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# Effect of Volatile Reactions on the Thermochemical Conversion of Biomass Particles

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## Abstract

A numerical and experimental study on the conversion of a biomass particle is carried out to quantify the effect of homogeneous volatile combustion on the biomass pyrolysis. The numerical domain consists of a particle and its surrounding and the model considers detailed chemical kinetic mechanism for reaction of pyrolysis products. A detailed pyrolysis model is employed which provides the composition of pyrolysis products. The effect of gas phase reaction on the conversion time and temperature of the particle is analyzed and it was shown that the gas phase reactions results in shorter pyrolysis time. H<sub>2</sub>O mole fraction and temperature above a biomass pellet from wheat straw (WS) and stem wood (SW) were experimentally measured using tunable diode laser absorption spectroscopy (TDLAS) while recording the particle mass loss. The TDLAS data were used to validate the numerical model developed for biomass conversion. The results showed that by considering the gas phase reactions a good agreement between the measurement and the model prediction for mass loss and temperature can be achieved. For H<sub>2</sub>O mole fraction on top of the particle, on the other hand, some discrepancy between the model prediction and the experimental data was observed. Nevertheless, the difference in H<sub>2</sub>O mole fraction would be much larger by neglecting the gas phase reaction at the particle boundary.

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**Keywords:** Biomass Particle; Boundary Layer; Combustion; Numerical Modeling

## 1. Introduction

Conversion of biomass particle can be divided into the processes occurring inside the solid structure of the particle and processes occurring in the particle boundary layer where chemical reactions and heat and mass transfer between the particle and the surrounding take place. The homogeneous reactions in the particle

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boundary layer are usually neglected while modeling the particle conversion [1-3]. The effect is modeled through boundary conditions for mass and heat transfer on the particle surface based on Nusselt and Sherwood numbers. Homogeneous reactions can affect the concentration of species and temperature in the boundary of the particle. The reasoning for neglecting the homogeneous reactions is that radiation heat transfer to the particle surface plays a more important role than the heat transfer from the chemical reactions of the surrounding gases during the pyrolysis process. Char combustion, on the other hand, is affected by the concentration of oxygen or gasifying agents at the particle surface. To take into account the effect of species concentration, single-film model and double-film model was developed. In the single film model, the combustion of CO is neglected and it is assumed that the char is reacting with oxygen directly. In the double-film model, char is reacting with CO<sub>2</sub>, which is produced from the homogeneous reaction of CO and O<sub>2</sub> in the particle boundary. The single-film model is commonly adopted for small particles (in micron size range) and the model has shown reasonable results [4, 5].

While there are some efforts to evaluate the errors from such model simplifications for small coal or char particles [5], the effect of homogeneous reactions on the conversion of large biomass particles during the pyrolysis and char reactions is not well investigated. In this paper, a joined numerical and experimental study is performed to investigate the effect of homogeneous reactions in the boundary layer of a biomass particle on the thermochemical conversion of the particle.

## 2. Numerical model

The computational domain is made up of a particle and its surrounding, far from the particle surface. The domain is divided to control volumes based on the original shape of the particle in a one-dimensional framework. The model considers the convective, conductive and radiative heat transfers inside the particle as well as heat transfer from or to the particle from the surrounding gas. The gradients of species and temperature are taken into account by solving the species and energy conservation equations with the respective source terms due to homogeneous and heterogeneous reactions inside and at the boundary of the particle. The temporal change in the particle volume is taken into consideration along with the changes in the thermos-physical properties. The governing equations for thermochemical conversion of biomass can be found in [1]. For homogeneous reactions, the combustion of pyrolysis products, secondary reactions of tar molecules and combustion of CO and H<sub>2</sub> from char reactions is considered. The rate of homogeneous reaction are presented in the following form,

$$\mathcal{R}_j = \sum_k \vartheta_{j,k} A_k \exp\left(\frac{E}{RT}\right) \prod C_j^{n_{j,k}}, \quad (1)$$

where  $\vartheta_{j,k}$  is the stoichiometric coefficient of species  $j$  in reaction  $k$ ,  $A_k$  is the pre-exponential factor,  $E$  is the activation energy,  $\mathcal{R}$  is the universal gas constant,  $C_j$  is the molar concentration of species  $j$  and  $n_{j,k}$  is the reaction order of species  $j$  in reaction  $k$ . For the gas phase reaction, a detailed mechanism (DRM19) was adopted [6].

