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Full Length Article

Experimental investigation on sorption enhanced gasification (SEG) of biomass in a fluidized bed reactor for producing a tailored syngas

I. Martínez*, V. Kulakova, G. Grasa, R. Murillo

Department of Energy and Environment, Instituto de Carboquímica (Spanish Research Council, ICB-CSIC), Miguel Luesma Castán 4, 50018 Zaragoza Spain

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ABSTRACT

Synthetic fuel production from renewable energy sources like biomass is gaining importance driven by the ambitious targets for reducing greenhouse gas emissions worldwide. Sorption enhanced gasification (SEG) proposes carrying out the gasification of biomass in the presence of a CO_2 sorbent, which allows producing a syngas with a suitable composition for a subsequent synthetic fuel production step. This study aims at analysing the effect of different operating parameters (e.g. steam-to-carbon (S/C) ratio, CO_2 sorption capacity and sorbent-to-biomass ratio) in the syngas composition and char conversion obtained in a 30 kW_{th} bubbling fluidized bed gasifier, using grape seeds as feedstock. The importance of reducing the formation of higher hydrocarbons through a high steam-to-carbon ratio and using a CO_2 sorbent with high sorption capacity is assessed. C_3-C_4 and unsaturated C_2 hydrocarbons contents below 1%vol. (in dry and N_2 free basis) can be achieved when working with S/C ratios of 1.5 at gasification temperatures from 700 to 740 °C. Varying the amount of the CO_2 separated in the gasifier (by modifying the temperature or the CO_2 sorption capacity of the sorbent) the content of H_2, CO and CO_2 in the syngas produced can be greatly modified, resulting in a module $M = (H_2\text{-}CO_2)/(CO + CO_2)$ that ranges from 1.2 to almost 3.

1. Introduction

Biomass derived biofuels can play an important role in the decarbonisation of the transport sector [1], as well as in the replacement of fossil fuels in common applications like heat and power production [2]. Gasification of biomass is the leading thermal conversion technology when focused on syngas production to be used as feedstock for synthetic biofuel production in a downstream catalytic process [3]. Steam and oxygen should be used as gasification agents when looking for the synthesis of biofuels in order to produce a high-heating value synthesis gas without N_2 as main diluting component [4]. However, oxygen-blown gasifiers require from an energy-consuming air separation unit (ASU), which may turn the process uneconomically when moving to small-to-medium scale.

Dual fluidized bed reactors have demonstrated a great potential in the field of synthetic biofuels production [4]. This gasification system is an indirect gasification process where the energy for the steam gasification is supplied by a stream of solids at high temperature circulating from a secondary reactor. Steam is usually used as gasification agent in this system since it improves the H_2 content in the syngas produced and reduces the amount of tar [5]. Unconverted char that leaves the gasifier is burnt with air in the secondary reactor or combustor in order to increase the temperature of the circulating solids that will be sent back to the gasifier acting as heat carriers. Typically, two fluidized bed reactors are used in this indirect gasification system, i.e. a bubbling fluidized bed reactor operating as gasifier and a circulating fluidized bed reactor as combustor [4]. This indirect biomass gasification concept has been demonstrated in several commercial scale plants in Austria (Güssing, Oberwart), Germany (Senden) and Sweden (Gothenburg) with plant capacities in the range of 2 MW_e (corresponding to that in Güssing) to 20 MW of synthetic natural gas in the Gobigas plant in Gothenburg [6–11]. In addition to these commercial plants that use woody biomass as fuel, there are smaller pilot plants that have investigated this dual fluidized bed system for alternative biogenic or residual biomass fuels [12–14] that have provided valuable information about such materials' performance and the impurities produced in each case.

The solid bed material used in the dual fluidized bed gasification system can act exclusively as heat carrier, providing the energy needed for the gasification reaction (i.e. sand), or can be a reactive bed material and so take part in the gasification process. In this latter case, the bed material can have good catalytic properties towards tar cracking (i.e. olivine or iron ores) and/or can improve the hydrogen content in the syngas by separating the CO_2 from the gas phase as it is formed (i.e.

* Corresponding author.
E-mail address: imartinez@icb.csic.es (I. Martínez).

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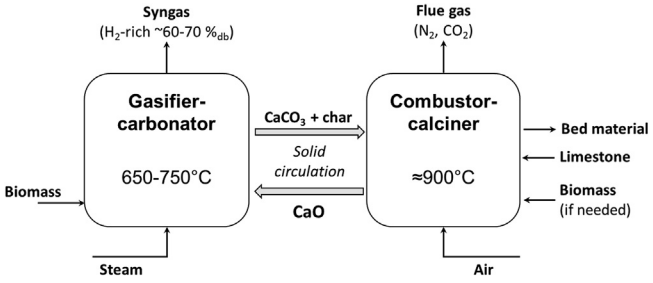


Fig. 1. Scheme of the sorption enhanced gasification (SEG) process.

dolomite and limestone are the most common). By coupling an *in-situ* CO_2 separation process, a sorption enhanced gasification (SEG) process is achieved. A CaO-based material is typically used in such SEG process, which reacts with the CO_2 produced according to the exothermic carbonation reaction of CaO (i.e., $CaO_{(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)}$). Fig. 1 shows a conceptual diagram of this SEG process. In order to favour this reaction, the gasifier is usually operated at temperatures between 650 °C and 750 °C, which are noticeably lower than those used in conventional gasification systems or in indirect gasification with olivine [15,16]. Despite this operation at lower temperatures, the CaO has demonstrated good catalytic properties towards tar cracking as demonstrated by the relatively low values of tar concentration in the syngas reported in the literature [14]. Hydrogen contents in the syngas produced through a SEG process using biomass can be as high as 75 % vol. (dry basis) when using CaO as CO_2 sorbent [17], due to the favourable effect of the carbonation reaction on the equilibrium.

When focused on synthetic fuel production, the relative amount of H_2, CO and CO_2 in the syngas should be adjusted depending on the desired final product and the type of catalyst used in the synthesis process. Typically, the M-module (i.e., the ratio $(H_2\text{-}CO_2)/(CO + CO_2)$) or the H_2/CO molar ratio are used as parameters for checking the suitability of the syngas produced for a given downstream synthesis process. Working with a proper amount of these gases allows optimising the performance of the synthesis process and so maximising its efficiency. In case of biofuels like dimethyl-ether (DME), methanol or Fischer-Tropsch biodiesel, the final H/C ratio, and therefore the desired M-module or H_2/CO ratio in the synthesis gas, is around 2. However, for synthetic natural gas production (i.e., methane) an M-module of 3 would be needed and so higher H_2 content in the syngas would be desirable. For conventional indirect gasification of biomass, a very poor H_2 content syngas is obtained, corresponding to H_2/CO ratios of 0.5–1.6 or M-modules of 0.1–0.8 [4], whereas for the SEG process these ratios are greatly above the values needed for a synthesis process. The idea of a flexible SEG, where the amount of CO_2 separated in the gasifier is regulated to obtain a tailored syngas composition, has been recently proposed [18]. In this way, the conditioning stages needed before the synthesis process would be greatly simplified with respect to the traditional biofuel synthesis routes, resulting in an intensified process. Furthermore, improved process safety may be targeted in SEG by comparison of conventional biomass gasification, since "simplification" – *Simplify—eliminate unnecessary complexity, design "user-friendly" plants*" – is one of the four driver keywords towards inherently safer processes, according to initial promoters of inherently safer design (ISD) of processes [19].

