THERMO-CHEMICAL CONVERSION OF SINGLE WOOD PARTICLE: A NUMERICAL STUDY

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Abstract

This paper reports the main findings of the first phase of our ongoing research on numerical study of oxy-fuel combustion of single biomass particle. The primary goal was to develop a detailed one-dimensional model based on mass, energy and momentum conservation principles, and to create a simulation code for investigation of biomass particle combustion at various conditions. Initially, the pyrolysis of a woody biomass particle was studied, since a deeper understanding of biomass pyrolysis was necessary to sufficiently model particle combustion. It was shown that an accurate formulation of energy equation would need to account for variation of enthalpy of reactions with temperature usually neglected in many past studies. In the next step, the endothermic heat of volatiles formation and the exothermic heat of char generation were considered using the correlations proposed in the literature. The improved pyrolysis model enabled us to capture various experimental data including internal temperature peak reported in some past works. A parametric study was subsequently conducted to investigate pyrolysis time and final char density of a single biomass particle with diameter up to 1mm at high heating environments.

The pyrolysis model was then extended to account for char gasification and oxidation and gas phase reactions within and in the vicinity of the particle to complete the particle combustion model, which was validated by comparing the predictions with different sets of experimental data reported in the literature. It was found that a correct selection of the pyrolysis kinetic data was a necessary step for accurately prediction of the biomass particle combustion. The reasonable agreement obtained between the predictions and experiments indicate that the particle model and the related simulation code can be used with sufficient accuracy to study combustion of wood particles.

Introduction

We have just passed the first decade of the 21st century while we have been facing with serious issues regarding uncertainties over longevity of fossil fuels and increasing concerns about environmental impact of fossil and nuclear energy-based technologies. Researchers in various parts of the globe have commenced fundamental investigation about feasibility of utilization of alternative and environmental-friendly fuels such as hydrogen and renewable fuels.

In the Netherlands, a research project supported by the Dutch Technology Foundation STW has been lunched with the objective of reduction of CO_2 emitted from coal-fired power plants. The proposed technique for achieving this goal is co-firing of a high fraction of torrefied biomass and coal at high oxygen concentration, but this technique has not been fully demonstrated on a large scale yet. In fact, a combination of co-firing at oxy-fuel conditions has the advantages of increasing the use of biomass of various sources to meet energy demands, and raising CO_2 concentration in the flue gases which would facilitate efficient capturing of carbon dioxide.

The project is a collaborative research between the scholars from Eindhoven University of Technology (TUe) and Twente University (UT) as well as industrial partners from KEMA, NUON-TSA and Dutch Utilities Industry. The ultimate goal of the research is to acquire knowledge and increase predictive capabilities of torrefied biomass combustion at high co-firing percentages under oxy-fuel conditions with respect to emissions, burnout time and fuel ignition through performing experimental and numerical studies. Our task at Combustion Technology group at Eindhoven University of Technology is to conduct detailed numerical investigation on combustion of a single biomass particle, and to identify dominant processes during thermo-chemical conversion of a biomass particle at the conditions similar to those found in industrial furnaces. This paper aims to present the main findings of the first stage of our research.

Description of the Process
Figure 1 illustrates various stages of combustion of a biomass particle with initial radius of r_{p0} exposed to a hot oxidative environment maintained at a fixed temperature with a constant oxygen fraction in the surrounding fluid passing over the particle. The problem is assumed to be described only in radial coordinate. As the first stage of the particle conversion, heat is transferred from the surrounding to the surface of the particle via convection and radiation mechanisms. The heating up process continues until the particle temperature reaches a certain level beyond which the virgin biomass begins to decompose to volatiles (e.g., H_2O, CO, CO_2, tar) and char residue.
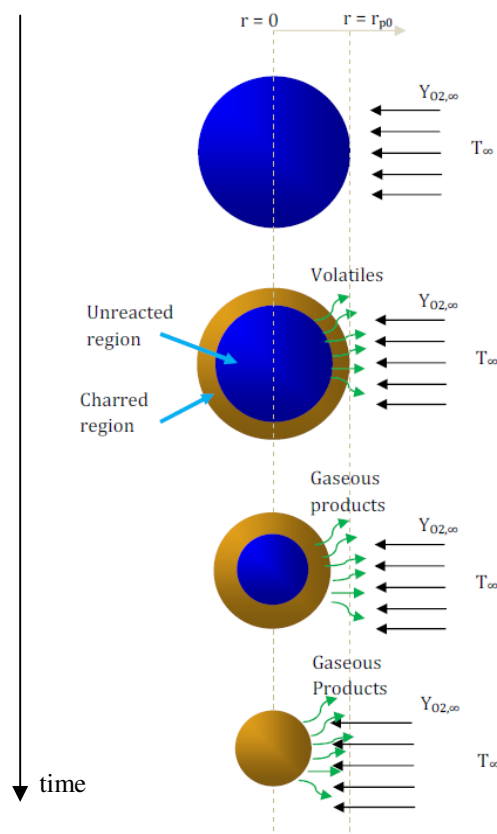

