A numerical and experimental study on fast pyrolysis of single woody biomass particles

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HIGHLIGHTS

- A novel two-zone pyrolysis kinetic model, transient at 350 °C, is proposed.
- Image processing of particles helped to identify the characteristic length of particles.
- Particles smaller than 0.5 mm do not have significant internal heat transfer limitation.
- Range of particle size valid for lumped formulation depends on operating temperature.

ARTICLE INFO

ABSTRACT

A one-dimensional unsteady-state heat transfer model coupled with time dependent mass loss equation of wood particles exposed to drying and pyrolysis conditions was developed. The kinetic parameters were determined experimentally and the regime and characteristics of the conversion were evaluated in terms of the particle size and reactor temperature. The order of mass loss exponent varied from $n = 1$ at temperatures lower than 350 °C to $n = 0.5$ at temperatures higher that 350 °C. The analysis of conversion time, the time when particles lost 90% of their mass, showed that thermal treatment of particles larger than 0.5 mm were controlled by internal thermal resistances. The valid range of particle size to use the simplified lumped model depends on the fluid temperature around the particles. The critical particle size was 0.6–0.7 mm for the fluid temperature of 500 °C and 0.9–1.0 mm for the fluid temperature of 100 °C.

1. Introduction

Pyrolysis is a thermal process that converts the raw biomass to the secondary fuels in an oxygen-free or an oxygen-deficient atmosphere. It is mostly a preceding step for gasification and combustion processes; although, it may also be an independent process to produce liquid biofuel [1]. As the temperature of particle increases, different stages of thermal treatment occur. First, the particle starts to dry up to the temperatures of about 150 °C [2]. At temperatures of 200–300 °C, various degrees of torrefaction happens and release volatile. At temperatures of higher than 300 °C, severe decomposition of biomass happens and lots of structural changes occur in the solid matrix of particle. Rate of particle heating significantly influences the product distribution of a pyrolysis process [3]. The size of particle [4–9], reactor temperature [10–12], heating rate of reactor [13,14] and the heating mechanisms involved in the process are the most important factors affecting the heating time of particle. Many researchers studied thermal decomposition of biomass by thermogravimetric analyzer (TGA) which is a slow pyrolysis process and is the most common technique used for kinetic analysis of devolatilization process [15–19].

During a fast pyrolysis process, the biomass particles are heated up rapidly to the temperatures of 400–600 °C. The external heat transfers to the particle surface by heat convection and/or radiation mechanisms and then diffuses toward the particle center [20]. Different heat resistances inside and outside of particle make a non-linear temperature profile inside the particle which affects the rate of mass loss in both drying and pyrolysis stages.

From the mathematical point of view, the wood thermal treatment process is investigated as a simultaneous kinetic, heat and mass transfer phenomenon in both solid and gas phases. The rate-controlling mechanism strongly depends on the particle size. As the particle size increases, the heat and mass transfer are

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Nomenclature

k_0	pre-exponential factor, $1/kg^{n-1}$ s
b	geometrical factor
$C_{p,s}$	particle specific heat capacity, J/kg K
d_p	particle diameter, mm
d_{gs}	grinder screen opening size, mm
d_{sv}	sieving mean particle size, mm
dr	radius step size, m
dt	time step size, s
E	activation energy, J/mol
Fo	Fourier number
h	heat transfer coefficient, W/m^2 K
H	overall heat transfer coefficient, W/m^2 K
i	model numerator in radius direction
j	model numerator in time direction
k_d	drying rate constant, 1/s
k_p	pyrolysis rate constant, $1/kg^{n-1}$ s
K_s	particle thermal conductivity, W/m K
n	order of pyrolysis mass loss
Py	pyrolysis number
$-q$	heat of reaction, J/kg

$-r_p$	rate of pyrolysis mass loss, kg/s
r	radial position, m
R	universal gas constant, J/mol K
t	time, s
T	particle local temperature, K
T_c	particle center temperature, K
T_h	heater temperature, K
T_f	fluid temperature, K
T_s	particle surface temperature, K
X	conversion

Greek symbol

α	thermal diffusivity
σ	Stefan-Boltzmann constant, W/m^2 K^4
ε	emissivity
ρ	particle density, kg/m^3
ρ_0	initial particle density, kg/m^3
ρ_e	biochar density, kg/m^3
τ	conversion time, min

getting slower and become rate controlling instead of the chemical kinetic. Slow mass transfer may influence the volatile yield of pyrolysis due to the possible secondary and tertiary reactions. These reactions convert the desired volatiles to the non-condensable gases, biochar and also non-desirable volatiles [21]. In the range of biomass particle sizes used in industrial thermal conversion applications, the mass transfer does not control the rate of pyrolysis [22].

