

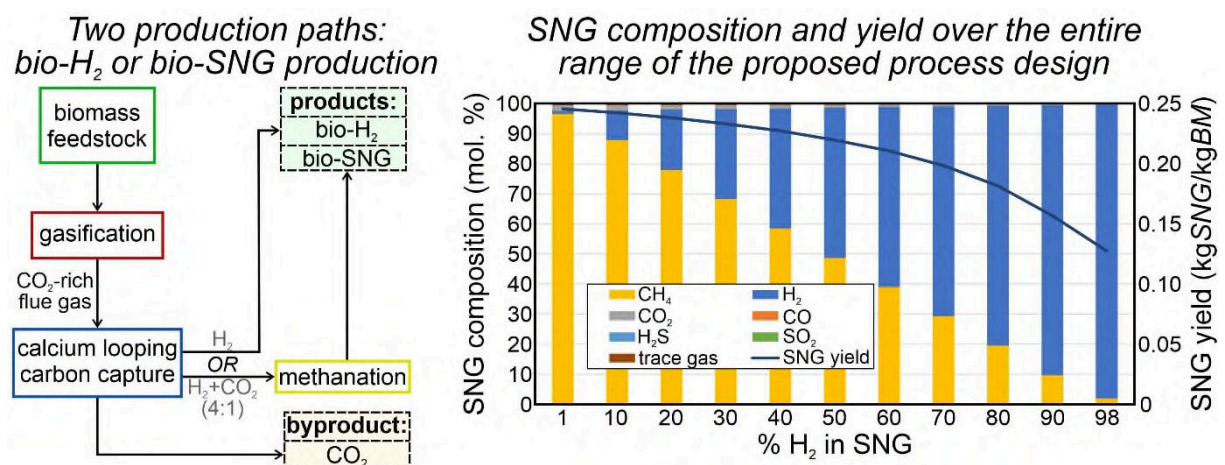
Process development and performance assessment of flexible calcium looping biomass gasification for production of renewable gas with adjustable composition

Domen Žalec^a, Dawid P. Hanak^b, Matic Može^a, Iztok Golobič^{a,*}

^aFaculty of Mechanical Engineering, University of Ljubljana, Aškerčeva 6, SI-1000 Ljubljana

^bEnergy and Power, School of Water, Energy and Environment, Cranfield University, College road, Cranfield MK43 0AL, UK

*Corresponding author: iztok.golobic@fs.uni-lj.si



ABSTRACT

In recent years, the field of biomass gasification as a method of transforming biomass into a more useable gaseous fuel experienced expedited development since it represents a prominent way to achieve sustainability goals and targets set by the Paris accord and more recently, the European Green Deal. The use of natural gas is projected to reduce with the transition towards exploitation of renewable gas, while a new area of hydrogen applications is also emerging. However, with uncertain production of current processes, and consumption patterns seen on the market, an opportunity for a new flexible process exists. This paper investigates a concept process design of sorption enhanced gasification (SEG) based on calcium looping. Aspen Plus® simulation software was used to develop and simulate the process models for flexible production of bio-SNG or bio-H₂. The process parameters can be manipulated to either achieve a high-purity bio-H₂ (> 96 mol.%) or high-purity bio-SNG (> 95 mol.%), as well as any other combination of the two main products. The concept process is based on a low-pressure, low-temperature dual fluidised bed reactor with steam as a gasifying agent, and an additional downstream Sabatier process reactor to achieve high CH₄ contents. The simulated process achieves process efficiency of up to 62.2%_{LHV} and 78.0%_{LHV} for H₂ and CH₄ production, respectively, with production yields reaching 0.112 kg H₂/kg BM and 0.23 kg CH₄/kg BM. These values were validated and benchmarked against comparable process designs, and the performance of the proposed process was found to be on par or superior. Overall, the proposed process design exhibits clear benefits of calcium looping gasification, with high process efficiency, negligible NO_x, SO₂ and H₂S content, and high flexibility. Therefore, the proposed process addressed and successfully solved some of the key challenges of achieving viability of a gasification plant on a commercial scale.

Key Words: hydrogen, biomethane, sorption enhanced gasification, calcium looping, process design, simulation

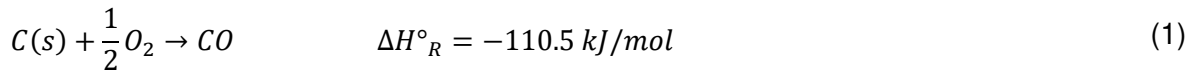
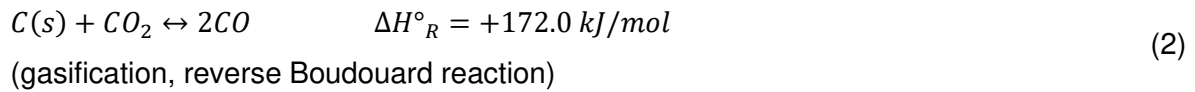
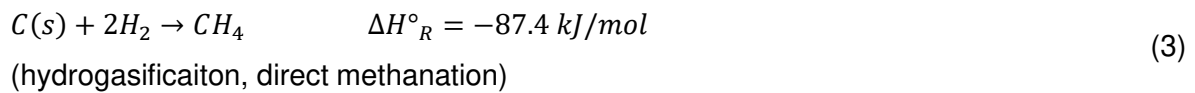
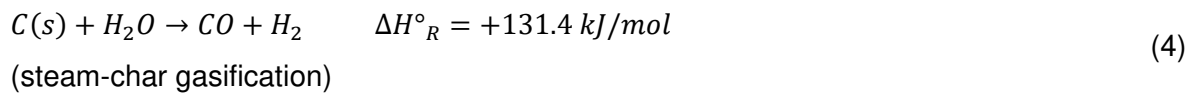
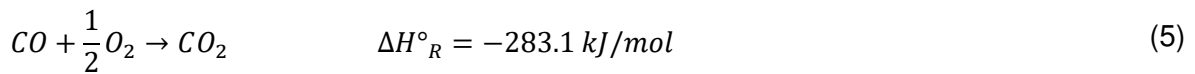
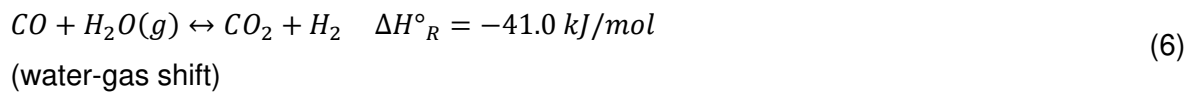
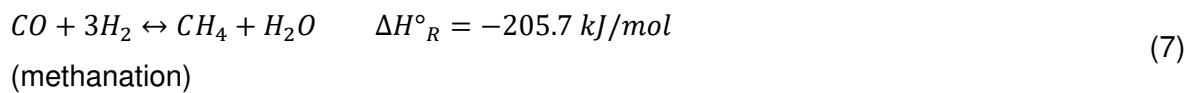
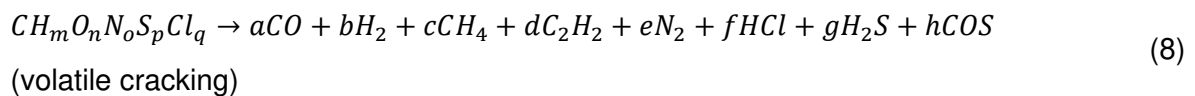
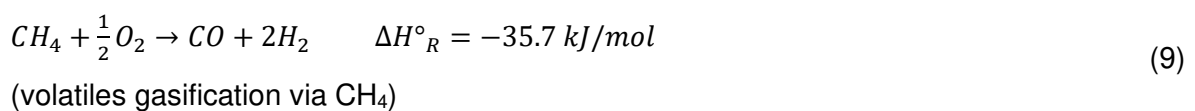
1 Introduction

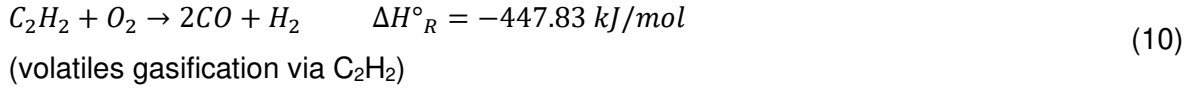
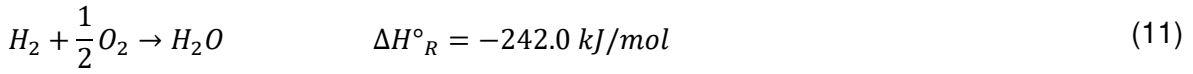
As the European Green Deal charts the course towards climate neutrality in 2050, rapid and extensive decarbonization of all sectors of economy is required if this goal is to be met. Achieving the emission reduction targets, along with the socio-economic ambitions, require near complete decarbonization of the energy and industrial sectors as more than 75% of EU's greenhouse gas (GHG) emissions stem from the energy sector [1]. Therefore, the key goal in achieving climate neutrality in the future decades is increasing the share of renewable energy sources in the energy supply chain. While to overall gas demand in the EU is projected to decrease by 20-60% in the long term, the role of renewable gases will increase in all scenarios as the natural gas use is projected to decrease significantly and green alternatives will be required [2]. Multiple studies [3–7] agree that emerging low-carbon gas production technologies will play a major role in decarbonization of EU's economy. By 2050, green gasses such as green H₂ and biomethane could represent 30-70% of the total gas use according to the Council of the European Union [8]. This requires both increasing the production capacities of renewable gases and adapting or replacing the gas infrastructure to allow the admixing of renewable gases or their exclusive use in the future [9]. Furthermore, the removal of CO₂ from biogas or other renewable gases (e.g., via carbon capture and storage technologies) needs further research attention alongside with additional studies of the effects of admixing renewable gasses to natural gas until complete decarbonization can be achieved.

Natural gas demand exceeded 148 EJ in 2017 and is forecasted to increase by as much as 60% by 2040 [10]. While hydrogen is being promoted as a clean energy vector, its total usage in 2013 was reported as only 7.2 EJ [11], meaning that decarbonisation of the industry sector is still a looming challenge [10]. Additionally, as reported by IEA in 2015 [12], only around 5% of world's hydrogen production is electrolytic and not necessarily produced using renewable energy sources. Nearly 48% of H₂ is currently produced via steam-methane reforming of natural gas, further 30% is a by-product in oil-refineries, and around 18% comes from coal [12]. This indicates that large amounts of CO₂ are emitted into the atmosphere during H₂ production.

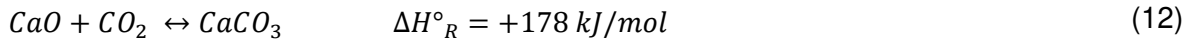
To ensure sustainable and net-zero supply of H₂, new renewable routes for H₂ and methane (CH₄) production are being investigated, including the use of wood biomass gasification and upgrading of the produced gas. This solution could especially benefit countries with a large supply of wood biomass and currently low share of renewable energy sources (RES) in their energy supply chain.

To exploit wood (or other) biomass for energy purposes, gasification may be employed to turn solid or liquid carbonaceous feedstock into synthesis gas (syngas) via a thermochemical conversion process [13]. Syngas consists primarily of carbon monoxide (CO) and hydrogen (H₂), with smaller fractions of CH₄, CO₂, and other hydrocarbons. Reactions governing the gasification process are presented in Eqs. (1) to (11) and can be classified as heterogeneous (Eqs. (1)-(4)) and homogeneous (Eqs. (5)-(11)). Enthalpy of each reaction (ΔH°_R) is also given at reference temperature of 298 K and pressure of 1 atm.





To enhance the syngas composition, sorption enhanced gasification (SEG) was developed in the last decades. It combines the gasification process with a simultaneous CO_2 removal to produce H_2 -rich syngas, as shown in Figure 1. A calcium looping (CaL) process is considered as an emerging technology for CO_2 capture, and is appropriate for integration with gasification in the pre-combustion carbon capture configuration [14,15]. Eq. (12) defines the reverse reaction of CaO carbonation. Enthalpy of the reaction (ΔH°_R) is given at reference temperature of 298 K and pressure of 1 atm.



