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In Situ Carbon Dioxide Capture during Biomass Fluidized Bed Gasification

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The necessity to contain CO_2 emissions has been leading to a growing interest in renewable and CO_2 free energy sources. So far, co-gasification of coal and biomass is appealing for the production of a valuable energy or chemical vector as syngas. However, depending on the specific end-use, further treatments of the producer gas are required in order to reduce impurities including tars, dust and inorganic substances and/or to adjust the $H_2/CO/CO_2$ ratio. In this respect, sorption enhanced water gas shift reaction process with in situ CO_2 capture by solid sorbents represents an intensified option for producing a H_2-rich product stream. In addition to enhanced H_2 production, due to a shift in the key equilibrium reactions of gasification, this process has, in fact, several advantages including: a) the production of a concentrated stream of CO_2, suitable for storage (sequestration), as a consequence of the reversibility that generally characterizes these processes.; b) the exothermic carbonation reaction can supply most of the heat demand of the endothermic gasification reactions; c) particles sorbents, such as limestone, dolomite, olivine and high-iron solids, show some catalytic activity for tar reforming and cracking.

The paper reports on the mutual influence in the reactor between coal/biomass steam-oxygen gasification and CO_2 separation by means of a chemical sorbent. Experimental tests in a BFB (Bubbling Fluidized Bed) gasifier demonstrate that using a CaO-alumina mixed bed the H_2/CO ratio can be strongly enhanced, provided that a good control of the temperature is assured because of the high thermal character of the carbonation. The use of CaO-alumina mixed bed offers the advantage of reducing the tar concentration and prevent the bed agglomeration typically observed when olive husk and quartzite sand are used.

1. Introduction

Due to global warming and climate changes caused mainly by fossil fuel consumption, hydrogen, as a clean and carbon-free fuel, and its production have recently become a very important topic of research. Currently, H_2 is largely produced from fossil fuels via steam methane reforming and coal gasification. The amount of hydrogen in the synthesis gas is up to 30 - 40 % vol. In addition the water gas shift reaction (WGS) can be also carried out to reduce the concentration of CO at a level required for the purification of stream by membranes for fuel cells application or for CO_2 sequestration process.

There are different techniques for removing carbon dioxide (CO_2) from the flue gases of power and chemical plants. Among these methods, high-efficiency dry sorption is a promising method. Calcium (Ca) based materials are the best candidates for CO_2 capture sorbents, due to their abundance, low cost and high CO_2 uptake at gasification temperatures (Florin and Harris 2007). The most recommended gasifying agent used to produce hydrogen (H_2) is pure steam. Moreover, the H_2 content can be as high as 40 – 60 vol% (dry basis) in the gasification of raw gas (Corella et al., 2008). The integration of the reaction and separation phases into one stage has several advantages over the conventional method; process simplification, enhanced energy efficiency, and increased reactant conversion and product yield (Lin et al., 2002). In sorption-enhanced

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process, a sorbent is added to the reaction mixture to remove one of the reaction products in order to shift forward the equilibrium of reversible reactions (Florin and Harris 2007). Coal gasification coupled with the presence of Ca-based sorbents increases the hydrogen production yield and has several advantages. First of all, the major portion of heat required for endothermic gasification reactions is supplied by the process itself, and the emission of pollutants containing sulphur, chlorine, and nitrogen (e.g., sulphur and nitrogen oxides and hydrogen chlorine) are mitigated. Therefore, this modified gasification process would not require an extensive gas clean-up unit.

The CO_2 capture can occur provided that the partial pressure of CO_2 is high enough to make possible the carbon uptake. Since the carbon monoxide is predominant at high temperature (i.e. > 1,073°C) during coal gasification with moderate equivalence ratio, the operating temperature should be between 923 and 1,023 K. In this range of temperature, a partial pressure of CO_2 higher than the equilibrium pressure for the CaO-CO_2 atmospheric system is attainable under certain conditions. Because of the medium temperature range, a detrimental effect of limited kinetics of both gasification and absorption reactions occurs. The conditions of optimized operation are strongly dependent on the reactivity of the fuel, catalytic effects exerted by the sorbent as well as reactor fluid-dynamics.

If a biogenic fuel is co-processed and subjected to carbon capture, a negative contribution to the CO_2 emissions in the atmosphere could be achieved, with possible credits for the industrial application. Among large number of biomass fuels, dry olive husks – abundant in the Mediterranean area - can be attractive as energy source because of their appreciable heating value and the easiness to be gasified.