This study aims at analysing the influence of the main operating parameters in a SEG process on the composition of the syngas obtained. SEG tests have been carried out in a 30 kW_{th} bubbling fluidized bed gasifier, using a by-product/waste of wine production (i.e. seeds) as biomass feedstock. This winery waste is a potential valuable source of oil to be used in food, cosmetics or healthcare industries, or a feedstock for the production of high valuable chemicals. However, most of this winery by-product is discarded as waste in landfills. Consequently, an added value to this work is demonstrating the possibility of producing a tailored syngas through a gasification process from this winery by-product. The sorbent-to-biomass ratio, the steam-to-carbon (S/C) ratio and the CO_2 sorption capacity of the Ca-based sorbent have been modified to elucidate their influence on syngas composition, and so on the possibility of adjusting syngas composition through any of these variables. Moreover, the variation of the char conversion with the main operating variables of this SEG process (i.e. gasification temperature, solid residence time and/or S/C ratio) has been also assessed, which would be useful for closing the global balances of a dual-reactor SEG process. Experiments carried out in this work have been carried out in the framework of the EU H2020 project FLEDGED whose main objective is the demonstration at TRL-5 of an intensified and flexible DME production process based on the SEG process of biomass [20]. As a result of the experiments carried out, indications of the aforementioned operating parameters needed for the SEG process would be given when focused on DME production.

2. Materials and methods

2.1. Materials description

The biomass used for the experiments was a by-product/residue of wine production process, i.e. grape seeds, with a particle size ranging between 4.5 mm and 6.8 mm. The ultimate and proximate analyses as well as the calorific value of the grape seeds were determined, obtaining the results compiled in Table 1. For determining the properties shown in this table, representative samples of the biomass were left to stabilise in air until constant weight before being analysed. Ultimate analysis was determined in a Thermo Flash 111 (UNE-EN-5104) whereas moisture, volatile matter and ash contents were calculated according to standards UNE-EN 18134-3, UNE-EN 14775 and UNE-EN 15148, respectively. Ash composition was also determined by ICP-OES, and Ca and K were detected as the major compounds in biomass ashes (8313 and 8639 ppm, respectively). Phosphorous and Silicon were the following most abundant elements in biomass ashes with contents of 2094 and 1359 ppm, respectively, in the ashes.

CO_2 sorbent used for the experiments was obtained from limestone calcination in the bubbling fluidised bed (BFB) reactor at around 910 °C by means of the combustion of A1 quality wood pellets (0.36%wt. of ash content, 0.02%wt. of Sulphur and a LHV = 17.6 MJ/kg) with air. Mean particle size of the calcined sorbent used for the SEG tests was 450 μm. Limestone used as a precursor of the CO_2 sorbent was analysed through an inductively coupled plasma-optical emission spectrometer (ICP-OES) to determine its chemical composition. Composition of the calcined material determined by ICP-OES is shown in Table 2. According to the information in this table, the limestone used has a high purity with more than 98%wt. of CaO in the solid residue after calcination. Minor impurities like MgO and Al_2O_3 are present. Calcined material was also texturally characterised for determining its porosity, BET surface and solid density, which have been also indicated in Table 2. Pore volume was determined using a Hg Porosimeter

Table 1
Ultimate and proximate analyses, as well as calorific value of the biomass used for SEG tests.

Ultimate analysis [%wt., dry-ash free basis]*		Proximate analysis [%wt.]*	
C	60.31	Moisture	6.30
H	6.58	Volatile matter	65.12
N	2.46	Ash	4.30
S	0.13	Fixed carbon	24.28
O	29.92		
Cl**	0.07	LHV [MJ/kg]*	20.51

* Referred to the weight of the samples after stabilisation in air until constant weight.

** Determined by ionic chromatography.

Table 2
Composition and textural characterization of the calcined limestone used as CO_2 sorbent precursor in SEG tests.

	Calcined limestone
CaO [%wt]	98.25
Al_2O_3 [%wt]	0.145
Fe_2O_3 [%wt]	0.002
K_2O [%wt]	< 0.001
MgO [%wt]	0.183
Na_2O [%wt]	< 0.001
SiO_2 [%wt]	0.132
Porosity [–]	0.52
Surface area [m^2/g]	8.8
Solid density [kg/m^3]	3139

Quantachrome Pore Master and solid density through a He pycnometer (Accupyc 1340 by Micromeritics). N_2 adsorption (Micromeritics ASAP2020) at 77 K was used to calculate the sorbent surface area by applying the Brunauer-Emmett-Teller equation. Finally, the CO_2 carrying capacity of the sorbent along consecutive calcination/carbonation cycles was determined in an atmospheric thermogravimetric analyser (TGA), which has been already described in [21,22] and specifically designed for high temperature multi-cycle testing. Calcination/carbonation cycles consisted of a calcination stage at 900 °C in air during 5 min followed by a carbonation period at 710 °C in a mixture of 15 % vol. of CO_2 in air during 5 min. As widely observed in the literature for natural CaO-based sorbents, the CO_2 carrying capacity of this material typically decreased with the number of calcination/carbonation cycles, achieving a residual activity of around 0.07 mol of CO_2/mole of CaO after hundreds of cycles. For the CO_2 sorbent used in this work, CaO conversion moved from 0.8 mol of CO_2/mole of CaO in first carbonation to 0.4 mol of CO_2/mole of CaO during fifth carbonation.