The attractiveness of CaL gasification process is in its ability to be implemented directly within the gasification reactor. Use of natural CaO sorbent presents low environmental risks, while offering clear advantages in carbon capture, promotion of hydrogen production, and tar cracking, as demonstrated in the following paragraphs.

A concept of CaL gasification based on dual fluidised bed reactor (DFB) was proposed by Mahishi et al. [16] and was highly successful as fluidised bed reactors are very suitable for both gasification and CaL carbon capture with the chief advantage of extensive interaction of gas and solid particles, and low pressure drops [15,17]. Mahishi et al. [16] performed experiments at various pressures and relatively low temperatures ($<700^\circ\text{C}$), achieving the maximum hydrogen yield at atmospheric pressure. Similar findings were reported by Correla et al. [18]. Parvez et al. [19] recently reviewed the current status of sorption enhanced gasification of biomass for tailored syngas production with in-situ CO_2 capture and the connected process scale-up experiences and future outlook. They found that the operating gasification temperature window for sorption enhanced gasification lies between 600°C and 750°C . Through optimization of process parameters, high H_2 concentrations (above 70%) can be obtained in addition to desired H_2/CO ratios for downstream processes. The authors point out that cheap and readily available natural sorbents such as limestone can enable satisfactory operation, although issues with attrition and

deactivation require further research attention. Li et al. [20] propose a two-step sorption enhanced staged gasification of biomass for H₂ production. Simulations in Aspen Plus® revealed that the two-stage process with separate gasification reactor for high temperature steam gasification and an additional reactor for sorption enhanced reforming (a carbonator reactor) is more advantageous for H₂ production compared to the conventional one-step process. Higher temperature in the gasification reactor promotes biomass conversion and water-gas shift reaction to produce more H₂, while the second reactor enriches the H₂ concentration further through CO₂ adsorption onto CaO and by shifting the water-gas shift reaction equilibrium to convert more CO into H₂.

Many studies were conducted on the topic of carbon conversion in fluidised bed reactors as the particle residence time can vary significantly. According to most studies, approximately 20-50% of carbon entering the reactor leaves unconverted as solid char [16,18,21,22]. While the cold gas efficiency (CGE) is consequently lowered, this is advantageous for sorbent regeneration in the calciner as the unconverted solid char can be used as a fuel to meet the heat requirement of the calcination process.

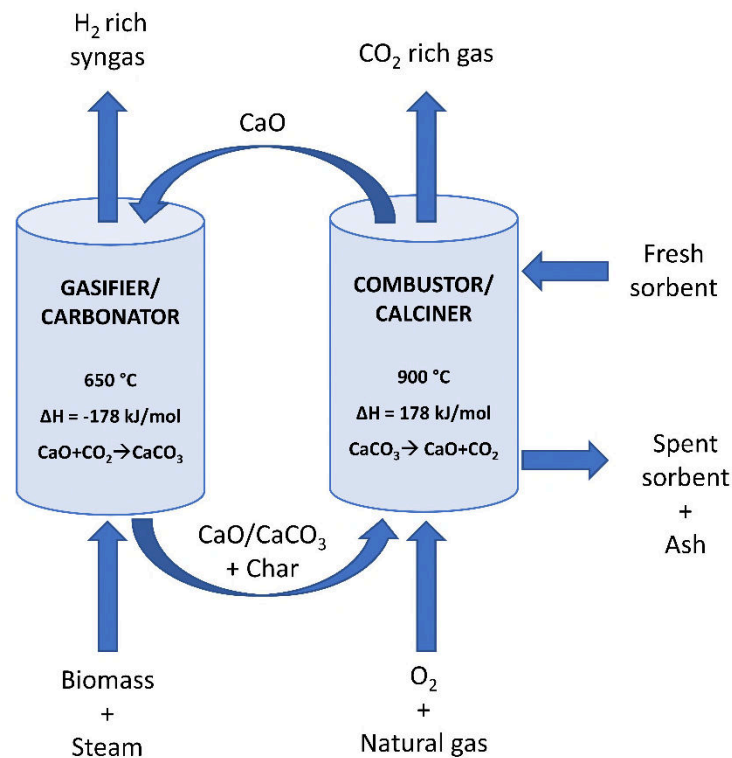


Figure 1: Scheme of SEG based on CaL process with DFB.

Another important advantage of SEG based on CaL is that CaO sorbent also acts as a catalyst for tar cracking; various studies report favourable results on the effectiveness of this process. For example, Mahishi et al. [16] report that the presence of CaO promoted carbon conversion, leading to noticeably lower tar formation in comparison with the base process (without CaO addition). On the contrary, Corella et al. [18] found only limited effects caused by low operating temperatures. However, they stated that high CaO/fuel ratios (>10) will reduce tar formation with noticeable effects. Additionally, CaO absorbs CO_2 and shifts the equilibrium of water-gas shift reaction to the right, which, as Udomsirichakorn et al. [23] report, further promotes H_2 production. Furthermore, CaO sorbent had been reported to have a high affinity to SO_x , thus reducing the concentration of one of the chief syngas contaminants [24].

Recently, Schweitzer et al. [25,26] proposed SEG coupling with in-situ CaL CO_2 capture. They performed process simulations, pilot-scale investigations and a techno-economic analysis of the process. A 200 kW_{th} DFB reactor was used with steam serving as the fluidising and gasifying agent, while limestone (>88 wt.% CaO) was utilized as the bed material. The experiments were conducted at atmospheric pressure with gasifier temperatures of 660-670 °C and regenerator temperatures of 900-950 °C. Under these conditions, syngas hydrogen content of up to 70 vol.%_{dry} with less than 7 vol.%_{dry} CO_2 content was achieved. Furthermore, low NO_x formation and SO_2 content below 3 ppmv in oxy-fuel combustion regenerator were observed together with positive effects of CaO on tar cracking. Udomsirichakorn et al. [27] performed similar experiments with comparable operating parameters, but with a different reactor design. They measured hydrogen concentrations up to 80 vol.%_{dry} and a CO_2 content of less than 5 vol.%_{dry}. Additionally, they also confirmed a tar reduction of more than 50% when utilizing CaO as the bed material as opposed to sand. Another process model for production of syngas with a high H_2 concentration was proposed by Chen et al. [15]. For this purpose, a novel compact fluidised bed was coupled with the CaL process. The proposed DFB design provided more optimal reaction conditions by effectively separating the gasifier reactor into two sections operating at different temperatures. Results showcase production of syngas with up to 94 vol.%_{dry} H_2 and a 58.5%_{LHV} hydrogen yield efficiency. Lin et al. [21,28,29] performed extensive experimental investigations into H_2 production through gasification, proving the technical feasibility of the CaLG process, although the process was primarily aimed at

coal and fossil fuel conversion. Müller et al. [30] explored the use of calcite as the bed material in dual fluidised bed steam gasification of wood to produce hydrogen-rich syngas. The proposed calciner temperature was 850 °C, while the gasification reactor was operated at 650 °C. Furthermore, the experimental results were compared to simulation predictions. The proposed sorption enhanced process exhibited greater cold gas efficiency of 71%, while the reference efficiency was 58%. The authors further demonstrate that H_2/CO ratio can be adjusted in the range from 9 to 2 by changing the operating temperature of the gasification reactor and that low bed material circulation is favourable for obtaining a high H_2 concentration in the syngas. Nam et al. [31] experimentally evaluated biomass air and air-steam gasification using a bench-scale fluidised bed reactor operating under constant conditions but with different biomass sources and bed materials. The presence of CaO directly in the gasification reactor bed made conditions for water-gas shift reaction and CO_2 carbonation more favourable, which increased the H_2 concentration in the syngas. When combined with air-steam gasification, the H_2 concentration increased to nearly 50% with 44 g of H_2 being produced per kg of input dry biomass. Bach et al. [32] also proposed a different concept of biomass gasification with torrefaction and CO_2 capture. Although not an SEG process, its interesting concept yielded efficiencies above 50%_{LHV}. Martinez et al. [33] analysed the effect of different operating parameters (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 fluidised bed gasifier, using grape seeds as feedstock. Furthermore, the importance of reducing formation of higher hydrocarbons was assessed, finding that S/C ration of 1.5 at gasification temperatures from 700-740 °C can be used for this purpose. It was also found that more active CO_2 sorbent further improves the amount of CO_2 separated and therefore pushes H_2 formation and the decomposition of hydrocarbons. Modifying the operating conditions through the sorbent-to-biomass ratio and the CO_2 sorption capacity of the sorbent showed great flexibility of the SEG process towards different synthetic fuel production processes.

To produce SNG (synthetic natural gas), syngas needs to be largely converted into methane via the methanation process. An overview of some of the most important studies in the field of numerical and experimental investigation of such processes and their performance is provided below. Three possibilities for SEG and power-to-gas

(PtG) integration for SNG production were assessed by Martínez and Romano [34] using biomass hydrogasification for syngas production and supplemental electrolytic hydrogen to achieve stoichiometric ratio of reactants. Similarly, three different configurations for an SNG plant utilizing biomass were proposed by Barbuzza et al. [35]. While the first proposed design relies on hydrogasification coupled with electrolysis for hydrogen production and the second one adds pressure-swing adsorption (PSA) for reduction of CO₂ content, the third design is perhaps the most interesting since it proposes a downstream Sabatier reactor for methanation. The authors reported that running the latter process at 15 bar and 300 °C resulted in CO₂-to-CH₄ conversion of almost 98%. Although this design does not incorporate SEG processes, the reported SNG production cost of 2.11 \$/Sm³ -2.76 \$/Sm³ and an overall efficiency of 69%_{LHV} are viable benchmarks. Another carbon capture and storage design in conjunction with SNG production was put forward by Bassano et al. [36]. Their design relies on gasification of feedstock followed by removal of excess CO₂ to meet the input requirements (stoichiometric ratio) for the Sabatier process. To reduce the concentration of contaminants, H₂S scrubbing was also employed. The study reports a methane content of approx. 94 vol.% with a process efficiency just above 50%_{LHV}.

In addition to numerical studies and laboratory scale experiments, multiple large pilot plants were also set up to investigate biomass-to-SNG conversion processes. GoBiGas demonstration plant [37] represents what was possibly the most successful project, reaching the commercial stage of development and operation in 2018. The project's gasifier is of a bubbling fluidised bed (BFB) design, while a circulating fluidised bed (CFB) is used as the combustor, meaning a DFB system is effectively present. TREMP™ methanation system by Haldor Topsøe [38] used to convert syngas into SNG with a maximum operating capacity of 20 MW_{biomethane} being reached through multi-stage upgrades during the commissioning [39]. Similarly, GAYA project was started in France in 2010 through cooperation of the ENGIE company and several partners. Biomass-to-biomethane conversion efficiency of 56% was reported [40] and was achieved with a fluidized bed reactor operating at 800-1000 °C. While the plant's capacity lies at 400 kW of SNG output, the specifics of the methanation process are not disclosed [38]. The town of Güssing in Austria is home to another successful demonstration plant, which was initially built as a combined heat and power plant and

received an upgrade in the form of a methanation fluidized bed reactor in 2008. The 1 MW_{SNG} reactor successfully operated for over 1000 continuous hours [38,41,42]. Another demonstration plant (GoGreenGas) utilizing an oxy-steam fluidised bed gasifier and Vesta methanation was set up in the UK to assess the feasibility of SNG production [43]. Excess CO₂ is removed via PSA and an operating capacity of 80–140 kW_{th} of SNG production was achieved during test runs [44]. A further 800 kW_{th} biomass-to-SNG demonstration plant was developed and built by the Energy Research Centre of the Netherlands (ECN), incorporating previously developed the MILENA™ gasification system and the OLGA™ gas cleaning section [45]. The pilot plant reportedly achieved biomass to grid-grade SNG production efficiency of approx. 70%_{LHV}. Liu et al. [46] proposed two processes for SNG production based on sorption enhanced steam hydrogasification (SE-SHR) using coal and biomass feedstock with a downstream water gas shift reactor (WGSR) or methanation reactor. They found the proposed processes can significantly increase H₂ yield beyond the initial H₂ input and minimize CO₂ production. Simulations of downstream upgrading processes in Aspen Plus® based on the preliminary bench-scale data were performed to obtain the final SNG composition, showing that SE-SHR-Methanation process results in high CH₄ production with self-sustained H₂ supply and near zero CO₂ emissions. The optimum gasification conditions for this process using lignite were H₂/C of 1.08 and steam/C of 2.22. A preliminary pilot-scale simulation of SE-SHR-Methanation process showed that carbon conversion efficiency to CH₄ was as high as 39.8%.