Literature reported that the heat transfer and reaction kinetics are the most rate-controlling mechanisms in pyrolysis reaction of a single biomass particle [23–27]. Babu and Chaurasia [28] did a comprehensive study to compare the complexity of the mathematical models on their agreement with experimental data. They reported that the most simplified model which ignores the particle shrinkage, mass transfer limitation inside the particle, and the convective and radiative transport mechanisms inside the particle agrees well with experimental data. Janse et al. [29] also supported the importance of heat transfer compared to the mass transfer inside the particle. Their work on particles in the size range of 0.2–1.0 mm shows that an extensive investigation of internal mass transport in fast pyrolysis modeling of biomass particles is not necessary, while accurate and stable heat transfer model and reaction kinetic scheme are crucial.

Pyle and Zaror [23] categorized the heat transfer models to be applied in different ranges of particle size. They used the dimensionless Biot (*Bi*) and Pyrolysis (*Py*) numbers to define the valid applicability region of simplified lumped model. Their experimental and modeling results showed as particle size increased in range of 0.25–13 mm, the reaction time increased. Pyle and Zaror [23] stated that the heat conduction model coupled with the mass loss kinetic gives a very good description of primary pyrolysis reactions. Simmons and Gentry [27] used the one-dimensional distributed heat transfer model to determine the particle size region free of heat transfer limitations. They showed that slower heating of particles at low reactor temperature (~300 °C) increases the critical particle size. Yang et al. [30] stated that isothermal reaction assumption is not valid for particles larger than 0.25 mm, and in practice the heating rate of particle is limited by its low thermal conductivity [31].

Majority of the pyrolysis modeling studies used the experimental data of Pyle and Zaror [23] and Koufopanos et al. [32]. Using a

one-dimensional heat transfer model coupled with the mass loss kinetic, Babu and Chaurasia [28] predicted the experimental data of Koufopanos et al. [32]. Babu and Chaurasia [23] modeled the pyrolysis of 0.25–13 mm biomass particles in the temperatures up to 730 °C. As particle size increased, the reaction time increased. But the increase depended upon pyrolysis temperature. Babu and Chaurasia [28] also showed that larger particles raised the yield of char and decreased the yield of volatiles for the primary reaction. Grioui et al. [33] modeled thermal treatment of thick pine wood (~2 cm) using a conduction heat transfer model coupled with the mass loss kinetic. The results showed a good agreement with experimental data of Pyle and Zaror [23]. Lu et al. [34] modeled devolatilization process in a heated nitrogen environment up to the temperature of 1350 °C. Their experimental and theoretical research showed that spherical particles react slower than the cylindrical and slab particles. Volatile yield also decreased with increase in particle size. Haseli et al. [35] numerically investigated the pyrolysis of a single biomass particle in the size range of 0.25–1.0 mm. Their model included a one-dimensional heat conduction, flow of gas within the particle and exothermic formation of char. Their results showed that increase in diameter caused a linear increase in both reaction time and char density.

1.1. Objectives

Based on the open literature [22–29], it is clear that heat transfer limitation inside the large particles play an important role in the rate of pyrolysis reaction. The objective of current study is to model the overall pyrolysis mass loss of a single wood particle. The presented model is validated with experimental pyrolysis data obtained in a thin layer pyrolyzer. In this paper, a one-dimensional heat transfer model is developed and solved instantaneously with a mass loss kinetic relation. The mass loss kinetic model presented in the current paper is a novel two-zone model which helps the one-dimensional heat transfer model to accurately predict the overall mass loss. The developed pyrolysis model determines the range of particle size valid for the simplified lumped model and the intrinsic reaction. Empirical correlations are also developed to model the pyrolysis of moist ground chip and moist ground pellet particles. The proposed correlations express a functional relationship between the mass loss rate and initial moisture content,