Figure 1. Schematic representation of thermo-chemical conversion of a biomass particle

Upon generation of volatiles inside the pores of the solid matrix, a flow of gaseous species is formed which moves through the pores towards the surface of the particle where they interact and mix with the surrounding fluid. This flow of the volatiles escaping from the surface of the particle causes a resistance against the diffusion of the surrounding oxygen to reach the particle surface and to react with the char formed during the pyrolysis process. The amount of oxygen mass transfer from the surrounding to the surface of the particle will depend on factors such as its concentration far from the particle, the mass flux of the volatiles leaving the particle, the Reynolds number representing the flow regime around the particle, and the rate of combustion of volatiles with oxygen. Thus, oxidation of char may or may not take place simultaneously with devolatilization and homogenous reactions in the vicinity of the particle.

During the pyrolysis process, the pores of the solid particle open up resulting in a higher porosity and increased inner surface area. Upon complete release of the volatiles, the remaining material is the char residue. Due to the porous structure of char, oxygen can react not only at the surface of the particle but also within the pores. As the char oxidation process continues, the porosity of the particle further increases and reaches unity upon complete conversion of the char at a given location within the particle. Depending on process conditions, char oxidation may obey a volumetric shrinking density model or a shrinking core model. In the former model, the char conversion takes place uniformly throughout the particle, whereas in the latter one its size decreases consistently as the particle conversion proceeds.

Pyrolysis of a Biomass Particle
As the first step towards modeling combustion of a single biomass particle, it was necessary to sufficiently understand the pyrolysis phenomenon. We believed that a deeper understanding of the biomass pyrolysis would enable us to sufficiently model biomass combustion. In particular, we found discrepancies in the reported kinetic data and enthalpy of pyrolysis used in different past studies on biomass pyrolysis. Moreover, discrepancies were found in measurements and experimental observations reported in various sources. For instance, center temperature showed to exceed the surface temperature of the solid particle before reaching thermal equilibrium in some past experimental works.

The kinetic scheme employed in this study to describe the chemistry of the decomposition of the particle is the well-known model of Shafizadeh and Chin [1] which suggests that the virgin biomass decomposes to light gases, tar and char. Thus, the kinetic model is coupled with one-dimensional (1-D) transport equations obtained from conservation of energy, species mass and momentum. It is assumed that the gas and the solid phases are locally in thermal equilibrium. Additionally, the gas phase is assumed to behave as a perfect gas so that its local pressure can be determined from the ideal gas law. Mass changes per unit volume of tar and gas phase are expressed as the sum of the convective flux due to the gas flow and mass conversion during the pyrolysis reaction. Darcy's law is employed to approximate the flow field within the porous matrix of the solid.

Almost all previous thermo-kinetic models of a pyrolyzing biomass particle consider an endothermic heat with an identical value for all reactions involved in the pyrolysis process. In these studies the source term in heat transfer equation is defined as

$$S_{pyr} = \rho_B \left(k_G + k_T + k_C \right) \Delta h_P \tag{1}$$

where k is the decomposition rate of biomass to the pyrolysis byproduct, and Δh_P is the enthalpy of pyrolysis.
Nevertheless, we showed that S_{pyr} has to be described as follows [2].

$$\tilde{Q} = \rho_B(k_G + k_T)\left[\Delta h_{B-g} + \int (c_B - c_g)dT\right] + \rho_B k_C\left[\Delta h_{B-C} + \int (c_B - c_C)dT\right] \qquad (2)$$

In fact, Eq. (2) suggests that the heat of char formation and the heat of volatile generation need to be computed as a function of temperature. Most values reported in the literature for the heat of pyrolysis have been found by fitting the predictions with experiments in previous works without considering the effects of sensible heat related to the specific heats differences. The proposed values for the pyrolysis heat have usually been endothermic.

The pyrolysis model accounting for the heat of reactions described in Eq. (2) was implemented in CHEM1D [3]. Various experimental data available in the literature were used to validate the accuracy of the model prediction. Illustrative comparisons between the model predictions and experiments are shown in Figs. 2 and 3, in which the effects of various kinetic data proposed by different researchers have been demonstrated. The normalized temperature in Fig. 2 is defined as $(T-T_r)/(T_0-T_r)$ with T_0 and T_r representing the initial and reactor temperatures.