Process modelling of biomass gasification is experiencing an extensive increase in the recent years. Safarian et al. [47] performed a review of recent advancements and identified strong and weak parts of this research area. Similar review was recently produced by Ramos et al. [48]. The process design models for methane and hydrogen production are advancing, but there is still a lack of new innovative approaches in combining both into a single flexible process. One of the key challenges that remain is achieving profitable commercial operation, therefore a process design which is less prone to failure due to project and market setbacks is needed fill this gap.

This paper proposes a novel concept process design of sorption enhanced gasification based on calcium looping for flexible production of two renewable gasses: bio-SNG and/or bio-H₂. The goal was to develop a high-efficiency calcium looping gasification (CaLG) process that can bridge the challenges towards scale-up and

commercialisation of this technology. The key novelty of the proposed process is that process parameters can be manipulated to either produce high-purity bio-H₂ (> 96 mol.%) or high-purity bio-SNG (> 95 mol.%), as well as any other combination of these two products. The product flexibility is achieved through appropriate conditions in the reactor, which grants control over the syngas composition. Thus, the H₂ concentration can be maximized, or the H₂/CO₂ ratio can be optimized to the stoichiometric value for downstream methane (CH₄) synthesis. Aspen Plus® simulation software was used to develop and simulate the process models with the numerical model incorporating recent advances from biomass gasification and calcium looping process research into a unified process design. Additionally, this work also proposes an extension to the key performance indicator that characterises the performance of gasification in order to quantify for an additional amount of fuel consumed in the CaL process for sorbent regeneration.

2 Methodology

2.1 Sorption-enhanced gasification model description

The proposed gasification process with two production paths [49] was designed in Aspen Plus® simulation environment. The gasification process is devised to be used for either hydrogen or methane production, with ability to adjust the extent of CO₂ capture, depending on the required syngas composition of downstream processes. The paths of the two possible production processes are shown schematically in Figure 2. For H₂, a nearly complete CO₂ removal is performed, whereas for CH₄, the H₂/CO₂ ratio in the syngas is maintained at 4, which is based on methanation stoichiometry. For the SNG production, a downstream fixed bed, once-through methanation reactor was modelled. Peng-Robinson equation of state with Boston-Mathias modification (PR-BM) was used as property calculation method in Aspen Plus®.

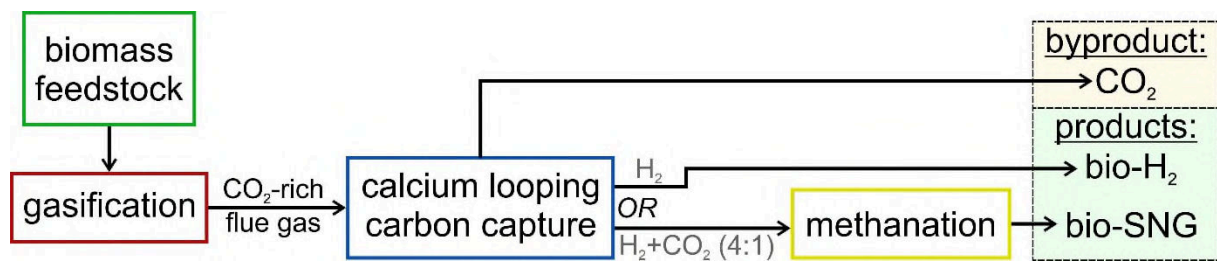


Figure 2: Schematic of sorption enhanced gasification of wood biomass with two production paths: bio-H₂ or bio-SNG production.

The SEG reactor was based on a DFB concept with steam fluidisation. A first fluidised bed reactor integrates gasifier and carbonator, operating at 650°C to achieve the balance between kinetics and equilibrium of the carbonation reaction [24]. When the process is set for H₂ production, the operating pressure was maintained close to atmospheric pressure, whereas for CH₄ production the pressure was increased to 10 bar. The SEG gasifier was modelled with *RYield*, *RGibbs*, and *RStoic* reactor blocks in Aspen Plus®. These blocks were connected with heat streams to unify the energy potential of the process. Biomass was fed into *RYield* block where its decomposition was performed, followed by *RGibbs* block for gasification and *RStoic* block to simulate WGS and CO₂ capture via the carbonation reaction. Similar CaLG models were

developed by Chen et al. [15] and Detchusananard et al [50]. It was assumed that the carbon conversion in the *RGibbs* reactor was 30%. This aimed to account for an incomplete carbon conversion that usually occurs in DFB reactors [51–53]. The steam to carbon (S/C) ratio in the gasifier was set to 1.8, which is comparable to other studies reported in literature as well as the values reported by Pitkääoja et al. [54]. Figure 3 presents the process flow diagram of the gasification section conceptualised in this study. With the proposed process design, no external heat source is needed to operate the gasifier, once the steady state operation has been achieved. The required heat to maintain the desired reaction temperature was supplied by both the highly exothermic carbonation reaction [Eq. (12)] and by the hot CaO circulating between the carbonator and the calciner. A relatively high solid-to-gas ratio of 6 was achieved in the gasifier in the proposed process, which may represent a technical challenge in ensuring fluidisation of the reactor bed. To mitigate this, 50% recirculation rate of syngas to the reactor was used. To compensate for pressure drop in the gasifier, the syngas was compressed to 1.2 bar.

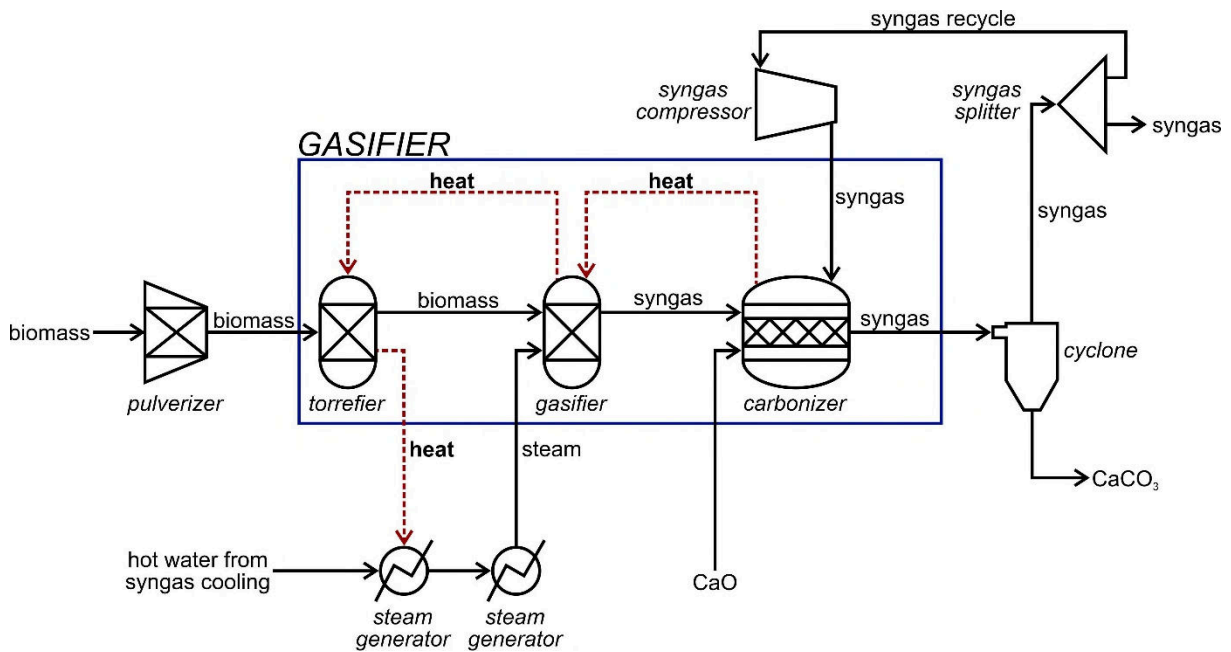


Figure 3: Process flow diagram of the sorption-enhanced gasification reactor.

In the hydrogen production case, the CO₂ capture level in the carbonator was set to 90% to achieve a high hydrogen content in the syngas. Solid particles (i.e., CaCO₃, CaO, ash, char), that leave the SEG gasifier, were separated using a cyclone, which was modelled using *Sep* block. The separated solids were then fed into the calciner,

modelled as the *RGibbs* reactor, for sorbent regeneration at 900 °C and atmospheric pressure. The process model to represent the CaL process was developed by Hanak et al. [24]. This model incorporated calculation of the maximum conversion of CaO in the SEG gasifier, based on the relative make-up ratio of the fresh limestone and using the correlation derived by Rodriguez et al. [55]. The activity of the sorbent reduces with the increasing number of carbonation and calcination cycles. Additionally, irreversible reactions with sulphur compounds also contribute to sorbent deactivation. Similar model where *RGibbs* reactor block was utilised as calcination reactors was developed by Detchusananard et al. [50]. Finally, real-life SEG is also affected by tar deposits on sorbent particles. However, tar production was neglected in this simulation due to simplification of the process models, as well as it being impossible to model the tar deposits across the system. Following the sorbent regeneration, another cyclone separator (modelled with a *Sep* block) was used to separate the solids from CO₂ stream. The solids are then recycled back to the SEG gasifier. The summary of the operating conditions for the CaL process is presented in Table 1.

Table 1: Operating conditions for the sorption-enhanced gasification based on calcium looping.

<i>Parameter</i>	<i>Value</i>
<i>Calciner temperature</i>	900 °C
<i>Calciner outlet pressure</i>	1.05 bar
<i>Total pressure drop in the calciner</i>	150 mbar
<i>Calciner combustion oxygen excess</i>	2 %
<i>Integrated carbonator temperature</i>	650 °C
<i>Integrated carbonator outlet pressure</i>	1.05 bar
<i>CaO make up/recycle ratio</i>	0.03
<i>Carbon capture (gaseous) efficiency – only for H₂ production</i>	90%
<i>H₂/CO₂ ratio – only for CH₄ production</i>	4.02
<i>Calcination conversion</i>	90%
<i>Carbonation conversion</i>	70%
<i>*Carbon capture refers to CO₂ and CO produced during gasification</i>	

