



Kinetic study of biomass char combustion in a low temperature fluidized bed reactor



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ABSTRACT

The purpose of this work is the kinetic study of biomass char combustion in a low temperature fluidized bed reactor. This char was obtained from fast pyrolysis of beech stick in an annex batch fluidized bed reactor at 923 K and atmospheric pressure. Operating conditions of the combustion were thoroughly characterized so that the reaction takes place in isothermal conditions and a constant oxygen partial pressure. The kinetic study was performed for temperatures up to 643 K, oxygen partial pressures ranging from 5065 to 21273 Pa and cylindrical char particles ($D = 4$ mm and $L = 9$ mm). The Volumetric 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 144 kJ/mol and 0.59. The reaction scheme during char combustion showed that char first reacts with oxygen to form CO which is further oxidized either at the particle surface or in the gas phase to produce CO₂. Besides, it was found that the char reactivity in combustion is higher in a fluidized bed reactor compared to TGA. This was explained by diffusional effects of oxygen and CO oxidation within the crucible in the TGA.

1. Introduction

Biomass is a possible alternative to the direct use of fossil fuel in gasification process as it has the advantage of being neutral in regard to the CO₂ emissions considering photosynthesis reactions. Biomass gasification produces synthesis gas which can be directly burned for heat and electricity production or used as a feedstock for the production of methane via Methanation process or liquid via Fisher-Tropsch process. Biomass gasification is a thermochemical conversion occurring at high temperatures with many simultaneous reactions. It occurs in two stages: (i) for temperatures above 623 K, biomass undergoes a fast thermal conversion. This pyrolysis step converts the biomass into volatile products either condensable (steam and tars) or non-condensable (H₂, CO, CO₂, CH₄ and C₂H₂) and a solid residue called char [1]; (ii) for temperatures greater than 973 K, the char reacts with steam and carbon dioxide. This gasification step converts the char into synthesis gas.

The reactive system of biomass conversion (i.e. pyrolysis + gasification) is an endothermic process. A contribution of energy is necessary in order to maintain the temperature and the different reactions in the reactor. Two types of technologies exist for biomass gasification according to the method of heat transmission [2]. Firstly, the heat can be supplied by partial combustion of the fuel in the gasifier itself. This process includes the fixed bed gasifiers (co- and counter-current) and the “bubbling fluidized bed” gasifiers. Secondly, the heat can be

provided from a source outside of the gasifier by external heat (plasma or solar) or internal recirculation of gas and char. In the latter approach, Fast Internally Circulating Fluidized Bed (FICFB) [3] is currently a promising process which uses a circulation of a medium between an entrained bed exothermic reactor and a dense endothermic reactor. In the exothermic reactor called combustor, a part of the char from the gasifier is burnt and heats the medium. In the endothermic reactor called gasifier, the medium provides the heat necessary for the biomass gasification.

During biomass gasification in dual fluidized bed, the char reacts with steam and carbon dioxide in the gasifier and with oxygen in the combustor. Information regarding the kinetic of char combustion in a fluidized bed reactor is then essential to better understand phenomena inside a combustor.

The char combustion proceeds 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 [4,5]. Together, these different steps are strongly affected by the physicochemical properties of the char, the combustion temperature, the oxygen partial pressure, the size of the solid char particles and the type of reactor.

The physicochemical properties and the reactivity of biomass char depend on the pyrolysis operating conditions. This has been discussed

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Nomenclature			
A_{VM}	pre-exponential factor for the Volumetric model ($\text{Pa}^{-n} \cdot \text{s}^{-1}$)	$S_{crucible}$	crucible surface (m^2)
$C_{O_2}^s$	oxygen concentration at the surface of the char particles ($\text{mol} \cdot \text{m}^{-3}$)	t_f	final time of the combustion (s)
$C_{O_2,i}$	oxygen concentration at the CSTR outlet i ($\text{mol} \cdot \text{m}^{-3}$)	T_p	particle temperature (K)
E_a	activation energy ($\text{J} \cdot \text{mol}^{-1}$)	$w(t)$	instantaneous sample weight (kg)
$f(X)$	structure function (-)	w_{ash}	final sample weight (kg)
H	height of the crucible (m)	w_i	initial sample weight (kg)
K_c	global mass transfer coefficient (m/s)	X	conversion rate (-)
n	reaction order with respect to oxygen (-)	X_c	carbon conversion rate (-)
$n_{char,crucible}$	initial amount of char in the crucible (mol)	$x_i(t)$	molar fraction of component i (-)
$(n_{carbon})_{char}$	initial amount of carbon in 2.2 g of STI650 (mol)	$Y_{H_2}^i$	normalized fraction of hydrogen at the outlet of CSTR i (-)
$\dot{n}_i(t)$	instantaneous total molar flow rate ($\text{mol} \cdot \text{s}^{-1}$)	Greek letters	
$\dot{n}_i(t)$	instantaneous partial molar flow rate of component i ($\text{mol} \cdot \text{s}^{-1}$)	δ_c	height of the char layer in the crucible (m)
$P_{O_2,s}$	oxygen partial pressure at the particle surface (Pa)	ε	porosity of the char layer in the crucible (-)
R	universal gas constant ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)	ε_p	particle porosity (-)
R_{app}	apparent reaction rate at $X = 0.5$ (s^{-1})	ρ_a	apparent density ($\text{kg} \cdot \text{m}^{-3}$)
		ρ_t	true density of the char particle ($\text{kg} \cdot \text{m}^{-3}$)
		τ	tortuosity of the char layer $\tau = \sqrt{2}$ (-)
		τ_{CSTR}	residence time of the CSTR (s)