2.2. BFB facility description

Sorption enhanced gasification (SEG) tests were carried out in the 30 kW_{th} (referred to the nominal thermal input of biomass in LHV-basis) bubbling fluidized bed (BFB) reactor depicted in Fig. 2. It consists of a 3 m height stainless steel reactor comprising two zones: a bottom dense zone of 1 m height (0.15 m of internal diameter) and a freeboard zone of 2 m height (0.20 m of ID). The reactor is externally heated through five electrical resistances and insulated with glass wool. Temperature and pressure distribution along the reactor are monitored through thermocouples and pressure transducers placed as shown in Fig. 2. CO_2 sorbent and biomass are fed separately into the reactor from two independent closed hoppers. As indicated in the figure, these hoppers are placed over two screw feeders that introduce the solids at the bottom of the reactor (right above the gas distribution plate). Both feeders are provided with a regulation system that changes the rotation speed of the electric motor for regulating the mass flow rate. For most of the experiments shown in this work, a constant biomass thermal input of about 21 kW_{th} (i.e. 3.6 kg/h flow rate) was used. However, some experiments with a lower thermal input of 13 kW_{th} were carried out for assessing the impact of char conversion in the gasifier. Biomass screw feeder is externally cooled with water in order to prevent its excessive heating due to conduction and so the prompt decomposition of the biomass in the screw. Solids ($CaO/CaCO_3$, unconverted char and ashes) leave the reactor through a lateral overflow (shown schematically in the left-hand side of the reactor in Fig. 2), and are collected in a hopper that is periodically discharged during operation. This overflow regulates the solid bed inventory in the bottom dense zone of the reactor, which resulted around 5–7 kg depending on the fluidization conditions.

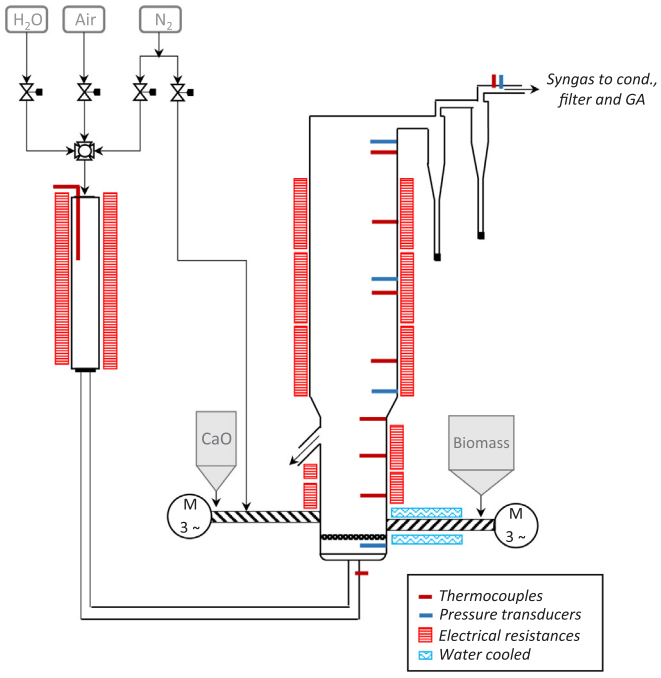


Fig. 2. Schematic of the 30 kW_{th} BFB gasifier.

The flow rate of steam or air fed to the reactor is controlled by means of the corresponding mass flow controllers. Liquid water contained in a pressurized process vessel passes through a tubular evaporator that is externally heated by an electric furnace, producing overheated steam at 160–180 °C that is fed through the bottom of the reactor. A constant flow rate of N_2 is fed together with the water at the entrance of the evaporator in order to facilitate the flow of H_2O through the evaporation system as well as to serve as an internal standard for calculating the syngas flow rate at gasifier outlet. Moreover, a constant flow rate of N_2 is also fed into the reactor through the screw feeder of the CO_2 sorbent in order to avoid the backflow of rich-H_2O syngas through the sorbent hopper, which would cause operational problems due to the premature hydration of the CaO. Both N_2 flow rates account for 0.0120 Nm^3/min, which has been accounted for in the N balance solved for calculating the syngas yield obtained in the experiments.

Downstream the gasifier, two high efficiency cyclones are placed in order to separate entrained particles of CO_2 sorbent and unconverted char generated during the gasification process. Each cyclone is provided with a hopper where fine particles are accumulated to be purged during operation. After passing through the cyclones, syngas is cooled down to around 35 °C in a shell and tubes condenser, where water at room temperature is used as coolant. Partially dried cooled syngas is then passed through a wet gas scrubber and a commercial dust filter, where fine particles not retained so far are separated. Right after the filter, the gas is sent to an online gas analyser that determines CH_4, CO, CO_2, H_2 and O_2 concentrations in filtered syngas. Tedlar sampling bags are also taken from this gas line during steady state operation to be analysed off-line by gas chromatography and so quantify higher hydrocarbons (up to C_4). An induced drive fan is placed downstream the filter in order to push the syngas produced out of the reactor. Finally, syngas is burnt in a flare and sent out to the atmopshere through the stack.

2.3. Experimental procedure

In the tests carried out in this work, the operation parameters analysed were: (i) the amount of steam introduced into the gasifier, that was quantified through the steam-to-carbon (S/C) ratio indicating the moles of steam introduced into the gasifier (i.e. without including the steam introduced with the moisture of the biomass) per mole of carbon in the biomass fed to the reactor; (ii) the amount of CO_2 sorbent introduced into the gasifier, which was quantified through the calcium-to-carbon (Ca/C) molar ratio that indicates the moles of CaO introduced with the CO_2 sorbent (which has a purity of about 98 %wt. of CaO as

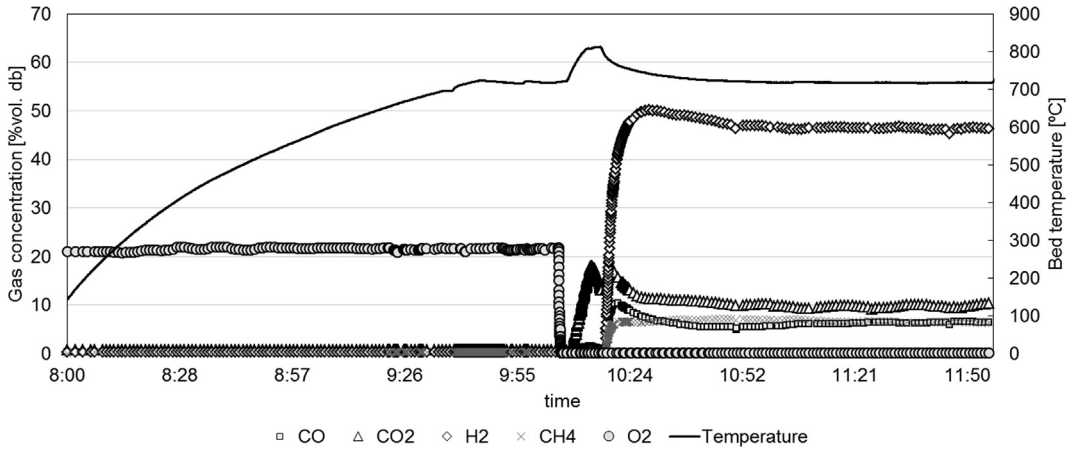


Fig. 3. Bed temperature and syngas composition evolution from start-up to the end of the steady state period in a SEG test.

indicated in Table 2) into the gasifier per mole of carbon in the biomass fed; and (iii) the CO_2 sorption capacity of the sorbent.

