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Gasification of lignocellulosic biomass char obtained from pyrolysis: Kinetic and evolved gas analyses

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ABSTRACT

Pyrolysis and gasification processes of three types of lignocellulosic biomass (Eucalyptus wood, fir wood and pine bark) and biomass main components (cellulose, xylan and lignin) were studied by thermogravimetric-mass spectrometric analysis. Biomass samples were pyrolyzed between 30 °C and 1000 °C obtaining a solid fuel (char) that was later gasified using steam as the reacting agent (5% vol.). The gasification temperature was set at 900 °C. Biomass samples reactivity profiles showed a catalytic effect at high conversion values, which was correlated with their ash composition. Three models were used to reproduce the gasification process. Cellulose and pine bark samples were the only ones that properly fitted to these models. This fact was attributed to their low ash content. This way, a semi-empirical model for predicting the gasification rates including the catalytic effect of ashes was proposed, which highly improved the obtained fitting. H_2, CO and CO_2 were the main products obtained. Furthermore, the detection of CH_4 indicated the existence of methanation reactions. NO_x were also observed, indicating that nitrogen was retained in the char after the pyrolysis process.

1. Introduction

The production of clean and sustainable fuels is the main challenge to tackle upcoming energy crises and global warming [1]. Among all renewable energy sources, biomass stand out as a potential alternative to increase energy independence on fossil fuels and minimize environmental pollution [2].

Thermochemical conversion of biomass is the most promising route for biomass utilization [3]. In this regard, pyrolysis and gasification are used to produce liquid and gaseous fuels that are suitable for feeding efficient gas engines and gas turbines [4]. Pyrolysis plays an important role in these processes, being the first chemical step in the gasification one.

Gasification is of special interest due to the fact that it is compatible with new applications in the area of biomass conversion, coal to liquid applications and superior environmental performance especially with regard to CO_2 capture and sulfur removal. Furthermore, it is economical in a wide range of capacities [5]. Biomass gasification can be defined as the conversion of biomass to a gaseous fuel by heating in a partial oxidation atmosphere [6]. Char gasification is of special interest because it represents the rate-controlling step in the process [7]. This step is a function of several factors such as particle size, porosity, gasifying agent chemical composition, gasifying agent partial pressure, reactor temperature, pore structure, number of active sites and ash content [8].

TGA (thermogravimetric analysis) coupled to MS (mass spectrometry) has been commonly used for the study of the thermochemical conversion of different types of solid fuels, such as biomass or coals [9–13]. In this regard, most studies have been focused on pyrolysis and combustion processes. Comparatively, gasification studies have been less reported in literature, being most of them focused on the study of coals [5,6]. TGA – MS is an excellent tool for determining the kinetics of process. In this regard, the kinetics of gasification are essential for modeling gasification processes at an industrial scale [14]. Furthermore, a knowledge of the process kinetics has great importance for a correct design and product yield control [15].

There are several studies dealing with the gasification of biomass [7,16–19]. Lv et al. [17], studied the effect of cellulose, lignin and alkali and alkali-earth metals on biomass pyrolysis and gasification. Their study revealed that the gasification process was mainly influenced by the interaction between AAEM (UCTR 100 289 Project: *CENIT VIDA-CEN-20101026*) and the cellulose lignin ratio. Umeki et al. [7], reported that the ashes had a catalytic effect on the steam gasification of rice straw enhancing the production of H_2 and CO_2 by promoting the water-gas shift reaction. In this regard, Di

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Blasi et al. [4], reported in an extensive review underlining the effect biomass ashes constituents on the gasification of biomass chars. The catalytic effect of biomass ashes on the gasification process affects both, the gasification rates and the gas product distribution. Marquez and Montesinos et al. [16], reported the effect of K on the gasification of char formed from grapefruit skin. However, the effect of ashes on the gasification process is still unresolved and most studies do not consider the kinetics of the process at high conversion values between 0.7 and 0.9, where the catalytic effect of ashes is predominant. Thus, models that analyze the process in the whole conversion range are required in order to properly evaluate the process.

This work deals with the gasification of different types of lignocellulosic biomass materials that were selected according to their potential to be used in thermochemical conversion processes. In a previous work [20], a large number of biomass fuels were placed into a ternary diagram according to their proximate analysis. In this regard, biomasses with high volatile matter and fixed carbon content and low ash content were selected. According to this criteria, eucalyptus wood, fir wood and pine bark showed the best characteristics to be used in thermochemical conversion processes.

The aim of this work was to study the pyrolysis and gasification of different types of lignocellulosic biomasses (fir wood, eucalyptus wood and pine bark) and their main components (cellulose, hemicellulose and lignin) by means of TGA. The pyrolysis of biomass samples was carried out to obtain a solid fuel (char), which was later gasified with steam. A preliminary kinetic analysis of the gasification process was performed in order to obtain the apparent gasification rates by using three standard models: volumetric model, shrinking core model and random pore model. In addition, a semi-empirical model was proposed in order to reproduce the process in the full range of conversion. Finally, the gases released during the gasification process were analyzed by MS.