In this work, firstly the operating and thermodynamic conditions are determined, for making possible the concurrent process of CO_2 uptake in an ideal gasification reactor where the chemical equilibrium is reached. Furthermore the experimental results of biomass/coal gasification in a fluidized bed containing CaO are presented and discussed with the aim to provide further insights into even more sustainable generation of syngas for different end-use. The Ca based sorbent has been used mixed with alumina which offers the additional possibility to prevent the sulphur poisoning of the CaO, since it has been reported that at low sulphur concentration the alumina could preferentially adsorb S compounds (Ammendola et al., 2012) in other process.

2. Experimental

2.1 Experimental Facility

The bubbling fluidized bed gasifier (BFBG) is composed of three main sections (the feeding system, the fluidized bed gasifier and the syngas treatment unit). The feeding system can be divided into: gasification agent feeding and fuel feeding. The gasification agent feeding consists of a two gas flow meter with a maximum load of 15 Nm^3/h controlled by a junction box and connected to a control computer. A steam generator to produce steam at a moderate gauge pressure (20 kPa) and at temperatures up to 673 K is used for the steam production. A wind-box before the gas distributor allows to mix the different gasification agents. The gas distributor at the bottom of the fluidizing gasifier has a conical shape to promote mixing of the solids. The fuel feeding system allows to feed the fuel into the reactor by a screw conveyor, 130 mm above the conical distributor. The fuel is fed under-bed in order to enhance the contact with the bed. The bubbling fluidized bed gasifier (BFBG) is composed of two vertical stainless steel tubes connected by a conical adapter. The lower tube has an Internal Diameter (ID) of 140 mm and 1,010 mm in height, and the upper tube has an ID of 200 mm and is 1800 mm in height. The syngas treatment unit can be divided into: gas de-dusting system, tar sampling and gas analyzer. A high efficiency cyclone and a heated ceramic filter (nominal aperture of 2 μm) are used for gas de-dusting. The dusts are collected, weighted and analyzed during post-process analysis. The transfer line and the cyclone were maintained at 723 K 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, CO_2 and CH_4 and a thermal conductivity detector (TCD) for H_2. 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 by Ruoppolo et al. (2009).

2.2 Bed materials and fuel characterization

Quartzite sand (density = 2,600 kg/m^3; average size 155 µm; minimum fluidization velocity 2.2 cm/s at 1,073 K),

γ-alumina (Al_2O_3) (density =1,800 kg/m^3; average size 150 µm; minimum fluidization velocity 0.6 cm/s at 1,073 K) and calcium oxide (CaO) obtained by an Italian high-calcium limestone ($CaCO_3$) commercially referred to as Massicci (density =1,650 kg/m^3; average size 650 µm; minimum fluidization velocity 8.4 cm/s at 1,073 K) are used as bed material. In particular CaO is mixed with alumina or quartzite in order to obtain a mixed bed (35 % wt. CaO and 65 % wt. of Al_2O_3 or quartzite). The chemical and physical properties of limestone were reported by Coppola et al. (2012). Olive husk/German brown coal pellets were used as fuel. The olive husk/coal pellets (OHGBC) 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 moisture, volatiles, fixed carbon and ash contents have been obtained by thermo-gravimetric measurements (TGA 701 LECO). The results of the analyses are reported by Ruoppolo et al. (2013).

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 (970 – 1,100 K). The fluidization oxygen flow is set at the assigned value and the steam generator is turned on. The water is pumped to produce the desired steam flow rate at around 673 K. Afterwards the fuel feeding system is started and an inertizing nitrogen flow of 0.65 kg/h is used. 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 liquid phase products are weighted, separately with respect to their dew point. Afterwards, 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. To characterize the gasification conditions different ratios are introduced: the SF (steam to fuel mass ratio) calculated as the ratio of steam supplied to fuel mass flow 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 steam-oxygen gasification which is the sum of fluidization agent (O_2 + steam) divided by the mass of the solid feedstock.

3. Results and discussion

3.1 Thermodynamic equilibrium of the combined process

The limitation that most directly affects the processes in which CaO is used as sorbent is the thermal equilibrium of the carbonation reaction (4). The equilibrium vapor pressure of CO_2 over CaO is given by Baker (1962):

$$\log_{10} Peq\ [atm] = 7.079 - \frac{8308}{T\ [K]} \tag{1}$$

The necessity of operating at typical gasification temperature (between 950 and 1,300 K) together with the aim at capturing carbon dioxide, narrows down the width of possible working conditions.