The experimental data shown in Fig. 2 are related to the pyrolysis of 20 mm dried wood cylinders at a reactor temperature of 623K; these data are obtained from Koufopanos et al. [4]. As shown in Fig. 2, the measured center temperature exceeds the reactor temperature. Interesting to note is that our pyrolysis model is capable of capturing this temperature peak observed in the experiments of Koufopanos et al. [4] without extension of the reaction mechanism. The experiments in Fig. 3 are taken from Rath et al. [5], who measured center and surface temperatures and mass loss profiles of 20 mm beech wood particles heated in a muffle furnace maintained at 850 °C.
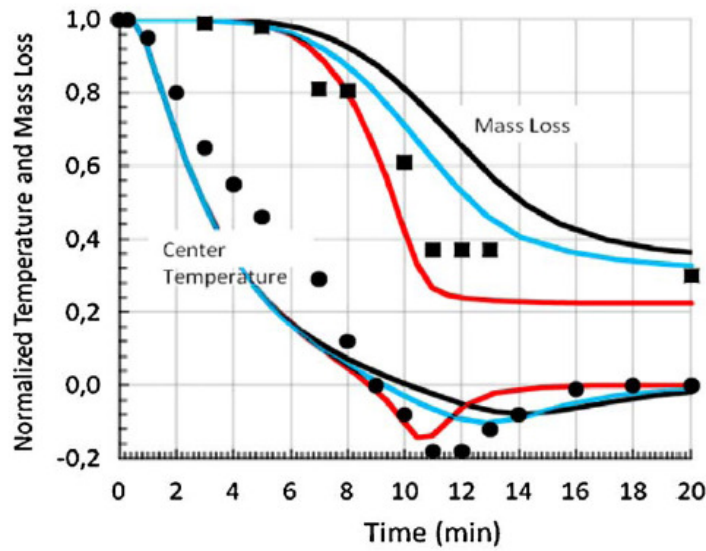

Figure 2. Comparison of predicted mass loss and center temperature with measurements of Koufopanos et al. [4] at a reactor temperature of 623 K. (●) measured temperatures; (■) measured mass losses; (━) Kinetic data of Chan et al. [6]; (━) Kinetic data of Thurner and Mann [7]; (━) Kinetic data of Di Blasi and Branca [8]
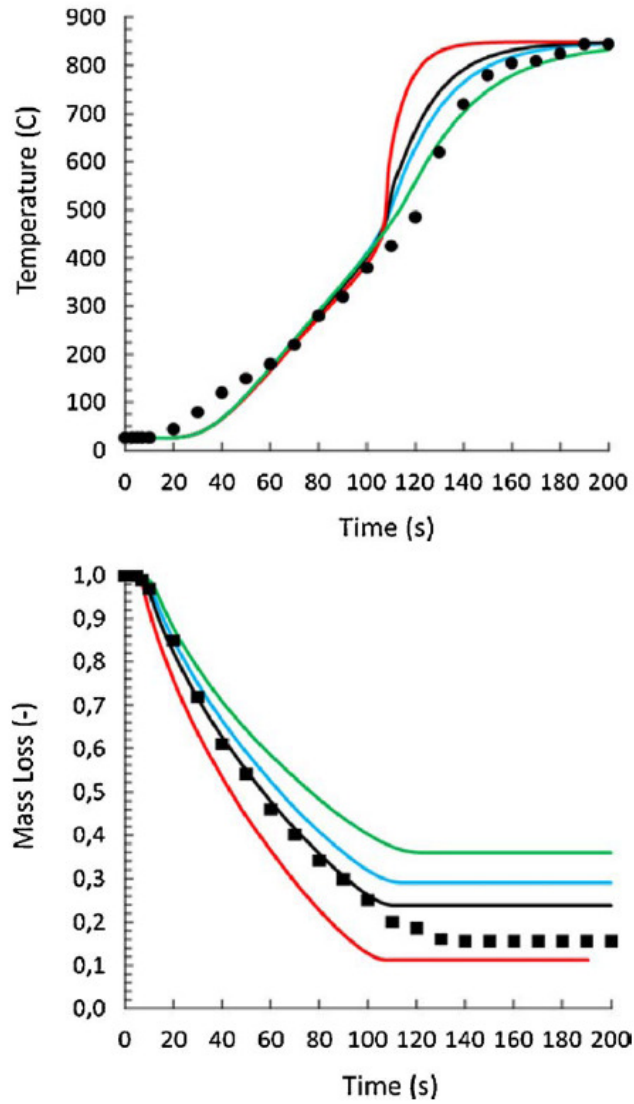
Figure 3. Comparison of the predicted center temperature and mass loss (lines) with measurements of Rath et al. [5] (symbols); (—) Kinetic data of Chan et al. [6]; (—) Kinetic data of Thurner and Mann [7]; (—) Kinetic data of Di Blasi and Branca [8]; (—) Kinetic data of Font et al [9]