The flow rate of biomass was maintained constant over the entire gasification test, and the amount of steam and CaO fed to the BFB were modified according to the S/C and Ca/C ratios defined for each experiment. A CO_2 sorbent whose maximum CO_2 sorption capacity corresponded to 0.2 g_{CO2}/g of calcined sorbent was used for these experiments. For the specific conditions of S/C = 1.5 and Ca/C = 0.34, the SEG experiment was repeated using a CO_2 sorbent with a CO_2 sorption capacity of 0.1 g_{CO2}/g of calcined sorbent, corresponding to the activity of a highly cycled limestone.

At the beginning of each SEG experiment, solid bed in the reactor corresponded to completely calcined CO_2 sorbent without any char particles obtained after complete combustion in air at the end of the previous SEG test. The experimental routine followed in each SEG test is represented in Fig. 3. A first heating period in air (using a flow rate of 0.1 Nm^3/min) is performed using the electric resistances until a temperature of around 700 °C is measured throughout the reactor. At this point, biomass is fed into the reactor to speed up the heating process up to 820–850 °C. The air flow rate is then increased up to 0.12 Nm^3/min and 1.3 kg/h of biomass is fed into the reactor during this second heating period. As shown in Fig. 3, this second heating period corresponds to the time frame where CO_2 concentration in the gas increases and O_2 concentration decreases due to biomass combustion. When the temperature set-point is reached, biomass and CaO flow rates are tuned to those desired for the SEG test. N_2 flowing into the evaporator and into the CO_2 sorbent screw feeder are switched on and the air flowing into the reactor is stopped. At this point, the desired flow rate of steam is set and when a constant flow of steam is produced, the flow rate of 3.6 kg/h or 2.2 kg/h of biomass (depending of the desired thermal input) is introduced. Bed temperature starts decreasing, as it is shown in Fig. 3, and H_2, CH_4 and CO are detected in the gas phase. Gas composition stabilises sufficiently fast whereas the bed temperature takes at least one hour to reach a constant value since the solid composition is still changing (CaO is being saturated in CO_2 and char is being accumulated and converted into syngas). Afterwards, steady state conditions are fulfilled and maintained during one hour in order to proceed with the gas and solid sampling. Gas sampling bags and solid samples are taken every 15 min from the beginning of the steady state.

For shutting down after the steady-state period, biomass is stopped and then steam is exchanged by an air flow rate of 0.12 Nm^3/min. Unconverted char in the solid bed is then burnt, making the temperature increase up to 920 °C. $CaCO_3$ contained in the CaO particles is also decomposed into CaO, and CO_2 is therefore released. When CO_2 is no longer present in the gas phase, complete combustion of the char and complete $CaCO_3$ calcination are fulfilled and the electric resistances are then switched off to cool down the reactor.

2.4. Characterization of solid and gas samples from the BFB facility

Permanent gases concentration (e.g. H_2, CH_4, CO and CO_2) is measured online using a SICK GMS810 analyser placed downstream the condenser. Solid and gas samples are taken every 15 min during the steady-state period. Tedlar sampling bags are taken to quantify higher hydrocarbons (up to C_4) present in the syngas. A Hewlett Packard series II gas chromatograph coupled to a TCD detector is used for determining the concentration of H_2, O_2, N_2, CH_4 and CO using a Molsieve 5 Å column, and the concentration of CO_2, C_2H_4 and C_2H_6 using a HayeSep Q column. The oven programmes used for both columns were isothermal at 60 °C and 90 °C for the Molsieve and Hayesep columns, respectively. In addition, C_3-C_4 hydrocarbons (C_3H_6, C_3H_8 and C_4+) are measured using a Varian 3400 gas chromatograph through a capillary column coupled to a FID detector according to the following temperature programmed method: isothermal at 60 °C for 5 min and then, a heating rate of 20 °C/min up to 120 °C, keeping that temperature for 5 min.

Solid samples are taken from the solids collected through the overflow. Coarse particles (> 2mm) corresponding to unconverted biomass particles are separated and their ultimate composition is determined using a Thermo Flash 111 (UNE-EN-5104), as done also for the biomass fed to the gasifier. Proximate composition (i.e. moisture, volatile matter and ash contents) of these coarse particles is also determined following the same procedures explained in section 2.1 for the biomass feedstock. Smaller particles (< 2 mm) containing char, $CaCO_3$ and CaO are characterised as follows: X-ray diffraction (XRD) analysis is done in a Bruker D8 Advance diffractometer to determine the relative amount of the crystalline phases $CaO/CaCO_3$ and so determine the conversion of CaO into $CaCO_3$; scanning electron microscopy (SEM) coupled with EDS (Energy Dispersive X-rays spectroscopy) is used for determining the total amount of Ca in the solids that is complemented with XRD analysis for quantifying the mass fractions of CaO and $CaCO_3$; and finally ultimate analysis is done for calculating the total amount of carbon and so calculate the mass fraction of carbon corresponding to char particles.

Based on the information on solid samples characterisation, biomass conversion in the gasifier (X_{OM}) is considered as the conversion of the organic matter of the biomass (i.e. fixed carbon and volatile matter), and it is calculated for the different solid samples taken during the steady-state operation according to Eq. (1). Based on this expression, X_{OM} is calculated referred to the organic matter fed with the biomass into the gasifier during 15 min and the corresponding organic matter collected from the gasifier overflow in the same period of time. This organic matter is calculated as the fixed carbon and volatile matter contents of the coarse particles (i.e. > 2 mm) determined by proximate analysis, and the C content associated to the char fraction in the < 2

mm particles, which is determined by subtracting to the total organic carbon the carbon associated to the $CaCO_3$.

$$X_{OM} = \left(1 - \frac{m_{FC+VM,>2mm} + m_{C(char),<2mm}}{m_{FC+VM,biomass}}\right)\cdot 100 \quad (1)$$

Fixed carbon conversion (X_{FC}) is also calculated according to Eq. (2), which is similar to X_{OM} but referred exclusively to the fixed carbon of the char contained in the different solid samples collected during the steady-state period. The fixed carbon content in the < 2 mm particles (i.e. $m_{FC(char)\ <2mm}$ in Eq. (2)) is calculated assuming that the char contained in these particles has the same fixed carbon and volatile matter contents as the coarse particles collected at the same time.

$$X_{FC} = \left(1 - \frac{m_{FC>2mm} + m_{FC(char)<2mm}}{m_{FCbiomass}}\right)\cdot 100 \quad (2)$$

Finally, solid residence time for the char particles in the BFB gasifier has been also estimated considering the inventory of char particles in the reactor (m_{char}) and the amount of fixed carbon and ashes fed with the biomass, according to Eq. (3). For the inventory of char particles in the gasifier, it is assumed that the fraction of coarse particles collected from the overflow corresponds to the fraction of char particles within the gasifier, which is reasonable considering the low fraction of C from the char measured in the particles < 2 mm (i.e., below 3%wt. for all the experiments included in this work).