For the gas phase beyond the particle surface, the gas velocity is calculated using the continuity equation by assuming constant pressure. Since the gas density can be changing due to the homogeneous reactions, in the transient term the gas density is substituted from the ideal gas law equation,

$$\frac{1}{r^n} \frac{\partial}{\partial r} (r^n \rho_g u_g) = \frac{\partial}{\partial t} \left( \frac{P}{\mathcal{R}_{mix} T} \right), r > R_p \quad (2)$$

where  $\rho_g$  is the gas density,  $u_g$  is the gas velocity  $\mathcal{R}_{mix}$  is the mixture molecular weight,  $r$  is the distance from the particle center and  $R_p$  is the particle radius.

At ambient surrounding gas far from the particle surface, the Dirichlet boundary condition for the species mass fraction ( $Y_j$ ), pressure and temperature are imposed,

$$p = p_{atm}, T = T_{\infty}, Y_j = Y_{j,\infty}. \quad (3)$$

At the interface of particle and the surrounding gas phase, all fluxes are continues except for the heat flux due to the radiation from the walls. The radiation heat flux is added at the particle surface,

$$q_{rad} = \sigma \epsilon (T_{wall}^4 - T_s^4), \quad (4)$$

where  $T_s$  and  $T_{wall}$  are the particle surface temperatures and the wall temperature, respectively.

### 3. Experimental measurements

Tunable diode laser absorption spectroscopy (TDLAS) based on calibration-free scanned wavelength modulation spectroscopy (CF-WMS) [9, 10] was used to simultaneously measure  $H_2O$  mole fraction and gas temperature above biomass pellets. A schematic of the experimental setup is shown in Fig. 1a. The sensor employed a fiber-coupled distributed feedback diode laser emitting at 1398 nm that was scanned at a frequency of 80 Hz and modulated at 8 kHz. Each recorded spectrum covered a spectral range of  $2.3 \text{ cm}^{-1}$  and was an average of ten scans. Temperature was assessed by two-line thermometry on  $H_2O$  transitions with linear T dependence in the range 1200–1800 K [10]. The CF-WMS curve fitting procedure allows simultaneous determination of wavelength-dependent modulation amplitude,  $H_2O$  mole fraction and temperature from a single least-squares fit to a group of  $1f$ - or  $dc$ -normalized  $2f$ -WMS lineshapes [9]. The detection limit for  $H_2O$  was 1000 ppmv. The repeatability of a temperature measurement was within 10 K and measurement uncertainties of 1% for  $H_2O$  and 50 K for temperature have previously been determined under homogenous conditions in a flat flame [10].

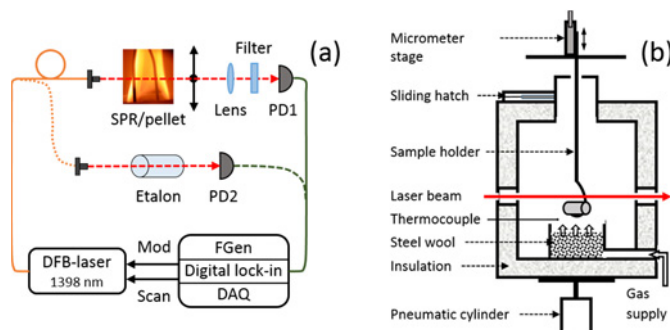


Fig. 1. Schematic of the experimental TDLAS setup (a) and the single-pellet-reactor (b).

Biomass pellets were combusted at 1123 K under atmospheric conditions in an electrically heated, laboratory-scale single-pellet-reactor (SPR) with optical access (Fig. 1b). The pellet holder was connected to an analytical balance to record the pellet mass loss during the combustion process. Two different pelletized fuels of relevance for the energy industry were used in the present study, one softwood derived fuel consisting of whole trees (stems) without bark, denoted as stem wood (SW), and a fuel containing agricultural residues, called wheat straw (WS). The moisture content of SW and WS was 6.4 and 10%, respectively, while the (chemical bound) hydrogen content was about 6% for both fuels. The pellets were of cylindrical shape with diameter 8 mm, and lengths 8 mm and 10 mm for SW and WS, respectively. The initial weights of the pellets used in the combustion experiments were  $500 \pm 5 \text{ mg}$  for both fuels.

