

BIO-SNG PRODUCTION BY MEANS OF BIOMASS GASIFICATION COMBINES WITH MCEC TECHNIQUE

Report from an f3 project

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PREFACE

This report is the result of a collaborative project within the Swedish Knowledge Centre for Renewable Transportation Fuels (f3). f3 is a networking organization, which focuses on development of environmentally, economically and socially sustainable renewable fuels, and

- Provides a broad, scientifically based and trustworthy source of knowledge for industry, governments and public authorities,
- Carries through system oriented research related to the entire renewable fuels value chain,
- Acts as national platform stimulating interaction nationally and internationally.

f3 partners include Sweden's most active universities and research institutes within the field, as well as a broad range of industry companies with high relevance. f3 has no political agenda and does not conduct lobbying activities for specific fuels or systems, nor for the f3 partners' respective areas of interest.

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SUMMARY

Biomass gasification is an attractive technology that efficiently converts forest biomass, biomass-based wastes and other types of renewable feedstocks into transportation fuels, chemicals or electricity. The technology has great potential to significantly contribute to the national targets of a fossil fuel independent vehicle fleet by 2030 and the vision of a fossil-free society by 2045. With regard to biomass gasification plants, one important bottleneck for commercialisation is the choice of engineering solutions for the downstream product gas cleaning and conditioning, before using the produced synthesis gas. The technologies for gas cleaning and conditioning processes are capital intensive, and the investment costs for these technologies in biomass gasification production systems are initially very large. Therefore, the consequently large business risks may hamper the introduction of biomass gasification. One way to promote its commercialisation is investments in small- to medium-scale plants, where the total costs are more reasonable and the financial risks are lower.

The main aim of this study is to make a preliminary evaluation of the technical and economic feasibility of combining biomass gasification with molten carbonate electrolysis cell (MCEC) technology in systems for production of biomass-based substitute natural gas (bio-SNG). The results presented are positive with regard to integrating a MCEC and can be considered a pre-study for a more rigorous techno-economic evaluation of the conceptual process. The study is based on a literature survey and a conceptual techno-economic investigation of using a MCEC as a gas cleaning and conditioning process step in a biomass gasification system for bio-SNG production. To enable a comparison with a real case, the GoBiGas plant was selected as a reference case. Five different scenarios were evaluated in relation to energy and economic performance.

The conclusion is the results are positive: the mass and energy balance shows that the production of bio-SNG can be boosted by up to 60% when integrating a MCEC, compared to the same biomass input in a standalone operation of a GoBiGas plant. Additionally, the economic assessments revealed price ranges for biomass, SNG and renewable electricity, allowing for a wider margin in terms of the Investment Opportunity (IO) index for the considered process configurations, as compared to the standalone SNG plant. The produced oxygen is also of high value, both as a product for sale or used internally by the gasification process in a direct gasifier, for example. This implies a use of direct gasifiers at smaller scales for synthesis gas production, as supply of pure oxygen is generally a cost-limiting factor in such cases. A direct gasifier is generally less complex compared to indirect systems, exemplified when comparing single direct and dual indirect fluidised bed gasifiers.

The introduction of a MCEC in the gas cleaning and conditioning process of a biomass gasification system provides with the opportunity for process intensification with a potential integration of three process units into one.

There is a number of technical issues related to the MCEC, such as sulphur tolerance and tolerance towards other impurities and extent of hydrocarbon steam reforming depending on process conditions, that need to be addressed before the potential of a MCEC can be concluded. An outline of investigations needed for a more rigorous and comprehensive analysis is specified.

SAMMANFATTNING

Förgasning av biomassa är en attraktiv teknik för effektiv omvandling av skogsbiomassa, biomassaavfall samt andra typer av förnybara råvaror till drivmedel, kemikalier eller t.ex. elkraft. Tekniken har en stor potential att bidra till omställningen enligt de nationella målen för en fordonsflotta oberoende av fossila bränslen år 2030 samt visionen om ett fossilfritt samhälle i 2045. Ett tekniskt hinder för implementering av förgasningstekniken förgasning är valet av tekniska lösningar för produktgasen i efterföljande gasrenings- och konditioneringssteg före den slutliga användningen av den producerade syntesgasen. Traditionell teknik för rening och konditionering av gaser är generellt kapitalintensiv med hög initial investeringskostnad. De stora affärsrisker detta innebär är förmodligen ett av de största hindren för införandet av teknik för förgasning av biomassa. Ett sätt att främja kommersialisering är därför investeringar i små och medelstora anläggningar, där de totala investeringskostnaderna blir mer rimliga och de finansiella riskerna lägre.

Huvudsyftet med innevarande studie har varit att göra en preliminär utvärdering av den tekniska och ekonomiska möjligheten att kombinera förgasning av biomassa med smältkarbonatelektrolyscell (MCEC) teknik i system för produktion av biobränslebaserad syntetisk naturgas (bio-SNG). Studien kan betraktas som en förstudie för en mer rigorös teknisk-ekonomisk utvärdering av den begreppsmässiga processen. Resultaten visar på att det är fördelaktigt att integrera MCEC.

Metodiken i studien baseras på en litteraturstudie och en konceptuell tekno-ekonomisk undersökning av användningen av MCEC, som ett gasrenings- och konditioneringsprocesssteg i en process för förgasning av biomassa för produktion av bio-SNG. För att möjliggöra en jämförelse med ett verkligt fall, valdes GoBiGas-anläggningen som ett referensfall. Fem olika scenarier utvärderades avseende energetisk och ekonomisk prestanda.

Den generella slutsatsen är att resultaten pekar i en positiv riktning, där material- och energibalanser visar att produktionen av bio-SNG kan ökas med upp till 60 %, vid integration av MCEC jämfört med referensfallet GoBiGas-anläggningen. Vidare så visade den ekonomiska analysen att prisklasserna för biomassa, SNG och förnybar el möjliggör en bredare marginal beträffande investeringsmöjligheterna (Investment Opportunity - IO) för de utvärderade processkonfigurationerna, jämfört med den fristående SNG anläggningen. Det producerade syrer har ett högt värde, både direkt som en produkt för försäljning eller för användning internt i förgasningsprocessen vid t.ex. direkt förgasning. Detta innebär att direkt förgasningsteknik för syntesgasproduktion i en mindre skala blir intressant, då kostnaderna för produktion av rent syre generellt är en begränsande faktor för sådana tillämpningar. En direkt förgasare är i allmänhet mindre komplex jämfört med indirekta system, exemplifierat av direkt förgasning i en fluidbädd jämfört med indirekt förgasning i en fluidbäddförgasare med två bäddar.

Integrering av MCEC i gasrenings- och konditioneringsprocessen i en förgasningsanläggning resulterar i en processintensifiering där tre processenheter reduceras till en enhet.

Innan en definitiv slutsats angående MCEC teknikens möjligheter kan tas finns ett antal tekniska frågor att studera, t.ex. svaveltolerans och tolerans mot andra föroreningar samt omfattningen av ångreformerings av kolväten beroende på processbetingelser. I rapporten finns en översiktlig beskrivning på förslag på FoU aktiviteter för en mer noggrann och omfattande analys.

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1 INTRODUCTION

Biomass gasification is an attractive technology to efficiently convert forest biomass, biomass-based wastes and other types of renewable feedstocks into transportation fuels, chemicals or electricity. The technology has a great potential to significantly contribute to the national targets of a fossil-fuel independent vehicle fleet by 2030 and the vision of a fossil-free society by 2045.

One major hurdle in reaching a commercial breakthrough is the economic viability surrounding current conditions. Therefore, it is important to find ways to improve the process economics. With regard to biomass gasification plants, one important bottleneck is the choice of engineering solutions for the downstream product gas cleaning and conditioning before using the produced synthesis gas. The technologies for gas cleaning and upgrading processes are capital intensive, and the investment costs for these technologies in biomass gasification production systems are initially very large. Therefore, the consequently large business risks may hamper the introduction of biomass gasification. One way of promoting commercialization is investments in small- to medium-scale plants, where the total costs are more reasonable and the financial risks are lower. Additionally, finding technical alternatives to reducing the costs for gas cleaning and conditioning would be beneficial.

The main aim of this study has been to make a preliminary evaluation of the technical and economic feasibility of combining biomass gasification with molten carbonate electrolysis cell (MCEC) technology in systems for production of biomass-based substitute natural gas (bio-SNG). The concept is to integrate MCEC technology as a process step for simultaneous conversion of undesired hydrocarbons via tar and gas conditioning to the required H₂/CO ratio prior to the methanation. The results from the study may provide a basis for a more in-depth study of the technical, economic, and environmental potentials and consequences. A number of system-wide issues of a general plan to assess the possibility of integrating MCEC technology in a gasification process for transportation fuel production have been addressed:

1. Are there opportunities for molten carbonate electrochemical cell technology to replace the process of gas cleaning and upgrading process?
2. What is an appropriate size ratio between the thermal gasifier and molten carbonate electrochemical cell technology?
3. What other gas cleaning and upgrading steps are required in connection with the molten carbonate electrochemical cell technology?
4. Are there opportunities to interact with the electrical system through the flexibility of switching between power-to-gas and gas-to-power?
5. What is the estimated investment and operating costs of a general system?

2 BACKGROUND

2.1 BIOMASS GASIFICATION

In biomass gasification for production of transportation fuel, the biomass feedstock is thermochemically converted at elevated temperatures (600-1400 °C) in the presence of an oxidant, such as oxygen or steam, to the main permanent gases H₂, CO, CO₂ and H₂O [1]. Besides these gases, a spectrum of light, mainly methane and heavier hydrocarbons, consisting of polyaromatics, also referred to as tars, and benzene, are formed. Additionally, a variety of undesired pollutants, including NH₃, H₂S, mercaptans, HCN, COS, and alkali salts, HCl, and carbon residue, as well as ash particles is also present in the product gas [1]. The preferred synthesis gas molecules are in the end mainly CO and H₂, in some cases also small amounts of CO₂ and perhaps methane if methane production is desired. This means that hydrocarbons should preferably be converted to synthesis gas molecules, but other non-desirable components, depending on requirements (often below the ppm level) of the end synthesis process, must be removed from the gas as much as possible. Of particular importance is minimising sulphur and nitrogen compounds, as well as alkali salts, which, among others, cause problems in downstream catalytic conversion processes. After gas cleaning, the final gas is generally conditioned to a relevant H₂/CO ratio in relation to the desired end product, for example a methanation process requires an H₂/CO ratio of approximately three.