$$\tau_{char} = \frac{m_{char}}{\dot{m}_{biomass}\cdot(y_{FC} + y_{ash})} \quad (3)$$

3. Results and discussion

3.1. Effect of the sorbent-to-biomass ratio

Fig. 4 shows the syngas composition measured by gas chromatography (GC) during the steady-state period for two different Ca/C ratios (0.34 and 0.49), which correspond respectively to 3.1 and 4.4 kg/h flow rates of CO_2 sorbent, and an S/C ratio of 1.5. As shown in this figure, solid bed temperature stabilised at a lower value of 705 °C for the test with higher Ca/C ratio since the amount of CaO fed to the BFB gasifier from the hopper was larger, and so the sensible heat absorbed by this solid stream for heating up. Concerning the permanent gas composition of the syngas shown in Fig. 4 (left), H_2 concentration resulted close to 60 %vol. (H_2O and N_2 free basis) for the experiment with larger Ca/C ratio, which was around 5 percentage points higher than the H_2 content fulfilled with Ca/C of 0.34. This behaviour is linked to the higher amount of CO_2 separated in the test with larger Ca/C ratio that pushes gasification reactions towards H_2 formation. Considering the solid inventory of solids in the BFB reactor and the flow rate of CO_2 sorbent used, solid residence time for the CO_2 sorbent particles was sufficiently high for fulfilling their maximum CO_2 carrying capacity in every experiment (it was observed in the TGA tests that the maximum CO_2 carrying capacity was attained in just 2–3 min). Therefore, varying the sorbent-to-biomass ratio the amount of CO_2 separated is modified, increasing as the Ca/C ratio increases. Estimating a Carbon Capture Ratio (CCR) as the fraction of the C fed with the biomass that is separated as $CaCO_3$ with the sorbent, a CCR of around 22% resulted for the test with a Ca/C = 0.34 and around 44% for the test with a Ca/C = 0.49, corroborating the trend observed for the H_2 content.

Concerning the CO_2 concentration in the gas phase, this will be exclusively affected by the operating temperature of the gasifier through the carbonation reaction equilibrium, i.e. larger CO_2 concentration as temperature increases [23]. As shown in Fig. 4 (left), CO_2 concentration for the test with the lowest solid bed temperature turns out into a lower value (≈10.8%vol.(db) vs. 14.1%vol.(db), which corresponds to around 4 %vol. vs. 6 %vol. when considering real syngas composition (including H_2O and N_2) at the BFB reactor outlet). At the same time, CO concentration is linked to that of CO_2 through the Water Gas Shift (WGS) reaction (i.e., $CO + H_2O \rightarrow CO_2 + H_2$), which is pushed towards H_2 as the separation of the CO_2 formed proceeds. Therefore, CO concentration would be reduced when the CO_2 concentration diminishes, as appreciated in Fig. 4 (left). Based on these effects, the M-module became around 2.5 for the test with Ca/C = 0.49, which would be close to the target value of 3 desired when looking for CH_4 production in a downstream synthesis process. For the experiment with Ca/C = 0.34 the M-module resulted in 1.7 since the amount of carbon in the form of CO and CO_2 in the syngas was higher, being more appropriate for a DME or Fischer-Tropsch synthesis.

The concentration of higher hydrocarbons for these experiments with different Ca/C ratio is depicted in Fig. 4 (right). As shown, the concentration of C_3-C_4 and unsaturated C_2 hydrocarbons remained below 0.8 %vol. in both experiments since the S/C ratio used was high. However, the concentration of C_2H_6 and CH_4 resulted in 10.3 and 12.9 %vol. (H_2O and N_2 free), respectively, for the test with larger Ca/C ratio, around 2 percentage points higher than the corresponding values found for the experiment with lower CaO excess. This effect is linked to the lower stabilisation temperature of the solid bed for this experiment

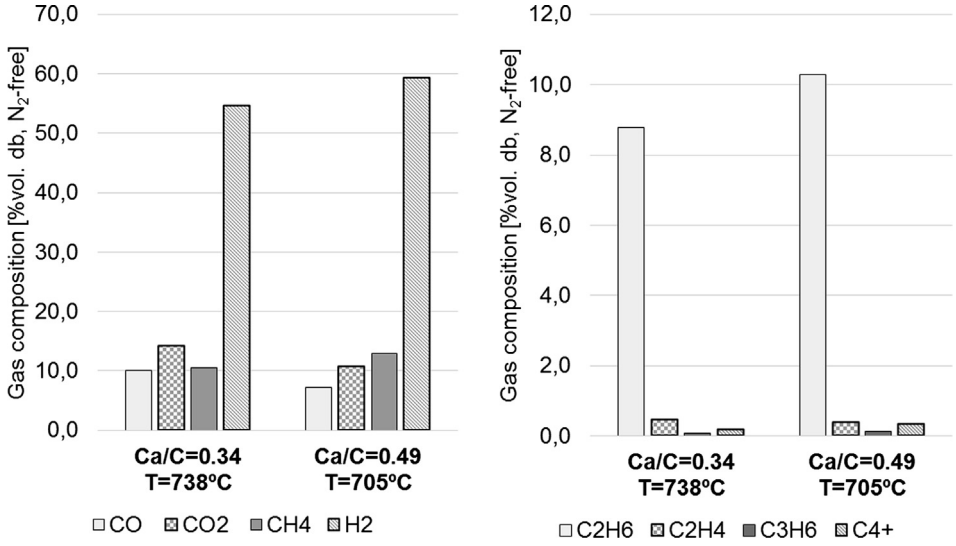


Fig. 4. Gas concentration (dry and N_2 free basis) during steady state measured by GC for two different Ca/C ratios of 0.34 and 0.49 for a thermal input of biomass of 21 kW_{th} and a constant S/C ratio of 1.5. Stabilization temperature of the solid bed during the experiments is shown in the X-axis.

