Thermochemical conversion of biomass in smouldering combustion across scales: The roles of heterogeneous kinetics, oxygen and transport phenomena

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HIGHLIGHTS

- Based on TGA, 3-, 5- and 9-step kinetics are proposed for biomass smouldering.
- The order of biomass oxidation is determined, which is less than one.
- 5-Step kinetics is suitable for biomass smouldering under various X_{O2} and scales.
- Proposed 1D model predicts burning rates in bench-scale biomass smouldering.
- Stochastic sensitivity analysis is applied to test model accuracy and reliability.

GRAPHICAL ABSTRACT
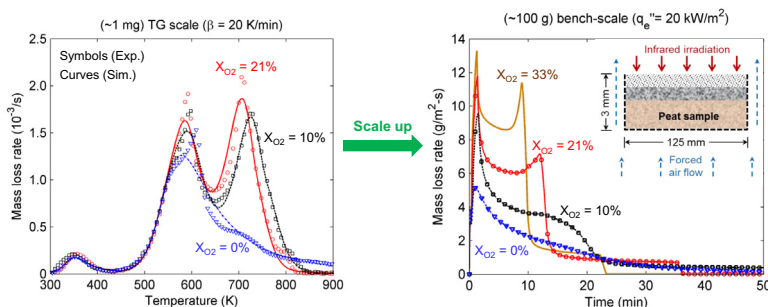
ABSTRACT

The thermochemical conversion of biomass in smouldering combustion is investigated here by combining experiments and modeling at two scales: matter (1 mg) and bench (100 g) scales. Emphasis is put on the effect of oxygen (0–33 vol.%) and oxidation reactions because these are poorly studied in the literature in comparison to pyrolysis. The results are obtained for peat as a representative biomass for which there is high-quality experimental data published previously. Three kinetic schemes are explored, including various steps of drying, pyrolysis and oxidation. The kinetic parameters are found using the Kissinger–Genetic Algorithm method, and then implemented in a one-dimensional model of heat and mass transfer. The predictions are validated with thermogravimetric and bench-scale experiments and then analyzed to unravel the role of heterogeneous reaction. This is the first time that the influence of oxygen on biomass smouldering is explained in terms of both chemistry and transport phenomena across scales.

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1. Introduction

Biomass is a solid fuel of natural origin that can present very high moisture and mineral contents (McKendry, 2002). Once heated, biomass dries and pyrolyzes (Anca-Couce, 2016), and if oxygen is present, it can ignite and support gas-phase homogenous combustion (flaming) or heterogeneous combustion (smouldering) (Ohlemiller, 1985; Rein, 2016). While most studies of biomass combustion have focused on flaming, this paper focuses on smouldering.

Smouldering is the slow, low-temperature, flameless burning of porous fuels and the most persistent type of combustion (Rein et al., 2006). The thermochemical process in smouldering includes drying, pyrolysis and oxidation steps (Ohlemiller, 1985; Huang and Rein, 2014). Therefore, compared to biomass pyrolysis (Di Blasi,

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Nomenclature

c	heat capacity
d_p	characteristic pore size
E	activation energy
h	enthalpy
h_c	convective coefficient
h_m	mass-transfer coefficient
ΔH	heat of reaction
k	thermal conductivity
K	permeability
L	sample size
$\dot{m}''$	mass flux
n	reaction order
P	pressure
$\dot{q}_e''$	irradiation
$\dot{q}_r''$	in-depth irradiation
R	gas constant
S	particle surface area
t	time
T	temperature
X	volume fraction
Y	mass fraction
z	distance
Z	pre-exponential factor

Greek

β	heating rate
γ	radiative coefficient
δ	thickness
ε	emissivity
κ	radiation absorption coefficient
ν	stoichiometric coefficient

ρ	bulk density
σ	Stefan–Boltzmann const.
χ	fraction factor
ψ	porosity
$\dot{\omega}$	reaction rate

Superscripts

$*$	critical or normalized

Subscripts

0	initial
∞	ambient condition
α	α-char
β	β-char
a	ash
b	biomass
c	cellulose
d	destruction
dr	drying
f	formation
g	gas
h	hemicellulose
i	condensed species index
j	gaseous species index
k	reaction index
l	lignin
o	oxidation
p	peat species, or pyrolysis reaction
s	solid
sm	smouldering
w	water

2008; Anca-Couce, 2016), smouldering is more complex and poorly studied. Particularly, biomass smouldering plays an important role in cooking fuels, biochar production, incineration of biowaste, fire hazards and wildfires (Carvalho et al., 2002; Blasi et al., 2004; Rein, 2013).

From a chemical point of view, biomass is a natural composite material, constituted by a mixture of three main components: hemicellulose (H), cellulose (C) and lignin (L) (Di Blasi, 1993; Ding et al., 2016; Anca-Couce, 2016). Neglecting the small amounts of extractives and other species, biomass composition can be approximated as:

$$\text{biomass} \approx Y_h \text{H} + Y_c \text{C} + Y_l \text{L} \tag{1}$$

where Y_i represents the mass fraction of component i. Fig. 1 compares thermogravimetric (TG) data for a series of biomass types under inert or oxidative atmospheres (Niu, 2014; Su et al., 2012; Zhao et al., 2014). A clear similarity in the decomposition process can be observed for pine needle, pine wood, forest peat and moss peat samples. Such similarity implies that there could be a general kinetic scheme to describe biomass thermochemical conversion in both inert and oxidative atmospheres.

Most studies in the literature investigate biomass kinetics using very small samples, at the 1 mg scale, in thermogravimetric (TG) experiments under either inert ambient or air, e.g. Huang and Rein (2014) and Ding et al. (2016). Fewer studies conducted TG experiments under other oxygen concentrations (X_{O_2}, percentage by volume). For example, Zhao et al. (2014) found that as the oxygen concentration decreased to sub-atmospheric levels, the mass-

loss rate of biomass decreased. Amutio et al. (2012) proposed a 6-step kinetics to explain the oxidative pyrolysis of lignocellulosic biomass. Anca-Couce et al. (2012) proposed 3- and 7-step kinetic schemes to explain the TG data of wood under sub-atmospheric oxygen levels. However, studies at the TG scale alone do not provide in-sight about the changing role of chemistry at larger scales where heat and mass transfer processes are also important.

This paper chooses peat as a representative biomass because the literature offers high-quality experimental data in both TG and bench scales. Peat is an organic soil formed through incomplete humification processes of various dead plants. It is porous and forms a char upon heating, thus peat is prone to smouldering combustion (Rein, 2016). Smouldering megafires of peatlands are a very important source of greenhouse gases, and result in the widespread destruction of valuable ecosystems and large regional haze events (Turetsky et al., 2015). Several bench-scale ($\sim$100 g) experiments have studied the influence of oxygen on peat smouldering. Belcher et al. (2010) found that in laboratory scale experiments, smouldering could not be sustained for peat below a critical X_{O_2} of 16%. Hadden et al. (2013) found that smouldering of dry moss peat (MC $\leq$ 10% and IC $\approx$ 2%[1]) exposed to wind could be initiated by an irradiation of 20 kW/m^2 within 1 min under X_{O_2} as low as 11%. In a previous study (Huang and Rein, 2014), a 5-step kinetic scheme (including drying) was proposed and successfully explained

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[1] Moisture content (MC) is defined here in dry basis as the mass of water divided by the mass of a dried soil sample, expressed as %. Inorganic or inert content (IC) is defined here in dry basis as the mass of soil inorganic matter (minerals) divided by the mass of a dried soil sample, expressed as %.