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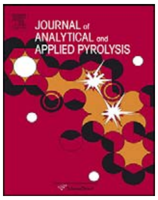

Modeling biomass particle pyrolysis with temperature-dependent heat of reactions

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ABSTRACT

An accurate formulation of energy conservation to model pyrolysis of a biomass particle needs to account for variations in the heat of reaction with temperature, usually neglected in most past studies. It is shown that by including this effect in a pyrolysis model with three parallel reactions yielding char, gas and tar, a wide range of experimental data can be accurately predicted. In particular, through comprehensive comparisons of the simulation results with various measurements, a consistent and single value of 25 kJ/kg is obtained for enthalpy of pyrolysis, which represents a lumped heat of volatiles and char formation at a reference temperature. It is found that the kinetic parameters of Chan et al. [W.C. Chan, M. Kelbon, B.B. Krieger, Fuel 64 (1985) 1505–1513] and Thurner and Mann [F. Thurner, U. Mann, Ind. Eng. Chem. Process Des. Dev. 20 (1981) 482–488] provide reasonable agreement between the model predictions and experiments compared to other reported kinetic constants. These comparisons also indicate that inclusion of tar cracking reactions to yield additional light gases does not give a better prediction of the process parameters. The presented thermo-kinetic model is capable of successfully predicting various experimental observations such as the internal temperature peak reported in some past studies. It is shown that the sensible heat released due to the conversion of virgin biomass to the reaction products is responsible for this phenomenon. Simulation results reveal that a temperature peak at an internal location of the particle may occur when the corresponding local temperature reaches the particle surface temperature while the local biomass conversion is not finalized yet.

1. Introduction

Increasing CO_2 emissions and uncertainties related to the ultimate availability of fossil fuels are major concerns which push industry and R&D sectors to seek solutions and new concepts to overcome these issues. Fossil fuel-based power plants, in particular coal fired power plants, contribute significantly to greenhouse gas emissions. A cost-effective CO_2 reduction method is co-firing of a high fraction of biomass in coal fired power plants. Because of the existing infrastructure of coal fired power stations, the extra investment costs for co-firing biomass takes advantage of the high efficiencies obtainable in large coal fired power plants. Therefore, it is necessary to increase our understanding and predictive capabilities of biomass combustion with respect to emissions, fuel ignition, burnout and ash quality.

Combustion of a biomass particle is quite complex as it undergoes various physical and chemical successive processes including heating up, drying (in case of a wet particle), devolatilization/pyrolysis and char burnout. However, depending on the heating conditions, particle size and composition, moisture content, etc., some of the above mentioned processes may occur simultaneously. As concluded by Williams et al. [1], accurate modeling of biomass combustion with quantitative reliability still remains a challenge.

The thermal characteristics of the pyrolysis process as one of the unavoidable steps during thermal decomposition of a biomass particle need to be carefully investigated at combustion conditions; even though this phenomenon has been previously studied theoretically and experimentally by many researchers, e.g. Di Blasi [2,3], Gronli and Melaaen [4], Bharadwaj et al. [5] and Larfeldt et al. [6]. During biomass pyrolysis, several physical and chemical processes take place including virgin biomass heating up, moisture evaporation and transportation, kinetics involving the decomposition of biomass to tar, char and light gases, heat and mass transfer, pressure build-up within the porous medium of the solid, convective and diffusive gas phase flow, variation of thermo-physical properties with temperature and composition, and change in particle size, i.e. shrinkage.

The detailed models available in the literature for biomass pyrolysis are based on coupled time-dependent conservation equations including kinetics of the biomass decomposition. In fact, the kinetic model directly influences the conservation equations. A lit-

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Nomenclature

A	pre-exponential or frequency factor, 1/s
c_P	specific heat, J/kg K
E	activation energy, kJ/mol
e	surface emissivity
h	convective heat transfer coefficient, W/cm^2 K
h_f	enthalpy of formation, kJ/kg
$\hat{h}$	total enthalpy, kJ/kg
K	permeability, cm^2
k	reaction rate, 1/s
k^*	effective thermal conductivity, W/cm K
MW	molecular weight, mol/g
n	Shape factor
P	pressure, Pa
$\tilde{Q}$	source term in energy equation, J/cm^3 s
q_x	external heat flux, W/cm^2
R	particle radius, cm
R_g	universal gas constant, kJ/mol K
r	radial (sphere and cylinder), axial (slab) distance, cm
T	temperature, K
t	time, s
u	superficial gas velocity, cm/s
Y_C	fraction of char in the products

Greek letters

ε	porosity
ρ	density, g/cm^3
Δh_{B-g}	enthalpy of $B \rightarrow G$ and $B \rightarrow T$ reactions, kJ/kg
Δh_{B-C}	enthalpy of $B \rightarrow C$ reaction, kJ/kg
Δh_{T-g}	enthalpy of tar cracking reaction, kJ/kg
μ	viscosity, kg/m s
σ	Stephan–Boltzmann constant