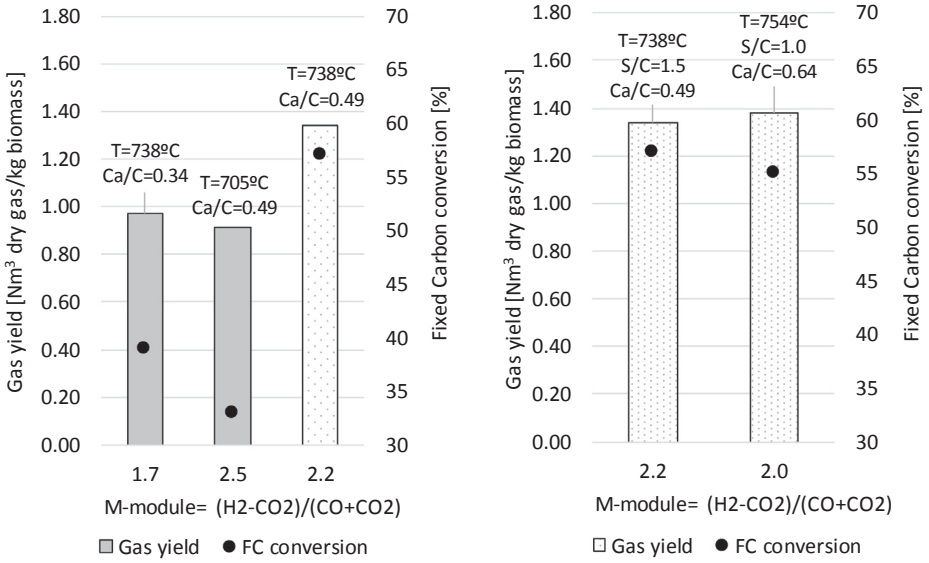


Fig. 5. Gas yield, fixed carbon (FC) conversion and M-module obtained under different operating conditions of biomass input, S/C and Ca/C ratios. Grey filled bars correspond to 21 kW_{th} of biomass input and white dotted bars to 13 kW_{th}. Results shown in left hand side figure keep an S/C ratio of 1.5. Ca/C ratio used in every test is indicated in the label.

with larger Ca/C ratio, which hampers the decomposition of C_2H_4 and CH_4 into lighter compounds. The higher CH_4 and C_2H_4 yields for the experiment at lower temperature would lead to a higher tar yield, as expected according to thermodynamics [24], which would increase the demand for downstream gas cleaning section.

3.2. Effect of char particles conversion

The amount of unconverted char that leaves the gasifier in a dual fluidized bed SEG system influences noticeably the overall efficiency of the SEG process. The higher the conversion of the char particles in the gasifier, the higher the efficiency of the biomass-to-syngas conversion process. However, certain amount of unconverted char flowing into the combustor is needed to provide the energy for $CaCO_3$ calcination, hence avoiding the need of additional biomass into this reactor, which would otherwise turn down the efficiency of the process. For these reasons, it is important to know which variables influence most the conversion of the char particles, as well as the influence of char conversion in the gas yield.

Fig. 5 shows the gas yield and fixed carbon conversion calculated for different biomass thermal inputs and Ca/C and S/C ratios. As noticed when comparing results obtained at different temperatures (left grey bars shown in Fig. 5 left, which correspond to experiments shown in Fig. 4), fixed carbon conversion (X_{FC}) is favoured with gasifier temperature (39% at 738 °C and 33% at 705 °C) and contributes to increasing the gas yield. The gas yield calculated for the test at 738 °C was 0.97 Nm^3(dry basis)/kg_{BS}, whereas it was 0.92 Nm^3(dry basis)/kg_{BS} for the experiment at 705 °C. Such variation in the gas yield is also influenced by the different CCR fulfilled in these tests, since the CO_2 separated from the gas phase as $CaCO_{3(s)}$ does not contribute to the gas production. Variation in the biomass conversion (X_{OM}) with the temperature (81% at 738 °C and 79% at 705 °C) was not as significant as the variation of X_{FC} in these two tests as the relatively high amount of volatile matter with respect to the fixed carbon content of the biomass (see analysis in Table 1) lessen the impact of such variation for fixed carbon conversion.

In addition to the gasifier operating temperature, residence time of char particles in the gasifier can significantly affect their conversion. With the aim of assessing the impact of the char particles residence time, results obtained for a thermal input of biomass of 13 kW_{th} and a Ca/C ratio of 0.49 have been included in Fig. 5 (left) (dotted bar in the right hand side), which resulted in the same solid bed temperature of 738 °C as the left hand side experiment with larger thermal input. As noticed, increasing the solid residence time in the reactor by reducing proportionally the feeding rates of biomass and CO_2 sorbent into the gasifier influences noticeably X_{FC} and, ultimately, the gas yield. An increase of about 60% in the solid residence time in the gasifier makes X_{FC} to increment from around 40% to 57% while the temperature and the S/C ratio remained constant and equal to 738 °C and 1.5, respectively. Such increase in X_{FC} translates into a large syngas yield of 1.34 Nm^3(dry basis)/kg_{BS} as shown in Fig. 5 (left). In this case, and due to the significant increase of X_{FC}, the increment in X_{OM} was also considerable (i.e. up to 88% for the test with 13 kW_{th} of biomass thermal input).

In Fig. 5 (right) it is shown the gas yield and X_{FC} when modifying the S/C ratio at BFB inlet from 1.5 to 1.0, which resulted also in slightly different temperatures in the gasifier. As noticed, regardless of the small differences in the gasifier temperatures, the excess of steam used for the gasification has an influence on the X_{FC} reached, making it to be reduced as the S/C ratio diminishes. However, compared to the effect that the gasification temperature had on X_{FC} in Fig. 5 (left), it can be appreciated that X_{FC} is less influenced by the S/C ratio than by the gasification temperature.

3.3. Influence of the S/C ratio

Fig. 6 shows the syngas composition measured by GC during the steady-state period for two different S/C ratios (1 and 1.5) and similar Ca/C molar ratio (0.4). Solid bed temperature in both experiments is also indicated in the figure. Slightly lower temperature was reached for the test with the higher S/C ratio of 1.5 due to the larger sensible heat required to heat up the fluidising gas and the endothermicity of the gasification reaction. As appreciated in the figure, the main effect of the S/C ratio relies on the C_2-C_4 concentration in the syngas as shown in Fig. 6 (right). The amount of C_3-C_4 and unsaturated C_2 hydrocarbons in the syngas is noticeably reduced below 1 %vol. (dry and N_2 free basis) when increasing the S/C ratio up to 1.5. Raising the amount of steam introduced into the gasifier favors the conversion of the higher C_3-C_4 hydrocarbons and unsaturated C_2 into C_2H_6 and CH_4, as shown in the figure. As a result, C_2H_6 concentration increases from 6.8 %vol. to 10.3 %vol. (dry and N_2 free basis) when moving from S/C = 1 to S/C = 1.5, and so does also CH_4 concentration that increases from 9.1% vol. to 12.9 %vol. The decomposition of each molecule of heavier hydrocarbon into lighter ones translates into a larger gas yield that resulted in 0.92 Nm^3(dry basis)/kg_{BS} for the test with S/C = 1.5 and 0.82 Nm^3(dry basis)/kg_{BS} for S/C = 1.

