Combustion and Flame 184 (2017) 117–135

Contents lists available at ScienceDirect

Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame

The role of gasification reactions during pulverized solid fuel combustion: A detailed char combustion model based on measurements of char structure and kinetics for coal and pre-treated biomass

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ARTICLE INFO

Article history:
Received 18 December 2016
Revised 23 May 2017
Accepted 29 May 2017

Keywords:
CFD modeling
PF combustion and gasification
Intrinsic reaction kinetics
Char structure evolution
Pre-treated biomass

ABSTRACT

A detailed char combustion model including gasification reactions with emphasis on char structural evolution is developed and validated using combustion experiments from a lab-scale entrained flow reactor burning a bituminous coal and torrified wood. The char combustion model is a single film model based on nth order Arrhenius type equations for char reactions. Diffusion through the particle boundary layer and inside the particle interior is considered by an effectiveness factor approach. Char reactivity towards O_2, H_2O and CO_2 is measured for five different char samples from four different parent fuels, being two bituminous coals and two pre-treated biomasses. Char samples are generated at high heating rates in an entrained flow reactor. Reaction rates and intrinsic reactivity values are quantified using a thermo-gravimetric analyzer. Reaction rates for pre-treated biomass samples are one to two orders of magnitude higher compared with the coal samples. The oxygen reaction is around four to five orders of magnitude faster than gasification reactions in the chemically-controlled reaction regime. The char combustion model is able to accurately describe char conversion and char structural changes. Model results reveal that there might be fragmentation effects in early stages of char conversion, presumably for cenospherical char particles. Particle reaction rates and reaction regimes are shown to vary strongly among different particle sizes and trajectories, and even for a single particle along its profile. Therefore, mean values calculated from CFD results have to be interpreted with care and can be misleading. A parameter study on temperature and stoichiometry shows the importance of gasification reactions. Depending on the conditions, gasification reactions are responsible for 2 up to 60 wt.-% of char conversion. They become relevant in regions of high temperatures and oxygen depletion, e.g. inside the flame. For typical furnace conditions of 1300 °C and a slightly over-stoichiometric flame, the Boudouard reaction accounted for approximately 10 wt.-% and the heterogeneous water-gas shift reaction for 4 wt.-% of char conversion. Therefore, gasification reactions cannot be neglected when predicting fuel conversion in PF systems, particularly in modern staged combustion systems with reducing furnace conditions.

1. Introduction

Solid fuels are still dominating today's power generation and are expected to play a key role for the next decades. Currently, the European Commission is trying to increase the share of biomass-fired combined heat and power stations with high efficiencies by replacing coal with 100% biofuels [1]. In particular, low-grade feedstocks such as forest or agricultural residues are gaining much attention. Often these fuels are pre-treated thermally, in order to increase energy density, transportability and grindability. The goal is to design new biomass-fired units with smaller size and higher efficiency. Therefore, reaction kinetics for biomass and pre-treated biomass are needed to predict their combustion behavior. In general, pulverized fuel (PF) combustion subdivides into the four main steps [2,3]: drying and release of fuel moisture, devolatilization (thermal decomposition and release of volatile matter), igni-

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http://dx.doi.org/10.1016/j.combustflame.2017.05.033
0010-2180/

Latin symbols

A	[m^2] area
A	[(m^3/kmol^{n-1})/s] pre-exponential factor
c_i	[mol/m^3] concentration of species i
c_p	[J/(kg K)] heat capacity
d	[m] diameter
$\bar{d}$	[m] mean diameter for Rosin–Rammler distribution
$D_{A,\ B}$	[m^2/s] diffusion coefficient of species A in species B
D_{Kn}	[m^2/s] Knudsen diffusion coefficient
E_A	[kJ/mol] activation energy
f_h	[-] fraction of heat absorbed by particle
h	[W/(m^2 K)] heat transfer coefficient (often introduced as α)
$\Delta H_{R,\ i}$	[MJ/kg] reaction enthalpy of reactant i
H_{reac}	[W] heat uptake of particle due to reaction
k	[W/(m K)] thermal conductivity
$k_{i,\ 0}$	[kg/(m^2 s atm^n)] pre-exponential factor
m	[kg] mass
$\dot{m}$	[kg/s] mass flow rate
M_i	[kg/kmol] molar mass of species i or symbol denoting species i
n	[-] number of particles or cells, Rosin–Rammler exponent
n_i	[-] reaction order of reactant i
N_i	[-] gravimetric stoichiometric coefficient
Nu	[-] Nusselt number
p_i	[Pa] partial pressure of species i
p	[-] porosity
Pr	[-] Prandtl number
r_i	[s^{-1}] reaction rate for reactant i (observed)
r_{intr}	[kg/(s m^2)] intrinsic reaction rate
rf	[-] roughness factor
R	[J/(mol K)] ideal gas constant
Re	[-] Reynolds number
S	[m^2/kg] specific surface area
Sc	[-] Schmidt number
Sh	[-] Sherwood number
t	[s] time
T	[K], [°C] temperature
$u,\ v,\ w$	[m/s] velocity component in direction x, y and z
w_i	[wt.-%] mass fraction of species i
$x,\ y,\ z$	[m] coordinates in all three spatial directions
x_i	[mol.-%] mole fraction of species i
x	[-] conversion of fuel (char, overall)
Y_d	[-] mass fraction undersize for Rosin–Rammler distribution

