Modeling the influence of potassium content and heating rate on biomass pyrolysis

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HIGHLIGHTS

- A single set of kinetic parameters was used for woody and herbaceous biomass.
- Heating rate and potassium content influence char yield the most.
- Particle shrinkage has a negligible effect on char yields.
- Catalytic effects of potassium on char yields most apparent at high heating rates.
- At high heating rates, lower mass fractions of metaplast were formed in the core.

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ABSTRACT

This study presents a combined kinetic and particle model that describes the effect of potassium and heating rate during the fast pyrolysis of woody and herbaceous biomass. The model calculates the mass loss rate, over a wide range of operating conditions relevant to suspension firing. The shrinking particle model considers internal and external heat transfer limitations and incorporates catalytic effects of potassium on the product yields. Modeling parameters were tuned with experimentally determined char yields at high heating rates ($>200 \, K \, s^{-1}$) using a wire mesh reactor, a single particle burner, and a drop tube reactor. The experimental data demonstrated that heating rate and potassium content have significant effects on the char yield. The importance of shrinkage on the devolatilization time becomes greater with increasing particle size, but showed little influence on the char yields.

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1. Introduction

Biomass firing is widely used for power generation. Danish pulverized fuel fired power plants are undergoing a transition to 100% biomass firing in order to reduce greenhouse gase emissions. Straw, wood pellets and wood chips are the most abundant biofuels in Denmark [1]. The annual consumption of biomass at Danish power stations is 1.2 million tones of straw and 0.2 millions of wood chips per year [2]. The advantage of utilizing wheat straw as a renewable energy source is that it is one of the most readily available Danish agricultural residues, while the wood pellet production depends on the supply of imported wood residues [3,4]. The drawback, however, is that the quality of agricultural wastes is lower than that of wood due to a higher ash content leading to

deposition and corrosion of the boiler units. In pulverized biomass combustion, short residence times are required for biomass devolatilization, which makes it difficult to examine the dynamics of the process. In addition, the lignocellulosic material reactivity is affected by the biomass composition, namely organic matter and minerals [5–7]. The differences in char properties generated under various pyrolysis conditions can lead to a range of challenges in a modeling of biomass conversion.

Fast pyrolysis at high temperatures and high heating rates is the initial step in suspension biomass firing. Fuel particles first undergo rapid drying, heating and devolatization with the formation of char and volatiles. Despite of numerous previous studies on biomass devolatilization mechanisms and particle models, there is no generally accepted model that can estimate the conversion rate and final char yield over a wide range of operating conditions. Existing kinetic models [8–14] were developed with experimental data using specific biomass samples and a narrow

Nomenclature

AR	aspect ratio
A_i	pre-exponential factor (s^{-1})
A_p	particle area (m^2)
c_p	specific heat capacity ($J\,(kg\,K)^{-1}$)
d_p	particle diameter (m)
d_{pore}	particle pore diameter (m)
D_r	reactor diameter (m)
E_i	activation energy ($J\,mol^{-1}$)
f_{sh}	shrinkage factor
g	gravity ($m\,s^{-2}$)
h	convective heat transfer coefficient ($W\,(m^{-2}\,K^{-1})$)
ΔH_{vap}	heat of vaporization ($J\,kg^{-1}$)
K_1, K_2	constants for the activation energy of the char formation reaction as a function of biomass potassium content
k_i	reaction rate constant (s^{-1})
L	reactor's length (m)
m	reaction order
n	dimensionality factor
R	gas constant ($J\,(K\,mol)^{-1}$)
r	reaction rate ($kg\,(kg\,s)^{-1}$)
R_p	particle radius at specified interior location (m)
r_p	particle radius (m)
T	temperature (°C)
t	time (s)
V_p	particle volume (m^3)
v_p	slip velocity between gas and particle ($m\,s^{-1}$)
X	conversion
$x_{Fe,max}$	Feret maximum diameter (m)
$x_{Ma,min}$	Martin minimum diameter (m)

Dimensionless numbers

Bi	Biot number
Nu	Nusselt number
Pr	Prandlt number
Re	Reynolds number

Greek symbols

α	particle thermal diffusivity ($m^2\,s^{-1}$)
κ	heating rate ($K\,s^{-1}$)
λ	thermal conductivity ($W\,(m\,K)^{-1}$)
μ	viscosity (Pa s)
Ω	correction factor for influence of potassium content on activation energy ($E_{a,3}$)
ω	K^+ concentration ($mg\,kg^{-1}$)
ψ	biomass fraction of solid phase
ρ	density ($kg\,m^{-3}$)
σ	Stefan-Boltzmann constant ($J\,(s\,m^2\,K^4)^{-1}$)
τ	holding time (s)
ε	emissivity
ξ	void fraction occupied by the gas phase

Subscripts

0	initial
b	biomass
c	char
g	gas
H_2O	water
K	potassium
M	metaplast
max	maximum
$mesh$	wire mesh
min	minimum
p	particle
pyr	pyrolysis
r	radiative
s	solid phase
$total$	overall
w	wall

set of low temperature reaction conditions. The application of lower temperatures makes extrapolation to higher temperatures in combustion/gasification processes.

Most of the existing biomass pyrolysis models [10,15–17] which describe both the devolatilization product composition and yields (light gases, tar and char) are mainly valid for low-ash fuels (hardwood, softwood); whereas considerably less work has been carried out with herbaceous lignocellulosic materials. In addition, these mathematical models are valid for biomass pyrolysis under slow heating rates (1–50 K min^{-1}) and long residence time (1–4 h). Many kinetic models for wood pyrolysis have been reported in the literature [18]. The simplest models are based on a single first order decomposition reaction, and are not able to estimate the influence of heating conditions on the product yields [19] (see Figs. 1 and 2).

Other models assume competing parallel reactions to predict the production kinetics of gas, tar and char, which is often valid only over a narrow temperature range [10,21]. Thurner and Mann [10] assumed that the activation energy for the char formation reaction is similar to the activation energy for mass loss reactions to gas and tar, and therefore, that the final residual weight (e.g. the char yield) is independent of the heating rate and heat treatment
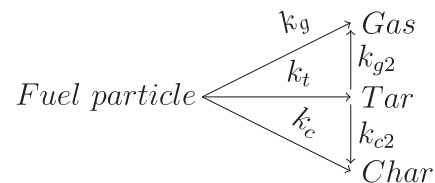
Fig. 2. Competing step global model with k_g - rate constant of gas release, k_c - rate constant of char formation, k_t - rate constant of tar formation, k_{g2} - rate constant for the formation of gas from tar and k_{c2} - rate constant for the formation of char from tar [10].

temperature. More complex models involve additional steps for tar decomposition in the gas phase [22] or an intermediate product derived from primary decomposition of biomass [15,23,24]. These models can be generally applied only for a specific type of biomass. Ranzi et al. [25,26] included the effect of holocelluloses, lignin and extractives on the product yields and composition. Previous models have not included the catalytic effect of alkali metals on biomass devolatilization, which has been shown to influence yields and product release rates significantly [7,27–29]. Extrapolation kinetics fitted under low heating rate conditions to the pulverized fuel firing conditions is difficult due to the changes in devolatilization kinetics with heating rate [20]. Previous pyrolysis kinetic models have failed to extrapolate to higher temperatures because the actual particle heating rate depends on parameters which are difficult to define quantitatively [20,30,31].

$$Fuel\ particle \longrightarrow Volatiles \cdot (1 - \gamma) + \gamma \cdot Char$$

Fig. 1. One-step global model [20].