Bio-syngas production from agro-industrial biomass residues by steam gasification

Tatiana Ramos Pacioni *, Diniara Soares, Michele Di Domenico, Maria Fernanda Rosa,
Regina de Fátima Peralta Muniz Moreira, Humberto Jorge José

Department of Chemical Engineering, Federal University of Santa Catarina, 88040-900 Florianópolis, SC, Brazil

ABSTRACT

This study evaluated the steam gasification potential of three residues from Brazilian agro-industry by assessing their reaction kinetics and syngas production at temperatures from 650 to 850 °C and a steam partial pressure range of 0.05 to 0.3 bar. The transition temperature between kinetic control and diffusion control regimes was identified. Prior to the gasification tests, the raw biomasses, namely apple pomace, spent coffee grounds and sawdust, were pyrolyzed in a fixed-bed quartz tubular reactor under controlled conditions. Gasification tests were performed isothermally in a magnetic suspension thermobalance and the reaction products were analyzed by a gas chromatograph with TCD/FID detectors. According to the characterization results, the samples presented higher carbon and lower volatile matter contents than the biomasses. Nevertheless, all of the materials had high calorific value. Syngas production was influenced by both temperature and steam partial pressure. Higher concentrations of H_2 and CO were found in the conversion range of 50–80% and higher concentrations of CO_2 in conversions around 10%, for all the gasified biochars. The H_2/CO decreased with increasing temperature, mainly in kinetic control regime, in the lower temperature range. The results indicate the gasification potential of Brazilian biomass residues and are an initial and important step in the development of gasification processes in Brazil.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Biomass is one of the most promising alternative sources for a sustainable energy future. According to the International Energy Agency's (IEA) World Energy Outlook 2014 (WEO, 2014) the share of renewables in global power generation will rise from 21% in 2012 to 26% in 2020, reaching about 33% in 2040. Energy from wastes, e.g. wood-based materials, forestry waste and agricultural residues, is advantageous due to their wide availability, distribution, low environmental pollution, etc. At the same time, it also represents an important element of waste management. In Brazil, the industrial and agro-industrial activities generate about 97.7 and 290.8 million tons of waste per year, respectively, according to the Brazilian Ministry of the Environment (BME, 2011). Two remarkable by-products generated every year, both in the country and worldwide, are spent coffee ground, generated in the production of soluble coffee, and apple pomace, generated in the manufacture of juice and cider. Currently, large amounts of these wastes are accumulated, remaining under-exploited. In this context, it is highly relevant to develop in-depth studies of enhanced energy production from sources such as biomass wastes, combined with the use of efficient and innovative processes, with minimum environmental impact.

Renewable energy technologies are expected to rapidly gain ground in coming years, as they constitute the central element for ensuring reliable, affordable and clean energy for all countries around the globe. Among the clean technologies capable of processing solid fuels, gasification of biochar is particularly interesting, since it allows both generating energy, primarily through an Integrated Gasification Combined Cycle (IGCC) power plant, and producing clean fuels, particularly hydrogen (Pettinau et al., 2010). Gasification processes are more efficient and environmentally friendly for the generation of low-cost electricity, among other products, and can be readily adapted to the process of capturing and storing CO_2. As commonly described, gasification involves the reaction between solid fuels, such as coal, biomass, and petroleum coke, and oxidants (air, oxygen, steam, carbon dioxide) at moderate pressure and temperatures exceeding 700 °C (Minchener, 2005; Collot, 2006). Under these conditions, a gaseous

product is generated, mainly composed of syngas (H_2 and CO) and CO_2, along with CH_4, N_2, H_2S, H_2O, trace sulfur and other light hydrocarbons and impurities. The gasification process can be separated into two main steps, known as pyrolysis (or devolatilization) and gasification, the latter being the rate-controlling step of the overall conversion process.

Few studies regarding steam gasification have been carried out to clarify the mechanisms and forecast syngas production from biomass fuels, thus the process is still not fully understood (Yan et al., 2010;Yip et al., 2010). Many parameters are acknowledged to influence gas yield and composition, such as the composition of the original biomass (mainly the three major components: cellulose, hemicellulose and lignin), the composting of the raw material, its moisture content, the temperature, pressure, gasifying agent, and catalyst (Wang et al., 2008; Barneto et al., 2009; Griffin and Schultz, 2012; Juchelková et al., 2015; Raheem et al., 2015). Portofino et al. (2013) evaluated the influence of temperature in the steam gasification of waste tyre. The authors found that higher temperatures resulted in higher syngas production (86 wt%), especially for hydrogen. Zhang et al. (2014) investigated hydrogen production in sorption enhanced gasification, catalyzed by different potassium precursors. Yip et al. (2010) evaluated the catalyst effect of the intrinsic mineral matter on steam gasification of biomass. Nevertheless, studies relating syngas production to the reaction regime and reactivity are scarce, especially those concerning the steam gasification of the biomasses used in this study.

The objective of this study was to investigate the syngas production of Brazilian biomass chars (apple pomace, spent coffee grounds and sawdust) during steam gasification at 1 bar, temperatures between 650 and 850 °C and steam partial pressure between 0.05 and 0.3 bar.

