

Fluidized Bed Gasification of Biomass and Biomass/Coal Pellets in Oxygen and Steam Atmosphere

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The oxygen and steam fluidized bed gasification of wood and olive husk/coal pellets was studied with preliminary experimental investigations in a pre-pilot scale bubbling fluidized bed reactor. Two different bed materials were adopted: inert quartzite and Ni-alumina catalyst. The gasification tests were carried out at steady state, under operating conditions typical for gasification paper. The gas analyses have been performed with dedicated instrumentations, like continuous analyzer and adopting a standard protocol for tar sampling and characterization. The influence of the equivalent ratio (ER), steam oxygen ratio (SOR) and bed temperature on the concentration of stable gas (e.g. H₂, CO₂, CO and CH₄) as well as on the efficiency of tar conversion and syngas heating value were studied. A comparison between air-steam and oxygen-enriched with steam gasification was also carried out. In particular, the oxygen enrichment of gasification atmosphere leads to highest char carbon conversion and, of course, limited dilution in nitrogen of the syngas. In contrast, the tar content is still somewhat high, even simpler tar species were detected, and a higher CO₂ level is attained in the syngas.

1. Introduction

Although biochemical technologies are well developed and most widely used for biofuels and biogas production (Basu, 2010), biochemical is not effective or feasible for any kind of application. For example, the production of biofuels (ethanol and biodiesel) from fermentation process is only possible with food crops (corn, sugarcane, sorghum, etc) as input feedstock, with consequent ethical issues. Biotechnologies also fail when fossil or plastic materials are included in the feedstock. In alternative, the thermochemical processes are effective and flexible. In particular the gasification is a promising technology that can exploit the embedded energy within various kind of biomass and convert into valuable intermediates with flexibility for many industrial market applications such as heat, electricity and liquid fuels (Chen et al., 2007). The gasification converts solid fuels into a gas mixture whose composition and heating value are greatly dictated by the type of gasifying agents. Among these, the most widely used is air due to simplicity and low cost operations. Due to nitrogen dilution, air blow gasification typically yields syngas with heating value in the range of 4-7 MJ/Nm³ which is suitable for heat and power generation but not for uses of synthesis processes to produce valuable chemicals and liquid fuels (Gil et al., 1997). Air blown gasification was intensively studied by many researchers and is well-developed. Steam is another possible gasifying agent that can yield medium heating value (10-16 MJ/Nm³) with H₂ rich gas (Ptasinski et al., 2009). However, the process would become more sophisticated, because indirect or external heating is needed for the endothermic reactions. The use of pure oxygen as gasifying agent can produce medium heating value syngas (Shuster et al, 2001) but the high capital cost for oxygen production is the main barrier for the industrial scale. The studies on pure oxygen (Zhou et al., 2009) and oxygen enriched air with steam (Compoy et al., 2009) fluidized bed gasification are relevant examples along this line. The use of enriched air reduces the nitrogen dilution effect, increasing the gasification temperature. The appropriate combination of temperature and steam leads to higher CO and H₂ yields, heating value, carbon conversion and gasification efficiency. Altogether, steam and oxygen gasification merits attention of the scientific

community because not completely investigated yet, in particular for meeting market demands for liquid biofuels and chemicals production. The aim of this research is to investigate and provide further technological and fundamental insights into understanding the effects and drawbacks of using oxygen and steam as gasifying agent during biomass and biomass/coal pellets in fluidized bed.

