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Kinetic study and modelling of char combustion in TGA in isothermal conditions

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HIGHLIGHTS

- Experimental study of biomass char combustion in TGA in isothermal conditions.
- Operating conditions: T < 400 °C, 5065 Pa < P_{O2} < 21,273 Pa, d_p = 25 µm.
- Response of the TGA to a concentration step included in the kinetic modelling.
- The GM and the RPM are the more appropriate models to represent kinetic data.
- Activation energy of 124 kJ/mol and reaction order with respect to oxygen of 0.74.

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ABSTRACT

The purpose of this work is the kinetic study of biomass char combustion in isothermal conditions in TGA. This char was obtained from fast pyrolysis of beech bark pellet in a fluidized bed reactor at 850 °C and atmospheric pressure. Kinetic study of isothermal char combustion was performed for temperatures up to 400 °C, oxygen partial pressures ranging from 5065 to 21,273 Pa and a char particles size of 25 µm. Mass transfer effects around and within the crucible were thoroughly characterized by naphthalene vaporization. Oxygen diffusion was found to have no effect on char combustion for temperatures below 400 °C. A novel method including the transfer function of the TGA which describes the variation of oxygen partial pressure just after switching the gas from inert to reactive in the TGA was taken into consideration in the kinetic modelling. Two kinetic models (the Grain Model and the Random Pore Model) were used to determine kinetic parameters. The Grain Model was found to be in very good agreement with experimental data. Values of activation energy and reaction order with respect to oxygen are respectively equal to 124 kJ/mol and 0.74. Besides, the maximum combustion rate commonly observed in the literature during char combustion was found to be the result of the non-uniform oxygen partial pressure in the TGA at the initial stage of the char combustion.

1. Introduction

With the growing environmental concern, biomass gasification is a promising alternative to fossil fuel for power generation. Recently, an increasing interest was showed for the production of methane via Methanation process and "Biomass to Fisher-Tropsch Liquids". Biomass gasification is a thermochemical conversion occurring at high temperatures with many simultaneous reactions. It occurs in two stages: (i) a fast pyrolysis step above 350 °C in which the biomass undergoes a thermal conversion leading to the formation of volatile products either condensable (steam and tars) or non-condensable (H_2, CO, CO_2, CH_4 and C_2H_x) and a solid residue called char [1]; (ii) a gasification step in which the char reacts with steam and carbon dioxide at temperatures greater than 700 °C to produce syngas.

Biomass gasification is an endothermic process. To maintain a fixed temperature in the reactor, a contribution of energy is required. Two types of technology exist for biomass gasification according to the method of heat transmission [2–5]. On the one hand, the heat can be provided by "in situ" combustion. This process includes the fixed bed gasifiers (co- and counter-current) and the "bubbling fluidized bed" gasifiers. In these types of reactor, the biomass undergoes drying, pyrolysis and partial combustion of

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Nomenclature

A	pre-exponential factor
A_{GM}	pre-exponential factor for the Grain Model ($mol.m^{-2}.Pa^{-n}.s^{-1}$)
A_{RPM}	pre-exponential factor for the Random Pore Model ($m.Pa^{-n}.s^{-1}$)
$C^s_{O_2}$	oxygen concentration at the surface of char particles ($mol.m^{-3}$)
$C^\infty_{O_2}$	oxygen concentration in the bulk ($mol.m^{-3}$)
$D_{O_2-CO_2}$	diffusion coefficient of oxygen into carbon dioxide ($m^2.s^{-1}$)
$D_{O_2-N_2}$	diffusion coefficient of oxygen into nitrogen ($m^2.s^{-1}$)
d_g	elementary grain diameter of char particle (m)
d_{pore}	average pore diameter (m)
E_a	activation energy ($J.mol^{-1}$)
$f(X)$	structure function (–)
H	height of the crucible (m)
K_c	global mass transfer coefficient (m/s)
L_0	Initial pore length per unit volume ($m.m^{-3}$)
M_c	molar weight of carbon ($kg.mol^{-1}$)
n	reaction order with respect to oxygen (–)
n_0	initial amount of char in the crucible (mol)
$P_{O_{2,s}}$	oxygen partial pressure at the particle surface (Pa)
R	gas constant ($J.mol^{-1}.K^{-1}$)
R_{app}	apparent reaction rate at X = 0.5 (s^{-1})
R_c	unreacted core of the char particle (m)
r_g	elementary grain radius of char particle (m)
$S_{crucible}$	crucible surface (m^2)
S_0	internal surface area per unit volume ($m^2.m^{-3}$)
S_{p0}	external surface area per unit volume ($m^2.m^{-3}$)
T_p	particle temperature (K)
$V_{crucible}$	crucible volume (m^3)
$w(t)$	temporal sample weight (kg)
w_{ash}	final sample weight (kg)
w_i	Initial sample weight (kg)
X	conversion rate (–)
x_c	mass fraction of carbon in the char particle (–)
$Y^i_{O_2}$	normalized fraction of oxygen at the outlet of CSTR i (i = 1, 2) (–)

