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Pyrolysis of biomass in a batch fluidized bed reactor: Effect of the pyrolysis conditions and the nature of the biomass on the physicochemical properties and the reactivity of char

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ABSTRACT

This work was carried out in order to understand the effect of the pyrolysis operating conditions and the nature of the biomass on the physicochemical properties of the char and its reactivity toward the combustion. The chars were obtained by fast pyrolysis of two types of cylindrical wood particle (beech stick: diameter of 6 mm, length of 10 mm and beech bark pellet: diameter of 10 mm, length of 15 mm) under an inert atmosphere of nitrogen in a fluidized bed reactor for three different temperatures (450, 650 and 850 °C) and at atmospheric pressure. The ultimate and FTIR analyses revealed that an increase in the pyrolysis temperature led to a raise of the carbon content and a decrease in the oxygen and hydrogen content. At high pyrolysis temperatures, Raman spectroscopy and XRD analyses showed that the char is more and more aromatic with a large size of the aromatic rings. The different chars prepared at a pyrolysis temperature of 850 °C exhibited a true density close to the one of graphite. The reactivity of chars was studied by isothermal combustion at 400 °C in TGA. The reactivity was found to be highly dependent on the pyrolysis temperature and the nature of the biomass. An increase in the pyrolysis temperature led to a decrease of the reactivity. Besides, char from fast pyrolysis of beech bark pellet is more reactive than char from fast pyrolysis of beech stick.

1. Introduction

Biomass gasification is a promising alternative to fossil fuels for the synthesis of highly energetic products via Fischer-Tropsch or Methanation processes. It is a thermochemical conversion occurring from medium to high temperatures with many simultaneous reactions. In the case of monodisperse particles, biomass gasification is done in two steps:

(1) For temperatures up to 200 °C, the biomass is dried. Above 350 °C, biomass undergoes a thermal degradation called pyrolysis or devolatilisation occurring in the absence of oxygen which leads 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 carbonaceous residue called char [1]. For instance, the product distribution of the fast pyrolysis occurring at 850 °C is about 5% of condensable gases, 85% of non-condensable gases and 10% of char [2].
(2) Then, the char reacts with steam, oxygen or carbon dioxide in an oxidizing atmosphere at temperatures greater than 700 °C to produce syngas.

The char is a complex solid residue composed of carbon, hydrogen, oxygen and inorganic matters (ashes). The fundamental carbon structure of the char is the aromatic ring structure. The hydroaromatic and aliphatic structures account for most of hydrogen while hydroxyl (—OH), carboxyl (—COOH) and carbonyl (=CO) forms are the major oxygen functional groups [3]. For instance, Laurendeau [3] observed that a typical bituminous coal consists of a series of aromatic and hydroaromatic clusters containing an average of 2–5 rings per cluster and joined together by methylene and aliphatic linkages. Char is also a porous material composed of micropores, mesopores and macropores which are usually classified by considering three cylindrical diameter ranges d_{pore}:

(1) Micropores: $d_{pore} < 2$ nm,
(2) Mesopores: $2 \text{ nm} < d_{pore} < 50$ nm,

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(3) Macropores: $d_{pore} > 50$ nm.

Biomass gasification is an endothermic process. Therefore, a contribution of energy is required to maintain a sufficient temperature in the reactor so that endothermic reactions can be carried out. Several technologies are used for biomass gasification [4–7]. These technologies can be divided into two categories depending on the mode of heat transmission:

- In the first case, the energy is provided by the partial combustion of biomass inside the reactor (in situ combustion). This first category includes: the fixed bed gasifiers (co-current – counter-current) and the "bubbling fluidized bed" gasifiers. They are used for the production of a synthesis gas that can be used for the production of heat and electricity or in cogeneration. Several mechanisms are present in these types of reactor including biomass drying and pyrolysis, the partial combustion of volatile matters and char and finally the gasification of char. Consequently, the energy necessary for the gasification is provided by the partial combustion of biomass inside the reactor [4,6,7].
- Another encouraging technology is dual or twin fluidized bed [8]. This process uses the ex situ combustion of char. Its principle relies on the circulation of a media (for instance: sand, olivine or catalyst particles) which acts as a heat carrier between an endothermic reactor and an exothermic reactor. In the former called gasifier, biomass gasification is carried out to produce syngas. In the exothermic reactor called combustor, a part of the char from the gasification process is burned to produce heat. The heat generated by the combustion provides the energy necessary for the gasification. Hence, the media soaks up the heat in the combustor to release it in the gasifier.

During these biomass gasification processes, char reacts with steam, carbon dioxide or oxygen. Thus, in order to better understand the phenomena occurring within the reactors, information concerning the influence of the nature of biomass and operating conditions of the pyrolysis step on the reactivity of char become essential. Char reactivity depends on three parameters: (1) the chemical structure of the solid, (2) inorganic matters content and (3) porosity of the particle [3]. Chemical structure of the solid promotes the formation of active sites which are highly dependent on the concentration of carbon edges, defects and dislocations as well as oxygen and hydrogen content. Inorganic constituents foster catalytic activity and further dislocations. Finally, the porosity corresponds to the total accessible surface area which control diffusion rate and the local concentration of gaseous reactants [3]. Together, these three parameters are affected by pyrolysis conditions.

