Energy 88 (2015) 703–710

Contents lists available at ScienceDirect

Energy

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

Thermogravimetric study on the influence of structural, textural and chemical properties of biomass chars on CO_2 gasification reactivity

Zeineb Bouraoui [a], Mejdi Jeguirim [a, *], Chamseddine Guizani [b], Lionel Limousy [a], Capucine Dupont [b], Roger Gadiou [a]

[a] IS2M, UMR 7361 CNRS, 15, rue Jean Starcky, Mulhouse, France
[b] CEA-LITEN, Laboratory of Technology of Biomass, 17 rue des Martyrs, Grenoble, France

ARTICLE INFO

Article history:
Received 3 February 2015
Received in revised form
7 May 2015
Accepted 13 May 2015
Available online 26 June 2015

Keywords:
Thermogravimetric study
CO_2 gasification
Biomass chars
Textural properties
Structural properties
Inorganic elements

ABSTRACT

The present investigation aims to examine the influence of textural, structural and chemical properties of biomass chars on the CO_2 gasification rate. Various lignocellulosic biomass chars were prepared under the same conditions. Different analytical techniques were used to determine the char properties such as Scanning Electronic Microscopy, nitrogen adsorption manometry, Raman spectroscopy and X Ray Fluorescence. Gasification tests were carried out in a thermobalance under 20% CO_2 in nitrogen at 800 °C.

Significant differences of the total average reactivity were observed with a factor of 2 between the prepared chars. Moreover, different behaviors of gasification rate profiles versus conversion were obtained. This difference of behavior appeared to be correlated with the biomass char properties. Hence, up to 70% of conversion, the gasification rate was shown to depend on the char external surface and the potassium content. At higher conversion ratio, a satisfactory correlation between the Catalytic Index and the average gasification rate was identified. The results highlight the importance of knowing both textural and structural properties and mineral contents of biomass chars to predict fuel reactivity during CO_2 gasification processes. Such behavior prediction is highly important in the gasifiers design for char conversion.

1. Introduction

The use of renewable energy has become crucial to overcome the fossil fuel depletion and the increasing energy demands in the world [1]. Among various renewable energies, biomass has a growing potential to decrease energy dependence on fossil fuel and minimize environmental pollution [1,2]. Energy can be obtained from biomass through various thermochemical and biochemical processes [3]. Biomass gasification is an emerging technology that generates gaseous fuels suitable for feeding gas engines and for biofuels synthesis [4–6].

The biomass gasification process is based on three successive steps: i) a drying step during which biomass loses its moisture, ii) a pyrolysis step which consists in biomass devolatilization at high temperatures leading to the formation of a solid residue called char and volatiles containing several compounds such as CH_4, CO_2 and CO iii) a char gasification step, in which char reacts with gasifying agents such as CO_2, H_2O and O_2 and gives rise to a syngas containing mainly CO and H_2 [7–9].

The study of char gasification reaction kinetics is of special interest since this reaction is the rate limiting step defining the solid residence time in the reactor chemical kinetics [10]. Consequently, the identification of the main parameters affecting the gasification mechanisms and kinetics is required for the gasifier design and operation from both process efficiency and environmental impact. Several experimental studies have examined the reactivity of steam and carbon dioxide with lignocellulosic biomass chars [11–19]. These investigations have revealed that the reactivity of char gasification is governed by many parameters such as pyrolysis operating conditions (temperature, pressure, heating rate) [11–13] and char properties (chemical structure, inorganic constituents, porosity) [14–19].

Min et al. have examined the effect of low pyrolysis temperatures and slow heating rates on the CO_2 gasification reactivities of chars prepared from agricultural wastes [11]. The authors showed that increasing pyrolysis temperatures leads to a decrease of char

* Corresponding author. Tel.: +33 3 89608661.
E-mail address: mejdi.jeguirim@uha.fr (M. Jeguirim).

http://dx.doi.org/10.1016/j.energy.2015.05.100
0360-5442/

gasification reactivities. They have observed that high temperature chars had many smaller pores with thinner cell walls and larger surface areas. Moreover, Min al noted that during FTIR spectroscopy analysis, the stretches caused by the C–O for the O–CH_3/C–OH, symmetric C–H stretch of lone C–H and O–H stretch of hydroxyl functional groups showed a continuous decrease in intensity with pyrolysis temperature increasing due to increased loss of these functionalities [11]. Min et al. have correlated the gasification reactivity with the influence of pyrolysis temperatures on char structure [11]. Okumura et al. have used Raman spectroscopy to study the influence of pyrolysis conditions (heating rate, pressure) on woody biomass char reactivity [14]. The authors have identified the correlation between the biomass char characteristics and the gasification rate. In particular, they have observed a relationship between the decrease in the gasification reactivity and the increase of the carbonaceous uniformity structure. Moreover, they have noted a correlation between the increase of gasification rate and the evolution of char surface texture and the internal texture of fiber bundles [14].