2. Experimental

2.1 Experimental Facility

The fluidized bed gasifier consists of two vertical stainless steel tubes connected by a conical adapter, the lower tube has an Internal Diameter (ID) of 140 mm and is 1010 mm in height, and the upper tube has an ID of 200 mm and is 1800 mm in height. The gas distributor at the bottom of the fluidizing column has a conical shape to promote mixing of the solids. The fuel is under-bed fed into the reactor by a screw conveyor, 130 mm above the conical distributor. A steam generator to produce steam at a moderate gauge pressure (20 kPa) and at temperatures up to 400 °C is used for the steam production. A high efficiency cyclone and a heated ceramic filter (nominal aperture of 2 μm) are used for gas de-dusting. The transfer line and the cyclone were maintained at 450 °C to avoid tar condensation. The concentrations of the permanent gases are measured on-line with an ABB continuous analyzer equipped with Infra Red (IR) detectors for CO, CO₂ and CH₄ and a thermal conductivity detector (TCD) for H₂. The tar sampling is performed according to the protocol UNI CEN/TS 15.439 (2006). The analysis of the condensed tar after it is extracted from the water with dichloromethane is performed off-line with a gas chromatograph (HP 9600 series) equipped with a Flame Ionization Detector (FID) using the same level of dilution of the dichloromethane for all samples. For each test, when steady state is reached, the average gas composition (on the basis of the last 10 min of analysis) has been evaluated. A more detailed experimental apparatus description is reported in (Ruoppolo et al., 2009)

2.2 Bed materials and fuel characterization

Quartzite sand (density =2600 kg/m³; average size 155 μm ; minimum fluidization velocity 2.2 cm/s at 800 °C) and a Ni dispersed on γ -alumina (Al₂O₃) catalyst (density =1800 kg/m³; average size 150 μm ; minimum fluidization velocity 0.6 cm/s at 800 °C) are used as bed material. The catalyst preparation procedure and characterization parameters are reported in Miccio et al. (2009). Wood pellets and olive husk/coal pellets were used as fuel. As regards the mixed pellets the pelletization procedure has proved suitable to give sufficient mechanical strength to coal/wood pellet (Ammendola et al., 2011). The wood pellets (SWP) contain 100 wt.% of spruce wood, the olive husk/coal pellets (OH/GBC) contain approximately 30 wt.% of German brown coal and 70 wt.% of olive husk. The carbon, hydrogen and nitrogen contents of different fuels have been determined with the elemental analyzer CHN 2000 LECO, the balance being the oxygen content. The moisture, volatiles, fixed carbon and ash contents have been obtained by thermo-gravimetric measurements (TGA 701 LECO). The results of the analyses are reported in Table 1.

Table 1: Elemental and proximate analyses and lower heating value (LHV) of the different fuels

Fuels	SWP	OH/GBC
Pellets dimensions (diameter x length), mm	6 x 20	6 x 20
Moisture, wt. %	8.5	9.4
Volatiles, wt. %	74.1	54.6
Fixed carbon, wt. %	17.1	32.4
Ash, wt. %	0.3	3.6
Carbon, wt. % on dry and ash free basis	49.4	49.2
Hydrogen, wt. % on dry and ash free basis	5.9	5.97
Nitrogen, wt. % on dry and ash free basis	0.1	0.22
Oxygen, wt. % on dry and ash free basis	44.5	44.6
Low heating value, MJ/kg	18.5	22.6

2.3 Test procedure

Steady state tests of gasification have been carried out following a standard experimental procedure. The reactor is heated up to the desired temperature (700–850 °C). Then, the fluidization oxygen flow is set at the assigned value, the steam generator is turned on and the water is pumped to produce the desired

steam flow rate at around 400 °C. Afterwards, the biomass feeding is started, together with an inertizing nitrogen flow of 0.75 kg/h. Under steady conditions of the monitored variables, namely temperatures and gas concentrations, the measurements (gas concentration, tar and fine elutriated) are taken and recorded. The solid particles collected in both the hot filter and the cyclone are weighed after the experiments and their elemental analysis performed with the same apparatus previously reported. The liquid phase products are weighed, separately with respect to their dew point. Then, both the condensate at ambient temperature and at low temperature are dissolved in dichloromethane, to separate water from tar. The speciation of the condensed heavy tars (dew point higher than 20 °C) is performed by a HP 9600 series gas chromatograph equipped with a HP 35 Phenyl Ethyl Methyl Siloxane, linked to an Agilent Technologies Chemstation Rev.A.10.01 (1635). The analysis is restricted only to the family of chemical species that are prescribed by the tar protocol of the CEN/TS 15439 normative.