Subscripts

0	initial condition
∞	surrounding condition
B	biomass
C	char
G	light gases
g	gas phase (tar + light gases)
T	tar

erature survey indicates that several kinetic schemes have been proposed and applied by different authors. The one-step global model, as the simplest kinetic model, considers decomposition of biomass into char and volatiles. This is the most frequently applied model, see for instance Galgano and Di Blasi [7]. An improved version of the one-step model with a single rate constant is a model according to which the main constituents of wood (cellulose, hemicelluloses and lignin) decompose independently into char and volatiles. Another decomposition scheme is the well-known Broido–Shafizadeh model for cellulose decomposition, which assumes that the formation of an intermediate phase is followed by two competing reactions; in one reaction tar is produced, while in the other one char and light gases are formed. The proposed mechanism of Koufopanos et al. [8] is similar to the kinetic scheme of Broido–Shafizadeh, in which the virgin biomass is first converted into an intermediate material (reaction 1) which then decomposes to gases and volatiles (reaction 2), and char (reaction 3). Shafizadeh and Chin [9] proposed a primary wood degradation mechanism which suggests three individual competitive reactions forming light gases, tar and char.

Another kinetic model of biomass degradation assumes that in addition to the primary reactions as suggested by Shafizadeh and Chin [9], tar undergoes homogeneous degradation producing additional light hydrocarbons and char. This is referred to as tar cracking or secondary reactions. This model was applied in detailed pyrolysis simulations conducted by Gronli and Melaaen [4], Di Blasi [2,10], Hagge and Bryden [11], Bryden and Hagge [12], Bryden et al. [13], and Chan et al. [14]. Moreover, Koufopanos et al. [15] took into account the nature of secondary reactions from a different viewpoint. In their model, virgin biomass undergoes primary reactions to decompose into volatile and gases (reaction 1) and char (reaction 2). The primary pyrolysis products participate in secondary reactions to produce also volatile, gases and char of different compositions (reaction 3). The kinetic mechanism of Koufopanos et al. [15] has been applied, for instance, by Babu and Chaurasia [16] and Sadhukhan [17,18] to model pyrolysis of biomass particles. In the recent comprehensive review studies by Di Blasi [19,20], the chemical kinetics of wood and biomass pyrolysis are critically discussed. The reader is also referred to the interesting paper by Di Blasi [21], in which the predictions of several kinetic mechanisms, which take into account the formation of char, tar and gas, are compared and discussed for the primary pyrolysis of cellulose and biomass.

Literature review indicates that there are also discrepancies in the reported kinetics and thermo-physical data applied in different theoretical investigations for predicting thermal degradation of a biomass particle. We have found five different data sets for activation energies and frequency factors of the primary reactions of the Shafizadeh and Chin [9] kinetic scheme, which are usually described as first-order with an Arrhenius type of temperature dependence. Moreover, the heat of these primary reactions is one of the most important parameters influencing the pyrolysis process, and it has been assigned various values. Hence, it remains a question for a pyrolysis modeler what set of kinetic constants and which value for the heat of reactions must be utilized in the simulation. Our attempt is to find reasonable answers for these uncertainties in this paper.

On the other hand, discrepancies have also been found in measurements and experimental observations reported in various sources. For instance, the particle inner temperature showed to exceed the surface temperature of the solid particle before reaching thermal equilibrium in the experimental studies of Koufopanos et al. [15], Park et al. [22] and Di Blasi et al. [23], whereas this phenomenon was not observed in measurements of other workers such as Larfeldt et al. [6], Chan et al. [14], Tan and White [24], and Lu [25].

In the current paper, assuming that the biomass decomposition takes place according to the Shafizadeh and Chin scheme, we investigate the accuracy of the pyrolysis models when using various kinetic parameters reported in the literature. The possibility of a tar cracking reaction to produce lighter gases is also examined. Moreover, it is intended to highlight advantages of an accurate formulation of the conservation of energy that allows computing the enthalpy of pyrolysis as a function of temperature. It will be shown that a pyrolysis model with the accurate energy equation is capable of predicting a wide range of experimental data including temperature peaks at internal positions observed in some past studies; e.g. [15].

2. Literature survey on kinetic parameters

The kinetic scheme utilized in our simulations assumes that the biomass particle decomposes to char, tar and gas according to the model of Shafizadeh and Chin [9]. Hence, the relevant kinetic constants that have been obtained experimentally by various past researchers are summarized. The accuracy of the particle pyrolysis model will be examined when using different sets of kinetic parameters. Moreover, this section provides data of the kinetic parameters