2. Materials and methods

2.1. Materials

Cellulose (microcrystalline cellulose with 50 μm average particle size), lignin (alkali lignin in brown powder form with 50 μm average particle size) and xylan (xylan processed from beechwood with 100 μm average particle size) were purchased from Sigma–Aldrich. Xylan was used as representative of the hemicellulose. The selected terrestrial biomasses (fir wood, eucalyptus wood and pine bark) were taken from the region of Castilla-La Mancha (Spain) on the basis of a preliminary analysis [20]. These samples were dried in an oven for 5 h at 100 °C, milled and sieved to an average particle size between 100 and 150 μm. Biomass samples were stored in a desiccator prior to their use in gasification experiments.

The proximate analysis, ultimate analysis and composition of biomass samples are shown in Table 1. The metal content in samples was determined by ICP (inductively coupled plasma) Spectrometry (Table 1).

The content of cellulose, hemicellulose and lignin in lignocellulosic biomass samples was calculated according to the experimental method reported elsewhere [21] (Table 1). The determination of the amount of extractives was carried out by solvent extraction (100 ml acetone for 1 g of dried biomass sample) at 60 °C. Then, the biomass sample was dried (110 °C) until a constant weight was obtained. The solid residue was then cooled to room temperature in a desiccator and weighted. The weight difference before and after the extraction is the amount of extractives. The hemicellulose content was determined by adding 1 g of extractive-free dried biomass sample to a 150 ml of NaOH solution (20 g/l), and boiled for 3.5 h with recycled distilled water. The residue was filtered and washed to remove Na^+. After the washing the residue was dried and weighted. The amount of hemicellulose was calculated by the weight difference before and after this treatment [22]. The determination of lignin was performed by the Klason method. 30 ml of H_2SO_4 (72%) were added to a 1 g extractive-free dried biomass sample. The mixture was heated and stirred for 2 h. After that, the mixture is diluted to 4% H_2SO_4 concentration. The resulting mixture was boiled for 4 h with recycled water. The residue was later filtered, washed and dried. The weight difference after and before the treatment is the amount of lignin. Finally, the amount of cellulose was calculated for weight difference from extractives, cellulose, hemicellulose and lignin.

2.2. Equipment and procedures

2.2.1. Thermogravimetric analysis for the gasification process

The pyrolysis and gasification of biomass components was carried out in a TGA apparatus (TGA-DSC 1, METTLER TOLEDO). The experimental setup used for the gasification experiments was described in a previous study [23]. The steam was generated by a bubbler system which consists of four bubblers connected in series in order to ensure the complete saturation of the reacting atmosphere. Ar was bubbled through degassed water heated to 33 °C.

Table 1
Characterization of lignocellulosic biomass samples (Cellulose, xylan, lignin, fir wood, eucalyptus wood and pine bark).

	Ultimate analysis (wt. %)					Proximate analysis (wt. %)				Biomass composition (wt. %)^{daf}[a]			
	C	H	N	S	O^{diff}[a]	Moisture	Ash	Volatile matter	Fixed carbon^{diff}[a]	Cellulose (%)	Lignin (%)	Hemicellulose (%)	Extractives (%)
Cellulose	42.18	6.15	0.01	0.06	51.61	3.0	0.8	90.7	6.0	100	–	–	–
Lignin	62.09	5.88	0.51	0.54	30.98	1.1	3.7	55.8	39.3	–	100	–	–
Xylan	38.41	6.18	0.01	0.11	55.30	6.4	2.8	71.6	19.2	–	–	100	–
Eucalyptus wood	41.62	4.88	0.38	0.03	53.09	2.6	6.8	73.8	16.8	52	17	24	7
Fir wood	50.12	6.14	0.44	0.00	43.45	2.6	3.4	74.4	19.5	38	24	30	8
Pine bark	52.71	5.52	0.01	0.08	41.70	4.4	2.7	61.6	31.3	13	31	37	19

	Mineral content (ppm)														
	Al	Ca	Cr	Cu	Fe	K	Mg	Na	Ni	Pb	P	Hg	V	Si	Ti
Cellulose	367	2711	16	66	106	575	255	1476	980	37	6869	411	10	237,816	84
Lignin	500	868	13	48	126	1069	219	7197	758	35	6100	350	36	181,504	150
Xylan	213	4343	7	77	77	456	124	13,828	382	17	3326	184	–	65,856	81
Eucalyptus wood	43	4116	16	131	33	5078	1062	1431	51	47	7819	408	9	247,228	18
Fir wood	557	10,921	22	71	717	1880	1774	1807	27	41	8608	492	22	353,166	62
Pine bark	946	2726	19	74	385	1254	776	2764	463	73	7360	524	26	474,344	70

[a] daf – dry and ash free basis; O^{diff} – Oxygen was calculated by difference from C, H, N and S; Fixed carbon^{diff} – Fixed carbon was calculated from difference from volatile matter, ash and moisture.