2.4 Investigating variables definition

To characterize the gasification conditions different ratios are applied: the ER (oxygen to biomass stoichiometric ratio) calculated as the ratio of oxygen supplied to the oxygen required for the complete stoichiometric combustion of the biomass on a dry basis; the SFR (steam to fuel mass ratio) calculated as the ratio of steam supplied to fuel supplied on an a.r. (as received) basis; the SOR (steam to oxygen mass ratio) calculated as the ratio of mass flow of steam supplied to mass flow of oxygen supplied; the GR (gasification ratio), often used for gasification with steam and oxygen in fluidized beds which is the sum of fluidization agent (O₂ + steam) divided by the mass of the solid feedstock. Apart from gas composition, two relevant results of gasification tests are the carbon conversion (CC%) and the cold gas efficiency (CGE%). CC% is defined as the ratio of fuel carbon, which is converted into non-condensable gaseous carbon components, to the total fed carbon, as reported in Eq (1).

$$CC\% = \left[\frac{m_{C, gas} \cdot \Phi_{m, gas}}{m_{C, fuel(dry)} \cdot \Phi_{m, fuel(dry)}} \right] \quad (1)$$

CGE% is defined as the ratio of the sum of the energy in cold syngas to the energy of fuel input, according to Eq(2) where the overall low calorific value (LHV) is calculated on the basis of syngas components and their LHVs.

$$CGE\% = \left[\frac{LHV_{gas}}{LHV_{fuel(dry)}} \cdot \frac{\Phi_{m, gas}}{\Phi_{m, fuel(dry)}} \right] \quad (2)$$

Finally, the overall lower calorific value is calculated as the weighted average of the low heat value for characteristic components of syngas.

2.5 Experimental conditions and results

Figure 1 shows the average concentrations of CO₂, CO, H₂ and CH₄ in the syngas for gasification tests carried out with a inert quartzite (tests 1-4) and Ni-alumina catalyst bed (test 5). The operating conditions of the gasification tests are reported in Table 2. The gas yield, carbon conversion, cold gas efficiency, low heating values of the syngas, unconverted carbon in the bed, and entrained char and dust are also reported in the same table. The gas yield was evaluated on the basis of a mass balance assuming the conservation of N₂ and is expressed as Nm³ of gas produced per kg of dry-biomass. The unconverted carbon was computed by time integration of CO and CO₂ profiles upon burning in air the accumulated char after each test; it is referred to the total fed fuel. Increasing gasification temperature is favourable for carbon conversion as it increases the gas-solid reaction kinetics (Figure 1, test 2 and test 3). Moreover, a temperature increase promotes thermal cracking of tars and their steam conversion (Pinto et al., 2009), as well as enhances the endothermic reactions between solid carbon, and volatile gases with steam increasing the total gas yields (Table 2, test 2 and test 3). In contrast, there is a very little effect of the temperature on gas composition (Figure 1, test 2 and test 3). Compared to coal, wood has higher volatile content and higher char reactivity, so an higher residual char is produced during oxygen-steam gasification of OH/GBC pellets although in presence of a higher oxygen content as evidenced by the different value of the steam to oxygen mass ratio (Table 2, test 1 and test 3). The dominance of CO concentration during steam-oxygen gasification is due to increased availability of O radicals to react with carbon in solid char

particles (the oxygen radicals are contributed from the breakdown of oxygen itself at high temperature). This is confirmed when comparing the composition of the syngas (Figure. 1, test 2 and test 4) obtained at higher temperature (> 800 °C) with the ones at lower temperature (Figure. 1, test 1 and test 3).

