Journal of Analytical and Applied Pyrolysis 107 (2014) 107–115

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

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

Investigations of the structure and thermal kinetic analysis of sugarcane bagasse char during non-isothermal CO_2 gasification

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ARTICLE INFO

Article history:
Received 29 December 2013
Accepted 9 February 2014
Available online 19 February 2014

Keywords:
Sugar cane bagasse
Gasification
Char structure
TGA/BET/FTIR
Reactivity
Activation energy

ABSTRACT

The CO_2 gasification reactivity, thermal behaviour and activation energies of sugar cane bagasse (SCB) chars prepared at 500, 800 and 900 °C were investigated by using thermogravimetric analysis (TGA) under non isothermal conditions at different heating rates of 20, 30 and 40 °C min^{-1}. The characteristics (physical and chemical structures) of the sugar cane chars as a function of pyrolysis temperature have been studied by applying Brunauer–Emmett–Teller (BET) surface area and Fourier transform infrared spectroscopy (FTIR) techniques. The results have demonstrated that the gasification of SCB chars took place almost completely in one-stage process as it has been shown by the presence of only one peak in DTG curve. The char reactivity is an inversely proportional to the pyrolysis temperature and directly to a gasification heating rate. As pyrolysis temperature increases, the char physical structures (BET surface area, pores characteristics) are directly proportional to the pyrolysis temperature. The hydroxyl, aliphatic C–H, carbonyl and olefinic C=C groups were lost at high pyrolysis temperatures (800 and 900 °C). The activation energies were estimated by using Vyazovkin and Ozawa–Flynn–Wall methods, which have resulted in the mean of activation energy values of 70.44–88.37, 89.16–101.55 and 107.20–115.29 kJ mol^{-1}, respectively for char prepared at 500, 800 and 900 °C. Finally, Vyazovkin and Ozawa–Flynn–Wall methods were effectively applied to predict the reaction mechanism of thermal gasification.

1. Introduction

Biomass resources as a potential renewable energy resource 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]. Bagasse is a fibrous residue of the cane stalk after crushing and extraction of the juice, which consists of approximately 26.6–54.3% cellulose, 22.3–29.7% hemicelluloses, 14.3–24.45% lignin and about 2–4% ash on a dry basis [4,5]. 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 harvesting from bagasse is attractive since it is a renewable resource of energy, and the combustion/gasification of sugarcane produces the same amount of CO_2 as it is consumed during its growth so it has a neutral carbon [2,4]. By implementing thermo chemical upgrading of bagasse, the energy efficiency can be increased significantly, resulting in energy saving and surplus energy products [6]. 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 its characteristics, directly as a fuel, fertiliser or precursor for activating carbon production, aluminium, copper, cement industries, for the production of chemicals and activation carbon [7,8].

The gasification of solid fuel can be divided into two main stages after the initial short drying: devolatilization (pyrolysis) and char gasification. 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 [9–12]. Char gasification consists of a series of heterogeneous reactions (e.g. Boudouard reaction) of the carbon in the chars with the gasification agent (carbon dioxide), and reactions among reactant and resultant gases. Hence, the char gasification directly depends on char reactivity with gasification agent. Reactivity is one of the most important parameters determining fuels suitability for the use in the gasification process at an industrial scale [13].

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http://dx.doi.org/10.1016/j.jaap.2014.02.010
0165-2370/

For this reason, the knowledge of the reactivity of char and its transformational stages during the reaction is vital for designing gasification reactors, because char gasification defines the overall rate of conversion [14]. The kinetic analysis of char is important for the projections that involve gasification reactors, because gasification is slower process than pyrolysis. Additionally, gasification causes continuous changes in the char structure and reactivity, therefore exhibits a tendency to change, depending on time and the stage of reaction. Reactivity of the char is quantified by kinetic parameters is also an important factor which can serve as an index for comparison of different coals and coal-biomass blends to predict the system performance. In thermal analysis activation energy mainly affects on the temperature sensitivity of the reaction rate. Char reactivity, therefore may be sufficiently characterised by its activation energy value alone [15]. The application of gasification process technologies involves 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 [8,10,12,16]. Among them, Min et al. investigated the effect of the pyrolysis temperature on the reactivity, physical and chemical structure of agricultural waste chars (corn straw and wheat straw) were generated under various lower pyrolysis temperatures (500, 600, 700 and 800 °C). They have reported that char gasification reactivity decreases with the pyrolysis temperature increase. The char particles which were generated under high pyrolysis temperatures had many smaller pores with thinner cell walls, larger surface areas, and some melting. The results have indicated that many functional groups' bands decreased and even disappeared with an increasing pyrolysis temperature. Idem et al. [16] studied the effect of the pyrolysis temperature and residence time on the char characteristics of flax straw. They have found that the pyrolysis temperature was found to have 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. Also they have found that the degree of porosity and graphitization had increased with increasing pyrolysis temperature and times. The chars which were formed at pyrolysis lower temperature were found to be more reactive than the chars produced at a higher pyrolysis temperature. The information and understanding of behaviour, kinetics, char reactivity and its variation during gasification are essential for proper designing the gasification reactors which play an important role in the large-scale gasification process. To these ends, thermogravimetric analysis (TGA) is useful, popular and simple. It provides information on activation energy and kinetic model [17]. TGA can be carried out under isothermal or non-isothermal conditions. The main disadvantage of the isothermal method is that, there is a small mass loss before reaching the desired temperature, causing a certain error when investigating the gasification reaction mechanism of the solid state. Therefore, non-isothermal method, which is used in this study has become a common analytical technique in recent decades due to the high sensitivity to experimental noise compared to the isothermal methods. In this paper and under this condition (non-isothermal) our study provides a novel result for estimation of kinetic thermal behaviour and reactivity.