Due to the product gas composition and the synthesis gas requirements, the gas cleaning and conditioning process is often complex with multiple steps positioned in a certain order for optimised efficiency. The different possible steps are outlined in Figure 1.

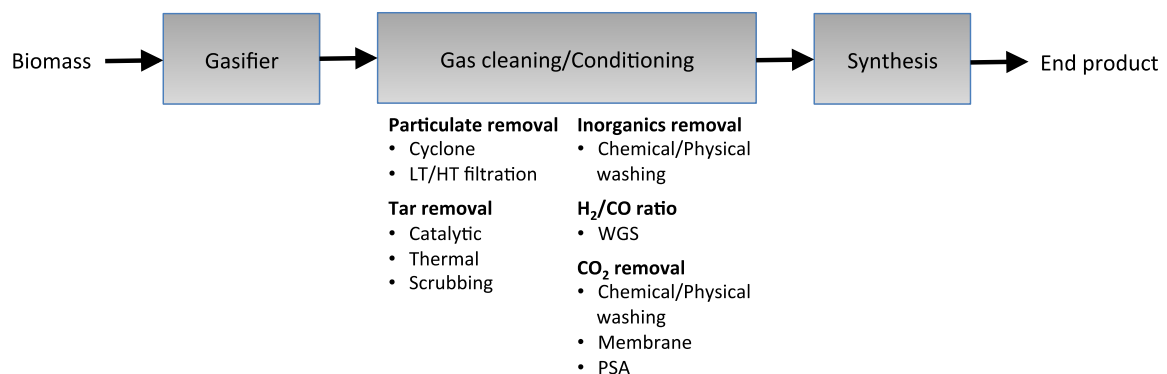


Figure 1. A schematic of selected gas cleaning and conditioning steps.

The capital cost for gas cleaning and conditioning is typically around 25% of the total capital cost for a biomass gasification-based biofuels plant. The proposed concept could potentially reduce the cost of gas cleaning and conditioning, and consequently improve the overall process economics.

The choice of process configuration depends generally on plant size, localisation, integration opportunities, desired end product, as well as the technical limitations of available process technology. Today's technology for gas cleaning and upgrading has its origin in the refinery industry, implying a use of the technology for large-scale production, which is difficult to scale down with reasonable investment costs. This and the lack of technology for production processes on a smaller scale have contributed to the general perception that large-scale production of transportation fuels is required for economic reasons. The need to demonstrate large-scale production for further scale-up and commercialisation involves high investment costs. This, together with the business risks,

may hinder the investment in new technologies, and thus complicating the commercialisation of the technique [2].

2.2 ELECTROCHEMICAL CONVERSION

The interest in using electrochemical conversion in power-to-gas applications has increased in recent years. The main focus has been on the production of H₂ by electrolysis of water, where the hydrogen is utilised in, for example, a methanation process together with CO [3] or directly as vehicle fuel. Today, hydrogen production by electrolysis takes place in relatively large processes, usually using alkaline type cells and operating at low temperatures with relatively low efficiency [4, 5]. Other alternatives is direct co-electrolysis of CO₂ and water to synthesis gas using the solid oxide electrolysis cell (SOEC) technology [3, 6-9], a technology increasingly being discussed as possibly enabling a greater share of intermittent renewable power into the energy supply system. Additionally, solid oxide fuel cell (SOFC) technology has been demonstrated as a promising low carbon technology to produce conditioned syngas from biogas feed [10]. A SOEC and SOFC generally use the same materials, implying operating temperatures of 600-1000 °C. The high operating temperatures change both thermodynamic and kinetic properties of the electrochemical process, resulting in improved overall conversion efficiency. In addition, the high temperatures also reduce the electric power requirement since part of the energy required for splitting the molecules is supplied as thermal energy. The downsides of using solid oxide cells are common electrode material problems leading to limited long-term stability [11]. Today, the SOFC is found as units of a size up to a few hundred kW, while electrolyzers are still only available at an experimental scale (few kW).

A promising alternative is the molten carbonate electrolysis cell (MCEC), a new technique recently developed and demonstrated at laboratory scale at KTH [12, 13]. The technology is based on the proven and already commercially introduced molten carbonate fuel cell (MCFC) [14], where units of up to 3.7 MW are currently sold on the market and several power plants of 10-60 MW are installed worldwide. MCFC technology is a SOFC operating at high temperatures of 600-800 °C, and therefore benefits from the same high overall conversion efficiency as a SOFC.

A molten carbonate cell consists essentially of two electrodes, commonly made of alloyed Ni and NiO, and an electrolyte, consisting of a molten alkali salt, including combinations of Li₂CO₃, K₂CO₃ and Na₂CO₃, suspended in a porous ceramic matrix made of LiAlO₂ [15]. The principal electrochemical reactions occurring in the cell converting electric power to an energy-rich gas, when fed with H₂O and CO₂, are shown in Figure 2. Water and carbon dioxide is converted to CO and H₂ in reactions R1 and R2. Carbonate ions are transported from the cathode to the anode in the electrolyte and decomposed to O₂ and CO₂. In the MCFC mode the reactions are reversed.

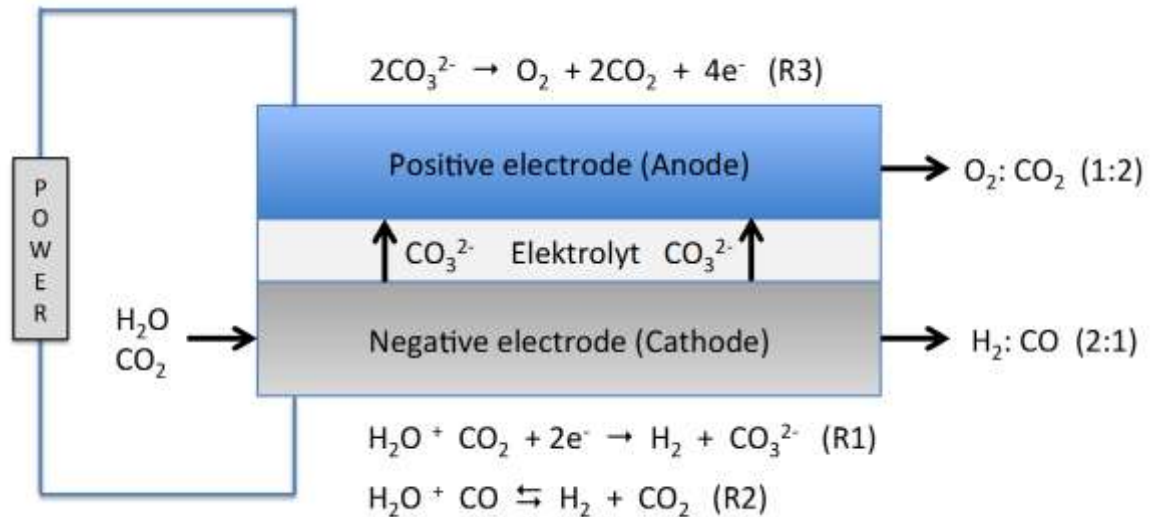
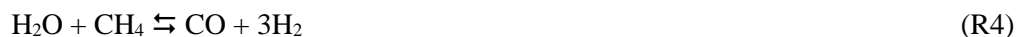


Figure 2. The principle for a molten carbonate electrolysis cell.

There are a number of advantageous of using molten carbonate electrochemical cell technology. A MCFC has the ability to withstand a high amount of CO content in the product gas. Another prospective advantage of integrating it in a gasification system is the internal reforming of hydrocarbons in the gas, especially, allowed by the high temperatures, when using catalytically active Ni electrodes [16]. The heat needed for the endothermic steam reforming of methane or higher hydrocarbons is taken from the cell stack, reducing the need for external cooling generally required in the stack. A final advantage of the MCEC is its reversibility [12, 13], implying a possibility using the cell technology both in power- to-gas applications and power production depending on needs.

Dayton [17] specified the levels of the tolerable amount of hydrocarbons in the feed to up to 10 vol-% saturated hydrocarbons (including methane) and less than 0.5 vol-% of aromatic and cyclic hydrocarbons, but large amounts of heavier hydrocarbons may create problems with deposits on electrodes, for example. How internal reforming works in the MCEC operational mode has, however, so far not been investigated. The reactions related to hydrocarbons are illustrated in R4-R6, where R6 represents the reforming reaction of tar, using a parametric compound.



The impact of pollutants such as ammonia, alkali metals and halides on a MCFC may, for instance, manifest as corrosion of cell components and increased loss of electrolyte by reaction and evaporation, impairing the balance of the electrolyte [17, 18]. Nevertheless, since molten alkali carbonate is used a certain tolerance of alkali metals is expected [19]. Also, particles may be a problem for the cell, where they, among other things, can clog the porous electrodes [17]. Furthermore, the presence of H_2S in the product gas could lead to degradation in performance and shorten cell life, particularly under low temperatures and high current density operation mode [18].

3 METHODOLOGY

This study has been based on a literature survey and a conceptual techno-economic investigation of using a MCEC as a gas cleaning and conditioning process step in a biomass gasification system for bio-SNG production. Aspects of the methodology for the conceptual study is briefly highlighted in this chapter but described in more detail in Appendix 1.

To enable a comparison with a real case, the GoBiGas plant has been selected as a reference case. The plant is a 32 MW_{feedstock} dual fluidised bed biomass gasifier, consuming 3 MW of electricity and 0.5 MW of RME (tar recovered from the process) during normal operation. The output is 20 MW of Biomethane, as well as 5 MW of excess heat for direct utilisation for district heating (DH) and 6 MW of upgraded heat (via a heat pump) to DH. The produced bio-SNG consists of more than 95% CH₄ and is distributed to consumers via the local natural gas grid. A detailed description of the GoBiGas plant is found in [20].