More specifically, the equilibrium vapor pressure of carbon dioxide at atmospheric pressure is equal to 3.5 % vol. at 973 K and grows up to 22 % vol. at 1073 K, for this reason the CO_2 capture can occur provided that no very high temperatures are adopted. On the other hand in a medium temperature range, a detrimental effect of limited kinetics of gasification reactions occurs. In order to taking account of this two different aspects we have fixed the operating temperature at about 973 K. Preliminary thermodynamic study has been carried out with the aim of assessing the “sorption-enhanced hydrogen production” or, in other words, the shift of the WGS reaction equilibrium by subtraction of CO_2,. In particular, the conversion of CO (in terms of H_{2out}/CO^{in} ratios), at different H_2O/CO ratios has been calculated under the hypothesis of equilibrium in presence or not of CaO on the basis of the four reactions following reported. The results obtained at 973 (a) and 1073 K (b) are plotted in Figure 1. It clearly appears that at temperature of 1,073 K the presence of CaO does not significantly enhance the H_2 production.

Carbonaceous materials gasification:

$$C\ (s) + H_2O(g) \rightarrow H_2(g) + CO(g) \qquad \Delta H^{\circ}_{923} = +131 kJ/mol \qquad (2)$$

Water gas shift:

$$CO\ (g) + H_2O(g) \Leftrightarrow CO_2(g) + H_2(g) \qquad \Delta H^{\circ}_{923} = -41.5\ kJ/mol \qquad (3)$$

CO_2 absorption:

$$CaO\ (s) + CO_2(g) \Leftrightarrow CaCO_3\ (s) \qquad \Delta H^{\circ}_{923} = -178.3\ kJ/mol \qquad (4)$$

Sorption-enhanced hydrogen production:

$$C\ (s) + CaO\ (s) + 2H_2O(g) \Leftrightarrow 2H_2(g) + CaCO_3\ (s) \qquad \Delta H^{\circ}_{923} = -88.8\ kJ/mol \qquad (5)$$

A different behavior is evident at 973 K; in this case an increase of around 28% is predicted for a syngas having $H_2O/CO = 2$. For this reason the operating temperature of experimental tests is fixed at 973K

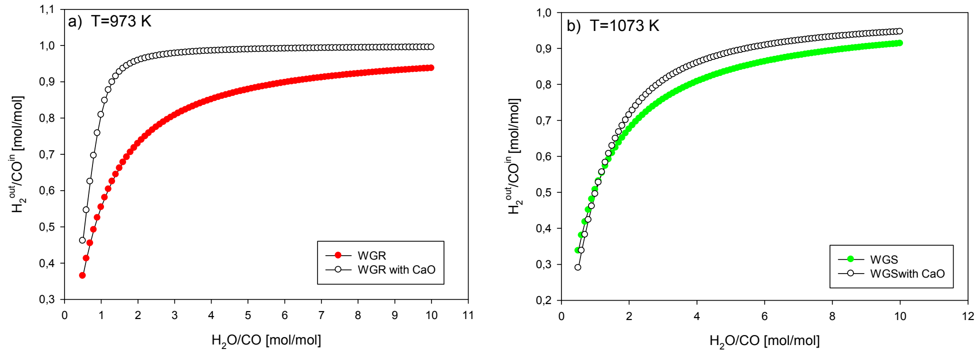

Figure 1: H_{2out}/CO^{in} ratio as function of H_2O/CO ratio evaluated on the basis of thermodynamic equilibrium in the presence or not of CaO at 973 K (a) and 1,073 k (b) and at atmospheric pressure.

3.2 Results of gasification tests

The result of the gasification test, carried out using a pure alumina bed and feeding OHGBC at 973 K and with a SF = 0.51, SOR = 0.94 and the GR = 1.05 in terms of dried CO, CO_2; CH_4 and H_2 concentration profiles are showed in the Figure 2.

As it is possible to see, a steady state condition is reached after 500 seconds, mainly due to the accumulation of a carbon load in the bed. Afterwards, a value of CO_2 (about 25 %vol in comparison to the 14 % estimated from the equilibrium at 973 K), compatible with its capture, is obtained under the chosen experimental conditions. The performance of alumina (in terms of average gas composition and tar concentration) differs from that previous reported (Ruoppolo et al. 2013) for a quartzite bed and the same fuel.