#### 4. Results and discussions

To validate the model, a comparison between the numerical results and experimental measurement of the mass of the particle for the two samples is presented in Fig. 2. The symbols are from the experiments and the lines are from the numerical model. Two different cases for the numerical simulations are considered. One with reactions at the boundary of the particle and the other without any reaction. By including the combustion of volatiles in the model, the model and the experimental data show a better agreement. In the case where the combustion of volatiles is considered, the mass loss rate is faster. Although the differences are small, but the mass loss shows a better match to the experiments towards the end of devolatilization for SW. For WS, the three step pyrolysis mechanism failed in prediction of mass loss. Different kinetic constants from the literature [11] were tested without showing any improvements in the results. To obtain the results in Fig. 2, the kinetic mechanism of Ranzi, et al. [12] for pyrolysis of WS was adopted. In this semi-detailed mechanism, 20 gaseous species have been carefully chosen to represent the gas and tar yields of the pyrolysis [12, 13]. According to this pyrolysis mechanism, cellulose, hemicellulose and lignin decompose independently. 43% cellulose, 36% hemicellulose and 21% lignin were presumed as the composition of WS [14]. The major difference between the experiment and the model prediction for WS is the amount of residual char, under-predicted by the model, which is due to the pyrolysis mechanism.

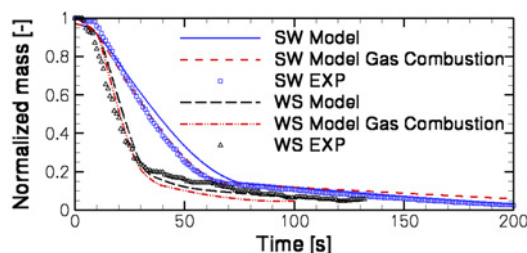


Fig. 2. Comparison between the results from the model and experiment for mass loss of WS and SW

The composition of some of the gases from the pyrolysis of WS is presented in Fig. 3. In addition to the species presented in this figure, CO, CO<sub>2</sub> and H<sub>2</sub>O and tar molecules are also considered in the model. The interesting observation from this figure is the formation of H<sub>2</sub>. H<sub>2</sub> is produced at the end of the pyrolysis from decomposition of lignin. This will show some effect on the temperature of the gas around the particle when considering homogeneous combustion. The main gas species from the pyrolysis of WS (except for CO, CO<sub>2</sub> and H<sub>2</sub>O) are formaldehyde (CH<sub>2</sub>O) and methane (CH<sub>4</sub>).

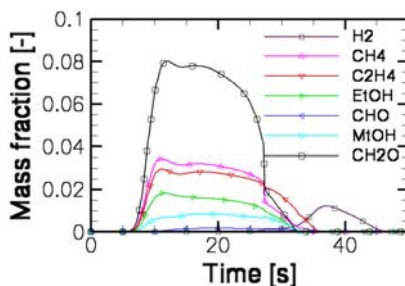


Fig. 3. Gas composition from pyrolysis of WS from detailed pyrolysis mechanism

The temperature of the gas at different heights above the particles is presented in Fig. 4. The experimental data are also included for comparison. Comparing the experimental data and the model prediction, one should bear in mind that the experimental data are from line-of-sight measurements which represents an average of the temperature at top of the particle, which is the reason that the experimental data show an almost constant temperature during the pyrolysis process. At first 20 seconds of the conversion, the temperature of the gas from the model is considerably lower than that from the experiment. The reason for this difference can be that in the model, the particle is treated one-dimensionally while in the experiment the corners of the particle can heat up much faster and pyrolysis can start from there. The volatiles released from these regions can ignite almost from the moment the particle is placed in the burner. However, in the model, since the particle is treated one-dimensionally, at first, the conversion is dominated by the moisture evaporation. At around 20 second, the pyrolysis starts and its products are ignited, when a sudden increase in the temperature is observed. Due to this reasons, the results of the model are shifted by 25 seconds.

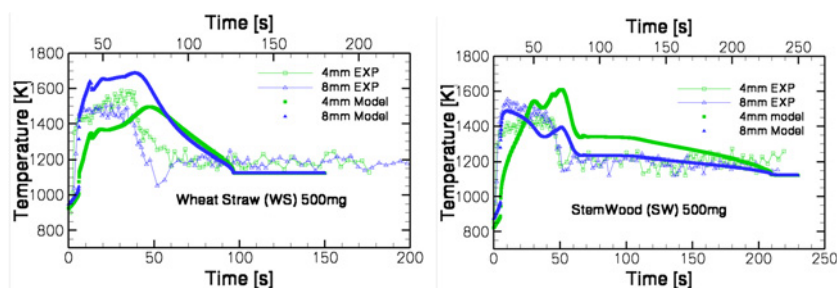


Fig. 4. Temperature at different heights above the particle from combustion of pyrolysis products; right: WS, left: SW

