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Full Length Article

Steam gasification behavior of tropical agrowaste: A new modeling approach based on the inorganic composition

Lina María Romero Millán[a,b,*], Fabio Emiro Sierra Vargas[a], Ange Nzihou[b]

[a] Universidad Nacional de Colombia – Sede Bogotá, Facultad de Ingeniería, Ciudad Universitaria, Bogotá, Colombia
[b] Université de Toulouse, Mines Albi, CNRS, Centre RAPSODEE, Campus Jarlard, Route de Teillet, F.81013 Albi Cedex 09, France

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ABSTRACT

The steam gasification and co-gasification reactivity and kinetics of coconut shells, oil palm shells and bamboo guadua were studied from an isothermal thermogravimetric analysis, with temperatures ranging from 750 °C to 900 °C, and steam partial pressures from 3 to 10 kPa. In the analyzed experimental range, inorganics were identified as the most influential parameter in biomass reactivity and kinetics. Accordingly, a new modeling approach is proposed to predict the gasification behavior of lignocellulosic agrowaste based on their inorganic composition. A good agreement between the experimental and modeled data was found, showing that the proposed approach is suitable for the description and prediction of the gasification behavior of biomasses with different macromolecular structure and within a wide range of inorganic composition, and H/C and O/C ratios near 1.5 and 0.8 respectively. This kinetic model could constitute a valuable tool for reactor design and scale-up of steam gasification facilities using tropical lignocellulosic feedstocks.

1. Introduction

Tropical regions are rich in biodiversity thanks to their geographic location and climate conditions. In this regard, they are appropriate for the development of agricultural activities and cultivation of a great variety of crops. Several developing countries in tropical regions base their economy in agriculture and farming and produce great amounts of agro-wastes that usually remain under-exploited. These residues could be valorized as biofuels or transformed into value-added products, giving new development opportunities for local communities.

In this regard, gasification is a very interesting thermochemical process for the recovery of energy from agrowaste. In particular, steam gasification produces high heating value fuel gases that can be used for the generation of heat and power [1–4]. However, the valorization of agrowaste could have some restrictions. One of the most important is probably the fact that agricultural residues availability often depends on seasonal crops. Consequently, most gasification facilities should operate intermittently, or work with different kind of residues or even blends.

Several authors have highlighted the differences in the gasification behavior of chars from different biomasses. In particular, the inorganic elements are reported to be the most influential parameter in the steam gasification reactivity and conversion profile [5,6]. Alkali and alkali earth metals (AAEM) like K, Na, Ca and Mg, which are present in indigenous biomass could have a catalytic effect on biomass gasification [7]. Among these elements, K has been reported to be the most active species for steam and CO_2 gasification of charcoal and biomass [8,9]. In contrast, Si, Al or P may inhibit this catalytic effect, as they tend to react with AAEM [10,11].

Most studies related to the impact of inorganics in the gasification behavior of biomasses use impregnation techniques to modify the composition of the samples [8,12–15]. In general, these treatments allow a good understanding of the effects of inorganics on gasification. However, the behavior of impregnated inorganic elements may differ from the one of inorganic elements in their natural form and distribution in biomass. In this regard, Dupont et al. [16] studied 21 samples of woody biomasses, confirming the beneficial impact of K and the inhibitory effect of Si in the indigenous biomass.

Generally, authors analyze the gasification behavior of biomasses individually. Nevertheless, most gasification applications in developing countries should work with different kind of residues or blends depending on their availability. In this context, the understanding of the impact of biomass characteristics and blends interactions in their gasification behavior is important in order to properly adapt the process parameters and conditions to the application.

To describe the steam gasification behavior of biomasses, several

* Corresponding author at: Universidad Nacional de Colombia – Sede Bogotá, Facultad de Ingeniería, Ciudad Universitaria, Bogotá, Colombia. Université de Toulouse, Mines Albi, CNRS, Centre RAPSODEE, Campus Jarlard, Route de Teillet, F.81013 Albi Cedex 09, France.
E-mail addresses: lina.romero_millan@mines-albi.fr, lmromerom@unal.edu.co (L.M. Romero Millán).

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Nomenclature

α	degree of conversion or reaction extent (−)
A	frequency factor or pre-exponential factor (min^{-1})
BG	bamboo guadua
CS	coconut shells
$d\alpha/dt$	decomposition rate (−)
daf	dry ash free
E_a	activation energy (kJ/mol)
OPS	oil palm shells
PH_2O	steam partial pressure (kPa)
R	ideal gas constant: 8.3144 J/mol K
t	time (min)
T	temperature (°C, K)