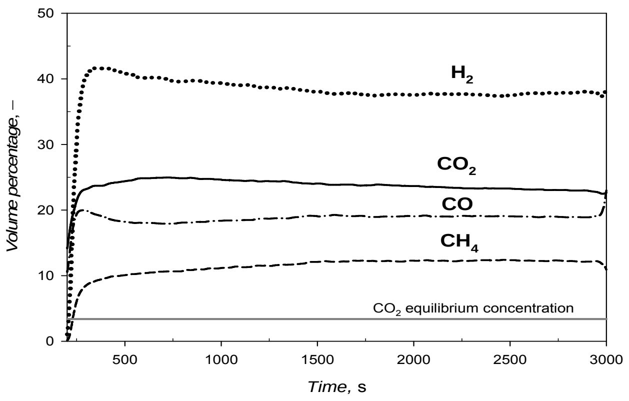

Figure 2: CO_2, CO, H_2 and CH_4 profile at the exit of gasifier obtained at 973 K, SOR = 0.94; SF = 0.51 and GR 1.05 with a bed of alumina and as fuel OHGBC pellets.

In particular the higher hydrogen (39 %vol instead of 22 %vol) and methane concentration (11.0 % vol. versus 7.0 % vol.) could be explained with a higher SOR adopted, which promotes the H_2 concentration, and by the tar cracking action of the alumina (tar concentration 27.3 g/Nm^3 rather than 76.3 g/Nm^3 in quartzite), which enhances the production of methane.

In Figure 3 the gas composition, obtained for OHGBC pellets under quite similar experimental conditions by partially substituting alumina with an amount of CaO (35 % wt), is shown.

As it is possible to see, at the beginning, higher value of H_2 and lower CO concentration in comparison with the experiment carried out without CaO have been obtained. This result can be related to a shift of the WGS reaction due to the subtraction of a product i.e the captured CO_2.

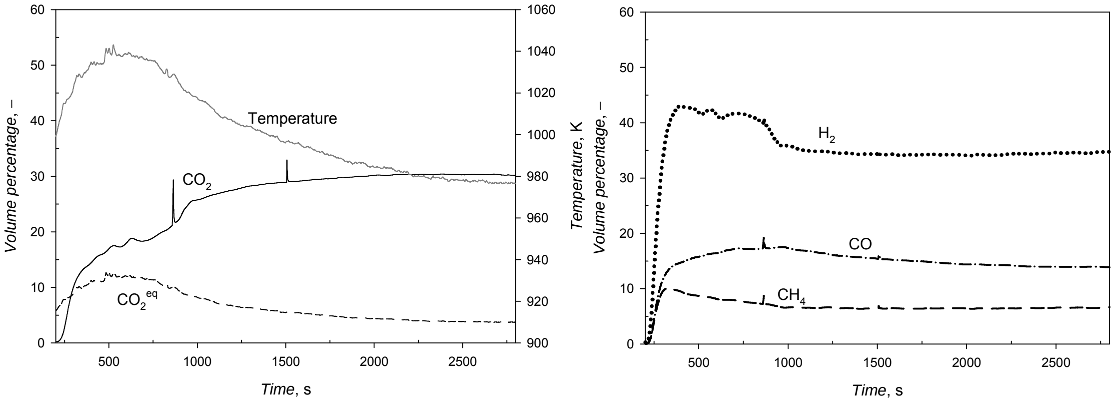

Figure 3: CO_2, CO, H_2 and CH_4 profile at the exit of gasifier at 1,013 K, SOR = 0.94; SF = 0.51 and GR 1.05 with a bed of 35 wt% CaO and 65 wt% of alumina and as fuel OHGBC pellets.