Different aspects of implementing MCEC technology, while assuming real conditions, have been simulated using the MATLAB Simulink environment. Figure 3 presents a schematic diagram of the integrated conceptual process. Upstream processes, including the gasifier, particle filtration, RME scrubber for tar removal (in some scenarios), and downstream processes — including syngas compression, methanation and bio-SNG drying — remain unaltered. Process units replaced by the MCEC are the RME scrubber (for scenarios when internal reforming is assumed), water-gas shift (WGS) reactor and carbon-dioxide scrubber. The thermal capacity (i.e., biomass) input and the raw gas production of the GoBiGas plant have been kept as is in the actual configuration. The MCEC has been modelled as an equilibrium electrochemical reactor consuming power as described in Appendix 1.

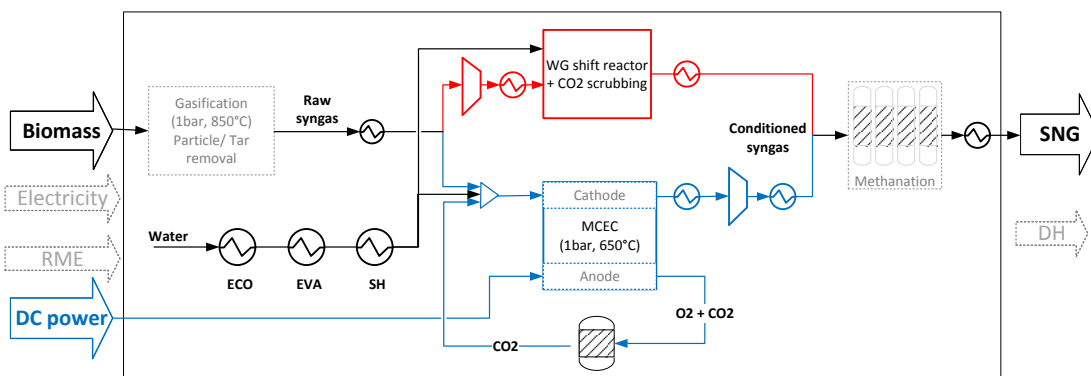


Figure 3. Schematics of the GoBiGas configuration (dark and red outlines) with an integrated conceptual MCEC process (dark and blue outlines). The black rectangle reflects the boundary for the energy performance analysis.

The different process scenarios evaluated in the modelling are:

Scenario I: represents the model run for standalone GoBiGas plant (without the integrated MCEC) in order to reproduce the actual plant operation.

Scenario II: represents the model run for integrated GoBiGas and MCEC with a DH option.

Scenario III: represents the model run for integrated GoBiGas and MCEC with a CT option.

Scenario IV: represents the model run for integrated GoBiGas and internal reforming MCEC with a DH option.

Scenario V: represents the model run for integrated GoBiGas and internal reforming MCEC with a CT option.

The scenarios considered have been evaluated in relation to energy and economic performance. The energy performance of the conceptual process has been evaluated based on the model outputs in accordance with the system boundary in Figure 3. As energy performance indicators, the bio-SNG efficiency (or the cold gas efficiency) is calculated as the ratio of the energy content (based on low heating value) of the produced bio-SNG to the biomass energy input, as well as the overall efficiency calculated as electricity equivalents, taking into account the qualities of the different energy streams. In terms of economic performance the Investment Opportunity (IO) has been used as an indicator of the potential economic feasibility. IO is an economic index of a design solution based on the difference between the algebraic sum of resource costs and product revenues. The higher the IO value, the wider the margins for investing more capital in a design solution, while the cash flow history of the project remains positive at the end of the economic lifetime. All input data and assumptions used in the evaluation are further described in Appendix 1.

4 RESULTS AND DISCUSSION

The results and discussion paragraph presents a summary of the technical conference paper in Appendix 1 and a literature survey to address issues not addressed in the conference paper. In the literature review, no results for application of MCEC technology, other than those reported by KTH [12, 13, 21-23], were discovered. Therefore, the evaluation is exclusively based on findings on the MCFC and when applicable on the SOFC and SOEC.

4.1 CONCEPTUAL STUDY

The overall results of the conceptual study, presented in detail in Appendix 1, show that the production of bio-SNG can be boosted by approximately 50% without the need for an additional carbon source, in other words for the same biomass input as in a standalone operation of the GoBiGas plant.

4.1.1 Process performance

The composition of the input and bio-SNG process streams are summarised in Table 1 for the MCEC with and without RME scrubber, that is with and without internal reforming, respectively. The results show that the reformation of tar and BTX in the MCEC consumes about 1 mol/s of additional steam, compared to the case without internal reforming, resulting in an increased bio-SNG yield of about 2.5 mol/s.

Table 1. Stream composition input to MCEC and SNG for a MCEC process with and without internal reforming.

	GoBiGas without RME (internal reforming)		GoBiGas with RME (no internal reforming)	
	Input gas	SNG	Input gas	SNG
Temp [K]	923.150	298.150	923.150	298.150
Pressure [bar]	1.013	6.000	1.013	6.000
Mole flow [mol/s]	150.130	42.451	146.240	39.981
O ₂ (vol. %)	0.000	0.000	0.000	0.000
N ₂	0.020	0.042	0.030	0.044
CO ₂	0.170	0.000	0.180	0.000
H ₂ O	0.190	0.000	0.220	0.000
CH ₄	0.035	0.957	0.040	0.955
H ₂	0.430	0.001	0.400	0.001
CO	0.155	0.000	0.130	0.000

The model was used to investigate the effects of different process conditions such as pressure and temperature on the MCEC. For both scenarios, with and without internal reforming, the H₂ and CO compositions in the synthesis gas increase with an increase in the operational temperature of the MCEC, while the steam and methane components simultaneously are depleted. Also, the tar reforming slightly increases the contents of CO and H₂, while the steam content is reduced.

In case of operating pressure, a gradual increase from atmospheric pressure up to a 30 bar reverse steam methane reforming (R4) is favoured, consuming H₂ and CO, and producing water and 27-30% methane for scenarios II-V. This could be advantageous if methane is desired. However, operational pressure is generally limited to below 8 bar for the MCFC to avoid initiation of accelerated

electrode dissolution failure, leading to early degradation [24]. There is, however, ongoing research aimed at developing more durable electrode materials for MCFC [25] and materials for applications, including internal reforming [26]. A similar reasoning applies to the MCEC. However, in the present study, this is not an issue since the gas compression before methanation is placed after the MCEC, i.e. the MCEC is operated at the same pressure of around 1 bar as the gasifier. Internal reforming of tar to CO and H₂ (R6) and formation of methane and steam through reverse steam reforming reaction (R4) occurs simultaneously.

4.1.2 Energetic performance

The energy balance of the scenarios and the results of their corresponding performance indicators are summarised in Tables 2 and 3. Table 2 shows the energy inputs to the system, and Table 3 the outputs of the main product bio-SNG and other energy carriers.

Table 2. Energy input.

	Input (GWh/year)					
	GoBiGas actual [20]	Scenario I	Scenario II	Scenario III	Scenario IV	Scenario V
Wood pellets	256.000	256.000	256.000	256.000	256.000	256.000
RME (bio-oil)	4.000	4.000	4.000	4.000	0.000	0.000
Compressor power	NA	20.944	17.872	17.872	17.680	17.680
Gasification power	NA	5.920	5.920	5.920	5.920	5.920
Total el. input	24.000	26.644	23.792	23.792	23.600	23.600
DC power MCEC	0.000	0.000	99.520	99.520	103.520	103.520

In terms of electricity equivalents in Table 3, scenario I resulted in higher electricity efficiency by about 10% for scenarios II and III and 7% for scenarios IV and V. This indicates that DC power required to operate the MCEC needs to be inexpensive from, for example, intermittent resources during periods of excess power generation.

Table 3. Energy output.

	Output (GWh/year)					
	GoBiGas actual [20]	Scenario I	Scenario II	Scenario III	Scenario IV	Scenario V
SNG	160.000	161.920	245.205	245.205	260.743	260.743
Net CHP power	0.000	13.120	11.520	16.272	10.240	14.240
District heating (DH)	25.000	17.500	20.000	2.500	17.500	5.000
El. Equivalency (%)	66.5	71.6	62.2	62.3	65.0	65.3
SNG efficiency (%)	62.5	63.3	95.8	95.8	101.9	101.9

In view of the difference between the electricity input to the process (Table 2) and the net power output from the CHP system (Table 3), it is clear all scenarios require external electricity supply for internal operations. The magnitude of this external electricity demand will, however, differ depending on the process configuration. Scenario III resulted in the highest net power generation due to the utilisation of scrubbed tar in the combustor, boosting the amount of generated steam for the CHP system.

4.1.3 Economy performance

Input data for the economic performance analysis is specified in Table 4 in Appendix 1. All scenarios have a positive IO index for MCEC input power prices in the range of 30–40 €/MWh, where the lower end belongs to cases without internal reforming. Scenario IV (Figure 7 in Appendix 1), including the MCEC with internal reforming coupled with the CHP system with district heating option, resulted in the highest IO index, with only a marginal difference compared to scenario V (Figure 7 in Appendix 1). This may be explained by the higher yield of both bio-SNG and district heating for this scenario. Nevertheless, in regions where there is no incentive for district heating, scenario V becomes the most attractive option.

When renewable intermittent power production such as wind, solar and wave power increases the need for electricity storage, the full potential can be utilised. This is no problem as long as the intermittent energy sources account for a minor share of the energy supply. However, when the intermittent power capacity is significantly increased, there will be times with a large surplus of electricity. A MCEC could help take advantage of this surplus and reduce the need for electricity storage. The targeted benefit is twofold. Firstly, the MCEC adds flexibility to energy production and use by linking naturally with the synthesis of gaseous fuels and electrical energy forms. Secondly, the intermittency of renewable electricity and subsequently its storage issue can be addressed with appropriated bio-SNG buffers.