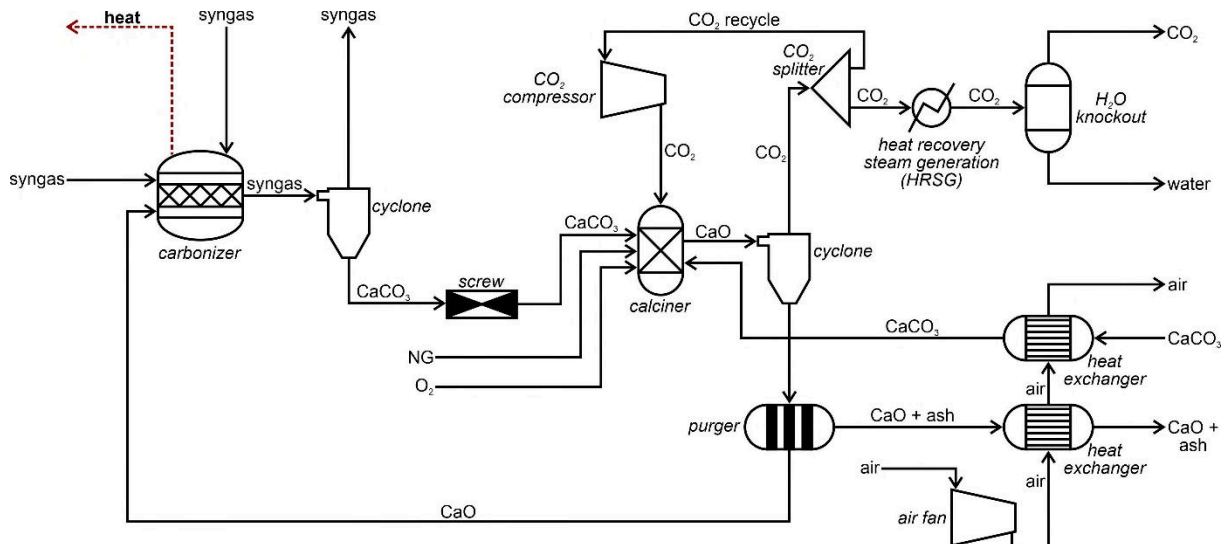


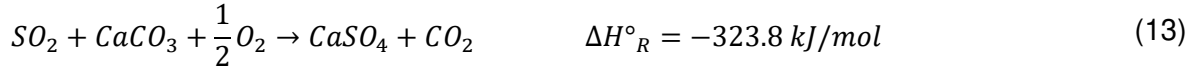
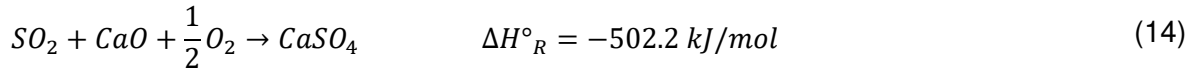
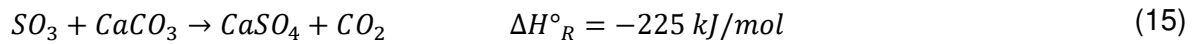
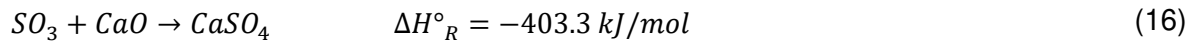
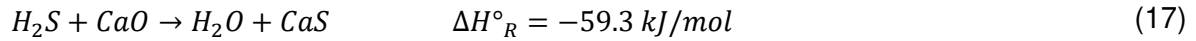
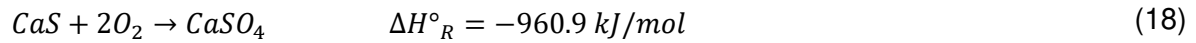
Figure 4: Process flow diagram of calcium looping process.

Figure 4 presents the process flow diagram of the CaL process, located downstream of the gasification process. A part of the high-purity CO₂ stream (20%) is recycled to fluidise the calciner bed with compression to 1.2 bar to compensate for the pressure drop in the reactor.

High-grade heat supply to the calciner reactor is required to regenerate the CaO sorbent due to the energy-intensive nature of the process. Importantly, the unconverted carbon (char) that left the CaLG gasifier with the sorbent can be burnt in the calciner to provide a fraction of the heat requirement for sorbent regeneration. O₂ at 98 mol.% purity was fed to the calciner to ensure that the only combustion products are CO₂ and H₂O. As the latter can be separated by condensation, a high-purity CO₂ stream, which is ready for compression and storage, can be produced. To make up the difference between the required heat for sorbent regeneration and heat released through char combustion, a small amount of natural gas (NG) is supplied to the calciner. Complete combustion and homogeneous heat distribution are ensured through intense mixing of solid particles, NG, and O₂. The O₂ requirement was assumed to be met by the O₂ supply from the air separation unit (ASU) with a specific power consumption of 200 kWh/to₂.

Tar cracking and efficient removal of SO_x and H₂S is ensured through the use of the CaLG process. Sulphur removal was considered using a *RStoic* reactor block and was modelled through the reactions (13) to (18). The reaction enthalpies (ΔH°_R) are given at reference temperature of 298 K and pressure of 1 atm. The sulphur removal method

and it's efficiency is implemented as in the validated model developed by Hanak et al. [24].



2.2 CO₂ compression model description

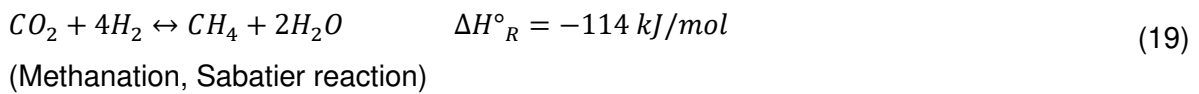
Conditioning of the produced high-purity CO₂ stream is required for transport and storage. First, water is separated from it using an integrated cooler and knock-out drum, which is modelled utilizing a *Flash2* block. Next, CO₂ is compressed to a critical pressure in a multi-stage intercooled compressor (*MCompr* block) and cooled (*Heater* block) to 20 °C to ensure transportation in a dense phase. Gas compression calculations were performed using the GPSA polytrophic method. Finally, the pressure of the CO₂ was increased using a pump (*Pump* block), achieving 110 bar. CO₂ compression train operating parameters are shown in Table 2. The CO₂ compression model in this process design is reused from previous work of Hanak et al. [24], available in the literature.

Table 2: Operating conditions for CO₂ compression section

<i>Parameter</i>	<i>Value</i>
<i>H₂O knock-out temperature</i>	30 °C
<i>H₂O knock-out pressure</i>	1.01325 bar
<i>Compressor discharge pressure</i>	80 bar
<i>Compressor stages</i>	5
<i>Comp. stage outlet temp.</i>	40 °C
<i>Compressor polytrophic eff.</i>	0.8
<i>Compressor mechanical eff.</i>	0.996
<i>Compressor – syngas outlet temperature</i>	50 °C
<i>CO₂ cooler pressure drop</i>	0.0 bar
<i>CO₂ cooler outlet temperature</i>	20 °C
<i>CO₂ pump discharge pressure</i>	120 bar
<i>CO₂ pump efficiency</i>	0.8
<i>CO₂ pump driver efficiency</i>	0.996

2.3 Methanation model description

A downstream reactor is used for methanation of the syngas in the methane production case. Methanation requires an optimum H₂/CO₂ ratio of 4, which is the stoichiometric ratio for the Sabatier process as described by Eq. (19). Enthalpy of the reaction (ΔH°_R) is given at reference temperature of 298 K and pressure of 1 atm.



Methanation part of the process setup is shown in Figure 5. First, the syngas is cooled down, regenerating the heat for steam generation for gasification. Cooling is performed using a multiphase heat exchanger (modelled with a *MheatX* block), with the syngas outlet temperature set to 80 °C to avoid temperature crossover. Next, further cooling and H₂O condensate removal is performed in a knock-out drum. This is followed by compression to 10 bar, performed with a multistage intercooled compressor. Finally, methanation reactor (modelled with a *Rstoic* block) is used to represent a fixed bed reactor with Ni-based catalyst, where catalytic methanation is performed. The Sabatier process was tuned according to validated research by Gao

et al. [56], while the design was simplified without explicitly modelling the catalyst. The Sabatier reaction is highly exothermic and favours lower temperatures. Methanation is therefore performed at 300 °C, with excess heat being recovered in a heat recovery steam generator (HRSG; *Heater* block) to further increase the efficiency of the system. Another knock-out drum (*Flash2* block) is used to dry the produced SNG. The operating parameters for the methanation reactor are presented in Table 3.

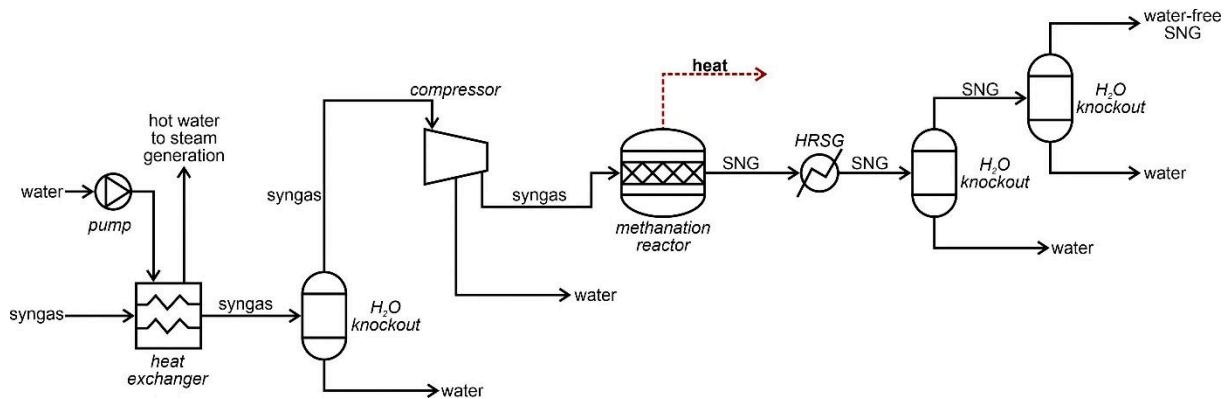


Figure 5: Process flow diagram of the methanation section.

Table 3: Operating conditions for the methanation section.

<i>Parameter</i>	<i>Value</i>
<i>Heat exchanger – syngas outlet temperature</i>	80 °C
<i>H₂O knock-out temperature</i>	30 °C
<i>H₂O knock-out pressure</i>	Equal to gasifier (min. 1 bar)
<i>Compressor discharge pressure</i>	10 bar
<i>Compressor stages</i>	3
<i>Comp. stage outlet temp.</i>	50 °C
<i>Compressor polytrophic eff.</i>	0.8
<i>Compressor mechanical eff.</i>	0.996
<i>Compressor – syngas outlet temperature</i>	50 °C
<i>HRSG pressure drop</i>	0.0 bar
<i>Methanation reactor temperature</i>	300 °C
<i>HRSG – syngas outlet temperature</i>	100 °C
<i>H₂O knock-out temperature</i>	20 °C

2.4 Biomass characteristics

Table 4 shows the composition of biomass used in the process simulation; the values are based on the experimental work of Mahishi et al. [16]. The heating values of southern pine bark were obtained from the ECN Phyllis2 database [57]. The higher heating value (HHV) of 21.52 MJ/kg and lower heating value (LHV) of 20.22 MJ/kg were determined as the mean values of 8 datasets for pine bark available in the aforementioned database. Biomass enters the process (specifically, the gasifier) at atmospheric pressure and 15 °C. Additionally, grinding of feedstock is considered and assumed to have a specific power consumption of 53.8 kJ/kg.

Table 4: Ultimate and proximate analysis of biomass [16].

<i>Element</i>	<i>Value [wt.%]</i>
<i>Moisture (ar.)</i>	9.22
<i>Volatile matter (dry)</i>	69.63
<i>Fixed carbon (dry)</i>	29.68
<i>Ash (dry)</i>	0.63
<i>Carbon (dry)</i>	51.13
<i>Hydrogen (dry)</i>	6.10
<i>Nitrogen (dry)</i>	0.14
<i>Sulphur (dry)</i>	0.04
<i>Oxygen (dry)</i>	41.96
<i>Chlorine (dry)</i>	0.0
<i>Ash (dry)</i>	0.63

2.5 Performance assessment

Any proposed process design needs to be thoroughly evaluated to determine its product stream compositions and thermodynamic performance. Two key parameters are typically considered when evaluating gasification processes. Firstly, carbon conversion efficiency (η_{CC}), defined through Eq. (20) based on molar flow rates of carbon out of the process ($\dot{n}_{carbon,out}$) and into it ($\dot{n}_{carbon,in}$), determines the conversion of feedstock's carbon content into syngas. In this study, the carbon conversion

efficiency was set at 70% as the reaction and particle kinetics were not explicitly modelled. Another critical parameter that evaluates the performance of the gasification process is the cold gas efficiency (CGE). The latter is usually defined as the ratio of heating values of syngas and feedstock fuel, as presented in Eq. (21). The lower heating values (LHV) used throughout the performance assessment were calculated on a mass basis at 15 °C and 15 °C reference temperature for petroleum mixture, based on RefSYS correlation property.

$$\eta_{CC} = \frac{\dot{n}_{carbon,in}}{\dot{n}_{carbon,out}} \cdot 100 \% \quad (20)$$

$$CGE_{LHV} = \frac{LHV_{syngas} \cdot \dot{m}_{syngas}}{LHV_{fuel} \cdot \dot{m}_{fuel}} \cdot 100 \% \quad (21)$$

In case of the SEG based on CaL, the CGE cannot be assessed using Eq.(21). The reason for this is that a significant amount of heat is provided to the SEG gasifier from the CaL process, which requires additional fuel to maintain the calciner at the desired operating temperature. It is therefore proposed to extend the traditional CGE definition to include the LHV of fuel (in this case natural gas) supplied to the regenerator reactor, as defined in Eq. (22). The natural gas is an additional input to the system, however, it is a key part of the CaL process and is therefore not considered an external heat source to the gasifier, as the calcination process is driving this demand, not the gasification.