In agreement with this hypothesis an increase of the temperature, due to the absorption, has been also observed. However, the value of CO_2 always remains higher than that estimated by theoretical equilibrium calculation at the given temperatures and reported together with the measured CO_2 concentration in the graph. During this test the steady state is not reached, as in absence of CaO, since the increase of the temperature depresses the CaO capture capacity and the system moves to a higher value of equilibrium concentration corresponding to the new value of the temperature. The increasing of CO_2 concentration is coupled with an increase of CO and a decrease of H_2 for the shifting of the WGS reaction to the reagents. When a stationary value of the temperature is reached, a further increment of CO_2 concentration is observed due to the progressive saturation of the sorbent that affects the CO_2 capture velocity. On the basis of the CO_2 profile the amount of carbon dioxide adsorbed has been calculated as difference between the steady state value (30.2 %vol) obtained at the end of the test, i.e. when the CaO is satured, and the actual concentration using the value of exit gas flow evaluated on the basis of N_2 conservation hypothesis. The amount of CO_2 captured is around 528 g which corresponds to a capture capacity of 0.46 $g_{CO2}/g_{sorbent}$ in agreement with values reported for a natural sorbent by Broda et al (2011), but lower than the theoretical value 0.78 $g_{CO2}/g_{sorbent}$.. A further test with a bed made of 35 % wt. of CaO and 65 % wt. of quartize, under the same operating condition of the former has been carried out in order to assess once again the role of the alumina in the tar cracking. After about 2,500 s a fast increase of the temperature (the temperature and pressure profiles obtained during the test are reported in Figure 4a) has been observed. The rapid increase of the temperature can be associated to the beginning of defluidization of the bed due to the occurrence of agglomeration phenomena. In fact,it is well know that the presence of alkalis in the ashes of the fuel, as in the case of olive husk, leads to the chemical formation of amorphous phases with the quartzite. The presence of CaO does not affect this behavior. On the basis of the ash content in the fuel and the value of the elutriation rate measured during the experiment the amount of ashes accumulated in the bed has been calculated. The value obtained is about 110 g which represents about 4% of the amount of quartzite loaded in the bed (2,600 g), a critical value that could be associated to the onset of agglomeration that can be extensive, leading to bed defluidization in agreement with findings reported by Scala and Chirone (2006). A further accumulation of the ashes in the bed gives rise to the more extensive agglomeration and defluidization associated to the very fast increase of the temperature and pressure. In figure 4b the photo of some agglomerates discharged from the bed after the shutdown of the reactor is proposed. The comparative analysis of the tests confirms that alumina prevents the formation of the agglomeration.

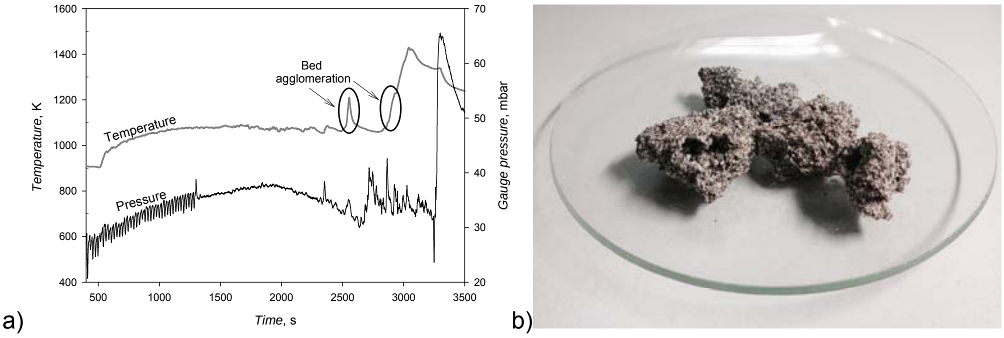

Figure 4: Temperature and pressure profiles at 1,013 K, SOR = 0.94; SF = 0.51 and GR 1.05 with a bed of 35 % wt. CaO and 65 % wt. of quartzite and as fuel OHGBC pellets (a); photo of agglomerates from the bed (b)

4. Conclusions

The computation of the chemical equilibrium for combined WGS and carbon capture reactions reveals that at temperature of 973 K the production of H_2 is largely enhanced by the presence of CaO: for instance, an increase of around 28% is predicted for a syngas having $H_2O/CO = 2$. This effect is depressed for higher temperature.

From the experiments carried out in BFBG, a significant change of the syngas composition was observed switching from a bed of pure alumina to a mixed bed of alumina/CaO: CO and H_2 increased confirming the CO_2 uptake until sorbent saturation. The large exo-thermal character of the carbonation reaction impacts on the energy balance of the reactor, an increase of T up to 50 K being recorded. The amount of CO_2 captured in alumina/CaO bed was high, corresponding to a capture capacity of 0.46 $g_{CO2}/g_{sorbent}$.

Alumina mixed with CaO prevents the formation of the agglomeration caused by alkali rich fuels. Further investigations are required to definitively assess the observed.

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