The  $H_2O$  mole fraction from the experiments at different heights above the particle along with the model predictions are presented in Fig. 5. The discrepancy between the experimental data for mole fraction of  $H_2O$  is larger than the temperature. At the beginning, the high value of  $H_2O$  is due to the moisture evaporation. During the pyrolysis, the  $H_2O$  concentration from the model decreases while the experimental data show constant or slightly decreasing trends. Until towards the end of the pyrolysis, when the  $H_2$  combustion starts resulting in an increase of the concentration of  $H_2O$ . The difference between the experiment and the model prediction can be due to several factors; one can be the uncertainty in the moisture content of the particle at the time of the experiment or the humidity of air. However, the main reason can be the entrainment of the moisture and combustion products from underneath of the particle to the top of the particle where the measurement is carried out. This phenomenon can considerably increase the concentration of  $H_2O$  at the top of the particle. The effect is more dominant at the highest mass loss rate, when the out-flow velocity of the pyrolysis products is high.

The profiles of  $CH_4$  mass fractions as well as temperature along the radius are presented in Fig. 6. The solid lines represent the case where the gas phase combustion is considered and the dashed lines represent the no combustion case. The symbols are added to distinguish results at different times. The gray area in the figure represents the particle. Comparing the combustion and non-combustion cases, at 16 s, the profiles of  $CH_4$  and temperature inside the particle for the two cases are almost identical, owing to that there is no homogeneous reaction inside the particle. However, the decrease in the  $CH_4$  mass fraction and increase in the gas temperature outside the particle indicates the existence of a flame at the particle boundary. At a later time ( $t = 32$  s), when the particle becomes more porous due to the mass loss and the temperature becomes higher, the homogeneous reactions are also occurring inside the particle. This can be clearly observed from

the profiles of  $\text{CH}_4$  and temperature inside the particle. Also the location of flame has moved to a shorter distance from the particle surface.

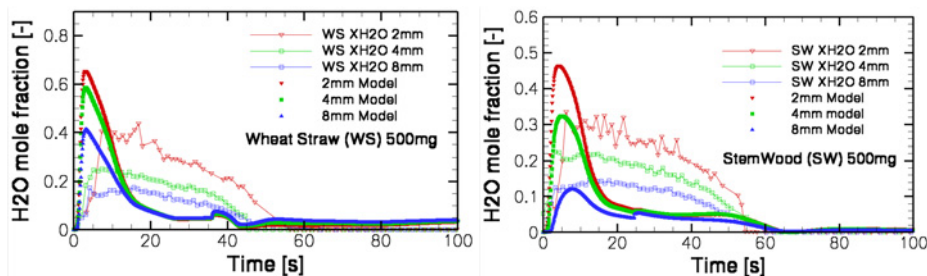


Fig. 5.  $\text{H}_2\text{O}$  mole fraction at different heights above the particle during combustion of pyrolysis products; right: WS, left: SW

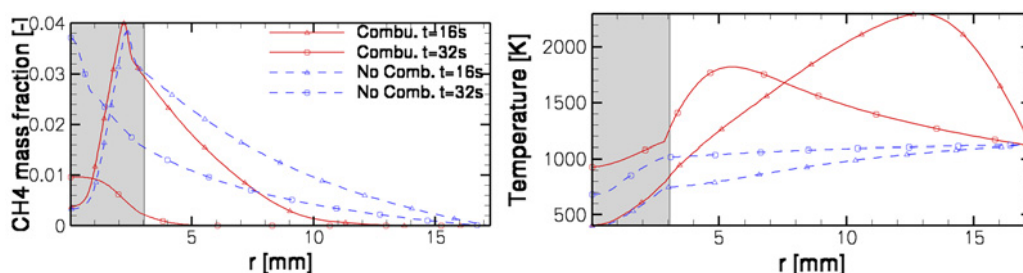


Fig. 6. Profiles of  $\text{CH}_4$  mass fractions and temperature at different times during the pyrolysis