4.1.4 Summary of conceptual study

The main conclusion is that a MCEC integrated with biomass gasification could boost the production of bio-SNG by up to 60% (for scenarios assuming internal reforming of tars) provided that the electricity power comes from low-cost sources.

The economic assessments further revealed the price ranges for biomass, bio-SNG and renewable electricity that would allow for a wider margin in terms of the IO index for the process configurations considered, as compared to the standalone SNG plant. Moreover, the sensitivity analysis shows that for renewable electricity price 26 €/MWh the biomass feedstock price needs to be below 26 €/MWh and for the natural gas market price above 30 €/MWh in order to get positive IO index for all the scenarios.

This is a pre-study. For a more thorough techno-economic evaluation of the conceptual process, experimental investigations of the MCEC fed with syngas are needed in order to justify thermodynamic chemical equilibrium assumptions when determining the composition of the process streams.

4.2 ADDITIONAL ASPECTS INTEGRATING A MCEC IN BIOMASS GASIFICATION CLEAN-UP AND CONDITIONING

As demonstrated by the conceptual study, a potential integration of a MCEC into the gas cleaning and conditioning process of a gasification system reducing the number of gas cleaning and conditioning steps is beneficial in terms of energy and economy performance, compared to current technology. In principle a MCEC has the potential to integrate three process units — catalytic steam reforming, WGS and CO₂ removal — into one unit. Nevertheless, a number of issues need to be further addressed before evident conclusions about the possibilities can be made. These issues relate both to technical limitations and opportunities, and are briefly reviewed below.

Internal reforming of hydrocarbons

This is a potential advantage of major importance, supported by the fact that MCFC is used for conversion of methane in natural gas [27, 28], where a reforming efficiency of up to 100% of methane may be obtained. However, in case of heavier hydrocarbons there is a limit to acceptable amounts (< 0.5 vol-% of aromatic and cyclic hydrocarbons) in the gas feed for a long-term stable operation of the MCFC [17]. Due to the complexity of the composition of tar and amount of tar produced, it is not easy to directly calculate the volume percentage of tar in the product gas. Typical values for benzene in a product gas are approximately 0.5-0.8 vol-% [29], where the benzene, together with toluene and xylene in case of the tar from the GoBiGas plant, amounts to 12.7 g/Nm^3 of 20.5 g/Nm^3 with the remaining 7.8 g/Nm^3 corresponding to heavier hydrocarbons (Appendix 1). This is too high for MCFC applications, implying that tar removal to a certain extent is needed before the product gas enters the MCFC. For example, this can be performed introducing an external catalytic pre-reforming step [30], but in such cases some of the advantage in process intensification is lost. Nevertheless, the discussion concerns a MCFC, and what is valid for a MCEC is at present unclear due to lack of experimental data.

Conditioning of H_2/CO ratio

The possibility to condition the H_2/CO ratio by the WGS reaction, R2 in Figure 2, is valuable. The extent of WGS may be controlled by the MCEC temperature, as reported by Peters et al. [31] for the SOFC. Temperatures closer to or below $600 \text{ }^\circ\text{C}$ promote H_2 and CO_2 formation, and higher temperatures promote methane decomposition. The latter also implies a possibility to control the extent of methane decomposition by changing the temperature.

CO_2 separation and production of O_2

The proposed MCEC enables separation of CO_2 from the main gas stream. The CO_2 and O_2 gas produced on the anode side passes a separation step from which the CO_2 is recycled back to the inlet cathode side of the MCEC. The separated oxygen is a product itself or may be utilised in the gasifier. In case of the dual fluidised bed technology, the oxygen can enrich the air used in the combustion process and thus reduces the need for heat to the nitrogen since less air is used. The available oxygen also opens up the possibility to utilising direct gasification where the produced oxygen is a significant advantage. Direct gasification systems used for syngas applications require in general a supply of oxygen from an air separation unit (ASU), which is expensive and costly to operate at a smaller scale. Therefore, are direct biomass gasification systems for syngas application often considered as suitable only for a larger scale? The oxygen produced in the MCEC process concept not only removes the need for a costly ASU, but also facilitates the use of less complex direct gasification technology, such as fluidised bed gasifiers, compared to indirect gasifiers for smaller gasification systems. Small-scale systems are further promoted by the possible process intensification by reducing the number of process steps in the gas cleaning and conditioning process.

Deactivation by impurities

A major limiting factor for the lifetime of the MCEC is probably the content of H_2S in the product gas. In case of MCFC operation, the presence of H_2S in the product gas could lead to degradation in performance and shorten cell life, particularly under low temperatures and high current density operation mode [18]. However, the particular limit is not evident and different requirements are re-

ported, ranging from less than 10 ppm on the anode side at atmospheric pressure and high gas utilisation (ca 75%) [32]. Other works report on identified H_2S limits on the anode side as low as 0.1 ppm [33, 17]. A solution would be to develop electrode materials with higher sulphur tolerance **and effective recovery capability, as exemplified by the SOFC [34]**. Since there is a lack of experimental data on MCEC operation, it is currently not possible to determine the effects of a H_2S contaminated product gas feed. A product gas from biomass gasification using a woody feedstock generally contains a H_2S content of 100-200 ppm [1]; therefore, a sulphur cleaning step before the MCEC is undoubtedly needed. The choice of sulphur cleaning technology depends on MCEC requirements but also on factors such as size of plant, gasification technology and end product. To perform a more thorough evaluation of needs, experiments investigating the sulphur tolerance at MCEC operation are needed.

Size of MCEC

Today, there is no available commercial MCEC technology, and similar applications have so far only been demonstrated at a laboratory scale [12, 13], investigating reversible use of MCFC with gas mixtures consisting of 64/16/20% $\text{H}_2/\text{CO}_2/\text{H}_2\text{O}$ and 15/30/55% $\text{O}_2/\text{CO}_2/\text{N}_2$ for the Ni hydrogen electrode and the NiO oxygen electrode, respectively. In the case of MCFC, the technology is commercially proven and currently available at a maximum unit size of 3.7 MW, and used in several power plants of 10-60 MW worldwide [14]. The fuel cell manufacturers are usually marketing modules of a few different sizes/power outputs, which are then added together to suit specific customer requirements with regard to power output. For a future commercial implementation of a MCEC a similar unit size of 3.7 MW is expected, as the cell should operate at dual mode and thus has the same limitations as MCFC. Consequently, utilising a MCEC in a biomass gasification plant does not have in principle a scaling limit, although handling or stacking too many units is technically challenging and will at a certain number of units not be cost efficient. The exact number depends of course on the investment and operational costs for other process equipment in the plant, as well as costs for feedstock (biomass and electricity) and end product.

MCEC operation in MCFC mode

The possibility to operate the MCEC in a reverse MCFC mode [13] increases the usefulness of the overall system and improves the economic benefits. MCFC mode operation could be utilized when the electricity or Bio-SNG price is at a level where power production is more beneficial or the bio-SNG price is not competitive. The reversibility of the cell technology also ensures that the cell technology, and also the system as a whole, can be operated nearly continuously, since shutdowns and startup of the cell, including cooling and heating is costly and also stress the cell technology, reducing the lifetime. The durability of the cell in reversible operation, i.e., alternately operating as an MCEC and MCFC, has been investigated in the longterm laboratory experiments [13]. The electrochemical evidence from these tests show that the performance of the cell and electrodes improves after up to approximately 1000 h in operation. Reversible mode operation will certainly influence the systems technical process configuration, including processes for handling the output gas after the MCEC/MCFC when operating in MCFC mode. Most likely the most straightforward solution would be to combust this gas to produce heat utilised, for example, for district heating.

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The overall conclusion is that the results are positive, as the mass and energy balance shows that the production of bio-SNG can be boosted by up to 60%, integrating a MCEC, compared to the same biomass input as in a standalone operation of the GoBiGas plant. The conclusions from the conceptual study are as follows:

- The mass and energy balance shows that the production of bio-SNG can be boosted by up to 60% for scenarios assuming internal reforming of tars without the need of an additional carbon source, in other words for the same biomass input as in a standalone operation of the GoBiGas plant.
- The economic assessments further revealed the price ranges for biomass, SNG and renewable electricity that would allow for a wider margin in terms of the IO index for the process configurations considered, as compared to the standalone SNG plant. Under the assumed economic conditions, renewable electricity prices higher than 26 €/MWh would make the integration of a MCEC infeasible. Furthermore, the sensitivity analysis shows that for a renewable electricity price of 26 €/MWh, the biomass feedstock price and the natural gas market price need to be below 26 €/MWh and above 30 €/MWh, respectively, in order to receive a positive IO index for all of the scenarios.
- The production of oxygen is also of high value, directly as a product for sale or to be used internally by the gasification process in a direct gasifier when production of a syngas is desired. This implies a possibility of using direct gasifiers at smaller scales for syngas production, as supply of pure oxygen is a cost-limiting factor in this case. A direct gasifier is generally less complex compared to indirect systems, as exemplified when comparing single direct and dual indirect fluidised bed gasifiers.
- The introduction of a MCEC in the gas cleaning and conditioning process of a biomass gasification system provides process intensification with a potential integration of three process units into one.
- Based on today's size of commercial MCFC systems, using 3.7 MW size units, stacked to power plants up to 60 MW, and utilising natural gas, a similar scenario for applying the MCEC technology is foreseen.
- The possibility to operate the MCEC in a reverse MCFC mode is beneficial and increases the usefulness of the overall system, promoting continuous operation of the cell technology and thus optimising the economy in relation to the price of electricity or Bio-SNG.
- There are a number of technical issues related to a MCEC such as sulphur tolerance and tolerance towards other impurities, and extent of hydrocarbon steam reforming depending on process conditions that need to be addressed before the potential of a MCEC can be concluded.