Besides studies on pyrolysis conditions influence on the gasification rate of lignocellulosic biomass chars, there have been several experimental studies dealing with the effect of mineral elements on the char gasification reactivity. These mineral elements were either present inherently in the raw biomass or added by impregnation with aqueous solutions. These investigations have shown that the reaction of the residual char with the steam gasifying agent is accelerated by alkaline (sodium, potassium) and alkaline earth (calcium, magnesium) elements [18]. Recently, an inhibiting effect of the phosphorus and silicon elements was observed during the steam gasification of chars prepared from algal and lignocellulosic biomasses [19].

Although the char properties influence on the gasification rate has been examined separately in larger extent, most studies have been focused on one char property (i.e. inorganic elements, surface area, structure, …) with the average gasification rate. However, recent investigations have shown that the average gasification rates of biomass chars vary with char conversion ratios. Such a behavior indicates that the char properties – including chemical, structural and textural properties – are changing along conversion and consequently impact the gasification char gasification reactivity. Moreover, the contribution of each property may change during the gasification reaction. Hence, there is still a need to better understand the coupled effect of chemical, structural and textural char properties effect on the gasification mechanism and reactivity.

The main objective of this work is therefore to identify the correlation between the char properties and the char gasification reactivity. In order to achieve this goal, chars prepared from various lignocellulosic biomasses were characterized using different analytical techniques to assess their structural, morphological, textural and chemical properties. The raw biomasses and the prepared chars were not exposed to any treatments in order to avoid the change in the sample structure. The non-isothermal CO_2 gasification of prepared chars was examined at 800 °C using TGA (thermogravimetric analysis).

2. Materials and methods

2.1. Materials

Five woody and agricultural samples of biomass were selected based on their difference of properties and composition. These samples include one herbaceous crop, namely miscanthus, two SRC (short rotation coppices) of poplar wood, and two mature woods, namely one mixture of softwood, spruce/fir, and one Brazilian wood, faveira. The samples physico-chemical characteristics were measured following the European standards for solid biofuels. The ultimate analysis and mineral contents of the selected samples are shown in Table 1.

The obtained results show that elemental compositions of the different samples are in the typical composition of biomass encountered in literature [19–24]. In particular, no significant difference is observed between samples on carbon, hydrogen and oxygen contents. However, significant differences are observed regarding ash content and inorganic element composition. In fact, the spruce/fir mixture has the lowest ash content and contains mainly potassium, calcium and small amounts of magnesium; silicon and chlorine. In contrast, the short rotation coppice samples contain a higher amount of ash, with the main part being calcium and potassium [23]. Faveira and miscanthus contain mainly silicon, then significant quantities of calcium and potassium and smaller amounts of magnesium.

2.2. Chars preparation

The analysis of the different char properties requests the preparation of homogenous chars in sufficient quantities. Therefore, chars preparation was performed in two steps. In a first step, $4 \cdot 10^{-3}$ kg of sample were placed in a tubular furnace (Thermolyne F 21100). Then, a nitrogen flow was continuously supplied at room temperature during 1800 s in order to remove residual oxygen. Afterwards, the temperature increased to the setting value fixed at 450 °C at 0.167 °C/s under nitrogen at a flow rate of $7 \cdot 10^{-6}$ Nm^3/s. The sample was kept one hour at 450 °C and cooled down to room temperature. In the second step, $1 \cdot 10^{-3}$ kg of the previously pyrolyzed sample was heated up to 800 °C at 0.167 °C/s under nitrogen atmosphere. Then, the produced char was grounded with a mortar and sieved below $50 \cdot 10^{-6}$ m.

2.3. Chars characterization techniques

Different analytical techniques were used to determine the textural, structural and chemical properties of the different prepared chars.

The mineral contents of the different chars were measured by XRF (X-ray fluorescence) spectrophotometer (PHILIPS PW2540) equipped with a rhodium target X-ray tube and a 4 kW generator. 100 mg of char were ground and mixed with 200 mg of boric acid, and then pressed into a pellet under a 8.83 10^8 Pa pressure for 45 min. The use of boric acid is required to pelletize the char powder since the char has a hydrophobic character and could not be densified without a binder. The acid boric signal is easily eliminated during the XRF analysis.

Scanning electron microscopy (Philips model FEI model Quanta 400 SEM) and energy dispersive EDX (X-ray spectrometry) were used to observe the morphology and the surface elemental analysis of the prepared chars, which allows determining the elemental mapping of the samples.

The textural properties of the chars were investigated with a Micrometrics ASAP 2020 instrument using N_2 adsorbate at 77 K. Prior to the analysis the char samples were out-gassed overnight in vacuum at 573 K. The TSA (Total Surface Area) was calculated from the linear plot in the relative pressure range of 0.05–0.15 while the micropore volume (Vmicro) was calculated following the αs-plot method. The mesopore volume (Vmeso) was obtained by subtracting the micropore volume from the total pore volume of N_2 adsorbed at a relative pressure of 0.95. The pore size distribution was determined using the DFT model on carbon slit pores [25].

Raman spectra of the chars were recorded with a BX40 LabRam, Jobin Yvon/Horiba spectrometer. Several char particles were sampled and deposited on a rectangular glass slide for the Raman