2. Material and methods

2.1. Material characterization and biochar preparation

Three types of residues from Brazilian agro-industry were selected for this study, including apple pomace (AP), spent coffee grounds (CG) and sawdust (Sd). As received, the biomasses were ground, sieved to particle sizes up to 300 µm and pyrolyzed in a fixed-bed quartz tubular reactor (DIST, Brazil). Operating variables applied during pyrolysis included: nitrogen flow of 400 ml/min (purity 99.996%), heating rate of 200 °C/min and residence time of 5 min at the final temperature of 900 °C. The resulting biochars were also ground, sieved to particle sizes up to 106 µm and used in the gasification tests.

Characteristics of the biomass and biochar samples, as determined by several techniques, are summarized in Table 1. Proximate analysis (ash, volatile matter and fixed carbon) was determined according to the standard ASTM E-1131 (ASTM, 2003) by thermogravimetry. Ultimate analysis (C, H, N, S and O) was determined according to the standard ASTM D-5373 (ASTM, 2002). Calorific values were estimated according to Channiwala and Parikh (2002). Porous structure analysis was carried out in liquid N_2 and at −196 °C, and surface areas were calculated using the BET method (Brunauer et al., 1938). Ash mineral composition was determined according to the DIN 51719 standard (DIN, 1997) by inductively coupled plasma mass spectrometry ICP-MS. The results were expressed relative to the total mass of the sample. Morphology structure was evaluated by scanning electron microscopy (SEM) using a JEOL JSM-14 6390LV microscope (USA). Fig. 1 presents SEM images of the biomasses and biochars under magnification of 500×.

Table 1
Characterization of the biomasses and biochars.

Sample	CG	CG-char	AP	AP-char	Sd	Sd-char
Proximate analysis (wt%, db[a])						
Ash	3.7	18.3	1.2	8.6	0.3	2.2
Volatile matter	77.7	14.5	83.1	15.0	86.3	9.2
Fixed carbon	18.7	67.2	15.7	76.4	13.4	88.6
Ultimate analysis (wt%, daf[b])						
Carbon (C)	56.4	84.7	50.0	83.9	46.7	81.8
Hydrogen (H)	7.0	1.5	5.6	1.6	5.3	1.6
Nitrogen (N)	2.1	2.9	3.0	3.6	1.6	1.8
Sulfur (S)	0.3	0.5	<0.1	0.2	0.1	0.1
Oxygen (O) (diff.)	34.3	10.4	41.3	10.6	46.3	14.7
Heating Value (kJ/kg, db)						
High	22,909	28,877	17,528	28,686	15,051	27,237
Low	21,342	28,488	16,242	28,267	13,831	26,859
Porous structure						
BET surface area (m^2/g)	<1	25.76	<1	12.47	<1	284.9
Pore volume[c] (cm^3/g)	0.0242	0.0323	0.0015	0.0214	0.0074	0.187
Mineral content (wt%)						
Fe	0.353	1.748	0.050	0.356	0.009	0.068
Ca	0.706	3.490	0.115	0.826	0.067	0.492
Mg	0.156	0.772	0.065	0.466	0.021	0.154
Na	0.021	0.106	0.008	0.059	0.004	0.027
K	0.159	0.784	0.312	2.233	0.026	0.191
Si	0.339	1.676	0.037	0.265	0.022	0.161
Al	0.206	1.017	0.017	0.121	0.020	0.143
Ti	0.006	0.030	0.018	0.128	0.007	0.052
P	0.144	0.710	0.097	0.695	0.004	0.026
Mn	0.028	0.138	0.002	0.016	0.005	0.035
S	0.053	0.261	0.014	0.099	0.003	0.022

[a] Dry basis.
[b] Dry ash free basis.
[c] Total pore volume at $P/P_0 = 0.99$.

2.2. Methods

2.2.1. Gasification reactions

Thermogravimetry is a technique frequently used to determine the kinetics of carbonaceous materials since it provides reliable data under well-controlled conditions. Accordingly, the gasification kinetic in this work was assessed by experiments in a thermobalance model Dyntherm-HP-ST (Rubotherm GmbH, Germany). The equipment has two main modules, a magnetic suspension balance and an automated gas dosing system. A schematic representation of the thermobalance system is depicted in Fig. 2. The position of the balance allows it to correct the baseline drift and to recalibrate during the entire procedure, and hence ensure highly accurate and stable weight measurements. This feature excludes the effect of buoyancy and the need for data correction by a blank experiment. Operating variables were in agreement with differential reactor conditions as previously determined experimentally (Domenico, 2013).

Tests were carried out isothermally at different temperatures, using 0.1 g of the char sample, placed in a thin layer into an alumina pan. This pan was a cylinder of 10 mm height and 15 mm diameter. Experimental procedure consisted of three consecutive steps: the system was first purged with an argon flow of 100 ml_N/min (purity 99.999%) for 2 h. The reactor was then heated at 20 °C/min, up to the desired reaction temperature, in the range of 650–850 °C. Finally, the inert gas was replaced by an argon/steam mixture flow of 300 ml_N/min with steam partial pressure range of 0.05–0.3 bar (steam concentration 5–30 vol%). Steam was generated and added to the system by an HPLC pump connected to a stainless steel block heated at 200 °C. All external tubes were heated to the same