Important to note is that Δh_{B-g} and Δh_{B-C} are unknown, given that appropriate correlations were used to compute specific heat of biomass, tar and light gases. The agreement between the model predictions and the experiments in Figs. 2 and 3 was obtained assuming $\Delta h_{B-g} = \Delta h_{B-g} = 25 \; kJ/kg$. An alternative way to evaluate enthalpy of pyrolysis was to use empirical correlations proposed by Milosavljevic et al. [10], Mok and Antal [11], and Rath et al. [12]. They correlated data of pyrolysis heat in the following form.

$$\Delta h_P = \Delta h_1 Y_c + \Delta h_2 (1 - Y_c) \tag{3}$$

where Y_c represents final char yield. Δh_1 and Δh_2 are apparent heats of the two lumped reaction pathways.

Although different values have been proposed in Refs [10-12] for Δh_1 and Δh_2, however, a common conclusion in these works is that the enthalpy of char formation is exothermic whereas that of volatiles generation is endothermic. Thus in the next step, we aimed to incorporate Eq. (3) in the pyrolysis model. It was found that employing the correlations of Milosavljevic et al. [10] and Mok and Antal [11] to compute the heat of pyrolysis together with kinetic constants of Di Blasi and Branca [8] in the model provides a good prediction of the final char yield and conversion time at high rector temperatures [13]. A typical comparison between the model prediction and the experiments of Rath et al. [5] is depicted in Fig. 4.

An important parameter when designing pulverized fuel combustors is the residence time of particles within the reactor. It is of technical importance to know the time of pyrolysis which is an unavoidable stage during combustion of a biomass particle. The fuel particles are usually small with diameters up to 1 mm. In practice, the shape of particles is usually aspherical which can be approximated as cylindrical-like particles. Thus, a parametric study was conduced to examine the effects of particle size and initial density and external heating conditions on the pyrolysis time and the final char density. The results led us to the following relationships:

$$t_{Pyr} = \begin{cases} 0.0003\rho_B\exp(1.966d_P)+0.01\exp(2.051d_P) & T_r = 1450K \\ 0.0002\rho_B\exp(2.190d_P)+0.008\exp(1.536d_P) & T_r = 1650K \end{cases} \tag{4}$$

$$\rho_C = \begin{cases} 0.0619\rho_B d_P^{0.2308}-5.5107d_P^{0.2004} & T_r = 1450K \\ 0.0552\rho_B d_P^{0.2360}-5.0809d_P^{0.2279} & T_r = 1650K \end{cases} \tag{5}$$

These results could be used to have an estimate on total conversion time and char yield if particles with various sizes and densities would undergo only a pyrolysis process.
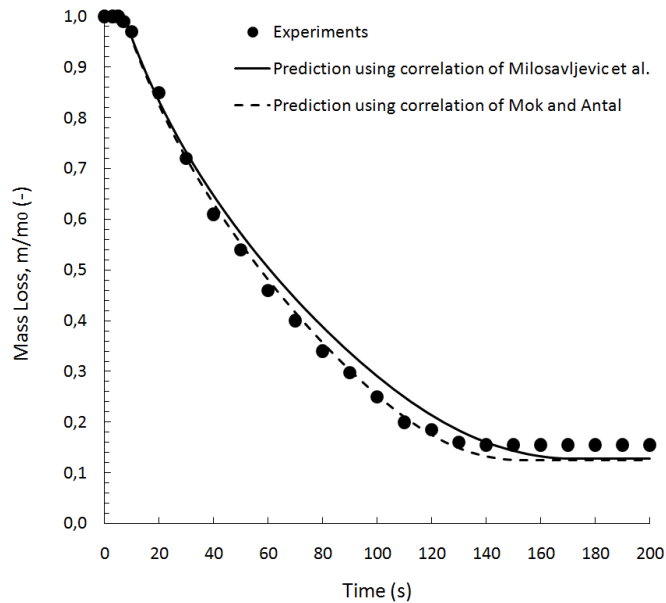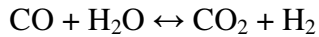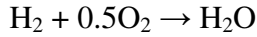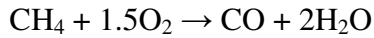

Figure 4. Comparison of predicted mass loss histories using empirical correlations of pyrolysis heat with experiments of Rath et al. [5]. Kinetic data: Di Blasi and Branca [8]

Combustion of a Biomass Particle

In a subsequent stage, the pyrolysis model was extended to account for additional processes involved in combustion of a biomass particle including char gasification and oxidation, and gas phase reactions within and in the vicinity of the particle.