5.2 RECOMMENDATIONS

The results presented in this work are positive when integrating a MCEC, and can be considered a pre-study for a more rigorous techno-economic evaluation of the conceptual process. An outline of

investigations needed for a more rigorous and comprehensive analysis is specified in Appendix 2. In summary, experimental investigations of the MCEC/MCFC fed with a relevant product gas is needed in order to determine the composition of the process streams, prior to and after the MCEC/MCFC. Once experimental investigations are conducted, the thermodynamic chemical equilibrium assumption may be justified, and the process economics can be performed in a more detailed manner. This will enable a thorough evaluation of different indicators such as net present value, internal rate of return, and the flexibility of switching between power-to-gas and gas-to-power of the proposed configuration.

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APPENDIX 1: CONFERENCE PAPER SUBMITTED TO ECOS 2017.

Integration of an electrolysis unit for producer gas conditioning in a bio-SNG plant

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Abstract:

Producer gas from biomass gasification contains impurities like tars, particles, alkali salts and sulfur/nitrogen compounds. As a result a number of process steps are required to condition the producer gas before utilization as a syngas and further upgrading to final chemicals and fuels. Here, we study the concept of using molten carbonate electrolysis cells (MCEC) both to clean and to condition the composition of a raw syngas stream, from biomass gasification, for further upgrading into SNG. A mathematical MCEC model is used to analyze the impact of operational parameters, such as current density, pressure and temperature, on the quality and amount of tailored syngas produced. Investment opportunity is evaluated as an economic indicator of the processes considered. Results indicate that the production of SNG can be boosted by approximately 50% without the need of an additional carbon source, i.e. for the same biomass input as in standalone operation of the GoBiGas plant.

Keywords:

SNG, process integration, electrolysis, techno-economics

1. Introduction

Biomass gasification is considered as a key technology to replace fossil fuels for transportation purposes as well as in the industrial sector. The upgrading of the producer gas or raw synthesis gas requires a high purity and precise composition to obtain optimal conversion rates. Hence, one of the challenges is cleaning and conditioning of the producer gas. Depending on reactor type and biomass feedstock, different impurities like particulates and tars are present in the producer gas, which need to be removed. The operational parameters (such as temperature and pressure) and the oxidizing agent (steam, air, enriched air or oxygen) of the gasification process have a strong influence on the gas composition and quality.

Concurrently, there is a growing consensus for increased integration of renewable energy sources such as solar and wind power in order to reduce the carbon intensity of the electricity sector. According to IEA [1], the share of renewables in the global electricity mix is projected to increase over the coming years (from 20% today to 65% in 2050, of which over 50% is intermittent in nature). However, power from solar and wind technologies is largely affected by the intermittency of availability of the resources, both in time and space. Moreover, renewables (such as wind, solar and hydro) are typically designed to produce electricity, which means that it can either displace fossil fuels usage in the electricity sector or it can power electrified transportation vehicles. This would limit the role of intermittent renewables in planning large scale decarbonization of energy supply systems, which emit CO₂ from a wide-range of sources outside of the power sector.

Electrolysis in the context of power-to-gas and power-to-liquid, e.g. [2–6], is increasingly being discussed as a technology that can enable greater share of intermittent renewable power into the energy supply system. These reports are focused on solid-oxide electrolysis cells (SOEC) technology, meaning that a pure feed stream of steam or mixture of steam and CO_2 is required. The concept is further expanded in this work, which instead considers molten carbonate electrolysis cells (MCEC) technology. The essential feature here is the potential ability of molten carbonate electrolyte to allow direct utilization of producer gas, including tar and H_2S , see e.g. [7,8].

The main objective of this work is to assess the techno-economic potential of integrating a MCEC in a dual fluidised bed gasification system for conditioning of the product gas and for boosting the production of bio-SNG by creating a link with intermittent renewable power, particularly during excess generation. As a reference case, a stand-alone bio-SNG production plant, without integrated MCEC is considered for comparison.

2. Process description

This study investigates a concept of using MCEC technology (described in section 2.2) to clean and to condition the composition of the producer gas stream from indirect biomass gasification, for further upgrading into bio-SNG. The investigation is based on a conceptual, steady-state model of a MCEC developed in MATLAB Simulink environment. The model focuses on the operational aspects of MCEC, while it assumes the actual operating conditions of the GoBiGas bio-SNG plant [9] for the rest of the subprocesses. Fig. 1 presents a schematic diagram of the integrated conceptual process. Accordingly, the upstream processes (i.e. gasification, particle filtration, RME scrubber for tar removal (in some scenarios)) as well as the downstream stream processes (i.e. syngas compression, methanation and bio-SNG drying) remain unaltered. The subprocesses of the actual bio-SNG plant that are altered are the water-gas shift reactor and carbon-dioxide scrubber, depicted in Fig. 1 in red outline. These processes are considered to be replaced with a MCEC, the sections in blue outline in Fig. 1. Moreover, the thermal capacity (i.e. biomass) input and the raw gas production of the GoBiGas plant (as described in section 2.1) is kept as is in the actual configuration.

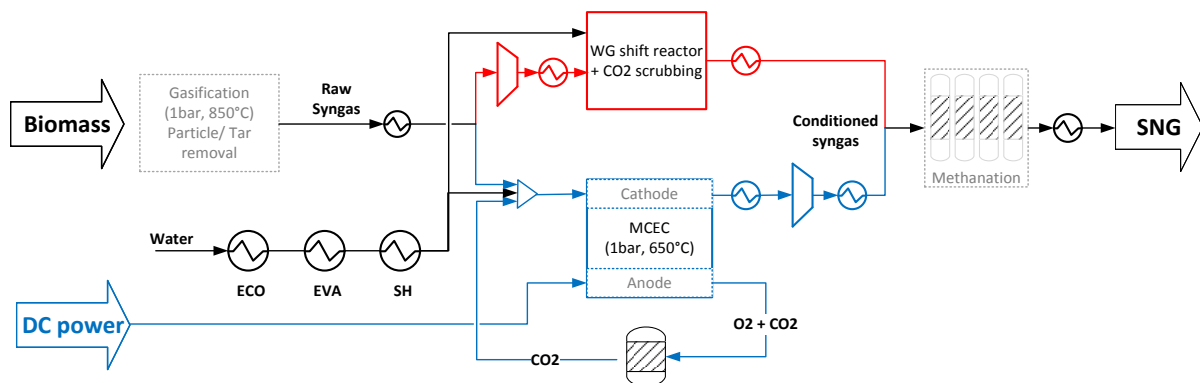


Fig. 1. Schematics of the actual GoBiGas configuration (dark and red outline) and with an integrated conceptual MCEC process (dark and blue outline).

2.1. GoBiGas plant

The GoBiGas plant is located in Gothenburg, Sweden, and has a production capacity of $20 \text{ MW}_{\text{SNG}}$. It converts wood-pellets (or forest residues) into bio-SNG using a Fast Internal Circulating Fluidised Bed Gasifier (FICFB) technology. The technology has a twin-bed, separate for gasification and combustion, resulting in high quality syngas free of nitrogen dilution except for the nitrogen in the biomass feed. The gasification reactor is steam-blown bubbling fluidized bed type, whereas the combustor, burning the residual char in order to generate the heat demand of the gasification process, is a circulating fluidized bed reactor.

The plant consumes 32 MW of biomass feedstock, 3 MW of electricity and 0.5 MW of RME (bio-oil recovered from the process) during normal operation and has a throughput of $20 \text{ MW}_{\text{SNG}}$. In addition to the 20 MW bio-gas the plant produces 5 MW of excess heat at a temperature high enough

to allow direct utilization for district heating (DH) and 6 MW of upgraded heat (via a heat pump) prior to being distributed as DH. The produced bio-SNG consists of more than 95% CH₄ and is distributed to consumers via the local natural gas grid.

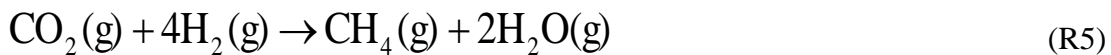
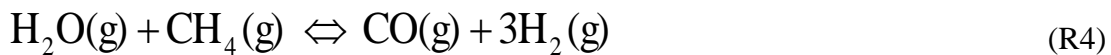
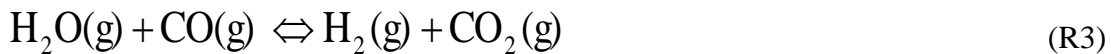
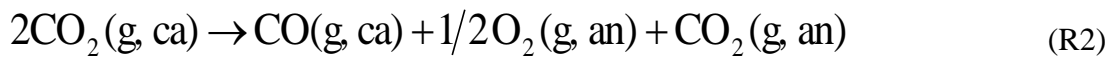
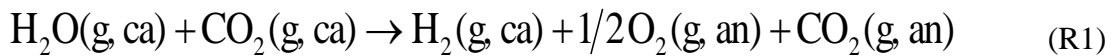
The producer gas composition from the gasifier, based on the raw gas composition from the GoBi-Gas plant before the reformer, is about (vol. %, dry) 42.1 H₂, 24.6 CO, 18.3 CO₂, 6.8 CH₄, 0.13 C₂H₂, 2 C₂H₄, 0.01 C₃H₆, and 4 N₂. In addition, about 20.5 g/Nm³ of tar and BTX (benzene, toluene and xylenes), 7.8 g/Nm³ excluding BTX, are produced.

2.2. Molten carbonate electrochemical unit

Experimental investigations have shown that high-temperature electrolysis of steam or co-electrolysis of steam and CO₂ in SOEC [6] or MCEC [7] benefits both thermodynamic and kinetic properties of the electrochemical process resulting in an improved overall conversion efficiency. In addition, a high temperature could also reduce the electric power requirement since part of the energy required for splitting the molecules is supplied as thermal energy. Besides, MCEC often use molten alkali metal carbonate salts as electrolyte, mandating operational temperatures in the range 600-800°C.

The operational benefits of high-temperature internal reforming molten carbonate fuel cells (MCFC) are well known [10]. Most notably, the heat needed for the endothermic steam reforming of methane or higher hydrocarbons is taken from the cell stack, reducing the need for external cooling. In addition, high-temperature operations diversify the feed spectrum a MCFC can utilize. For instance, the use of a bio-gas feed to produce conditioned syngas in a MCFC is demonstrated as promising low-carbon technology, see e.g. [11]. By reversing the direction of the electric current flow, MCFC can be operated in an electrolysis mode. Electrolysis mode will essentially reverse the direction of the chemical reactions compared to a fuel cell mode.