$$CGE_{LHV} = \frac{LHV_{syngas} \cdot \dot{m}_{syngas}}{LHV_{fuel} \cdot \dot{m}_{fuel} + LHV_{NG} \cdot \dot{m}_{NG}} \cdot 100 \% \quad (22)$$

In the latter equation, the lower heating value (LHV) and mass flow rate ($\dot{m}$) of each material flow are taken into account. Overall energy efficiency (η_{th}), as defined in Eq. (23), was used to assess the overall thermodynamic performance of the proposed process design. Such definition of efficiency considers both the syngas heating value (LHV_{syngas}) and the heat recovered in HRSGs that is utilised for power generation with the assumed power cycle efficiency of 40% [i.e., $0.4 \sum \dot{Q}_{HRSG}$]. This consideration is important, as the process is designed to fully utilise the potential of thermal energy in the system. SEG and CaL run at high temperatures, therefore, heat recovery from the products and by-products before they exit the system is crucial to achieve energy efficiency. Furthermore, Eq. (23) considers heating values of feedstock fuel (LHV_{fuel})

and natural gas (LHV_{NG}) used in calciner, while the power consumption of auxiliary systems not modelled within this study is taken into account by increasing the equipment power consumption by 10% (as $1.1 \sum P_{equip}$). The equipment power consumption parameters include water and CO₂ pumps, air, syngas, and CO₂ compressors, as well as biomass grinder power consumption. These can amount to significant values and are therefore important to consider.

$$\eta_{th} = \frac{LHV_{syngas} \cdot \dot{m}_{syngas} + 0.4 \sum \dot{Q}_{HRSG} - 1.1 \sum P_{equip}}{LHV_{fuel} \cdot \dot{m}_{fuel} + LHV_{NG} \cdot \dot{m}_{NG}} \cdot 100 \% \quad (23)$$

3 Results and discussion

3.1 Hydrogen production

Firstly, the evaluation of the H₂ production path line within the proposed process design is shown together with the comparison of simulation results with reports of numerical and experimental studies found in literature (Table 5).

The CGE for the process designs proposed in this study (69.1%_{LHV}), which was determined using Eq. (22), was shown to be comparable with that reported in the literature (70%_{LHV}). However, the overall process efficiency ($\eta_{th,1}$) was substantially higher (62.2%_{LHV}) compared to that reported in the literature (43.7%_{LHV}). This can be primarily associated with the assumption that the high-grade heat available in the CaLG reactor is utilised for power generation. Furthermore, the analysis of the H₂ stream composition is presented in Table 5, which shows that H₂ by far represents the main constituent, while CO₂, CH₄, and CO are the major remaining components. It should be noted that sulphuric components are present in practically untraceable amounts, demonstrating the CaO sorbent's *in situ* sulphur removal capabilities. The HHV and LHV of the biomass fuel (as calculated by Aspen Plus® using the PR-BM equation of state) and of the product stream (mainly containing H₂) are also compared in Table 5. The results clearly demonstrate the benefits of thermochemical conversion methods as the heating values of the syngas are increased fourfold, marking a major increase in energy density.

Table 5: H₂ production process results comparison.

<i>Parameter</i>	<i>This study</i>	<i>Schweitzer et al.</i> <i>[25,26]</i>	<i>Udomsiric-Hakorn et al.</i> <i>[27]</i>	<i>Han et al.</i> [58]
<i>Reactor type</i>	DFB	DFB	BFB	BFB
<i>Temperature, °C</i>	650	660	650	684
<i>Pressure, bar</i>	1.05	1.013	1.013	1.013
<i>S/C ratio, mol/mol</i>	1.8	1.5	1.8	1.7
<i>CaO/C ratio, mol/mol</i>	4.7	N/A	N/A	1
<i>Notes</i>	Simulation	Pilot & Simulation. Add. PSA in simulation	Experimental	Experimental
η_{CC} , %	70.0	N/A	N/A	55.6
CGE_{LHV} , %	69.1	70	N/A	N/A
η_{th} , % (LHV)	62.2	43.7	N/A	N/A
<i>H₂, mol. %</i>	96.8	68.8	78	57
<i>CO₂, mol. %</i>	2.0	8.3	4.5	7
<i>CO, mol. %</i>	0.3	7.8	6.3	12
<i>CH₄, mol. %</i>	0.8	12.4	11	16
<i>SO₂, mol. %</i>	0.0	N/A	N/A	N/A
<i>H₂S, mol. %</i>	0.0	N/A	N/A	N/A
<i>Other trace gases, mol. %</i>	0.1	2.7	0.2	8
<i>H₂ yield, kgH₂/kgBM</i>	0.112	0.05	0.04	N/A
<i>LHV_{fuel}, MJ/kg</i>	20.22	16.9	N/A	N/A
<i>HHV_{fuel}, MJ/kg</i>	21.52	N/A	18.7	N/A
<i>LHV_{syngas}, MJ/kg</i>	78.7	N/A	N/A	N/A
<i>HHV_{syngas}, MJ/kg</i>	93.0	N/A	N/A	N/A

Comparison with literature reports reveals that slight differences in the results are present even though all SEG processes featured similar designs and operating parameters. Especially important is the comparison with results reported by Schweitzer et al. [25,26], who compared numerical predictions with experimental results and obtained an experimental CGE very similar to the one obtained in the present study. The main difference arises from the comparison of syngas products, since the present proposed process design grant much higher H₂ content compared

to other reports found in the literature and shown in Table 5. It needs to be noted that the present study is unvalidated and does not consider true reaction kinetics. Nevertheless, a high CaO/C ratio realised within this study is comparable with the commonly reported values, such as the study by Magoua Mbeugang et al. [59], thus offering a good potential for CO₂ removal.

Other studies listed in Table 5 report CH₄ concentrations above 10 mol.%, which is most likely the reason for the much higher H₂ yield found in the present study, as the available hydrogen atoms are not bound to carbon and are instead synthesised to H₂. This is achieved through steam reforming in the present process design, with which the CH₄ content is intentionally lowered.

Since no major biomass-to-H₂ plant exists at the time, further comparison with experimental results is limited. Nevertheless, the GoGreenGas project (as described within the literature review subsection) is somewhat comparable as it was adapted to produce H₂ from waste [43,44]. While limited data is available, the operators reported a process efficiency of 70 %_{HHV}, which is comparable to the values achieved in the present study.

3.2 Synthetic natural gas production

Results presented in Table 6 reveal that higher overall process efficiency and higher CGE are obtained for the SNG production path line in comparison with H₂ production path line. This is mainly caused by a lower extent of CO₂ capture since a significant amount of it is utilized for CH₄ synthesis. This further decreases the natural gas requirement for sorbent regeneration and results in less energy used for CO₂ compression, lower flowrates in the CaL system and consequently also lower power consumption of various subsystems. In this mode of operation, CH₄ concentration of just over 95 mol. % was achieved together with a presence of approx. 3 mol. % H₂. As with the H₂ production path line, the concentrations of sulphuric compounds are negligible. Although the HHV and LHV of the produced gas are appreciably higher than that of the biomass feedstock, the values are below those of the H₂ product path line, since the latter possesses a higher energy potential and higher reactivity, being a purer chemical substance than CH₄.

Again, alternative processes found in the literature were compared to the proposed SEG process to compare the performance. Specifically, the comparison is made with one pilot plant and two numerical models although only one of the studies features a SEG process due to limited data available on biomass to biomethane conversion. The results are summarized in Table 6.

Table 6: CH₄ production process results comparison.

<i>Parameter</i>	<i>This study</i>	<i>Barbuzza et al. [35] – basic process</i>	<i>Martínez & Romano [34]</i>	<i>GoBiGas project [37,39]</i>
<i>Reactor type</i>	DFB	N/A	DFB	DFB
<i>Temperature, °C</i>	650	300	645	870
<i>Pressure, bar</i>	10 (1)	30	1.15	1
<i>S/C ratio, mol/mol</i>	1.8	N/A	0.42*	N/A
<i>CaO/C ratio, mol/mol</i>	2.33	N/A	4.96	N/A
<i>Target content of H₂, mol. %</i>	3	N/A	N/A	N/A
<i>Notes</i>	Simulation	Simulation, hydrogasification not SEG process	Simulation, SEG, PtG, *S/BM ratio (mass based)	Pilot, not SEG
<i>η_{CC}, %</i>	70.0	N/A	N/A	54
<i>CGE_{LHV}, %</i>	76.83	N/A	67.8	71.7
<i>η_{th}, % (LHV)</i>	77.99	69.84	41.2	57.7
<i>H₂, mol. %</i>	3.1	1.3	1.2	2.3
<i>CO₂, mol. %</i>	1.2	5.7	0.3	0.1
<i>CO, mol. %</i>	0.0	13.6	0,0	N/A
<i>CH₄, mol. %</i>	95.4	79.1	98.09	97.1
<i>SO₂, mol. %</i>	0.0	N/A	N/A	N/A
<i>H₂S, mol. %</i>	0.0	N/A	N/A	N/A
<i>Other trace gases, mol. %</i>	0.3	0.01	0.42	0.5
<i>CH₄ yield, kgCH₄/kgBM</i>	0.23	0.63	0.24	N/A
<i>LHV_{fuel}, MJ/kg</i>	20.22	19.26	19.09	N/A
<i>HHV_{fuel}, MJ/kg</i>	21.52	N/A	N/A	N/A
<i>LHV_{syngas}, MJ/kg</i>	48.37	N/A	49.45	N/A
<i>HHV_{syngas}, MJ/kg</i>	53.76	38.88	N/A	N/A

The achieved CGE of the SNG production path line within the present study is comparable with other results listed in Table 6. However, the overall plant efficiency of the proposed conversion process is significantly higher. Nevertheless, it should be noted that the overall efficiency depends on a multitude of factors including unit operations and process specifications as disclosed in the table. In all cases with the exception of the study by Barbuzza et al. [35], methane content above 95 mol.% CH₄ is achieved. The results by Martínez and Romano [34] are especially comparable with the present study. The main difference stems from the use of an electrolyser in their study for PtG, where hydrogen intended for hydrogasification is produced. While a comparable CGE is reported by Martínez and Romano [34], the use of an electrolyser significantly reduces the overall plant efficiency.

Methane yields recorded in different studies show significant scatter, which can be attributed both to different biomass feedstock and to differences in the process design. For example, the results of the present study indicate a H₂/CO₂ ratio in the first-stage syngas below stoichiometric, necessitating CO₂ removal, while Barbuzza et al. [35] avoided excessive CO removal by adding hydrogen through PtG. Martínez and Romano [34] also relied on PtG to achieve hydrogasification, but a much lower effective S/C ratio was maintained. In contrast with other studies, H₂ was not introduced externally in the present study and sufficient quantities were instead realized by pushing the WGS reaction towards a higher H₂ content upstream of methanation. Consequently, similar methane yields were achieved.

Furthermore, biomethane production plant presented in the literature review can be compared here as well. A comparison can also be made to the GoBiGas [37] biomethane production plant, which is possibly the most developed pilot-scale gasification biomass-to-biomethane facility. It should be noted, however, that data on all operating parameters of this plant is not published. Nevertheless, the proposed SEG process is shown to have a high potential for achieving superior performance of biomethane production in the form of a higher overall plant efficiency.

Evaluating the presented process models further, in terms of SNG production, interesting results were obtained. Figure 6 shows the overall process efficiency and LHV value of the obtained SNG in case of various H₂ contents in the produced SNG. As can be seen, the changes are nearly linear. While higher H₂ content produces a

SNG with higher heating values, an efficiency penalty increases due to greater CO₂ removal, thus reducing the process efficiency for less than one per cent point.

