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Air-steam and oxy-steam gasification of hydrolytic residues from biorefinery

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ABSTRACT

This paper reports the use of lignin-rich solid, derived from enzymatic hydrolysis of lignocellulosic biomass, to produce syngas and pyrolysis oil. The tested process was an updraft gasification carried out at pilot scale of about 20 kg/h as solid feed. The reactivity of two residues, one from straw and one from cane, was investigated by TGA in air, oxygen, nitrogen, using a heating program simulating the thermal gradient in the gasifiers. Below 400 °C the residues completely burned in air or oxygen with an apparent reaction order of 0.1–0.2. The 75%–80% of the organic mass was pyrolysed at 700 °C, when the gasification with H_2O and CO_2 started. In the plant tests, the residue was completely converted in gaseous and liquid energy carriers with an overall energy efficiency of up to 87%. Ten conditions were examined with different air flow (19.0, 25.5, 26.5 kg/h), O_2 (4.0, 4.5, 5.5 kg/h) or H_2O (as steam at 160 °C: 1, 2.5, 4.0, 4.5, 5.5, 8.5 kg/h). The experimental data were analyzed using the Response Surface Analysis (RSA) in order to highlight the dependence on the Equivalence Ratios of oxidation. The molar ratio H_2/CO in the syngas increased by using steam as co-gasification agent, and reached the value of 2.08 in oxy-steam gasification. Steam was necessary to stabilize the process when using oxygen as it was effective in lowering the average temperature in the gasifier. Another positive effect of using steam was the shift of the temperature maximum far from the grate where ash melting could occur. Oxy-steam gasification provided the best results in terms of syngas heating value (LHV 10.9 MJ/m^3) and highest thermal power output of the plant (67 kW_{th}). The tar yield was inversely correlated with the residence time of the gas in the bed, in according with a zero order reaction for tar cracking into incondensable hydrocarbons and hydrogen.

1. Introduction

The current biorefining process is focused mainly on the conversion of carbohydrates into sugars and then into biofuels or platform chemicals. Lignin is not involved in these processes and remains substantially unconverted; it is usually recovered by filtration as solid together with residual fibers, or it is found partially solubilized in the liquid waste streams. This residue can be exploited for producing additional chemicals, power, combined heat and power (CHP). Hydrolytic lignin residue of biomass (HR) was largely available in the former USSR and in the Countries of East Europe as byproduct of fuels and chemicals production from lignocellulosics via acidic routes; it was estimated that the aggregate excess reached 1.5 Mt/y in the 1980s [1]. At that time, the production of carbon sorbents was successfully realized at large scale and continued for decades before the drop of oil prices. In addition, cessation of state subsides made that industry economically unsustainable. Currently, lignocellulosics materials are pretreated, preferentially with low burden processes like steam explosion, allowing the substitution of strong acids with enzymes in the hydrolysis step. The obtained lignin is chemically more similar to the native macromolecule than that obtained from the acid route and different approaches have to be set to exploit it. The optimal use of excess lignin is a key factor for the economic and environmental sustainability of a Biorefinery, not only disposal costs can be avoided but additional incomes can be provided [2,3]. To overcome the structural and chemical complexity of HR, synthetic routes were developed to break HR down in smaller molecules, liquid or even gas. Thermochemical conversions are suitable processes for this purpose although depends on what target is planned; specific breakdown in a limited product pool is still complicated. Gasification produces a gas mixture that can be used for electricity generation, synthesis of liquid fuels and chemicals [4]. Several types of gasifiers are available, primarily classified on the type of bed where the biomass reacts, which can be either fixed or not. Fluidized bed, as well as entrained flow gasifiers, are more suitable for large scale and continuous operations thanks to their higher gasification intensity, but require high investment cost and high quality feedstock, first in terms of homogeneity [5]. On the other hand, gasification plants equipped with fixed beds have several advantages such as simple structure, low

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investment cost and easy maintenance. Depending on the way of drafting of the producer gas, these plants are classified as downdraft or updraft. Medium and small scales, up to 10–15 MW of thermal input, are suitable for distributed energy production. Several reports are available in the literature on the use of coal as feedstock, whereas few examples are available for biomass gasification by updraft plants at a scale approaching this target [6]. In a previous paper we reported the gasification of fermentation residues in the updraft mode with air as medium [7]. In this work we investigated the effect of using oxygen and steam with the objective of improving plant efficiency and gas quality and to achieve a higher production of hydrogen with a molar ratio H_2/CO close to 2, which is required for the production of synthetic biofuels in catalytic processes [8,9].

2. Experimental

2.1. Feedstock

The tested materials were produced from enzymatic hydrolysis of straw (*Triticum aestivum*) or cane (*Arundo donax L*) and will be referred throughout the manuscript as HRS and HRC respectively, or generically as HR. The residues were collected by filtering the slurry contained in a 3 m^3 bioreactor and then dried outdoor on canvas. The dried residues were constituted of very fine particles aggregated in lumps; the large lumps were broken down in small pieces of about 4 cm in size. The two bulks were sorted and sampled following the procedure CEN/TS 14778. About 1 kg of HRS and HRC were used to determine their physical and chemical properties and to carry out TGA. The bulk density was measured using the ASTM E873 method. The particle density was estimated by measuring the displaced volume of about 50 g of HR when immersed in a sand bath of 500 ml contained in a graduated cylinder. The feedstocks were analyzed to determine the heat values, proximate and ultimate composition. The proximate analysis was carried out in covered crucibles at 900 °C, according to the method ASTM D 3175. The Higher Heating Value (HHV) was determined by calorimetry, using benzoic acid as reference. The Lower Heating Value was calculated from the content of hydrogen assuming complete conversion into water. The analysis with respect to carbon, hydrogen and nitrogen was performed according to the method UNI EN 15104, oxygen was determined by difference. The content of carbohydrates was determined using the method NREL/TP-510-42,623. Insoluble lignin was dried at 105 °C and its amount measured by weight. Soluble lignin was determined by UV spectrophotometry (TAPPI Useful Methods 250). All the analytical determinations were carried out in triplicate.