The gas phase reactions used in this study are:

$$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O$$
$$H_2 + 0.5O_2 \rightarrow H_2O$$
$$CO + 0.5O_2 \rightarrow CO_2$$
$$C_{3.878}H_{6.426}O_{3.561} + 0.1585O_2 \rightarrow 3.878CO + 3.213H_2$$
$$CO + H_2O \leftrightarrow CO_2 + H_2$$

The combustion rates of methane, hydrogen and carbon monoxide were determined using the correlations reported by Dryer and Glassman [14], de Souza Santa [15], and Howard et al. [16], respectively. The empirical formula of tar represented by $C_{3.878}H_{6.426}O_{3.561}$ was obtained using the measurements of Rath and Staudinger [17] who investigated vapor phase cracking of tar obtained from the pyrolysis of small particles (0.5 – 1 mm) of spruce wood. The combustion rate of tar was assumed to be the same value as C_nH_m oxidation given by Smooth and Smith [18]. The correlation used for determination of the water-gas shift reaction rate was taken from de Souza Santos [15].

The heterogeneous reactions in terms of char gasification with water vapor and carbon dioxide, and char combustion with oxygen considered are

$$C + CO_2 \rightarrow 2CO$$
$$C + H_2O \rightarrow CO + H_2$$
$$C + 0.5O_2 \rightarrow CO$$
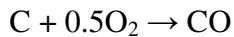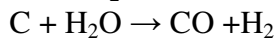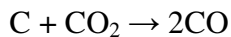
The kinetic rate constants of char gasification with carbon dioxide and steam were taken from Hobbs et al. [19], whereas the reaction constants of char oxidation adapted in this work are those reported by Evans and Emmons [20].

To fully describe combustion of a woody biomass particle, the one-dimensional transport equations are coupled with the kinetic models of pyrolysis, homogenous and heterogonous reactions discussed previously. The transport equations include mass conservation of biomass, char, tar, methane, hydrogen, carbon monoxide, carbon dioxide, water vapor, oxygen and nitrogen (considered to be an inert gas).

The experimental data used for validation of the model were taken from Wurzenberger et al. [21] and Porteiro et al. [22]. A comparison of the predicted and the measured mass loss histories is depicted in Fig. 5. The experimental data shown in Fig. 5a are related to the combustion of spherical beech wood particles with diameters of 20mm and 10mm in air at a reactor temperature of 1223 K. The mass loss history illustrated in Fig. 5b was obtained from burning of cylindrical Laguna Helada briquette particles of 50 mm diameter in air at a reactor temperature of 973 K. In both cases, a very good agreement is achieved between the model prediction and the experiments, indicating that the combustion model of a woody biomass particle developed in this work can be sufficiently used to numerically investigate combustion of wood particles.

The effect of kinetic constants of pyrolysis on the combustion of biomass particles at both experimental conditions outlined above was further examined. The best fit with measurements of beech wood particles in Fig. 5a was obtained using the kinetic data of Di Blasi and Branca [8]. On the other hand, only with the kinetic constants of Thurner and Mann [7] was sufficient

agreement achieved between model predictions and experimental data related to the combustion of a Laguna Helada particle (Fig. 5b) exposed to a reactor temperature of 973 K.