Greek symbols

α_{swirl}	[rad] angle of swirl generator
β	[-] diameter exponent
β	[-] mass transfer coefficient
γ	[kg/s^2] surface tension (sometimes defined as σ)
γ_i	[-] volume fraction
ε	[-] emissivity
η	[-] effectiveness factor
$\bar{\eta}$	[-] mean reaction rate weighted effectiveness factor
λ	[-] air-to-fuel equivalence ratio
ν	[-] stoichiometric coefficient
ρ	[kg/m^3] density
ρ_{app}	[kg/m^3] apparent density
ρ_{true}	[kg/m^3] true density
σ	[W/(m^2 K^4)] Stefan Boltzmann constant
τ_{pore}	[-] tortuosity of pores
ϕ	[-] Thiele modulus
Θ	[K] radiation temperature
Ψ	[-] structure parameter for specific surface area

Subscripts

0	initial
10, 50, 90	percentage under this value
a, ash	ash
app	apparent
c, char	char
eff	effective
EFR	entrained flow reactor
f, fuel	fuel (as received)
g	gas
i	species or reactant i
intr	intrinsic
I, II, III	regimes of heterogeneous char conversion
liq	liquid, moisture in the fuel
max	maximum
m, mineral	mineral matter
min	minimum
p	particle
PI, SI	primary or secondary inlet
R	radiation
RT	reaction tube
s	surface
v, vol	volatiles
w	water
W	wall
∞	free-stream, bulk conditions

tion and combustion of volatile matter, and char combustion. Char combustion is known as the slowest step, requiring up to several seconds. Thus, char combustion determines the size of the furnace and the boiler efficiency. A high degree of burnout is needed in order to achieve high boiler efficiencies. Furthermore, carbon in ash should be as low as possible for ash utilization purposes. The process of char conversion is illustrated in Fig. 1. The first step is the diffusion of the reactant to the particle surface (steps 1-2), called boundary layer diffusion or film/bulk diffusion. In the next step, the reactant either reacts with available active carbon sites (3-5) or diffuses into the particle pore systems (2-3), referred to as pore diffusion. The chemical reaction of solid char and gaseous reactant can be separated into adsorption (3-4), chemical reaction (4), and desorption (4-5). In the final steps, the product is transported out of the pores (5-6) and through the particle boundary layer (6-7). The chemical reaction leads to an increase in gas volume in the particle, causing the so-called “Stefan flow”, where the gas flow out of particle openings is driven by the chemical reactions. Each of the above mentioned steps can be the slowest one and thus the limiting step for char conversion. At low temperatures the chemical reaction rate is the slowest step, referred to as regime I. At very high temperatures and for large particles, the diffusion of the reactant to the particle is becoming the slowest step, denoted as regime III. In regime II, the diffusion of the reactant into the particle pores is the rate controlling step. The main parameters influencing the reaction rate and the regime are particle temperature, particle size, surface reactivity and availability of active carbon sites per unit surface area, as well as concentration of reactants. Heterogeneous char reactions can be divided into combustion and gasification reactions according to Table 2. Reactions 1 and 2 from Table 2 are the dominant reactions in PF combustion systems. Both reactions are exothermic with a strong heat production, resulting in increased particle temperatures compared with surrounding gas temperatures. It is often discussed in literature