The Vyazovkin method based on the Coats-Redfern approximation and Ozawa–Flynn–Wall method based on the Doyle's approximation were applied in order to determine the activation energy, find the optimum mechanism for char reaction and to describe the reactive behaviour of the samples. The literature on the Sudanese sugar cane bagasse char gasification does not provide an understandable relationship between pyrolysis conditions, char structure and char reactivity. This remains a relatively unexplored area of research. Based on these points, the aims of this study are:

(1) To investigate the non-isothermal CO_2 gasification thermal behaviour of sugar cane char generated at different temperatures.
(2) To characterise (reactivity, physical and chemical structures) the sugar cane chars as a function of pyrolysis temperature.
(3) To estimate the activation energy and find the optimum reaction mechanism of the samples.

2. Experimental methods

2.1. Raw material

The raw material, which was used in this study, was the Sudanese sugar cane bagasse (SCB). The SCB was air dried to moisture less than 10%. This material was crushed, ground and sieved to a particle size between 180 and 450 μm. The proximate, ultimate analysis and atomic ratios are given in Table 1, however, the ash composition of SCB was presented in Table 2. The SCB is available at huge amounts in Sudan.

2.2. Char preparation

The chars were prepared by devolatilization of SCB in a horizontal tube furnace (46 mm internal diameter, 600 mm length) under pure nitrogen atmosphere (99.99% purity) at flowing of nitrogen 1 L min^{-1} for required time (20 min) at a designed temperature 500, 800 and 900 °C, which were further denoted as SCB 5, SCB 8 and SCB 9, respectively. After the furnace was heated to the desired temperature, about 1 g of SCB in a ceramic container (50 × 30 × 10 mm) was placed on the outlet side of the tube and then the N_2 was purged into the furnace. When there was no oxygen in the tube, the container was pushed to the central section (heating zone) of the tube rapidly. After a given residence time, the container (resulting char) was immediately moved out of the heating zone, cooled in a nitrogen flow to room temperature and stored in desiccator to prevent moisture absorption. Proximate analysis of samples was carried out in the TGA-2000 (Navas Instruments, Spain) using the American Society for Testing and Materials (ASTM) D5142. The ultimate analysis was determined in an Euro-CA 3000 (HEKA tech, Italy) elemental analyser. The relevant data are also presented in Table 1.

2.3. CO_2 gasification of SCB chars

The CO_2 gasification of SCB chars were carried out in a thermogravimetric analyser (TG/DTA 6300; SEIKO-JAPAN) under non-isothermal conditions. Pure CO_2 was used as a gas agent at a flowing rate of 100 mL min^{-1}, about (17–20 mg) of sample was used in each experiment. The samples were heated up to 1300 °C at a constant heating rate of 20, 30 and 40 °C min^{-1}. Based on the active site concept the following reaction mechanism (Eqs. (1)–(4)) is considered for char gasification in carbon dioxide which is popularly known as the Boudouard reaction [18,19].

$$C + CO_2 \leftrightarrow 2CO \quad (1)$$

$$C_{fas} + CO_2 \xrightarrow{k_{b1}} C(O) + CO \quad (2)$$

$$C(O) + CO \xrightarrow{k_{b2}} C_{fas} + CO_2 \quad (3)$$

$$C(o) \xrightarrow{k_{b3}} CO \quad (4)$$

where k_i is the rate of the ith reaction.