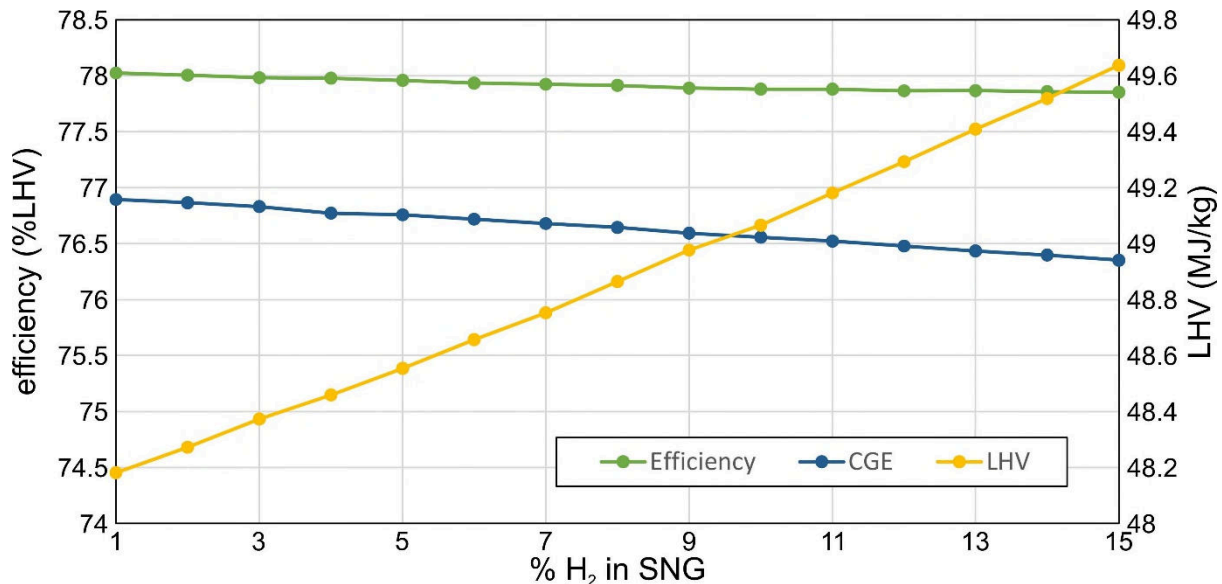


Figure 6: Effect of different H₂ contents in SNG on overall process efficiency and SNG's LHV.

Figure 7 depicts molar composition of the produced SNG, as well as its yield. Again, the presence of the H₂ changes linearly, as this was a design specification, and so does the SNG yield. The latter, however, decreases when more H₂ is present, as more carbon atoms, which are heavier compared to hydrogen, is removed during the process. Consequently, lower CH₄ content directly translates into lower SNG yield. Considering both LHV and SNG yield, the trend is slightly in favour of higher H₂ content in the SNG.

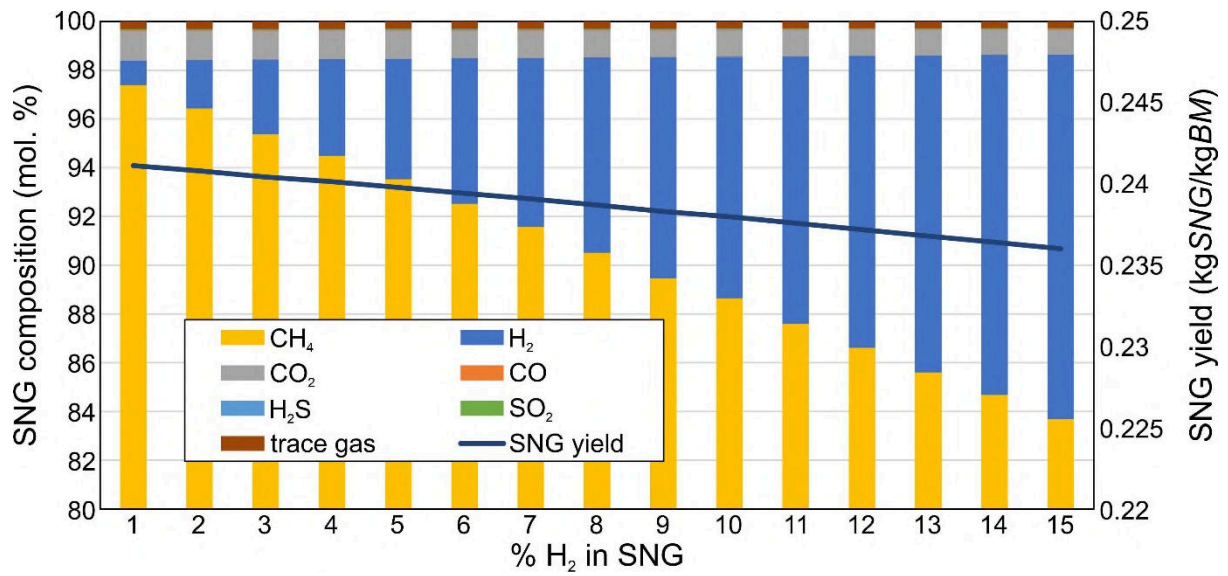


Figure 7: SNG composition and yield.

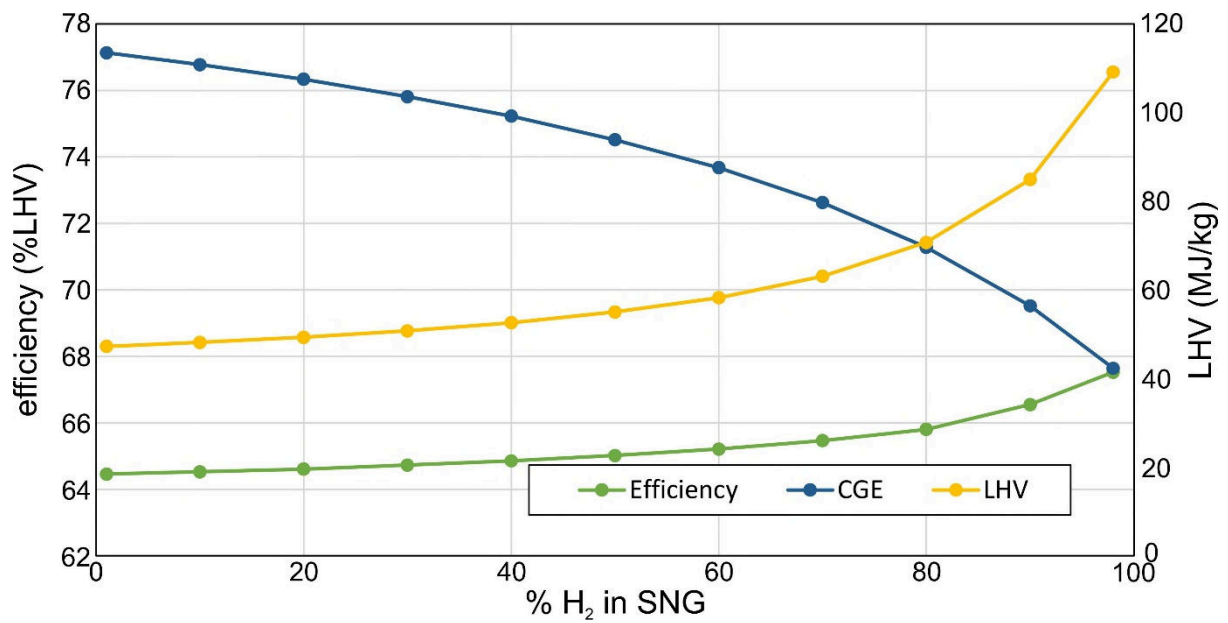


Figure 8: Effect of different H₂ contents in SNG on overall process efficiency and SNG's LHV over the entire range of the proposed process design.

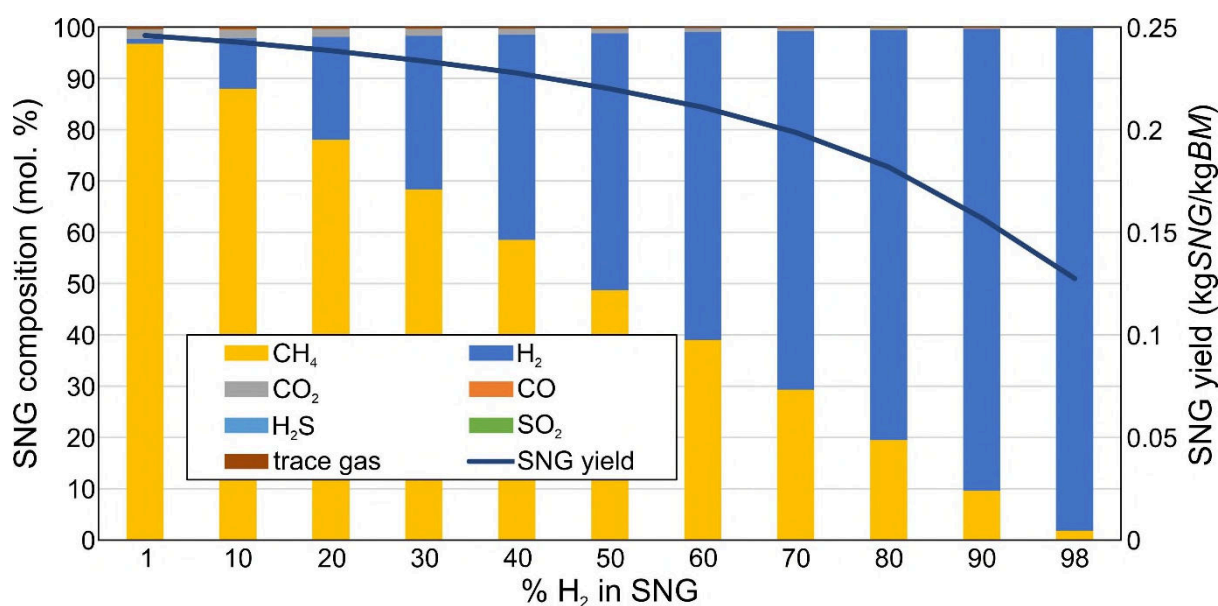


Figure 9: SNG composition and yield over the entire range of the proposed process design.

Figure 8 and Figure 9 show the response of the system over the entire range of its operational capabilities. The limiting values of 1 mol. % and 98 mol. % H₂ are a limitation of design, as it is impossible to achieve 100% purity or absence of hydrogen on such relatively simple design. To be able to achieve this kind of end-to-end composition flexibility, the gasification pressure was reduced to 1 bar, as higher pressures favour CH₄ production and therefore limit the target of achieving high-purity H₂. While being able to operate the system in such way may be challenging to achieve from the engineering and operating point of view, a system like that can have tremendous advantages. In the wake of new “green gas” policies and new research into higher H₂ content in the natural gas networks, this design could easily adapt to new standards.

Moreover, as taking the proposed process design a step further, we can also deactivate the CaL section of the process and thus retain the entire gas content in the syngas. This can be advantageous in case when renewable electrolytic H₂ is available from power production surplus. To keep the methanation stoichiometric balance in check, additional H₂ is then injected into the methanation reactor, to achieve higher SNG yields. This represents not only a viable RNG production method, but also plays an important part in renewable power surplus storage. Main advantage here is wide

usability of SNG, as opposed to currently very limited use of hydrogen in energy sector. Figure 10 shows the increased yield and composition of SNG for gasification process coupled with PtG to eliminate CaL, compared to earlier presented CaLG. With additional H₂ being injected into methanation reactor, SNG yields more than doubles, while composition changes only slightly. The main difference in residual H₂ actually arises from process control and could be further adjusted with different stoichiometry.