The major chemical reactions believed to take place inside the MCEC unit during co-electrolysis of steam and CO₂ are [7]:



The MCEC is modelled as an equilibrium electrochemical reactor that consumes power in order to deposit oxygen molecules onto the anode from a syngas feed stream that is rich in steam and CO₂.

It is evident from reaction (R1) that for every mole of oxygen transferred from the feed stream to the anode; two moles of CO₂ are consumed at the cathode side and transferred onto the anode side. In the MCEC, CO₂ should be present in the cell in order to produce carbonate ions, the ionic conductor in the electrolyte [7]. Direct reduction of CO₂ (via R2) may also take place generating CO, however the kinetics of this reaction is reported to be much slower than water electrolysis or co-electrolysis of steam and CO₂ [7,12]. As a result, the formation of CO is considered to proceed through reverse water gas shift reaction (WGS) (R3). In the model, the stoichiometry of R1 is set to control the balance of CO₂ used to generate the carbonate ion conductor. The fate of the remaining species at the cathode outlet (i.e. H₂O, H₂, CO, CO₂ and CH₄) is determined by assuming thermodynamic equilibrium. Thermodynamic equilibrium is assumed because the mechanism by which the oxygen and CO₂ transfer takes place is not well known. The model assumes steam-methane reforming (SMR) (R4) and WGS (R3) reactions in order to determine the composition of the cathode exhaust. The assumption of SMR is justified due to the fact that in the presence of methane in the feed stream, R4 may also proceed in forward direction.

Basically, what the model does is that it calculates the power required to remove oxygen from the syngas feed stream so that the equilibrium composition of the syngas after the MCEC meets certain condition. In this case, as the final product is SNG, the syngas prior to methanation needs to maintain a composition that meets the following criterion:

$$\frac{[\text{H}_2] - [\text{CO}_2]}{[\text{CO}] + [\text{CO}_2]} = 3.001$$

The exhaust from the anode is a mixture of O_2 and CO_2 in the ratio 1:2, respectively. This stream is assumed to undergo a purification process wherein the two species are separated. In order to improve the performance of the MCEC and to increase the yield of SNG, it is important that the CO_2 stream is recycled back to the unit after being mixed with the producer gas feed stream. In the model, about 75% of the CO_2 exhaust from the anode is considered to be recycled back to the MCEC.

Obviously, with about 75% of CO_2 recirculation, the syngas feed stream needs to be supplemented with steam in order to meet the pre-methanation composition criteria. In the model, an integrator controls the addition of steam to the feed stream. The integrator controller takes O_2 transfer rate as input signal. Chemical equilibrium is also assumed for the feed syngas stream pre-MCEC, including the CO_2 recirculation and the steam addition.

The power requirement of the MCEC is calculated based on the Faraday's law of electrolysis, i.e. the reactants consumption in an electrochemical cell is related to the electric current flowing through it according to the following expression:

$$n_r = \frac{I_F}{n_e \times F} \quad (1)$$

Where n_r is the amount of reactant flow effectively undertaking electrochemical reduction (mol/s), n_e is the number of electrons involved in the reaction ($n_e=2$, since both H_2O and CO_2 , which undergo electrochemical reduction, involve two electrons), F is the Faraday constant ($F= 96\,485\text{ C/mol}$ ($=\text{sA/mol}$)) and I_F is the faradic current (A).

The Nernst potential (also known as the reversible potential) is calculated based on the gas composition after the MCEC, the operating temperature and pressure according to the following expression:

$$V_N = \frac{-\Delta G_{f, \text{H}_2\text{O}}^{\circ}(T)}{2F} - \frac{RT}{2F} \ln \left[\left(\frac{y_{\text{H}_2\text{O}}}{y_{\text{H}_2} y_{\text{O}_2}^{1/2}} \right) \left(\frac{P}{P_{\text{std}}} \right)^{-1/2} \right] - \frac{RT}{2F} \ln \left(\frac{y_{\text{CO}_2, \text{an}}}{y_{\text{CO}_2, \text{ca}}} \right) \quad (2)$$

Where ΔG is Gibbs free energy, R is universal gas constant, y represents molar fraction of the respective gases at the exit of the MCEC and P is operational pressure of the unit.

The operational voltage, V_{op} , of an electrolysis cell is then calculated as the sum of the Nernst potential and the energy loss due to resistance of the electrolyte (also known as ohmic loss, R_o) and due to polarization resistance of the electrodes. R_o , depending on the internal resistance of the $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$ electrolyte and operating temperature, is calculated according to Eq. 3. A saturation value of $0.25\ \Omega\text{-cm}^2$ is set in the model so as to avoid over-estimation of the operating voltage [7,13]. For the sake of simplicity, polarization resistances are not considered here. Experimental investigations of MCEC with nickel electrodes have shown that polarization resistances are low for hydrogen-rich feed [14].

$$R_o = 9.84e - 3 * \exp \left[\frac{23800}{RT} \right] \quad (3)$$

$$V_{op} = V_N + i \times R_o \quad (4)$$

Where i is the current density (A/cm^2). In the model the current density is a variable parameter and it was assigned a value of $0.75\ \text{A/cm}^2$ for the main case.

Finally, the power required for the electrochemical reduction process is calculated as the product of operational voltage and faradic current. Table 1 summarizes the main parameters of the electrochemical unit at 650°C and 1 bar.

Table 1. Electrochemical and stack parameters.

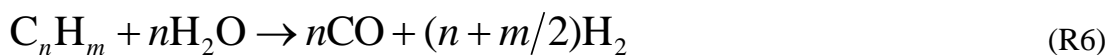
Parameter	MCEC	Unit
V_N	1.054	V
R_o	0.22 ^a	$\Omega\text{-cm}^2$
i	variable	A/cm ²
I_F	10020	kA

^aWith upper saturation value 0.25 (in case equation 3 results in R_o higher than 0.25 $\Omega\text{-cm}^2$)

3. Methodology

3.1. Process Integration

One of the potential advantages of integrating MCEC in a gasification system is the internal reforming of the tar, especially, when using Ni electrodes. In order to simplify the process modelling, all tar compounds with a molecular weight above 78 g/mol are assumed to be decomposed into CO and H₂ using steam (R6). All other hydrocarbons (C₂-C₅) are neglected from the analysis. Experimental data [15] indicate that the tar concentration primarily depends on the operating temperature. Ultimate analysis of tar, typically for a gasification temperature in the range of 700-815°C, contain about 78% carbon, 6% hydrogen, 0.7% nitrogen, 12% oxygen, less than 0.5% sulphur, and the rest being solids. Furthermore, the presence of H₂S in the product gas could lead to degradation in performance and shorten cell life, particularly under low-temperature and high current density operation mode [8]. Due to the lack of experimental data on MCEC operation under H₂S contaminated feed, the effect of H₂S is not considered in this study.



The bio-SNG process involves high-temperature processes (such as gasification and methanation) involving several exothermic reactions generating a number of hot streams. In this work, however, only the major thermal streams of the GoBiGas plant (such as syngas cooling after gasification, syngas cooling after compression, and SNG cooling) are reproduced by running the model with and without the integrated MCEC. The latter is done in order to establish a reference scenario for a fair comparison between the standalone and integrated scenarios. It should be noted that the thermal streams considered in the analysis are only the ones depicted by a heat exchanger symbol in Fig. 1.

Moreover, steam is required in the shift gas reactor (in the case of standalone operation) and in the MCEC (integrated operation). Since the SNG plant is operated at atmospheric pressure, the shift gas reactor and the MCEC are also operated at 1 bar. The steam demand of these units is assumed to be supplied at 2 bar (in order to avoid reverse flow) and superheated to the temperature at which both units are operated, 650°C. Consequently, it is considered important to assess the possibility of utilizing the thermal energy of the hot process streams to generate the process steam demand and, in case of surplus heat, to produce other energy services such as DH and electricity, bringing additional income to the plant.

In this case, a steam Rankine cycle can be suitably designed to exploit the heat pocket created by the hot process streams and to satisfy the steam requirement of the process via steam extraction from the steam turbine at the relevant temperature levels. Such configurations allow the use of superheated steam to co-generate electricity prior to its extraction.

With this in mind, the HEATSEP method [16,17] is applied to the flowsheets of the processes (including the SNG and the steam Rankine cycle) in order to assess the synergy among them. The HEATSEP method allows one to focus on the basic process units of a system configuration by replacing the potential heat transfer devices with the so-called “thermal cuts”. The thermal streams (hot and cold) across the cuts are then grouped into a “black box” where heat exchange interactions are

assumed to take place without predefined stream matches. A Problem Table Algorithm of Pinch Analysis is used to check the heat transfer feasibility within the “black box”.

The extracted process streams are presented in Table 2. The initial and final temperatures of these streams remain the same, however, the thermal loads differ since the mass flow rates of the conditioned syngas, SNG and process steam could vary depending on the process configuration. Due to the investigative nature of the study, this work explores different operating options of the MCEC and also considers different configurations for the steam turbine.

The description of the different process configurations is as outlined below:

Scenario I: represents the model run for standalone GoBiGas plant (without the integrated MCEC), in order to reproduce the actual plant operation.

Scenario II: represents the model run for integrated GoBiGas and MCEC with a DH option.

Scenario III: represents the model run for integrated GoBiGas and MCEC with a CT option.

Scenario IV: represents the model run for integrated GoBiGas and internal reforming MCEC with a DH option.

Scenario V: represents the model run for integrated GoBiGas and internal reforming MCEC with a CT option.

Table 2. Thermal streams (including the streams of steam consumed in the process).