Pyrolysis corresponds to a complex chemical transformation. It is well established today that operating conditions during pyrolysis of biomass – such as nature of the biomass, heating rate, final temperature, pressure, soaking time and gas atmosphere – influence the amount and the nature of volatile products and the physico-chemical properties of the produced char [1,3]. In the literature, several techniques were used to study the structure and properties of chars either from pyrolysis of coal or fewer from pyrolysis of biomass.

The heating rate has an influence on the pyrolysis products. Williams et al. [9] reported that a higher heating rate leads to the formation of lower yields of char and higher yields of gas and liquid. For instance, during the pyrolysis of pine wood at a final temperature of 720 °C, the amount of CO increases from 0.070 mol to 0.230 mol from 5 to 80 K/min, respectively [9]. The heating rate is also known to influence the char reactivity. Some authors [10–14] concluded that an increase in the heating rate increases the reactivity of char. Guerrero et al. [10] observed that a char obtained by slow pyrolysis of eucalyptus under a constant heating rate of 10 °C/min is less reactive toward oxygen than char from fast pyrolysis in a fluidized bed reactor. The authors suggested that a higher heating rate enables higher surface area, higher oxygen and hydrogen content and higher availability of active sites. Cetin et al. [11] mentioned that the higher reactivity of char at high heating rate is due to the higher total surface areas of the char. Mermoud et al. [14] also pointed out that the char prepared at low heating rate (2.6 °C/min) is denser and has a reactivity 2.6 times lower than the char obtained at high heating rate (900 °C/min). Lu et al. [15] showed that chars prepared at low heating rate exhibit higher ordering in structure which is further developed.

The final pyrolysis temperature plays a significant role on the pyrolysis products as well as on the structure and the reactivity of char. An increase in the pyrolysis temperature increases the yield of gas and decreases the yield of char [16,17]. Liquid yields are maximized under flash pyrolysis conditions and present a maximum yield around 500 °C before decreasing. Most of the molar fractions of the component in the gas also increase [16]. Hémati et al. [18] observed that the amount of CO_2 is reduced by increasing pyrolysis temperature which is due to the Boudouard reaction favored at higher temperatures. The different authors [19–22] agreed that an increase in the final pyrolysis temperature leads to a decrease in the char reactivity. This is due to the improvement in structural ordering of the char and the presence of larger aromatic rings system by increasing pyrolysis temperature. By using characterization techniques such as FTIR and NMR spectroscopy, Sharma et al. [23,24] concluded that char has a higher hydrogen and oxygen content at low pyrolysis temperature (below 400 °C) and becomes more and more aromatic by increasing pyrolysis conditions.

The pyrolysis pressure has an effect on the yield of char and volatile products. For instance, an increase in the pyrolysis pressure from 1 to 5 atm increases the yields of char and CO_2 but decreases the yeilds of CO, CH_4 and H_2 [25]. According to several authors [11,26], a higher pyrolysis pressure yields to a decrease in the char reactivity. Okumura et al. [26] studied the effect of pyrolysis pressure from 0.1 to 3 MPa at 800 °C during the pyrolysis of Douglas-fir chips on the reactivity of char with carbon dioxide. They attributed the decrease of char reactivity with pyrolysis pressure to the raise of carbonaceous structure of the char. In the case of coal devolatilisation, Roberts et al. [27] concluded that char made from high pyrolysis pressure of Australian coal is more reactive towards H_2O and CO_2 than char produced at atmospheric pressure and attributed this effect to the increase of surface area at high pyrolysis pressure.

The soaking time corresponds to the residence time of the char at the final pyrolysis temperature. Some authors studied the effect of this parameter on the char reactivity [12,14,28,29]. After biomass devolatilisation, the residence time at the final pyrolysis temperature leads to the modification of the solid structure of the char which influences the reactivity. According to several researchers [12,28], this time decreases the char reactivity. For instance, Kumar et al. [12] observed that the reactivity of both acacia and eucalyptus chars decreases as the soaking time increases. This phenomenon is also called thermal annealing. This is due to the fact that prolonged heating at the final pyrolysis temperature improves structural ordering of the char and the loss of active sites. By carrying out slow and fast pyrolysis of wood and agricultural residues, Zanzi et al. [28] concluded that char obtained by rapid pyrolysis contains a fraction that can be volatilized further by slow pyrolysis. Consequently, the authors divided the pyrolysis into two steps: an initial fast pyrolysis step completed within seconds followed by a slower step including some chemical rearrangements of the char which takes several minutes to be completed. Senneca et al. [29] studied the effect of carbonization time – from 1 to 300 min – at a given temperature of a bituminous coal on the reactivity with carbon dioxide. They found that thermal annealing has a larger effect in the early stage of the char gasification and vanished at conversion