authors have proposed different kinetic approaches, some of them incorporating the impact of inorganic elements. In this regard, Kajita et al. [17] considered that gasification occurs in a parallel reaction scheme and developed a dual Langmuir-Hinshelwood model, identifying K as the main catalytic element. This study highlighted the beneficial impact of K, but did not deal with other inorganic elements present in biomasses. For their part, Zhang et al. [10] analyzed the influence of AAEM and Si in the gasification behavior of different biomasses. They proposed a modified random pore model, introducing two dimensionless parameters that depends on the inorganic content of samples. Even when the calculation method of these parameters was not explicitly presented, the authors concluded that the gasification reactivities of biomasses are governed mainly by the amount of inorganic species. More recently, Dupont et al. [6] proposed a kinetic approach with two different kinetic laws for biomasses with inorganic ratio K/Si + P > 1 and K/Si + P < 1. A zeroth-order and a volumetric first-order model were found to describe the behavior of samples, respectively. Furthermore, in the case of biomasses with K/Si + P > 1, the authors suggest that the gasification kinetics can be predicted simply through the knowledge of the K content of the sample. Even when the proposed approach in this work can satisfactorily estimate the behavior of biomasses within a wide range of inorganic compositions, the conversion of samples with intermediate values of inorganic ratio (K/Si + P ≈ 1) is not completely described. The authors stated that the decomposition of these biomasses can be estimated either with a zeroth or a first order law. Additionally, concerning the analysis of the simultaneous steam gasification of different kind of biomasses and their kinetic modeling, no studies have been found in the literature until now.

Accordingly, the aim of this work is to study the steam gasification behavior of three tropical lignocellulosic biomasses and their blends, from an isothermal thermogravimetric analysis. The influence of the gasification temperature and steam partial pressure on the gasification reactivity of biomasses was discussed. Also, the impact of biomasses and blends composition on the gasification reactivity and kinetics was analyzed. An approach using model-free isoconversional methods and generalized master plots was used to determine the gasification kinetic parameters of the samples and compare their decomposition behavior. As a result, a new model with a unique kinetic equation is proposed to describe and predict the steam gasification behavior of tropical lignocellulosic agrowastes based on their inorganic composition.

2. Materials and methods

2.1. Biomass samples

Three tropical lignocellulosic feedstocks were selected for this study: oil palm shells (OPS), coconut shells (CS) and bamboo guadua (BG). The samples were collected in Colombia, South America, and were provided by a palm oil extraction plant, a food processing industry, and a furniture and handicraft construction site, respectively. The origin of selected samples has been detailed on a previous work [18]. The chemical composition of the biomasses was determined according to the standards of solid biofuels with at least three replicates, and is presented in Tables 1 and 2.

Elemental composition (C, H, N, S, and O) was determined using a Themoquest NA 2000 elemental analyzer, while inorganic speciation was determined using an HORIBA Jobin Yvon Ultima 2 inductively coupled plasma optical emission spectrometer (ICP-OES), based on EN 16967 standard. Proximate analysis was calculated according to the standards EN ISO 18134-3, EN ISO 18123 and EN ISO 18122, respectively. Molecular composition of the biomasses is referred to literature reported values [19–21].

The raw biomasses were milled and sieved to a size range between 100 µm and 150 µm before TGA. The characteristic time analysis of the experiments showed that under the presented conditions, limitations by heat or mass transfer can be neglected. Bi-component biomass blends were prepared after milling and sieving using different proportions.

2.2. Isothermal TGA gasification experiments

Raw biomasses and biomass blends gasification under steam was performed using a Seratam TG-ATD 92 thermal analyzer, coupled with a Wetsys humid gas generator. Approximately 20 mg of each sample were placed in an aluminum crucible and heated from 25 °C to the final gasification temperature (750 °C, 800 °C and 900 °C) at a heating rate of 10 °C/min, under an inert atmosphere. After 10 min, the measured mass loss of the sample was below 0.01%/min and then, it was considered that the pyrolysis stage has finished. The atmosphere was then switched to a mixture of H_2O/N_2 (steam partial pressure from 3.7 kPa to 10 kPa). The total flow rate was 4 L/h for all the experiments.

TGA experiments were conducted twice and averaged to verify their repeatability. A blank test was made for each experimental condition to exclude buoyancy effects. For each experimental condition, the repeatability was found to be satisfactory, as the calculated standard deviation of the mass loss was below 1%.

2.3. Reactivity and kinetic study

2.3.1. Theoretical background

The isothermal gasification experiments described are the basis of the kinetic analysis of biomasses decomposition under a steam atmosphere. The degree of conversion or reaction extent during gasification is defined as in Eq. (1):

Table 1
Organic composition of studied biomasses.

		OPS	CS	BG
Elemental Analysis (wt% daf)	C	46.7 ± 0.2	46.8 ± 0.2	42.7 ± 0.3
	H	6.5 ± 0.1	5.8 ± 0.1	5.4 ± 0.1
	O*	46.2 ± 0.1	47.1 ± 0.1	51.5 ± 0.1
	N	0.6 ± 0.1	0.3 ± 0.1	0.4 ± 0.1
	O/C	0.7 ± 0.1	0.7 ± 0.1	0.9 ± 0.1
	H/C	1.7 ± 0.1	1.5 ± 0.1	1.5 ± 0.1
Proximate analysis (wt% dry basis)	Volatile Matter	77.2 ± 0.3	79.5 ± 0.3	75.1 ± 0.2
	Fixed Carbon*	20.9 ± 0.3	19.1 ± 0.2	19.9 ± 0.3
	Ash	1.7 ± 0.2	1.4 ± 0.1	5.0 ± 0.4
Molecular composition (wt % daf)	Cellulose	30.4	32.5	53.9
	Hemicellulose	12.7	20.5	13.5
	Lignin	49.8	36.5	25.1

* Calculated by difference.