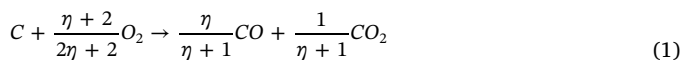
in a previous paper [6]. It was shown that the pyrolysis operating conditions such as the heating rate, the pyrolysis temperature and the biomass nature strongly influence the amount of hydrogen, oxygen, carbon and ash content in the char as well as the presence of aromatic and amorphous carbons. Besides, a raise of the heating rate during biomass pyrolysis increases the char reactivity while a raise of the final pyrolysis temperature decreases the reactivity. The amount of ash in the char matrix may also catalyze the reaction of combustion.

The reaction of combustion can be divided into three main regimes according to the temperature, the oxygen partial pressure and the char particles size [5]. In Regime I (i.e. low temperatures), the intrinsic chemical reaction is low with respect to oxygen diffusion inside the pores and external transfer around the particle. The intrinsic chemical reaction is the limiting step. The Regime II (i.e. medium temperatures regime) is the transition regime where both the intrinsic chemical reaction and the diffusion of oxygen play a significant role. In Regime III (i.e. high temperatures regime), the intrinsic reactivity of the solid is very high and oxygen molecules react as soon as they have passed the boundary layer around the particle. External mass transfer is then the limiting step. Consequently, to determine char- O_2 combustion kinetic, many authors [7–9] minimized mass and heat transfers by carefully choosing the combination of combustion temperature, oxygen partial pressure and particles size so that the combustion occurs in the chemical control regime (i.e. Regime I).

The char combustion is highly dependent on the combustion temperature and the oxygen partial pressure. It is well known in the literature that the combustion rate increases by raising these two parameters [7,8,10–15]. Several authors [9,16–18] also showed that the char particles size influences oxygen diffusion inside the particle which

may lead to a non-uniform oxygen concentration. Consequently, the combustion temperature, the oxygen partial pressure and the char particles size influence the regime of combustion (i.e. Regime I, II or III).

The most widely used treatment to represent char-oxygen reaction is based on a simple global reaction [19–24]:



where η represents the product ratio of CO over CO_2 .

However, there has been much controversy in the literature [23] to identify whether the reaction involved is



followed by CO oxidation in the gas-phase to form CO_2 , or, alternatively, the reaction may be



Overall, the authors [25–29] focused on the determination of the CO/CO_2 product ratio in order to determine whether the carbon dioxide is a primary product of the carbon-oxygen reaction or a secondary product resulting from the gas-phase oxidation of carbon monoxide.

Table 1 summarizes some previous works in regard to the CO/CO_2 product ratio. In these studies, the researchers used several techniques such as low oxygen partial pressures, high gas velocities, gaseous inhibitors and low temperatures of the surrounding gas in order to minimize the CO oxidation in the gas phase. Consequently, they exclusively measured the heterogeneous reaction between carbon and oxygen. For instance, Tognotti et al. [25] avoided oxidation of CO to

Table 1
Expression of CO/CO_2 product ratio from the combustion of carbon in the literature.

Ref	Carbon type	Reactor	Temperature (K)	P_{O_2} (bar)	Expression CO/CO_2
[25]	Spherocarb char	Electrodynamic balance	670–1670	0.05–1	$50 \cdot \exp\left(-\frac{3070}{T}\right) \cdot P_{O_2}^{-0.21}$
[26]	Soot particle	TGA	663–893	0.05–1	$A \cdot \exp\left(-\frac{3200}{T}\right) \cdot P_{O_2}^{-0.27}$
[27]	Graphon	Static system	798–948	$1.3 \cdot 10^{-5}$ $2.6 \cdot 10^{-4}$	$A \cdot \exp\left(-\frac{3200}{T}\right) \cdot P_{O_2}^{-0.22}$
[28]	Artificial graphite Coal char	Flow system	733–1173	0.05–0.25	$2500 \cdot \exp\left(-\frac{6240}{T}\right)$
[29]	Petroleum coke	Fluidized bed	850–970	0.21	$1340 \cdot \exp\left(-\frac{7640}{T}\right)$

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