Regarding to the syngas concentration of H_2, CO and CO_2, small differences can be noticed in Fig. 6 (left). Similar amount of CaO was

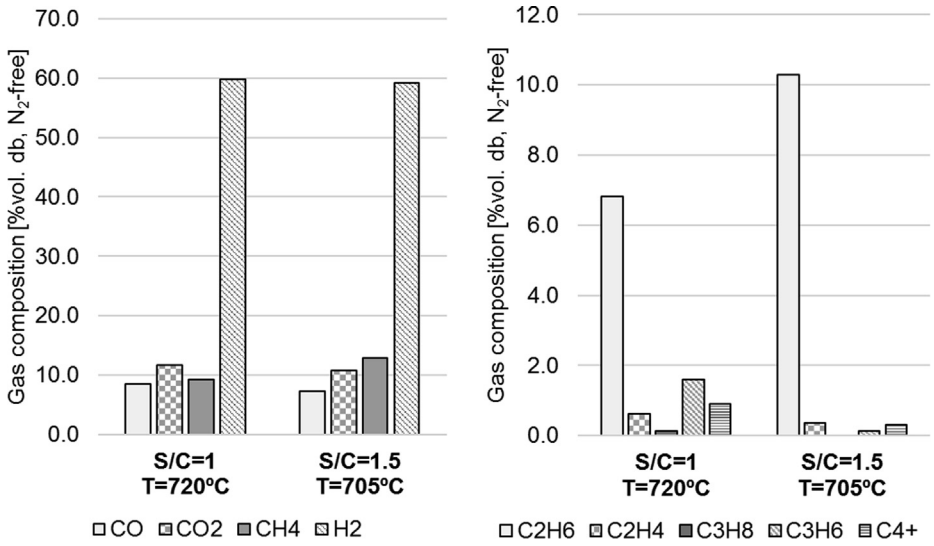


Fig. 6. Gas concentration (dry and N_2 free basis) during steady state measured by GC for two different S/C ratios of 1 and 1.5, keeping a constant Ca/C ratio of 0.40 and a biomass thermal input of 21 kW_{th}. Stabilization temperature of the solid bed during the experiments is shown in the X-axis legend.

fed to the gasifier in both experiments (≈3.7 kg/h) with respect to the C fed with the biomass (i.e. same Ca/C ratio), which makes the amount of CO_2 separated in both cases to practically match, resulting in this way into similar H_2 content as shown in the figure. As seen before, CO_2 concentration is influenced by the temperature through the $CaO/CaCO_3$ equilibrium, and the small differences observed in the CO_2 content (11.6 %vol. vs. 10.8 %vol. both in H_2O-N_2 free basis) are therefore linked to this temperature difference of 15 °C. Finally, the larger amount of H_2O and the smaller CO_2 content in the syngas for the experiment with S/C = 1.5 turn into a slightly lower CO content in the syngas. On the whole, and due to the smaller differences in the H_2, CO and CO_2 contents in the syngas when modifying the S/C ratio, almost the same module M = $(H_2\text{-}CO_2)/(CO + CO_2)$ of around 2.4–2.5 was fulfilled in both tests. Considering the information calculated from the solids characterisation, X_{OM} and X_{CF} calculated resulted around 80 and 32%, respectively, for both tests since the differences in temperature and solid residence time were negligible.

3.4. Activity of the sorbent

Finally, the effect of the CO_2 absorption capacity of the sorbent introduced into the gasifier was analysed. Table 3 summarises the results obtained for two different experiments with different CO_2 sorption capacities for the CaO, keeping the same Ca/C ratio of 0.34 and the S/C ratio at 1.5 at the gasifier inlet. The calculated maximum CO_2 sorption capacity of the CaO introduced in the BFB reactor for the tests shown in this table was 0.2 and 0.1 g_{CO2}/g_{CaO}. According to the typical CO_2 sorption capacity decay curve of different limestones reported in the literature [25], the CO_2 carrying capacity of 0.1 g_{CO2}/g_{CaO} corresponds to the activity of a highly cycled limestone. Stabilisation temperature in both cases was equal to 740 °C. As shown in Table 3, the use of a more cycled CaO sorbent turns into a lower amount of CO_2 separated from the gas phase, and so WGS and gasification reactions are less pushed towards H_2 formation. As a result, H_2 concentration in the syngas decreases from 55.2 to 50.7 %vol.(dry and N_2-free basis) and CO becomes larger. CH_4 content in the syngas is kept constant at around 11.0–11.7% regardless of the CaO particles conversion since the temperature is the same for both experiments. Moreover, the amount of C_3-C_4 hydrocarbons and C_2H_4 increased up to 6.2 %vol. (dry and N_2-free basis) for the experiment using more deactivated CaO since less H_2 is produced and the conversion of these compounds is therefore less favoured. When looking into a downstream synthetic fuel production process, it would be important to reduce the presence of these higher hydrocarbons in the syngas since they would act as inerts, reducing the synthetic fuel conversion per pass and so decreasing the efficiency, or they may decompose into carbon affecting the activity of the catalyst used. For these reasons, it is important operating this SEG process with active CaO-based sorbent that would enhance the production of H_2 and the cracking of higher hydrocarbons in the gasifier. Finally, no significant differences were detected for the char conversion reached due to the similar stabilisation temperature resulting in both tests.

Table 3
Results obtained for two experiments with different CO_2 sorption capacity of the CaO introduced in the gasifier, keeping a constant ratio of Ca/C = 0.34 and S/C = 1.5.

	CaO sorption capacity of 0.2 g_{CO2}/g_{CaO}	CaO sorption capacity of 0.1 g_{CO2}/g_{CaO}
Gas concentration (dry and N_2 free basis)		
H_2 [%vol.]	55.2	50.7
CO [%vol.]	9.8	14.8
CO_2 [%vol.]	14.0	15.0
CH_4 [%vol.]	11.0	11.7
C_2H_6 [%vol.]	9.1	1.7
C_2H_4 [%vol.]	0.6	4.8
C_3H_8 [%vol.]	–	0.1
C_3H_6 [%vol.]	0.2	1.0
C_4+ [%vol.]	0.2	0.3
Solid bed temperature [°C]	740	740
Gas yield (dry basis) [Nm^3/kg_{BS}]	0.95	0.84
X_{CF} [%]	41	41
τ_{char} [min]	49–50	47–50
CaO conversion (mole $CaCO_3$/mole Ca) [%]	24	15
M-module [–]	1.7	1.2

4. Conclusions

The operation and performance results of a sorption enhanced gasification (SEG) process of biomass in a 30 kW_{th} BFB gasifier are shown. Gasification tests using grape seeds as biomass and CaO-based sorbent obtained from calcined limestone as a precursor have been carried out to assess the effect of different operating parameters such as the sorbent-to-biomass ratio, the steam-to-carbon ratio and the CO_2 sorption capacity of the sorbent. Based on the results obtained, it has been corroborated the effect of varying the amount of CO_2 separated through

the sorbent-to-biomass ratio on the quality of the syngas produced, and so on the M-module. Steam-to-carbon ratios of at least 1.5 are needed in order to reduce the presence of C_3-C_4 and unsaturated C_2 hydrocarbons in the syngas produced below 1 %vol.(dry and N_2 free basis), which will act as undesirable inerts in the subsequent fuel production process. Gasification temperature influences the content of C_2H_6 and CH_4 in the syngas, making them to increase as temperature diminishes. Moreover, the importance of working with active CO_2 sorbent has been also assessed: more active CO_2 sorbent further improves the amount of CO_2 separated and therefore pushes H_2 formation and the decomposition of hydrocarbons. Concerning the fixed carbon conversion, it is clearly influenced by the gasification temperature as well as by the particles residence time used in the BFB reactor, being less influenced by the steam-to-carbon ratio used. Finally, M-modules ranging from 1.2 to almost 3 were obtained in this work when modifying the operating conditions through the sorbent-to-biomass ratio and the CO_2 sorption capacity of the sorbent. Such variability of the M-module confirms the flexibility of the SEG process towards different synthetic fuel production processes.