Illustrative simulation results related to combustion of spherical beech wood particle with diameter of 10mm corresponding to the experimental conditions of Fig. 5a are presented in order to enable one to get a deeper insight into the complete thermal conversion of a woody biomass particle. Figure 6 depicts time and space evolution of temperature and oxygen mass fraction during the combustion process of a 10 mm beech particle. The corresponding biomass and char densities are illustrated in Fig. 7. Notice that the simulation results are presented for the half thickness of the particle due to the symmetry assumption.
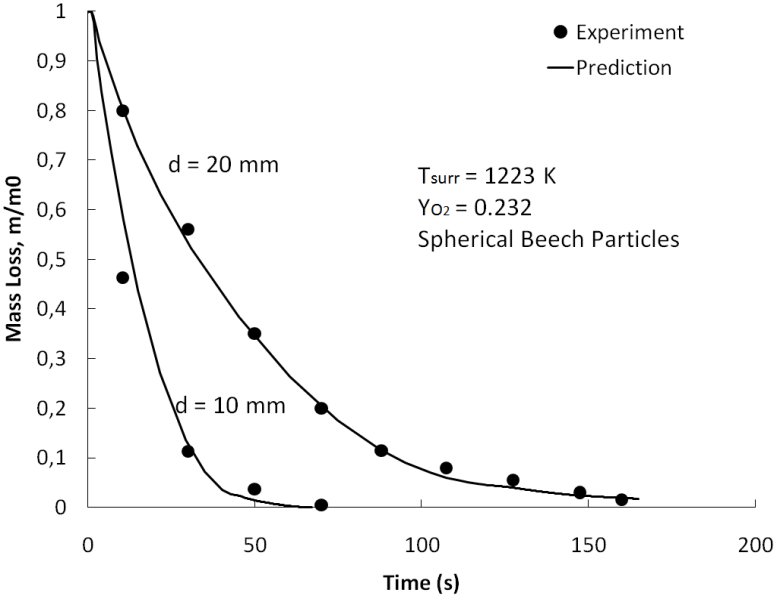
(a)
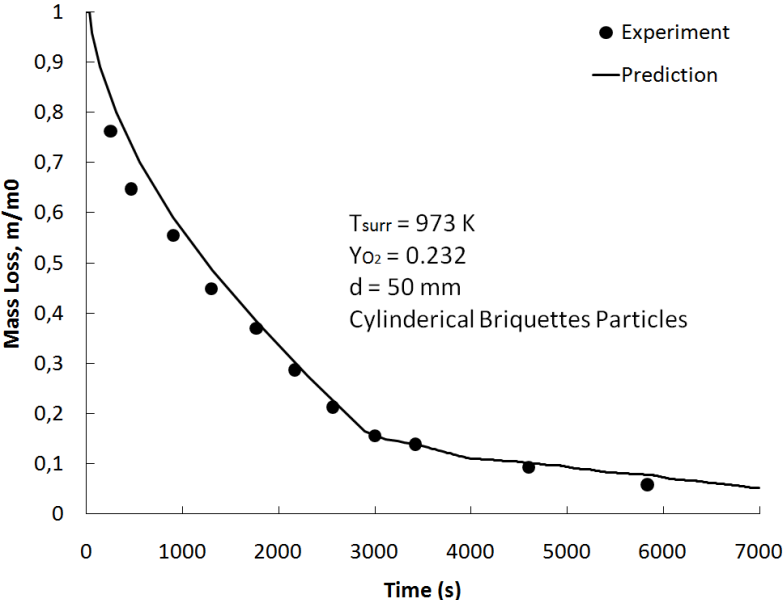
(b)