T_i [°C]	T_f [°C]	$\Delta T_{\min}/2$ [°C]	Heat [kW]	Type	Stream description
Combustor					
850	850	10	216.642	Hot	Radiative segment of RME combustion (Scenarios I, II, and III)
850	150	10	283.358	Hot	Convective segment of RME combustion (Scenarios I, II, and III)
Gas line streams					
850	650	10	$m_{\text{syn}}C_p\Delta T$	Hot	Producer gas cooling after gasification
836	650	10	$m_{\text{syn}}C_p\Delta T$	Hot	After cooling of compressed raw syngas (Scenario I)
650	220	10	$m_{\text{syn}}C_p\Delta T$	Hot	Cooling of conditioned syngas pre-methanation (Scenario I)
650	450	10	$m_{\text{syn}}C_p\Delta T$	Hot	Conditioned syngas cooling Pre-compression (Scenarios II to V)
890.4	220	10	$m_{\text{syn}}C_p\Delta T$	Hot	After cooling of compressed syngas (Scenario II to V)
220	158.8	10	$m_{\text{SNG}}C_p\Delta T$	Hot	SNG sensible cooling before condensation of its moisture content
158.8	158.8	2	$m_{\text{con}}\Delta h_{\text{fg}}$	Hot	Condensation of water from SNG at T_{sat} (@p=6bar)
158.8	25	10	$m_{\text{SNG}}C_p\Delta T$	Hot	SNG sensible cooling after condensation of its moisture content
Process steam (st) to MCEC or shift reactor					
T_{sat}	T_{sat}	2	$m_{\text{st}}\Delta h_{\text{fg}}$	Cold	Evaporation of water at maximum cycle pressure (P_{max})
T_{sat}	T_{max}	2	$m_{\text{st}}\Delta h_{\text{SH}}$	Cold	Superheating of steam to maximum temperature (T_{max}) at P_{max}
352.8	T_{max}	2	$m_{\text{st}}\Delta h_{\text{RH}}$	Cold	Reheating of Steam to T_{max} at 30 bar
233.9	650	2	$m_{\text{st}}\Delta h_{\text{SH}}$	Cold	Superheating of steam at 2 bar to MCEC operating temperature
5	T_{sat}	5	$m_{\text{st}}\Delta h_{\text{FW}}$	Cold	Preheating of feed water at P_{max}

The thermal energy of the process hot streams and RME combustor (only in scenarios I through III) is the limiting constraint on the size of the heat pocket in the GCC representation of the Pinch Analysis thermal cascade. The steam cycle is designed to optimally exploit this heat pocket. The configuration of the steam cycle is as follows:

- steam generation at the maximum cycle pressure (P_{\max}),
- steam superheating to the maximum cycle temperature (T_{\max}) and reheating to the maximum cycle temperature at 30 bar,
- superheating of steam to the shift reactor or MCEC operating temperature levels (650°C) at 2 bar
- condensation of the steam that remains in the Rankine cycle at 2 bar (for scenarios with DH option) and 0.05 bar (for scenarios with CT option).

The design parameters of the steam Rankine cycle (steam mass flow rate that remains in the power cycle, maximum cycle pressure and temperature) are the decision variables of the optimization problem, which is run to maximize the power output of the combined cycle. In order to compensate the steam consumed in the process, an equivalent amount of water needs to be continuously supplied to the steam Rankine cycle, which here is assumed to be available at a temperature of 5°C and 1 bar.

3.2. Energy performance evaluation

The energy performance of the conceptual process is evaluated based on the model outputs according to the system boundary shown in Fig. 2. Moreover, the electric power required to drive the gasification and methanation processes is calculated by assuming a reported value of $0.037 \text{ MJ}_{\text{el}}/\text{MJ}_{\text{SNG}}$ [18].

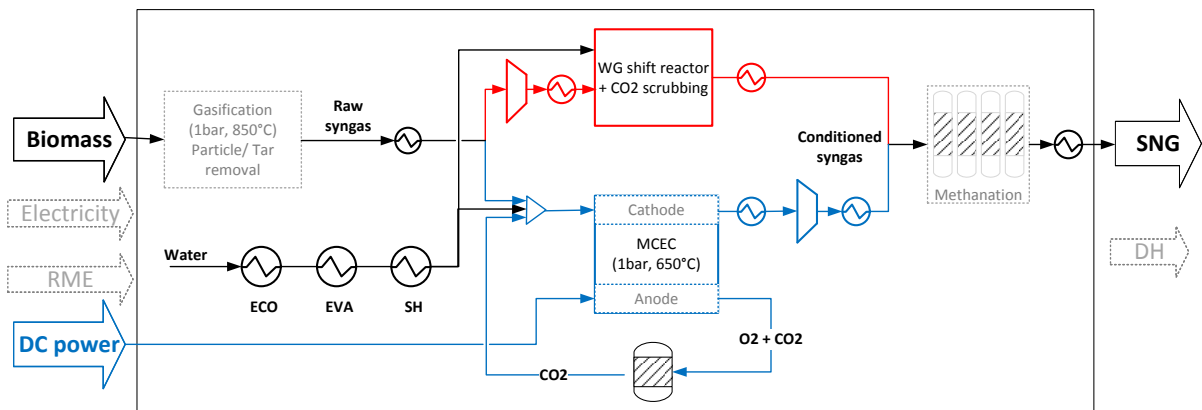


Fig. 2: System boundaries for energy performance analysis.

As performance indicators, two different efficiency terms are defined. The bio-SNG efficiency also termed as the cold gas efficiency, calculated as the ratio of the energy content of the produced bio-SNG (based on LHV) to the biomass energy input (based on LHV). The electricity efficiency, qualitatively measures the significance of the different energy streams in terms of their electricity equivalents, as summarize in Table 3.

Table 3. Power generation efficiencies used for calculating electricity equivalents [19]

Source	$\eta_{\text{el. source}} [\%]$
Biomass	46.2
Bio-SNG	57.6
RME	50
DH	15

$$\eta_{\text{SNG}} = \frac{\dot{m}_{\text{SNG}} \cdot \text{LHV}_{\text{SNG}}}{\dot{m}_{\text{BMF}} \cdot \text{LHV}_{\text{BMF}}} \quad (5)$$

$$\eta_{el,eq} = \frac{\dot{m}_{SNG} \cdot LHV_{SNG} \cdot \eta_{el,SNG} + DH \cdot \eta_{el,DH}}{\dot{m}_{BMF} \cdot LHV_{BMF} \cdot \eta_{el,BMF} + \dot{W}_{el,net} + RME \cdot \eta_{el,RME}} \quad (6)$$

3.3. Economic performance evaluation

The scenarios considered are evaluated from the economic point of view using Investment Opportunity (IO) as an indicator of the potential economic feasibility. IO is an economic index of a design solution based on the difference between the algebraic sum of resource cost and product revenue. The higher is the IO value the wider are the margins for investing more money in a design solution while the cash flow history of the project remains positive at the end of the economic lifetime.

$$IO = \sum \langle \text{Product revenue} \rangle - \sum \langle \text{Commodity cost} \rangle \quad (7)$$

Table 4. Economic parameters.

Parameter	Base value	Unit
Operational time ^a	8000	hours/year
Wood pellets	16	€/MWh
Natural gas price ^b	42	€/MWh
Grid electricity price ^b	59	€/MWh
DH price	26	€/MWh
Deionized water cost	1	€/ton
MCEC DC power input price ^c	Variable	€/MWh

^aDH is assumed to be operated for 5000 hours per year

^bSource Eurostat for the second half of 2015 (electricity €59/MWh and natural gas €42/MWh, both values represent for industry)

^cPower input to the MCEC is assumed to come from renewable resources (RE) such as wind or solar

4. Results

4.1. Process streams

The model is initially run at a temperature and pressure of 650°C and 1.031 bar. The resulting composition of the major streams depicted in Fig. 1 are presented in Tables 5 and 6, for the MCEC with and without internal reforming, respectively.

Table 5. Stream composition for MCEC with internal reforming at 650°C and 1.013 bar.

	GoBiGas + internal reforming	Additional feed + recycle	Pre MCEC	Post MCEC cathode	Post MCEC anode	SNG
Temp [K]	923.150	923.150	923.150	923.150	923.150	298.150
Pressure [bar]	1.013	1.013	1.013	1.013	1.013	6.000
Mole flow [mol/s]	150.130	61.604	220.699	145.576	80.524	42.451
O ₂ (vol. %)	0.000	0.000	0.000	0.000	0.333	0.000
N ₂	0.020	0.000	0.014	0.021	0.000	0.042
CO ₂	0.170	0.654	0.174	0.013	0.667	0.000
H ₂ O	0.190	0.346	0.330	0.087	0.000	0.000
CH ₄	0.035	0.000	0.003	0.079	0.000	0.957
H ₂	0.430	0.000	0.229	0.613	0.000	0.001
CO	0.155	0.000	0.250	0.187	0.000	0.000

Table 6. Stream composition for MCEC without internal reforming at 650°C and 1.013 bar.

	GoBiGas	Additional feed + recycle	Pre MCEC	Post MCEC cathode	Post MCEC anode	SNG
Temp [K]	923.150	923.150	923.150	923.150	923.150	298.150
Pressure [bar]	1.013	1.013	1.013	1.013	1.013	6.000
Mole flow [mol/s]	146.240	59.409	216.141	146.808	77.891	39.981
O ₂ (vol. %)	0.000	0.000	0.000	0.000	0.333	0.000
N ₂	0.030	0.000	0.020	0.030	0.000	0.044
CO ₂	0.180	0.656	0.178	0.015	0.667	0.000
H ₂ O	0.220	0.344	0.343	0.104	0.000	0.000
CH ₄	0.040	0.000	0.003	0.063	0.000	0.955
H ₂	0.400	0.000	0.220	0.606	0.000	0.001
CO	0.130	0.000	0.236	0.182	0.000	0.000

The results show that the reformation of tar and BTX in the MCEC consumes about 1 mol/s of additional steam (compared to the MCEC without internal reforming), resulting in an increased yield of SNG by about 2.5 mol/s.