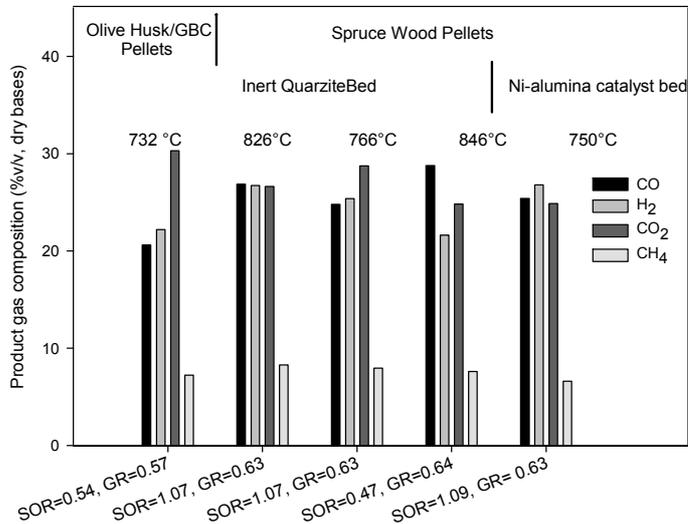
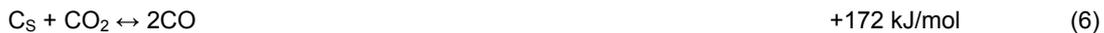


Figure 1: Effects of different operational conditions on the composition (dry basis) of syngas from biomass and biomass/coal using a quartzite inert bed

Heterogeneous reactions are reactions that arise from the interaction of char particles with gasifying agent as well as reaction between char particles and volatile gases. The main heterogeneous reactions and standard enthalpy change are:



The first two equations, Eq(3) and Eq(4), are combustion reactions that occur in the lower region of the bed. The Boudouard reaction, Eq(6), involves the gasification of carbon with CO₂. This reaction has three steps and the reaction rate is several orders of magnitude slower compared to the combustion reactions. Gasification of char in the presence of steam is represented by Eq(7), the water-gas reaction. This reaction is also slower than the combustion reactions, however, it is faster compared to the Boudouard reaction. The relative carbon conversion rate is as follows (Basu, 2010): $R_{C+O_2} \gg R_{C+H_2O} \gg R_{C+CO_2} \gg R_{C+H_2}$. Even though higher ER offers higher carbon conversion, too high of ER (Table 2, test 2 and test 4) will have adverse effects of oxidizing part of fuel gas and will result in excessive complete combustion products (CO₂ and H₂O) which lower the gas heating value. On the other hand the use of oxygen with steam removes the nitrogen dilution effect, thus increasing product gas heating values respect to the ones obtained with simple air steam mixtures (Ruoppolo et al., 2012). The comparison of the experimental results of this study with the ones obtained by Ruoppolo et al. (2012), using air-steam mixtures as gasifying agents, suggests that when pure oxygen is introduced in the reactor the carbon conversion increases because a higher partial pressure of O₂ establishes in the emulsion phase of the bed; thus lower unconverted carbon is obtained. Negative drawbacks of O₂ gasification seem to be the rather low cold gas efficiency, as consequence of the high CO₂ concentration in the syngas. Again, the increased partial pressure of O₂ in the emulsion phase could favour the full oxidation of C to CO₂ that is released in

freeboard where limited residence time and slow kinetics hinder the reduction to CO. A possible countermeasure could be a staged gasification scheme.

Table 2: Effect of different GR, OSR and temperature on CC%, CGE%, lower heating value of syngas, tar formation and residue/entrained char during biomass and biomass/coal gasification with a quartzite bed

Test	1	2	3	4	5
Fuel Pellets	OH/GBC	SWP	SWP	SWP	SWP
Temperature (°C)	732	826	766	846	750
SOR (kg/kg)	0.54	1.07	1.07	0.47	1.09
GR (kg/kg)	0.57	0.63	0.63	0.64	0.63
ER (kg/kg)	0.22	0.25	0.25	0.33	0.25
SFR (kg/kg)	0.23	0.34	0.34	0.21	0.41
Bed	quartzite	quartzite	quartzite	quartzite	Ni-alumina
U (m/s)	0.30	0.27	0.25	0.11	0.23
Tar Content (g/Nm ³)	76.8	23.7	62.7	37.5	23.0
Gas Yield (Nm ³ /kg _{dry})	0.79	0.81	0.73	1.06	0.60
Carbon Conversion (% , kg/kg _{fuel})	32.2	43.4	37.8	51.2	27.8
Cold Gas Efficiency (% , MJ/MJ)	18.2	40.5	34.4	42.3	59.9
Gas LHV (MJ/Nm ³)	4.14	4.99	4.71	4.72	4.78
Entrained Char (g/Nm ³)	1.65	6.26	12.4	4.91	2.64
Entrained Dust (g/Nm ³)	1.32	2.55	2.82	6.46	3.38
Unconverted Carbon (kg/kg _{fuel})	0.18	0.04	0.05	0.02	0.04

