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Original Article

Kinetic thermal behaviour and evaluation of physical structure of sugar cane bagasse char during non-isothermal steam gasification

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ABSTRACT

In the current study, the steam gasification reactivity, thermal behaviour and activation energies of sugar cane bagasse (SCB) chars prepared at 500, 800 and 900 °C were investigated via thermogravimetric analyser (TGA) under non isothermal conditions at different heating rates of 10, 15 and 20 °C min^{-1}. The physical structures of SCB chars as a function of pyrolysis temperature have been studied by using Brunauer–Emmett–Teller (BET) surface area technique. The achieved results explore that the gasification of SCB chars took place almost completely in one-stage process. The char reactivity is directly proportional to gasification heating rate and inversely to the pyrolysis temperature. The pyrolysis temperature significantly affected on the physical char structures. The activation energies were estimated by Vyazovkin and Ozawa–Flynn–wall methods. The Vyazovkin and Flynn–Wall–Ozawa methods show mean activation energies of 131.20–141.61 kJ mol^{-1} for SCB 5, 195.40–203.17 kJ mol^{-1} for SCB 8 and 246.84–252.66 kJ mol^{-1} for SCB 9. Finally, Vyazovkin and Ozawa–Flynn–Wall methods are efficiently utilized to predict the experimental data and the reaction mechanism of SCB chars steam gasification.

1. Introduction

Biomass is one of the most environmentally friendly fuels. It is a potential renewable energy resources to replace the depletion of fossil-fuel have attracted attention [1], which allows energy generation from biological, by-product material and agricultural residues such as sugar cane bagasse (SCB) [2,3]. In comparison to other agricultural residues, bagasse is considered as a rich solar energy reservoir due to its very high yields. Bagasse offers the advantage of being a cheap, plentiful and low polluting fuel. In addition, chemical energy

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harvesting from bagasse is attractive since it is a renewable source of energy, and the combustion/gasification of sugarcane produces the same amount of CO_2 as it consumes during its growth so it has a neutral carbon [4]. By implementing thermo chemical upgrading of bagasse the energy efficiency can be increased significantly, resulting in energy saving and surplus energy products [5]. The biomass char is a solid carbonaceous residue with a high content of fixed carbon, which can be used as a potential resource in diverse industries, depending on their characteristics, directly as a fuel, fertilizer or precursor for activated carbon production, aluminium, copper, cement industries, for the production of chemicals and activation carbon [6,7].

Gasification can be divided into two main stages: pyrolysis and char gasification. Since char gasification determines the final conversion achieved in the process, the char gasification process is a much slower conversion process compared to the initial pyrolysis. Thus, it is dominant in the whole gasification process and is very much dependent on the development of a porous char structure in the pyrolysis stage [8–11]. Char gasification consists of a series of heterogeneous reactions (e.g. the steam reaction) of the carbon in the chars with the gasification agent (steam), and reactions among reactant and resultant gases. Hence, the char gasification directly depends on char reactivity with a gasification agent.

Steam gasification reaction (Eq. (1)) is endothermic. So, for practical applications of the steam-only gasification, it is necessary to produce heat from an external source [12].

$$C + 2H_2O \rightarrow CO + H_2 \quad \Delta H = 131.4\,\text{kJ mol}^{-1} \tag{1}$$

Based on the active site concept [13,14], the steam gasification of char takes place according to two basic mechanisms indicated as the oxygen exchange mechanism and the hydrogen inhibition mechanism [13]. The steps to be considered are:

$$\text{Step 1} \quad C_{fas} + H_2O \xrightarrow{k_1} C(O) + H_2 \tag{2}$$

$$\text{Step 2} \quad C(O) + H_2 \xrightarrow{k_2} C_{fas} + H_2O \tag{3}$$

$$\text{Step 3} \quad C(O) \xrightarrow{k_3} CO \tag{4}$$

$$\text{Step 4} \quad C_{fas} + H_2 \xrightarrow{k_4} C(H)_2 \tag{5}$$

$$\text{Step 5} \quad C(H)_2 \xrightarrow{k_5} C_{fas} + H_2 \tag{6}$$

$$\text{Step 6} \quad C_{fas} + 0.5H_2 \xrightarrow{k_6} C(H) \tag{7}$$

$$\text{Step 7} \quad C(H) \xrightarrow{k_7} C_{fas} + 0.5H_2 \tag{8}$$

where k_i is the rate of the ith reaction.

The oxygen exchange mechanism consists of steps (1)–(3). The hydrogen inhibition mechanism may consist either of steps (1), (3) and (4), (5) or steps (1), (3) and (6), (7). For the oxygen exchange mechanism, hydrogen inhibition is due to the equilibrium of the dissociation reactions (1) and (2). For the first hydrogen inhibition mechanism, the formation of the C(H)$_2$ complex is the reason of the inhibition. In the other case, a dissociative chemisorption of H_2 on the active sites occurs and in this way the active sites become not accessible for the oxygen transfer with steam.

Reactivity is one of the most important parameters determining fuels suitability for the use in the gasification process at industrial scale [15]. For this reason, the knowledge of the reactivity of char and its transformation stages during the reaction is vital for designing gasification reactors because char gasification defines the overall rate of conversion [16]. The kinetic analysis of char is important for the projections that involve gasification reactors because gasification is a slower process than pyrolysis. Additionally, gasification causes continuous changes in the char structure, and char reactivity therefore exhibits a tendency to change, depending on the time and the stage of reaction. Reactivity of the char quantified by kinetic parameters is also an important factor which can serve as an index for comparison of different coals and biomass to predict system performance. In thermal analysis activation energy mainly affects the temperature sensitivity of the reaction rate. Char reactivity, therefore, may be sufficiently characterized by its activation energy value alone [17]. The application of gasification process technologies involving biomass, petroleum coke and coal for power generation requires a proper understanding of the thermal properties and reaction kinetics of them.

The effect of pyrolysis conditions such as (heating rate, pressure, residence time and temperature) on the structure and gasification reactivity of biomass chars were investigated by several authors [7,9,11,18,19]. Among them, Fanfei Min et al. [11] investigated the effect of the pyrolysis temperature on the reactivity, physical and chemical structures of agricultural waste chars (corn straw and wheat straw) generated under various lower pyrolysis temperatures (500, 600, 700 and 800 °C). They reported that char gasification reactivity decreases with the pyrolysis temperature increases. The char particles generated under high pyrolysis temperatures had many smaller pores with thinner cell walls, larger surface areas, and some melting. Raphael Idem et al. [18] studied the effect of the pyrolysis temperature on the char characteristics of flax straw, they found that the pyrolysis temperature has a significant impact on the micro-structure of chars and has a stronger influence on the char reactivity compared to pyrolysis residence time in the isothermal regime. They also found that the degree of porosity and graphitization increased with an increasing pyrolysis temperature. The chars formed at pyrolysis a lower temperature were found to be more reactive than the chars produced at a higher pyrolysis temperature.

Edreis et al. [19]. studied the effect of gasification heating rate and the kinetic thermal behaviour of sugar cane bagasse chars prepared at 500, 800 and 900 °C during CO_2 gasification, they found that the gasification of SCB chars occurred in one-stage process. They also found that the maximum rate of mass loss and its corresponding temperature are directly proportional to pyrolysis temperature and gasification heating rate.

The information and understanding of behaviour, kinetics, char reactivity and its variation during gasification are essential for proper designing of gasification reactors. These play an important role in the large-scale gasification process.