Figure 5. Validation of the combustion model; a) spherical beech wood particles, reactor temperature: 1223 K, source of data: Wurzenberger et al. [21]; b) cylindrical Laguna Helada briquette, diameter: 50 mm; reactor temperature: 973 K, source of data: Porteiro et al. [22]
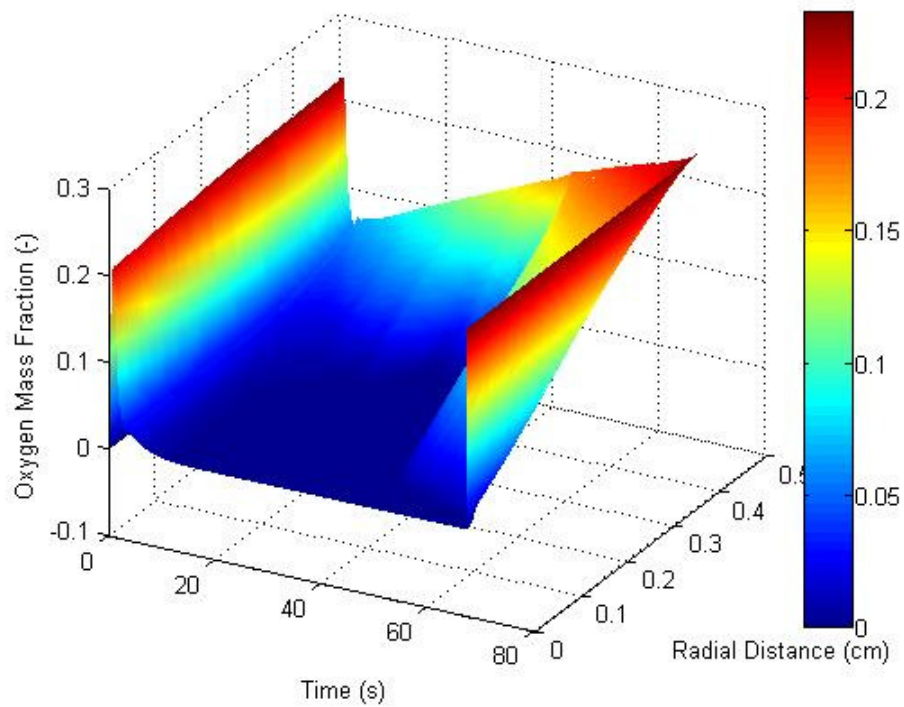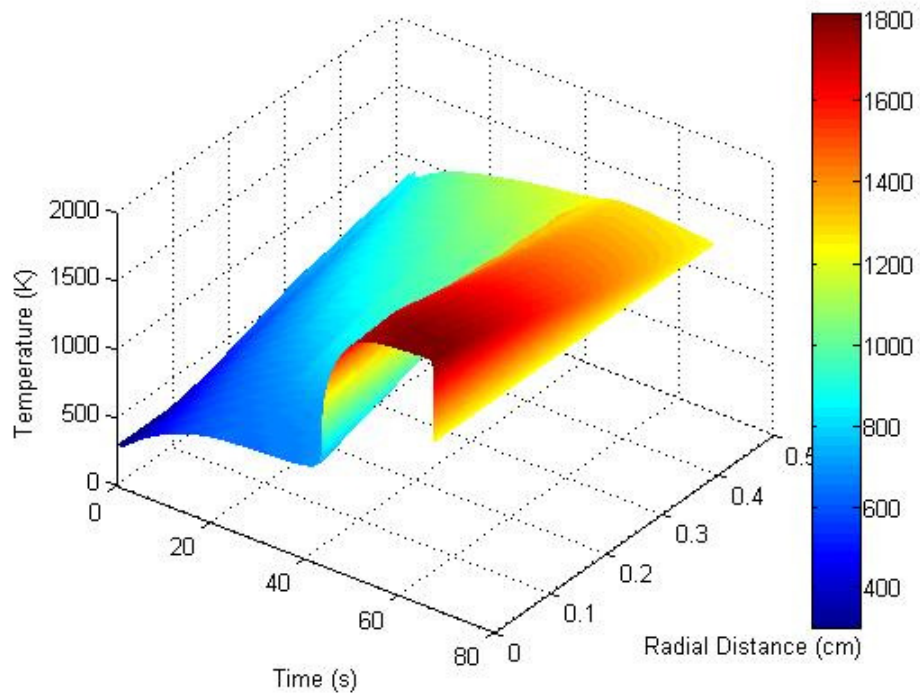
Figure 6. Typical simulated temperature and oxygen mass fraction corresponding to combustion of a 10 mm spherical beech wood particle burnt in air at a reactor temperature of 1223 K
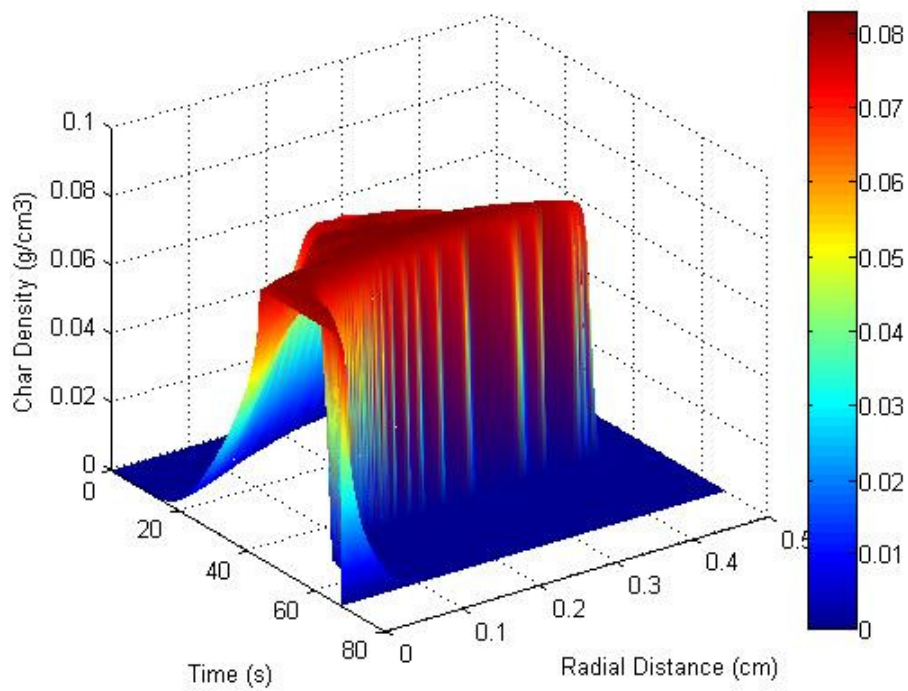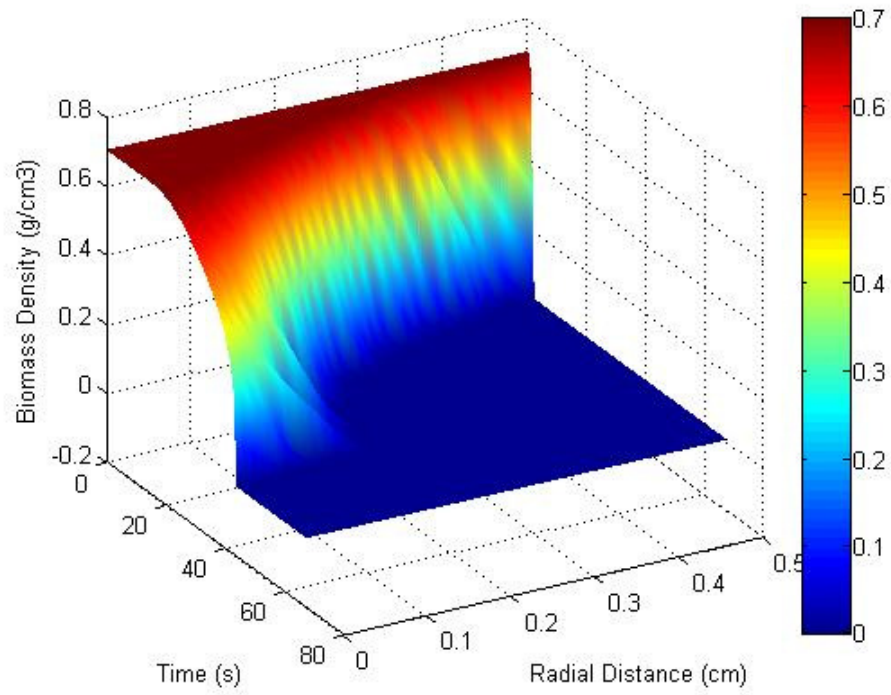
Figure 7. Typical simulated virgin wood density and char density corresponding to combustion of a 10 mm spherical beech wood particle burnt in air at a reactor temperature of 1223 K