It is worth noting that the total tar content produced from biomass gasification using oxygen enriched atmosphere with steam is generally higher than the one resulting from simple air steam gasification (Ruoppolo et al., 2012), suggesting an activity in tar removal of the carbon present in the reactor mostly during air steam atmosphere. It is likely that the porous carbonaceous particles adsorb the tar and, in turn, the increased residence time in the reactor enhances the tar conversion, mainly by steam reforming (Ruoppolo et al., 2009).

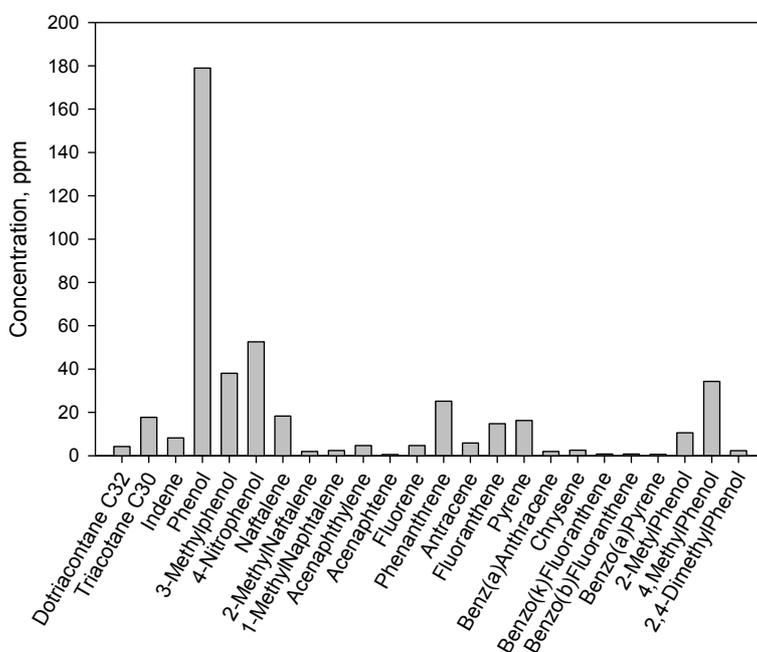


Figure 2: Tar speciation of the sample collected during the gasification test 5.

It is also confirmed the effect of the catalytic bed in reducing the tar yield, even at low temperature (Table 2, test 5). The composition of the tar as determined by GC-MS analysis is displayed in Figure. 2 for the

test 5 (Table 2). By comparison with results reported by Ruoppolo et al. (2012), it appears that the increased oxygen availability favors the formation of phenol, which is dominant, and other single ring compounds, with lower molecular weight and higher boiling point. Tars produced in air gasification are more refractory than those produced in steam (Corella, 1996), whereas steam gasification gives rise to more phenolics and C-O-C bond tars, which are easier to be reformed (Orio et al., 1997b). It is likely that the combined effect of pure oxygen and steam is beneficial, providing an explanation for the observed simplification of the produced tar suite.

3. Conclusion

The concept of oxygen and steam has been demonstrated as a feasible choice for FB gasification agent due to its positive effect on the carbon conversion, tar simplification and syngas calorific value. In contrast, the H₂/CO ratio is moderately low for synthesis processes such as Fischer-Tropsch for conversion into liquid fuels, where the required H₂/CO ratio is typically 2 (Higman and Burgt, 2003). A more extensive test matrix is needed in order to find the optimum combination of oxygen percentage in air, steam to biomass/coal ratios, equivalent ratios, gasification ratio and bed temperatures that give the highest carbon conversion, gas LHV and required H₂/CO ratio. A staged gasification scheme could be also an effective measure for limiting some drawbacks of excessive carbon conversion to CO₂.

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