## 5. Conclusion

A numerical model was developed for the conversion of large biomass particles by taking into account the combustion of volatile at the boundary of the particle. A detailed chemical kinetic mechanism consisting of 19 species and 84 reactions for the gas phase reactions was employed. To have a better estimate of the composition of pyrolysis products, a detailed pyrolysis mechanism was adopted from the literature. The results of the model was compared with the experimental measurement of  $\text{H}_2\text{O}$  mole fraction and temperature above a biomass pellet from wheat straw (WS) and stem wood (SW) using tunable diode laser absorption spectroscopy (TDLAS). Despite the good agreement between the model and the experiment in terms of the mass loss of the particle and the temperature,  $\text{H}_2\text{O}$  mole fractions are only in qualitative agreement with the experiments. The results show that the homogeneous volatile reactions at the boundary of the particle affect the particle temperature and conversion time, resulting in a shorter pyrolysis process. From the model results one can observe that at the beginning of the pyrolysis process, no homogeneous reaction is taking place inside the particle and the flame around the particle is formed far from the particle surface. As the pyrolysis process carried on, the flame converging the particle surface and part of the



pyrolysis products react with oxygen inside the particle. The shrinkage of the flame towards the particle surface at the end of the pyrolysis was also observed during the experiments.

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## References

- [1] H. Fatehi, X.S. Bai, A comprehensive mathematical model for biomass combustion, *Combustion Science and Technology*, 186 (2014) 574-593.
- [2] H. Lu, W. Robert, G. Peirce, B. Ripa, L.L. Baxter, Comprehensive study of biomass particle combustion, *Energy & Fuels*, 22 (2008) 2826-2839.
- [3] Y.B. Yang, V.N. Sharifi, J. Swithenbank, L. Ma, L.I. Darvell, J.M. Jones, M. Pourkashanian, A. Williams, Combustion of a single particle of biomass, *Energy & Fuels*, 22 (2007) 306-316.
- [4] R.E. Mitchell, R.J. Kee, P. Glarborg, M.E. Coltrin, Twenty-third symposium (international) on combustion the effect of co conversion in the boundary layers surrounding pulverized-coal char particles, *Symposium (International) on Combustion*, 23 (1991) 1169-1176.
- [5] E.S. Hecht, C.R. Shaddix, J.S. Lighty, Analysis of the errors associated with typical pulverized coal char combustion modeling assumptions for oxy-fuel combustion, *Combustion and Flame*, 160 (2013) 1499-1509.
- [6] A. Kazakov, M. Frenklach, <http://www.me.berkeley.edu/drm/>.
- [7] B.M. Wagenaar, W. Prins, W.P.M. Swaaij van, Flash pyrolysis kinetics of pine wood, *Fuel Processing Technology*, 36 (1993) 291-298.
- [8] M.L. Hobbs, P.T. Radulovic, L.D. Smoot, Modeling fixed-bed coal gasifiers, *AIChE Journal*, 38 (1992) 681-702.
- [9] Z. Qu, R. Ghorbani, D. Valiev, F.M. Schmidt, Calibration-free scanned wavelength modulation spectroscopy – application to h<sub>2</sub>o and temperature sensing in flames, *Opt. Express*, 23 (2015) 16492-16499.
- [10] Z. Qu, F.M. Schmidt, In situ h<sub>2</sub>o and temperature detection close to burning biomass pellets using calibration-free wavelength modulation spectroscopy, *Applied Physics B*, 119 (2015) 45-53.
- [11] C. Di Blasi, Modeling chemical and physical processes of wood and biomass pyrolysis, *Progress in Energy and Combustion Science*, 34 (2008) 47-90.
- [12] E. Ranzi, S. Pierucci, P.C. Aliprandi, S. Stringa, Comprehensive and detailed kinetic model of a traveling grate combustor of biomass, *Energy & Fuels*, 25 (2011) 4195-4205.
- [13] E. Ranzi, A. Cuoci, T. Faravelli, A. Frassoldati, G. Migliavacca, S. Pierucci, S. Sommariva, Chemical kinetics of biomass pyrolysis, *Energy & Fuels*, 22 (2008) 4292-4300.
- [14] J.C. del Río, J. Rencoret, P. Prinsen, Á.T. Martínez, J. Ralph, A. Gutiérrez, Structural characterization of wheat straw lignin as revealed by analytical pyrolysis, 2d-nmr, and reductive cleavage methods, *Journal of Agricultural and Food Chemistry*, 60 (2012) 5922-5935.

## Biography

Prof. Xue-Song Bai leads a research group working on CFD modeling of turbulent reacting flows. Current research of the group aims at developing models for simulation of combustion processes of gas, liquid and solid fuels with industrial application to internal combustion engines, gas turbines and furnaces.