As the particle, initially at room temperature, is exposed to a reactor temperature of 1223K with (flowing) air as the surrounding gaseous fluid, the heating up process begins. Prior to the pyrolysis process, oxygen from the surrounding diffuses inside the particle and reaches its ultimate amount as in the surrounding air. However, upon beginning of the biomass decomposition process after the temperature reaches a certain level, volatiles and char are formed. Subsequently, the mass fraction of oxygen reduces due to the formation of other gaseous species as well as its partial transference because of the outflow of volatiles.

As the pyrolysis process continues and a large amount of volatiles is released, diffusion of oxygen from the outside through the gaseous boundary layer around the particle experiences a delay. It can be inferred from the temperature graph in Fig. 6 that the final stages of the particle pyrolysis overlaps with the conversion of char at the outer layers of the particle. This may occur at low mass fluxes of the volatiles at latter stages of the pyrolysis, where there also exists a chance for the oxygen to reach the particle surface at a higher external mass transfer coefficient.

After all virgin biomass has completely converted to char, and the volatiles have left the particle, the diffusion of the oxygen inside the particle increases. Due to the high porosity of the remaining char, oxygen may react not only at the particle surface but also inside the pores. One may recognize from Fig. 7 that the char consumption proceeds from the outer layers towards the center of the particle indicating that the size of the particle decreases as the combustion process continues. During the combustion of char, the particle temperature takes a peak and remains at a certain level (around 1800 K in Fig. 6) until complete conversion and disappearance of char, after which the temperature drops to the surrounding temperature and remains in thermal equilibrium. Notice that in the present work, a negligible percentage of ash is assumed as in most woody biomasses, which has been regarded to fall off the particle upon its formation.

Conclusions

The main conclusions from this study can be summarized as follows.

- Employing empirical correlations of pyrolysis heat proposed by Milosavljevic et al. [10] and Mok and Antal[11] together with kinetic constants of Di Blasi and Branca [8] in the pyrolysis model allow reasonable predictions of conversion time of a single biomass particle and final char density at high operational temperatures.

- The correlations obtained from the parametric study; i. e., Eqs. (4) and (5), should enable designers to estimate the pyrolysis time and final char density of a biomass particle undergoing thermo-chemical conversion at the conditions of industrial combustors.

- The reasonable agreement obtained between the predictions and the different experiments indicate that the biomass combustion model and the related code developed using CHEM1D can be used with sufficient accuracy to study combustion of wood particles.

- A proper set of kinetic constants for the pyrolysis process needs to be selected carefully, since the later stages of the combustion process are greatly dependent on the amount of char and volatiles released during particle pyrolysis. In the case of absence of experimental data for a specific application, the kinetic constants of Thurner and Man [7] can be used for low to moderate reactor temperatures; whereas the kinetic data of Di Blasi and Branca [8] may be utilized at higher reactor temperatures; i. e. $T_r > 1100$ K.

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