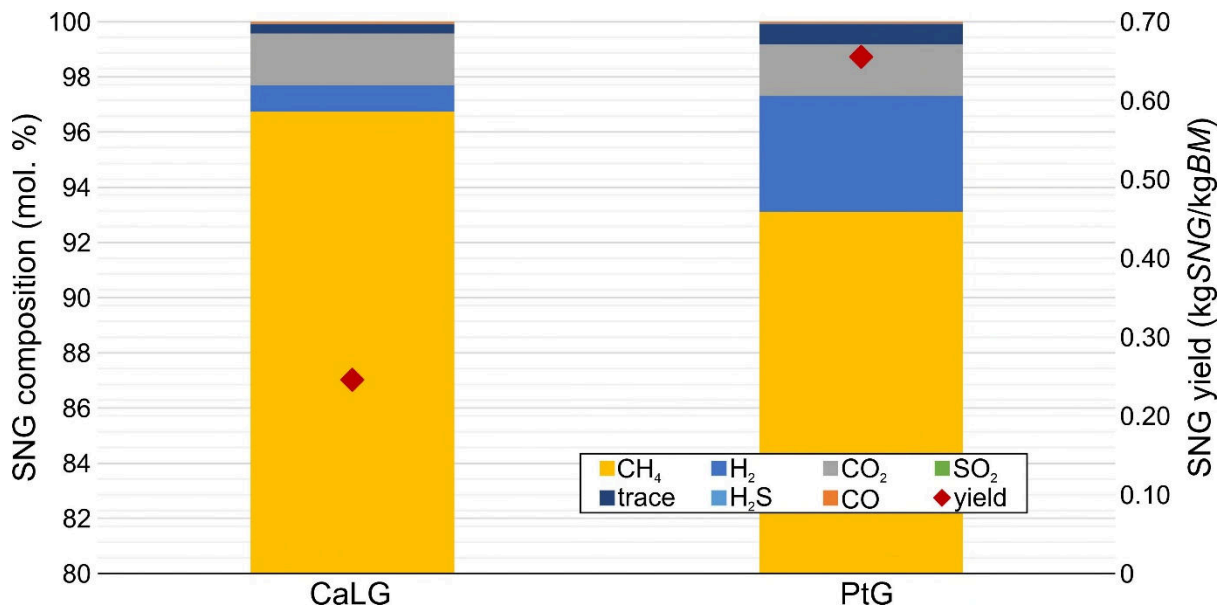


Figure 10: Yield and SNG composition for methanation combined with CaLG or PtG, respectively.

Overall, SEG processes utilizing CaLG for biomethane production benefit from a simpler process design compared to traditional solutions (such as PSA CO₂ capture) and higher (or at least equal) process efficiency. This is consistently reported by all major biomass-to-biomethane pilot plants as mentioned in the literature review subsection. However, a major CaLG pilot plant with a methanation subsystem for biomethane production is yet to be constructed and operated to experimentally validate simulation results.

4 Conclusions

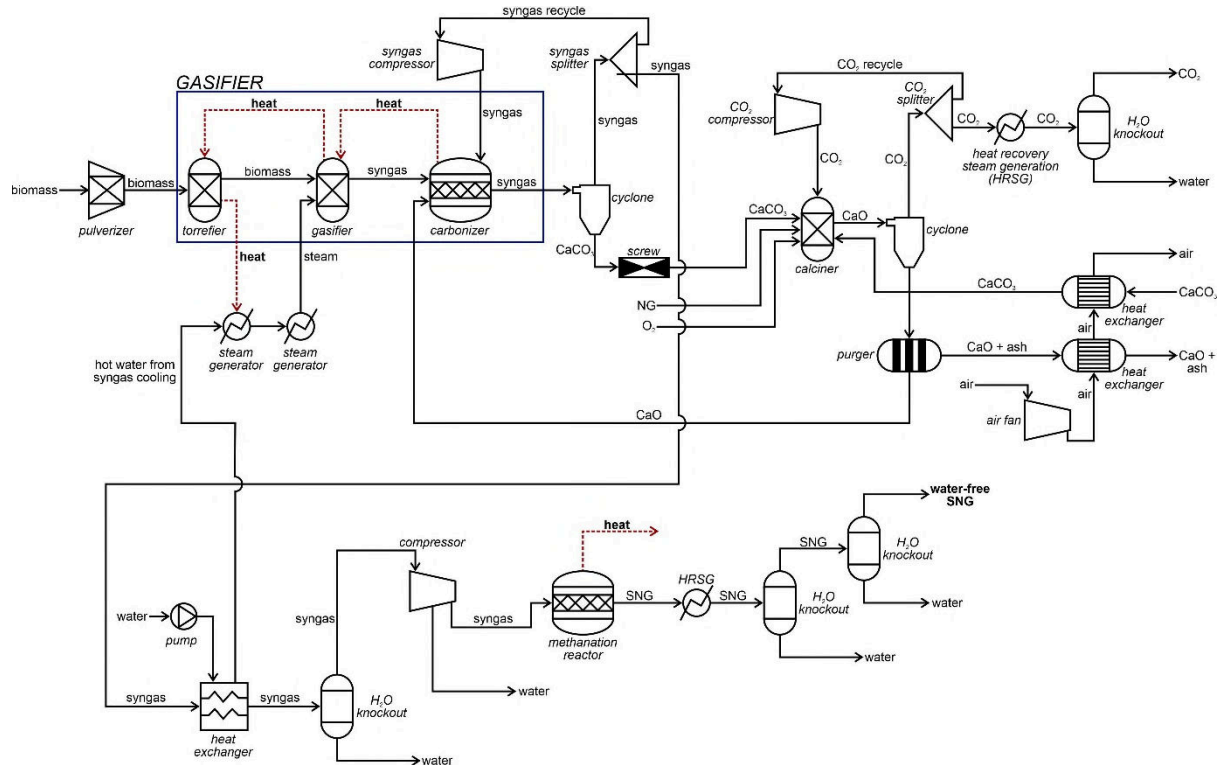
This study proposes a novel calcium looping gasification process design for bio-H₂ and bio-CH₄ production. The main advantage of the proposed design are two production path lines, enabling switchable production of two gasses and their mixtures with highly flexible composition. The proposed process was proven through thermodynamic assessment to not only be feasible but also potentially superior to alternative processes. Furthermore, both possible products have a negative carbon footprint due to the utilization of biomass feedstock and integration of the CaL process.

Overall process efficiency of 62.2%_{LHV} and 78.0%_{LHV} for H₂ and CH₄ production was achieved, respectively. Compared to alternative and/or similar H₂ and CH₄ production processes, the proposed process design was found to offer higher overall efficiencies, higher product purities, and on par product yields. Specifically, the H₂ production path line provided a yield of 0.112 kg H₂/kg BM with a purity over 96 mol.% and a LHV value of 78.7 MJ/kg. On the other hand, the CH₄ production path line yielded 0.23 kg CH₄/kg BM with a purity over 95 mol.% and a LHV value of 48.37 MJ/kg.

Calcium looping (CaL) process for carbon capture was found to be a beneficial choice for SEG. Both production path lines yielded products with negligible amounts of NO_x, SO₂ and H₂S, successfully proving the multi-effectiveness of the CaO sorbent. Consequently, the need for an additional desulphurisation unit was eliminated, thus simplifying the process and potentially lowering its price.

Overall, the proposed process design allows not only production of either H₂ or CH₄, but also production of SNG with almost any desired ratio of the two gases. The novelty of the design comes in end-to-end product flexibility, which to our knowledge has not been proposed before. This unique flexibility might be the key in solving the future dynamic demands for gas, as well as successfully complement other PtG technologies. Moreover, the concept proves technical viability of multi-purpose system design, with capability and adaptability to possible future regulation changes regarding SNG specifications.

Appendix A: Complete Flow Diagram of the Proposed Process



Appendix Figure 1: Complete flow diagram of the proposed process.

Nomenclature

Symbol	Unit	Explanation
CGE	/	Cold gas efficiency
η	/	Efficiency
HHV	kJ/kg	Higher heating value
ΔH°_R	kJ/mol	Enthalpy of reaction
LHV	kJ/kg	Lower heating value
$\dot{m}$	kg/s	Mass flow
$\dot{n}$	mol/s	Molar flow
P	W	Power
$\dot{Q}$	W	Heat flow rate
S/C	mol/mol	Steam to carbon ratio

Index	Explanation
CO_2	Carbon dioxide
CC	Carbon conversion
<i>dry</i>	Dry gas
<i>equip</i>	Equipment
<i>fuel</i>	Fuel
HHV	Higher heating value
$HRSG$	Heat recovery steam generation
LHV	Lower heating value
NG	Natural gas
O_2	Oxygen
<i>syngas</i>	Synthesis gas
<i>steam gen</i>	Steam generator
Th	Overall thermodynamic

Abbreviations

ASU	Air separation unit
BFB	Bubbling fluidised bed
BM	Biomass
CaL	Calcium looping
CaLG	Calcium looping gasification
CFB	Circulating fluidised bed
CGE	Cold gas efficiency
DFB	Dual fluidised bed
GHG	Greenhouse gas
HHV	Higher heating value
HRSG	Heat recovery steam generator
LHV	Lower heating value
NG	Natural gas
PR-BM	Peng-Robinson equation of state with Boston-Mathias modification
PSA	Pressure-swing absorption
PtG	Power to Gas
RES	Renewable energy sources
SEG	Sorption enhanced gasification
SE-SHR	Sorption enhanced steam hydrogasification
SNG	Synthetic natural gas
WGS	Water-gas shift
WGSR	Water-gas shift reactor

Acknowledgements

The authors acknowledge the financial support from the state budget by the Slovenian Research Agency (Program No. P2-0223). This publication is based on research conducted within the “Redefining power generation from carbonaceous fuels with carbonate looping combustion and gasification technologies” project funded by UK Engineering and Physical Sciences Research Council (EPSRC reference: EP/P034594/1).

Data availability

Further data, details and specifications on the simulation models can be obtained by request to the corresponding author.

References

- [1] European Parliament. Renewable energy directive. Eur Wind Energy Conf Exhib 2008 2008;1:32–8. https://ec.europa.eu/energy/topics/renewable-energy/renewable-energy-directive/overview_en.
- [2] Nuffel L van, Dedecca JG, Yearwood J, Smit T, Bünger U, Altmann M, et al. Impact of the use of the biomethane and hydrogen potential on trans-European infrastructure 2019:7. <https://www.europeangashub.com/wp-content/uploads/2019/11/Trinomics-biomethane-and-hydrogen-study.pdf>.
- [3] Trinomics. The role of Trans-European gas infrastructure in the light of the 2050 decarbonisation targets. 2018.
- [4] Frontier Economics. The Value of Gas Infrastructure in a Climate-Neutral Europe - A study based on eight European countries. 2019.
- [5] Navigant. Gas for Climate. The optimal role for gas in a net-zero emissions energy system. 2019.
- [6] Tahir F, Joos M, Freeman E, Foster S, Slater S, Alexandri E, et al. Towards fossil-free energy in 2050. 2019.
- [7] ICCT. The potential for low-carbon renewable methane in heating, power, and transport in the European Union. 2018.
- [8] Council of the European Union. Smart sector integration: Promoting clean energy - Policy debate 2019. <https://data.consilium.europa.eu/doc/document/ST-13854-2019-INIT/en/pdf>.
- [9] ACER. ACER Report on NRAs Survey - Hydrogen, Biomethane, and Related Network Adaptations. 2020.
- [10] International Energy Agency. World Energy Outlook 2018. Paris, France: OECD/IEA; 2018. <https://doi.org/10.1787/weo-2018-en>.
- [11] IHS Markit. Chemical Economics Handbook. London, UK: IHS Markit; 2017.
- [12] International Energy Agency. Technology Roadmap: Hydrogen and fuel cells. 2015.
- [13] Guo M, Song W, Buhain J. Bioenergy and biofuels: History, status, and perspective. Renew Sustain Energy Rev 2015;42:712–25. <https://doi.org/10.1016/j.rser.2014.10.013>.
- [14] Hanak DP, Manovic V. Techno-economic feasibility assessment of CO₂ capture from coal-fired power plants using molecularly imprinted polymer. Fuel 2018;214:512–20. <https://doi.org/10.1016/j.fuel.2017.10.107>.
- [15] Chen S, Wang D, Xue Z, Sun X, Xiang W. Calcium looping gasification for high-concentration hydrogen production with CO₂ capture in a novel compact fluidized bed: Simulation and operation requirements. Int J Hydrogen Energy 2011;36:4887–99. <https://doi.org/10.1016/j.ijhydene.2010.12.130>.
- [16] Mahishi MR, Goswami DY. An experimental study of hydrogen production by