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References

[1] IEA. Technology roadmap- Delivering Sustainable Bionenergy. 2017.
[2] Molino A, Chianese S, Musmarra D. Biomass gasification technology: The state of the art overview. J Energy Chem 2016;25:10–25. https://doi.org/10.1016/j.jechem.2015.11.005.
[3] Rauch R, Hrbek J, Hofbauer H. Biomass gasification for synthesis gas production and applications of the syngas. Wiley Interdiscip Rev Energy Environ 2014;3:343–62. https://doi.org/10.1002/wene.97.
[4] Göransson K, Söderlind U, He J, Zhang W. Review of syngas production via biomass DFBGs. Renew Sustain Energy Rev 2011;15:482–92. https://doi.org/10.1016/j.rser.2010.09.032.
[5] Corella J, Toledo JM, Molina G. A Review on dual fluidized-bed biomass gasifiers. Ind Eng Chem Res 2007;46:6831–9. https://doi.org/10.1021/ie0705507.
[6] Aichernig C, Hofbauer H, Rauch R, Koch R. Biomass gasification CHP plant Güssing (Austria): Research centre for 2nd generation biofuels. 8th World Congr. Chem. Eng. Inc. 59th Can. Chem. Eng. Conf. 24th Interam. Congr. Chem. Eng., 2009.
[7] Koppatz S, Pfeifer C, Rauch R, Hofbauer H, Marquard-Moellenstedt T, Specht M. H2 rich product gas by steam gasification of biomass with in situ CO2 absorption in a dual fluidized bed system of 8 MW fuel input. Fuel Process Technol 2009;90:914–21. https://doi.org/10.1016/J.FUPROC.2009.03.016.
[8] Thunman H, Seemann M, Berdugo Vilches T, Maric J, Pallares D, Ström H, et al. Advanced biofuel production via gasification – lessons learned from 200 man-years of research activity with Chalmers' research gasifier and the GoBiGas demonstration plant. Energy Sci Eng 2018;6:6–34. https://doi.org/10.1002/ese3.188.
[9] Larsson A, Seemann M, Neves D, Thunman H. Evaluation of performance of industrial-scale dual fluidized bed gasifiers using the chalmers 2–4-MWth gasifier. Energy Fuels 2013;27:6665–80. https://doi.org/10.1021/ef400981j.
[10] Kotik J, Rauch R, Hofbauer H, Bosch K, Schwenninger F. 8.5 MWth CHP plant in Oberwart, Austria - based on DFB steam gasification of solid biomass – achieves continuous full load operation through stringent optimization. 20th Eur. Biomass Conf. Exhib. 2012:1033–7.
[11] Heidenreich S, Müller M, Foscolo PU. Advanced biomass gasification. New concepts for efficiency increase and product flexibility. Elsevier; 2016.
[12] Pfeifer C, Koppatz S, Hofbauer H. Steam gasification of various feedstocks at a dual fluidised bed gasifier: Impacts of operation conditions and bed materials. Biomass Convers Biorefinery 2011;1:39–53. https://doi.org/10.1007/s13399-011-0007-1.
[13] Schweitzer D, Gredinger A, Schmid M, Waizmann G, Beirow M, Spörl R, et al. Steam gasification of wood pellets, sewage sludge and manure: Gasification performance and concentration of impurities. Biomass Bioenergy 2018;111:308–19. https://doi.org/10.1016/j.biombioe.2017.02.002.
[14] Soukup G, Pfeifer C, Kreuzeder A, Hofbauer H. In situ CO2 capture in a dual fluidized bed biomass steam gasifier - bed material and fuel variation. Chem Eng Technol 2009;32:348–54. https://doi.org/10.1002/ceat.200800559.
[15] Florin NH, Harris AT. Enhanced hydrogen production from biomass with in situ carbon dioxide capture using calcium oxide sorbents. Chem Eng Sci 2008;63:287–316. https://doi.org/10.1016/j.ces.2007.09.011.
[16] Heidenreich S, Foscolo PU. New concepts in biomass gasification. Prog Energy Combust Sci 2015;46:72–95. https://doi.org/10.1016/j.pecs.2014.06.002.
[17] Pfeifer C, Puchner B, Hofbauer H. Comparison of dual fluidized bed steam gasification of biomass with and without selective transport of CO2. Chem Eng Sci 2009;64:5073–83. https://doi.org/10.1016/j.ces.2009.08.014.
[18] Martínez I, Romano MC. Flexible sorption enhanced gasification (SEG) of biomass for the production of synthetic natural gas (SNG) and liquid biofuels: Process assessment of stand-alone and power-to-gas plant schemes for SNG production. Energy 2016;113:615–30. https://doi.org/10.1016/j.energy.2016.07.026.
[19] Kletz TA, Amyotte P. Process plants: a handbook for inherently safer design. 2nd ed. Boca Raton; 2010.
[20] Fledged project n.d. http://www.fledged.eu/ (accessed August 10, 2018).
[21] Grasa G, Murillo R, Alonso M, Abanades JC. Application of the random pore model to the carbonation cyclic reaction. AIChE J 2009;55:1246–55. https://doi.org/10.1002/aic.11746.
[22] Martínez I, Grasa G, Murillo R, Arias B, Abanades JC. Kinetics of calcination of partially carbonated particles in a Ca-looping system for CO2 capture. Energy Fuels 2012;26:1432–40. https://doi.org/10.1021/ef201525k.
[23] Barker R. The reversibility of the reaction CaCO3 ⇄ CaO + CO2. J Appl Chem Biotechnol 1973;23:733–42. https://doi.org/10.1002/jctb.5020231005.
[24] Schildhauer TJ, Biollaz SMA, editors. Synthetic Natural Gas from Coal, Dry Biomass, and power-to-gas applications. Wiley; 2016.
[25] Grasa GS, Abanades JC, Alonso M, González B. Reactivity of highly cycled particles of CaO in a carbonation/calcination loop. Chem Eng J 2008;137:561–7. https://doi.org/10.1016/j.cej.2007.05.017.