Greek letters

δ_c	height of the char layer in the crucible (m)
$\delta_{C_{10}H_8}$	height of the naphthalene layer in the crucible (m)
ε	porosity of the char layer in the crucible (–)
ε_p	particle porosity (–)
ρ_a	apparent density of grinded char particles ($kg.m^{-3}$)
$\rho_{t,c}$	true density of char particle ($kg.m^{-3}$)
τ	tortuosity of the char layer $\tau = \sqrt{2}$ (–)
τ_{CSTR}	residence time of the CSTR (s)
φ	structural parameter of the Random Pore Model (–)

volatile matters and char and finally the gasification of char. On the other hand, the heat can be supplied by "ex-situ" combustion of char. One of the most promising technologies which uses "ex-situ" combustion is dual or twin fluidized bed (FICFB: Fast Internally Circulating Fluidized Bed) [6]. Its principle relies on the circulation of a medium (sand, olivine or catalyst particles) which acts as a heat carrier between an endothermic reactor and an exothermic reactor. In the former (called gasifier) which operates around 750 °C–850 °C, biomass gasification is carried out to produce syngas. In the exothermic reactor (called combustor) which proceeds at 900 °C–950 °C, a part of the char from the gasifier is burned to produce heat.

During biomass gasification, especially with FICFB, char reacts with steam and carbon dioxide in the gasifier and oxygen in the combustor. Information regarding the kinetic of char combustion is then essential to better understand phenomena occurring inside the combustor and to design this process.

Char combustion corresponds to a complex chemical transformation which occurs in several steps: the external transfer of oxygen from the bulk to the external surface of the particle, the diffusion of oxygen within the pores of the solid, the oxygen chemisorption on an active site (adsorption), the intrinsic chemical reaction and finally the products desorption [7,8]. These different steps are strongly affected by the physicochemical properties of char, the combustion temperature, the oxygen partial pressure and the size of the solid particles.

A previous study was carried out to highlight the effect of pyrolysis operating conditions on the physicochemical properties and reactivity of two biomass chars [9]. We showed that the physicochemical structure of char is strongly dependent on the pyrolysis conditions (heating rate, pyrolysis temperature and the nature of the biomass). These parameters influence hydrogen, oxygen, carbon and ash content in the char as well as the presence of aromatic and amorphous carbon. The presence of inorganic matters (i.e. ash) in the char matrix was found to catalyze the reaction of combustion [9]. In addition, bibliographic works showed that:

1) An increase in the particle heating rate during biomass pyrolysis increases the reactivity of char [10–14].
2) A higher pyrolysis pressure yields to a decrease of char reactivity [11,15].
3) The effect of the soaking time is not well understood yet. The soaking time represents the residence time of char at final pyrolysis temperature. This parameter was found to decrease char reactivity for certain authors [12,16] and to have no effect on char reactivity for other researchers [14].
4) A raise of the final pyrolysis temperature leads to a decrease of char reactivity. The char reactivity greatly depends on the nature of the biomass. It is strongly influenced by the char chemical structure and ash content [9].

The reaction of combustion may be divided into three main regimes according to the temperature, the oxygen partial pressure and the particles size [8]. In Regime I, the intrinsic reactivity of the solid is low with respect to oxygen diffusion inside the pore and external transfer around the particle. The concentration of oxygen is considered as uniform inside the particle and equal to that in the bulk gas stream. The intrinsic chemical reaction is then the limiting step. The Regime II is the transition regime where both the diffusion of oxygen and the intrinsic chemical reaction play a significant role. These two phenomena must be taken into account to represent the char reactivity. In Regime III, the intrinsic reactivity of the solid is very high and oxygen molecules react at the particle surface as soon as they have passed the boundary layer around the particle. Therefore, the concentration of oxygen at the external surface of the particle is zero and the reaction rate is controlled by external mass transfer. Hence, to determine char-O_2 combustion kinetic, many authors [17,18] minimized mass and heat transfers. This can be achieved by carefully choosing the combination of combustion temperature, oxygen partial pressure and particles size so that char combustion occurs in chemical kinetic controlled regime (Regime I).