- gasification of biomass in the presence of a CO₂ sorbent. *Int J Hydrogen Energy* 2007;32:2803–8. <https://doi.org/10.1016/j.ijhydene.2007.03.030>.
- [17] Cormos A-M, Simon A. Assessment of CO₂ capture by calcium looping (CaL) process in a flexible power plant operation scenario. *Appl Therm Eng* 2015;80:319–27. <https://doi.org/10.1016/J.APPLTHERMALENG.2015.01.059>.
 - [18] Corella J, Toledo JM, Molina G. Steam gasification of coal at low-medium (600–800 °C) temperature with simultaneous CO₂ capture in a bubbling fluidized bed at atmospheric pressure. 2. Results and recommendations for scaling up. *Ind Eng Chem Res* 2008;47:1798–811. <https://doi.org/10.1021/ie0714192>.
 - [19] Parvez AM, Hafner S, Hornberger M, Schmid M, Scheffknecht G. Sorption enhanced gasification (SEG) of biomass for tailored syngas production with in-situ CO₂ capture: Current status, process scale-up experiences and outlook. *Renew Sustain Energy Rev* 2021;141. <https://doi.org/10.1016/j.rser.2021.110756>.
 - [20] Li B, Fabrice Magoua Mbeugang C, Liu D, Zhang S, Wang S, Wang Q, et al. Simulation of sorption enhanced staged gasification of biomass for hydrogen production in the presence of calcium oxide. *Int J Hydrogen Energy* 2020;45:26855–64. <https://doi.org/10.1016/j.ijhydene.2020.07.121>.
 - [21] Lin S, Harada M, Suzuki Y, Hatano H. Process analysis for hydrogen production by reaction integrated novel gasification (HyPr-RING). *Energy Convers Manag* 2005;46:869–80. <https://doi.org/10.1016/j.enconman.2004.06.008>.
 - [22] Gil J, Corella J, Aznar MP, Caballero MA. Biomass gasification in atmospheric and bubbling fluidized bed: Effect of the type of gasifying agent on the product distribution. *Biomass and Bioenergy* 1999;17:389–403. [https://doi.org/10.1016/S0961-9534\(99\)00055-0](https://doi.org/10.1016/S0961-9534(99)00055-0).
 - [23] Udomsirichakorn J, Salam PA. Review of hydrogen-enriched gas production from steam gasification of biomass: The prospect of CaO-based chemical looping gasification. *Renew Sustain Energy Rev* 2014;30:565–79. <https://doi.org/10.1016/j.rser.2013.10.013>.
 - [24] Hanak DP, Manovic V. Calcium looping combustion for high-efficiency low-emission power generation. *J Clean Prod* 2017;161:245–55. <https://doi.org/10.1016/j.jclepro.2017.05.080>.
 - [25] Schweitzer D, Albrecht FG, Schmid M, Beirow M, Spörl R, Dietrich RU, et al. Process simulation and techno-economic assessment of SER steam gasification for hydrogen production. *Int J Hydrogen Energy* 2018;43:569–79. <https://doi.org/10.1016/j.ijhydene.2017.11.001>.
 - [26] Schweitzer D, Beirow M, Gredinger A, Armbrust N, Waizmann G, Dieter H, et al. Pilot-scale demonstration of oxy-SER steam gasification: Production of syngas with pre-combustion CO₂ capture. *Energy Procedia* 2016;86:56–68. <https://doi.org/10.1016/j.egypro.2016.01.007>.
 - [27] Udomsirichakorn J, Basu P, Abdul Salam P, Acharya B. CaO-based chemical looping gasification of biomass for hydrogen-enriched gas production with in situ CO₂ capture and tar reduction. *Fuel Process Technol* 2014;127:7–12.

<https://doi.org/10.1016/j.fuproc.2014.06.007>.

- [28] Lin SY, Suzuki Y, Hatano H, Harada M. Developing an innovative method, HyPr-RING, to produce hydrogen from hydrocarbons. *Energy Convers Manag* 2002;43:1283–90. [https://doi.org/10.1016/S0196-8904\(02\)00014-6](https://doi.org/10.1016/S0196-8904(02)00014-6).
- [29] Lin S, Kiga T, Nakayama K, Suzukib Y. Coal power generation with in-situ CO2 capture—HyPr-RING method—Effect of ash separation on plant efficiency. *Energy Procedia* 2011;4:378–84. <https://doi.org/10.1016/J.EGYPRO.2011.01.065>.
- [30] Müller S, Fuchs J, Schmid JC, Benedikt F, Hofbauer H. Experimental development of sorption enhanced reforming by the use of an advanced gasification test plant. *Int J Hydrogen Energy* 2017;42:29694–707. <https://doi.org/10.1016/j.ijhydene.2017.10.119>.
- [31] Nam H, Wang S, Sanjeev KC, Seo MW, Adhikari S, Shakya R, et al. Enriched hydrogen production over air and air-steam fluidized bed gasification in a bubbling fluidized bed reactor with CaO: Effects of biomass and bed material catalyst. *Energy Convers Manag* 2020;225. <https://doi.org/10.1016/j.enconman.2020.113408>.
- [32] Bach QV, Gye HR, Song D, Lee CJ. High quality product gas from biomass steam gasification combined with torrefaction and carbon dioxide capture processes. *Int J Hydrogen Energy* 2019;44:14387–94. <https://doi.org/10.1016/j.ijhydene.2018.11.237>.
- [33] Martínez I, Kulakova V, Grasa G, Murillo R. Experimental investigation on sorption enhanced gasification (SEG) of biomass in a fluidized bed reactor for producing a tailored syngas. *Fuel* 2020;259. <https://doi.org/10.1016/j.fuel.2019.116252>.
- [34] 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>.
- [35] Barbuzza E, Buceti G, Pozio A, Santarelli M, Tosti S. Gasification of wood biomass with renewable hydrogen for the production of synthetic natural gas. *Fuel* 2019;242:520–31. <https://doi.org/10.1016/j.fuel.2019.01.079>.
- [36] Bassano C, Deiana P, Pacetti L, Verdone N. Integration of SNG plants with Carbon Capture and Storage Technologies modeling. *Fuel* 2015;161:355–63. <https://doi.org/10.1016/j.fuel.2015.08.059>.
- [37] Thunman H. GoBiGas demonstration – a vital step for a large-scale transition from fossil fuels to advanced biofuels and electrofuels 2018.
- [38] Rönsch S, Schneider J, Matthischke S, Schlüter M, Götz M, Lefebvre J, et al. Review on methanation - From fundamentals to current projects. *Fuel* 2016;166:276–96. <https://doi.org/10.1016/j.fuel.2015.10.111>.
- [39] Alamia A, Larsson A, Breitholtz C, Thunman H. Performance of large-scale

- biomass gasifiers in a biorefinery, a state-of-the-art reference. *Int J Energy Res* 2017;41:2001–19. <https://doi.org/10.1002/er.3758>.
- [40] Raphaël Schoentgen, Michy A, Guerrini O. *Gaya Project*. 2017.
 - [41] Bolhàr-Nordenkamp M, Rauch R, Bosch K, Aichernig C, Hofbauer H. Biomass CHP Plant Güssing – Using Gasification for Power Generation. *Proceeding 2nd Reg. Conf. Energy Technol. Towar. a Clean Environ.*, 2003, p. 566–72.
 - [42] Rehling B, Hofbauer H, Rauch R, Aichernig C. BioSNG-process simulation and comparison with first results from a 1-MW demonstration plant. *Biomass Convers Biorefinery* 2011;1:111–9. <https://doi.org/10.1007/s13399-011-0013-3>.
 - [43] Pickering D. *GoGreenGas: BioSNG Demonstration Plant: Summary of Plant Design*. London, UK: National Grid Gas Distribution; 2018.
 - [44] Pickering D. *GoGreenGas: BioSNG Demonstration Plant: Summary of Technical Results*. London, UK: National Grid Gas Distribution; 2018.
 - [45] Meijden CM van der, Könemann JW, Sierhuis W, Drift A van der, Rietveld G. *Wood to Bio-Methane demonstration project in the Netherlands*. 2013.
 - [46] Liu Z, Norbeck JM, Raju ASK, Kim S, Park CS. Synthetic natural gas production by sorption enhanced steam hydrogasification based processes for improving CH₄ yield and mitigating CO₂ emissions. *Energy Convers Manag* 2016;126:256–65. <https://doi.org/10.1016/j.enconman.2016.08.008>.
 - [47] Safarian S, Unnpórrsson R, Richter C. A review of biomass gasification modelling. *Renew Sustain Energy Rev* 2019;110:378–91. <https://doi.org/10.1016/j.rser.2019.05.003>.
 - [48] Ramos A, Monteiro E, Rouboa A. Numerical approaches and comprehensive models for gasification process: A review. *Renew Sustain Energy Rev* 2019;110:188–206. <https://doi.org/10.1016/j.rser.2019.04.048>.
 - [49] Žalec D. *Enhanced sorption biomass gasification for hydrogen and biomethane production*. Univeristy of Ljubljana, 2019.
 - [50] Detchusananard T, Im-orb K, Maréchal F, Arpornwichanop A. Analysis of the sorption-enhanced chemical looping biomass gasification process: Performance assessment and optimization through design of experiment approach. *Energy* 2020;207. <https://doi.org/10.1016/j.energy.2020.118190>.
 - [51] Lin S, Harada M, Suzuki Y, Hatano H. Continuous experiment regarding hydrogen production by Coal/CaO reaction with steam (II) solid formation. *Fuel* 2006;85:1143–50. <https://doi.org/10.1016/J.FUEL.2005.05.029>.
 - [52] Lin S, Harada M, Suzuki Y, Hatano H. Continuous experiment regarding hydrogen production by coal/CaO reaction with steam (I) gas products. *Fuel* 2004;83:869–74. <https://doi.org/10.1016/J.FUEL.2003.10.030>.
 - [53] Corella J, Toledo JM, Molina G. Steam Gasification of Coal at Low–Medium (600–800 °C) Temperature with Simultaneous CO₂ Capture in Fluidized Bed at Atmospheric Pressure: The Effect of Inorganic Species. 1. Literature Review and Comments. *Ind Eng Chem Res* 2006;45:6137–46.

<https://doi.org/10.1021/ie0602658>.

- [54] Pitkääja A, Ritvanen J, Hafner S, Hyppänen T, Scheffknecht G. Simulation of a sorbent enhanced gasification pilot reactor and validation of reactor model. *Energy Convers Manag* 2020;204:112318. <https://doi.org/10.1016/j.enconman.2019.112318>.
- [55] Rodríguez N, Alonso M, Abanades JC. Average activity of CaO particles in a calcium looping system. *Chem Eng J* 2010;156:388–94. <https://doi.org/10.1016/j.cej.2009.10.055>.
- [56] Gao J, Wang Y, Ping Y, Hu D, Xu G, Gu F, et al. A thermodynamic analysis of methanation reactions of carbon oxides for the production of synthetic natural gas. *RSC Adv* 2012;2:2358. <https://doi.org/10.1039/c2ra00632d>.
- [57] Energy Research Centre of The Netherlands. Phyllis2, Database for Biomass and Waste 2016. <https://www.ecn.nl/phyllis2>.
- [58] Han L, Wang Q, Yang Y, Yu C, Fang M, Luo Z. Hydrogen production via CaO sorption enhanced anaerobic gasification of sawdust in a bubbling fluidized bed. *Int J Hydrogen Energy* 2011;36:4820–9. <https://doi.org/10.1016/j.ijhydene.2010.12.086>.
- [59] Magoua Mbeugang CF, Li B, Lin D, Xie X, Wang S, Wang S, et al. Hydrogen rich syngas production from sorption enhanced gasification of cellulose in the presence of calcium oxide. *Energy* 2021;228:120659. <https://doi.org/10.1016/j.energy.2021.120659>.



DSpace

<https://dspace.org/>

Process development and performance assessment of flexible calcium looping biomass gasification for production of renewable gas with adjustable composition

Žalec, Domen; Hanak, Dawid P.; Može, Matic; Golobi, Iztok

2021-12-28

Wiley

<https://doi.org/10.1002/er.7558>

Žalec D, Hanak DP, Može M, Golobi I. (2022) Process development and performance assessment of flexible calcium looping biomass gasification for production of renewable gas with adjustable composition. *International Journal of Energy Research*, Volume 46, Issue 5, April 2022, pp. 6197-6215