Extension of apparent devolatilization kinetics from thermally thin to thermally thick particles in zero dimensions for woody biomass

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ABSTRACT

This work aims to provide an accurate and simple model, predicting the time dependent devolatilization of woody biomass at conditions (T_{gas} < 2000 K) and particle sizes (<2 mm) relevant to suspension fired boilers. The zero dimensional model is developed from reference calculations with a one-dimensional heat transport model coupled with a drying and a devolatilization model. The model output has been used to generate pyrolysis kinetics corrected for non-isothermal effects, i.e. intraparticle heat transport limitations. Analysis of the modeling results indicate that heat transport corrections of even small particles are necessary. The current work divides a given particle size distribution into suitable size categories based on their internal heat transport properties. The devolatilization is described by size category specific rate constants based on a single first order reaction mechanism. This approach allows for significantly more accurate devolatilization predictions of any particle size distribution to be described by simple kinetic mechanisms and isothermal particle heat balances. Such an approach is easily implemented into most commercial CFD (computational fluid dynamics) codes without adding any additional strain to the computational requirements.

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1. Introduction

The number of studies on thermal degradation of biomass material is extensive. The application covers a wide range of fields from wildfire simulations, fire protection, stoves, to utility boilers. Thus, the condition at which the models or experiments are developed or carried out at are very diverse. As a result quite a few biomass particle conversion models exist sharing common features while developed for different purposes. The most detailed single particle devolatilization models couple multiphase transport of heat and mass with volumetric gas-phase reactions, cracking reactions, and multiple competing multi-step reactions.

Hong et al. [1] developed a single particle one-dimensional model taking heat and mass transfer into account and including both drying, devolatilization, and char burn-out. Calculations using the non-isothermal model indicated significantly longer reaction times compared to those of the corresponding isothermal model for particles exceeding a few hundred microns in diameter. Similarly Groenli and Melaan [2] developed a single particle model for large particles (2−3 cm) and found that the addition of secondary cracking reactions are necessary in order to capture the ratio between gas, tar, and char formed for variations in the heating conditions. Bharadwaj et al. [3] mathematically investigated the influence of particle internal heat and mass transport and concluded that the drying and devolatilization to some extent was controlled by heat transport alone. Johansen et al. [4] showed through high heating rate experiments of particles less than 125 μm in diameter that the time scale for particle heat-up is comparable to that of complete devolatilization at high temperatures. Wagenaar et al. [5] combined slow heating rate thermogravimetric methods with flash pyrolysis drop tube experiments, and they were able to derive a single set of kinetic parameters capable of describing the pyrolysis of both set-ups at temperatures below 873 K.

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The objective of this work is to describe the rate of total devolatilization process at suspension firing conditions for non-isothermal particles using a zero-dimensional model with a global kinetic expression correcting for the heat transport limitations. This approach will reduce the computational cost of implementing single-dimensional particle models to CFD (computational fluid dynamics) simulations of larger systems, providing a method to do complex multiphase calculations with modest hardware requirements. The work provides a link between the complex multidimensional models found in the single particle literature and the isothermal assumption often made in burner simulations.

This work is divided into the following parts listed in chronological order:

1. Model description
2. Acquisition of validation material (literature study)
3. Model validation
4. Calculation of averaged devolatilization conversion and temperature profiles for non-isothermal particles (model output)
5. Single step, first order reaction devolatilization kinetic fitted to the calculated averaged conversions for different particle sizes

2. Modeling

In the present work the devolatilization of a fuel particle of spherical shape is described by a pyrolysis and a drying model coupled with a heat transport model taking both external and internal particular transport limitations into account.

The modeling is based on the following assumptions:

1. The model is solved in one dimension
2. Only primary pyrolysis takes place
3. The heat of pyrolysis sums to zero
4. No convective heat transport takes place inside the particle
5. There are no mass transfer limitations
6. Particles are spherical
7. Only the reactor walls contribute to the radiative external heat flux

The assumptions are generally accepted in the particle modeling literature [1,5–7]. Although some of the assumptions have been suggested to play an influence, e.g. multidimensional spread of energy, momentum, and mass [8], the influence of secondary reactions and heat of pyrolysis [9,10], the level of assumptions is generally considered valid for mass loss simulations similar to the objective of the current study.

2.1. Governing equations

The drying of the particles is described by a kinetic model [11]:

$$\dot{w} = k_Y(Y^* - Y(t))\rho_w \tag{1}$$

where $\dot{w}$ is the rate of water evaporation, ρ_w is the density of water, and Y^* and Y are the water content of the virgin fuel and the released amount of water at time t. The rate constant, k_Y, is expressed as:

$$k_Y = A_Y T_p^{1/2} \exp\left[\frac{-E_{a,Y}}{RT_p}\right] \tag{2}$$

where A_Y and $E_{a,Y}$ are the pre-exponential factor and the activation energy for the water evaporation model and T_p and R are the local particle temperature and the universal gas constant.

The devolatilization is solely driven by the thermal breakdown of the organic structure and is described by a single global reaction:

$$\text{parent fuel} \xrightarrow{k} \text{solid} + \text{volatiles} \tag{3}$$
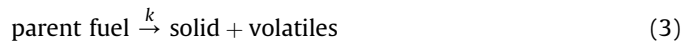
As such, only the primary pyrolysis [12,13], is taken into account neglecting any secondary reactions [14,15].

The rate of reaction is described by a single SFOR (step first order reaction)

$$\frac{dV(t)}{dt} = k(V^* - V(t)) \tag{4}$$

where V and V^* are the fraction of volatile matter released and the ultimate fraction of volatile matter respectively. V^* has been obtained experimentally in entrained flow reactors to yield the true high temperature, high heating rate value which is known to deviate significantly from low temperature, low heating rate experiments often used in fuel characterization standards [16].

The rate constant, k, obeys an Arrhenius type expression

$$k = A \exp\left[\frac{-E_a}{RT_p}\right] \tag{5}$$

where A and E_a are the pre-exponential factor and the activation energy respectively, for the pyrolysis step while R and T_p denote the universal gas constant and the local temperature of the solid.

The heat balance accommodates the intra-particular heat transport limitations coupled with a transport model for the external heat flux. If a quasi-steady-state is considered and the heat transport is described by Fourier's law, then

$$c_P\rho\frac{\partial T(t,r)}{\partial t} = \frac{2\lambda}{r}\frac{\partial T(t,r)}{\partial r} + \lambda\frac{\partial^2 T(t,r)}{\partial r^2} - \dot{w}_w\Delta_{vap}H \tag{6}$$

describes the heat transport through the particle. Here c_P, ρ, and λ are the specific heat capacity, density, and thermal conductivity of the solid phase, respectively.

The initial condition is given by the particle temperature at time zero, T_0:

$$T(0,r) = T_0 \tag{7}$$

The boundary conditions are defined as adiabatic behavior at the particle center, and the heat flux from the surrounding to the particle, q_{ext}, given by the total contribution from a convective flux, q_c, and a radiative flux, q_r. This yields the spatial boundaries of the particles as:

$$\lambda\frac{\partial T}{\partial r}\bigg|_{r=0} = 0 \tag{8}$$

$$\lambda\frac{\partial T}{\partial r}\bigg|_{r=R} = q_{ext} \tag{9}$$

2.2. Algebraic equations

In addition to the governing equation describing the energy balance of the system, a number of algebraic equations must be defined in order to describe the transport properties of the transient system.

2.2.1. Heat of evaporation of water

Because the model aims at describing particles used for suspension fired boilers, only bound water is taken into consideration.