2.2. TGA tests

About 2–3 mg of each sample was used for TGA performed with a Perkin Elmer TGA7 apparatus. The calibration of the apparatus was based on the Curie point of Nickel (354 °C) and Iron (970 °C). The reproducibility of the tests was on average within 0.5% of the weight at given temperature. More details about the apparatus are reported elsewhere [10]. The tests were carried out with variable heating rate to simulate the heating that biomass particles undergo in the updraft gasifier. Based on the average thermal profile measured inside the reactor during the gasification tests, the heating rate was set at 5.5 °C/min at the beginning of the run, from 60 °C (stable weight) up to 260 °C; then 6 °C/min up to 380 °C; 7.5 °C/min up to 510 °C; 7.5 °C/min up to 630 °C; 17 °C/min up to 900 °C. The gas flow in TGA was 20 ml/min and it was kept stationary at the inlet. The mixtures of gas were purchased in cylinders, the purity of N_2 and O_2 was 99.999%. From each run a set of 5500 couples of data was available, that is weight and temperature recorded at regular time intervals; the data were exported and worked out in Excel worksheet. The 3D plots and RSA were carried out with the program Essential Regression and Experimental Design for Chemists and Engineers.

2.3. Description of the plant and procedures

The gasification tests were carried out using the pilot plant PRAGA (uP dRAft GAsification) at the ENEA Research Center of Trisaia. The rig and the main components are shown in Fig. 1. Beside the gasifier, the facility is equipped with a cleaning section, based on organic (biodiesel) scrubbing that cools the syngas to about 50 °C and performs the primary tar and ash removal, as well as two coalesce filters to remove entrained droplets. The syngas can be enriched in H_2 by an integrated water gas shift (WGS) reactor and CO_2 capture by MEA. The core of the plant is the fixed bed updraft gasifier which is operated slightly above atmospheric conditions. It is shaped as a 2.4 m high cylinder with an internal diameter of 0.3 m, further a 10 cm refractory layer covers the steel casing. The facility is equipped with probes to monitor and control temperatures, pressures, mass flows and liquid levels. The signals are conveyed to a PC and monitored with specific software allowing instrument calibration and data recording. The plant is equipped with a real time measurement of non-condensable gases (H_2, CO, CO_2, CH_4, O_2) by online GC analysis. Moreover, the syngas is sampled at the exit of the gasifier for offline analysis of water and organic volatiles. The trials with the pilot plant were carried out with a mix of HRS:HRC in a 1:1 ratio, in order to have enough feedstock to do all the planned gasification tests. The biomass was fed into the gasifier by screws in a semi continuous mode, in batches of 4.2–4.5 kg, under N_2 atmosphere at intervals of about 12 min, and completed in few seconds. Details about the plant and the procedures are described elsewhere [7,11].

2.4. Gas analysis

The composition of the clean and dry syngas was assessed by sampling the gaseous stream at the exit of the scrubber and by analyzing its composition with GC equipped with a TCD detector. The organic volatiles products and water were adsorbed in isopropanol following the CEN/TS 15439 method. Part of the solution was analyzed by HPLC and HPIC to determine the content of acetic acid, formic acid, 2-furaldehyde, furfuryl alcohol, 5-hydroxymethyl furaldehyde, 4-hydroxy benzaldhyde, syringaldehyde. Other organic molecules were determined by GC–MS, and the mass spectra were matched with the NIST library in order to identify the chemical species; the peak area was used to quantify the amount of each molecule having set as standards benzene, phenol, cresol, 1-methyl-naphthalene. The water content in the isopropanol solution was determined by Karl Fisher titration. The offline analyses of the solid and liquid samples were carried out in triplicate and the average values are reported. The flows of gas and steam were measured with calibrated instruments credited for a maximum error of 1% on the measured mass. In this paper the reported gas volume is referred to the standard temperature and pressure conditions (STP, 273.15 K and 10^5 Pa). More details about the chemical analysis are provided elsewhere [7,11].

3. Results and discussion

3.1. Reactivity of the HR

Gasification is the result of a series of reactions occurring at the interface solid-gas and in the gas phase. Mass and heat transfer play important roles that depend on several factors including particle size, temperature and pressure. At low temperature the kinetics depends on the intrinsic reactivity of the solid and on the concentration of the gaseous reactants. At high temperature the reactivity of the solid is exponentially enhanced because of the Arrhenius dependence of the kinetic constant and the mass transfer could be the only limiting step. The knowledge of the kinetic parameters is fundamental to understand the behavior of the system and to design the gasifier. The TGA is a powerful tool to study combustion and gasification of carbonaceous solids and to determine conversion rates and kinetic constants. In this