In order to assess the impact of operating temperature and pressure, the model was run for different conditions. Fig. 3a presents the molar composition of the cathode exhaust as a function of the operating temperature. The solid-lines represent the MCEC without internal reforming (scenarios II and III) whereas the dashed-lines correspond to the composition results for the MCEC with internal reforming (scenarios IV and V). Accordingly, for both scenarios, with increasing operational temperature of the MCEC the H₂ and CO compositions in the syngas increase, while the steam and methane components are depleted. In Fig. 3a, it can be observed that tar and BTX reforming slightly increases the concentrations of CO and H₂ while it reduces that of steam.

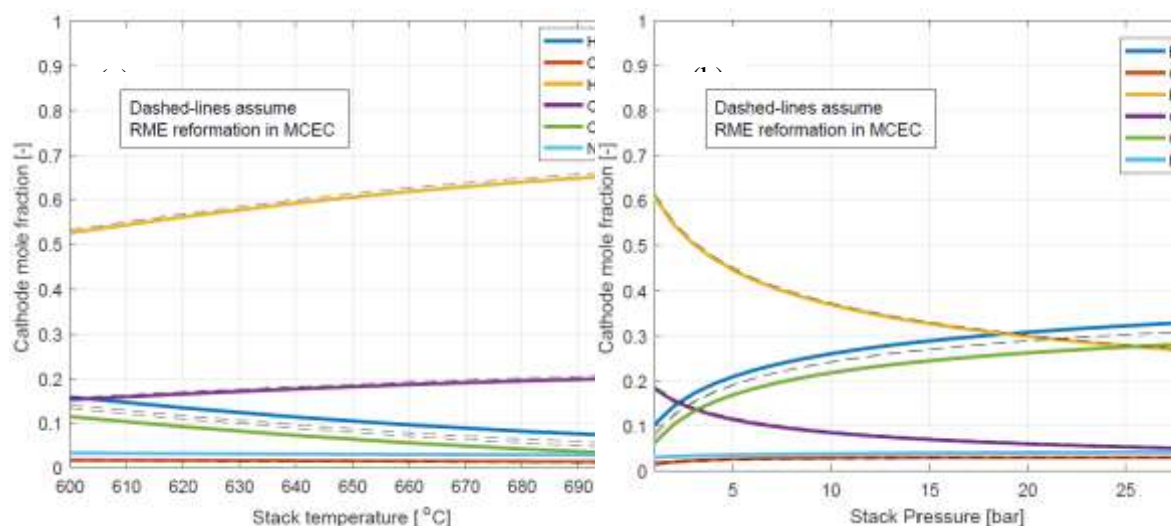


Fig. 3. Cathode outlet gas composition as function of: (a) MCEC operating temperature at 1.013 bar, (b) MCEC operating pressure at 650°C.

Fig. 3b shows that when the operating pressure is gradually raised from atmospheric up to 30 bar the SMR favours methane and steam formation consuming H₂ and CO, with methane concentration reaching above 27% vol. (scenarios II and III) and above 30% vol. (scenarios IV and V) of the cathode exhaust gas at 30 bar. Knowing that the desired final product is methane, its early formation in the MCEC could be advantageous. However, MCEC operational pressure is generally limited to below 8 bar to avoid initiation of accelerated electrode dissolution failure mechanism leading to premature degradation [20]. In Fig. 3b, the dashed-lines for steam (which reduces in concentration)

and methane (which increases in concentration) overlap almost for the entire pressure range considered. It seems that internal reforming of tar and BTX to CO and H₂ (R6) and formation of methane and steam through SMR (R4) occurs simultaneously.

4.2. Process Integration

The streams listed in section 3.1 generate the profile of the red curve in the so-called integrated grand composite curves (IGCC), Figs. 4 through 6. The steam Rankine cycle (blue curve) is designed to exploit the heat made available by the process streams (red curve) and co-generate electricity while providing process steam and heat demands. In this case, the CHP system provides the steam demand of the shift reactor or MCEC unit depending on the configuration.

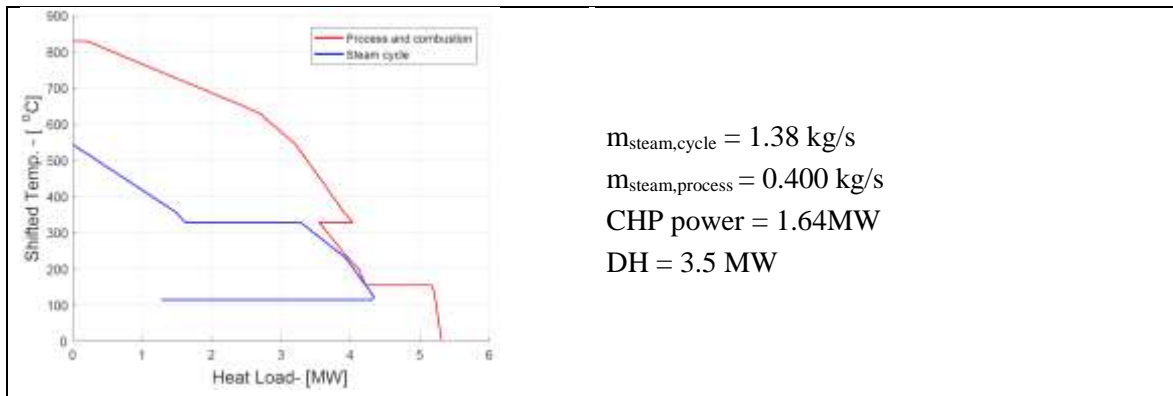


Fig. 4. IGCC for the reference scenario I.

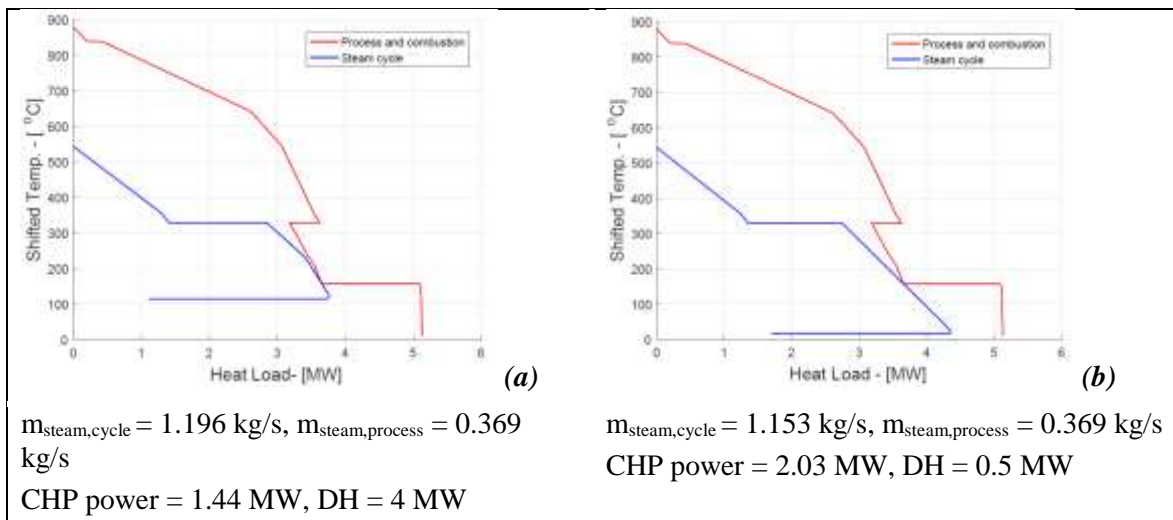


Fig. 5. IGCC for scenarios without internal reforming: (a) scenario II, (b) scenario III.

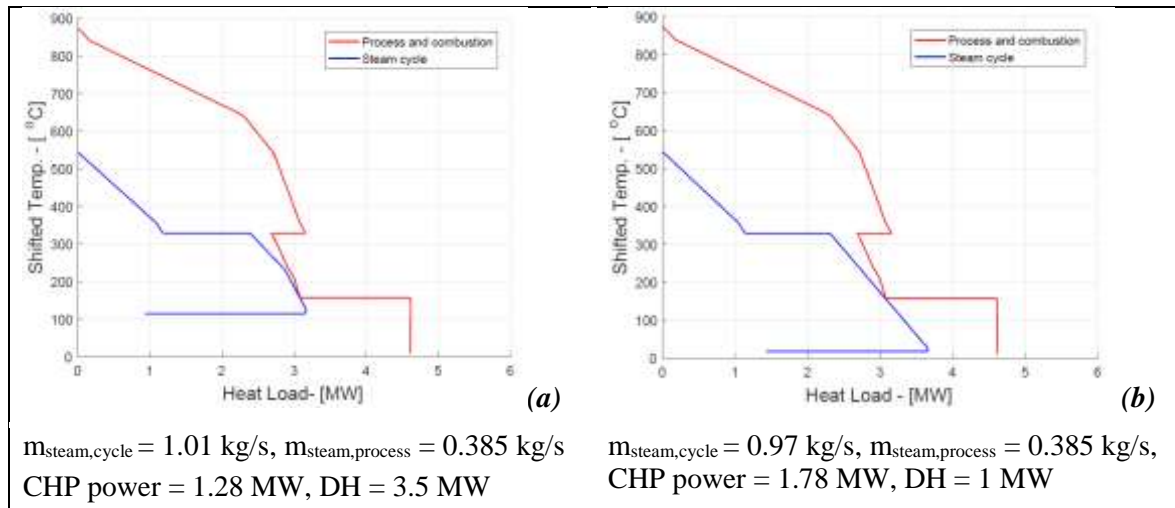


Fig. 6. IGCC for scenarios with internal reforming: (a) scenario IV, (b) scenario V.

The IGCC are graphical representations showing how well the steam Rankine cycle is exploiting the excess process heat. The optimal values of the decision variables and the different energy products are also presented with the respective IGCC of the scenarios, Figs. 4 to 6. The results of the thermal integration are used as a basis for the evaluation of the energy performance in the following section.

4.3. Energetic performance

The energy balance of the scenarios and the results of their corresponding performance indicators are summarized in Tables 7 and 8. Table 7 shows the energy inputs to the system where as Table 8 presents the outputs of the main product (bio-SNG) and other energy carriers.

As shown in Table 8, the integrated scenarios perform better in terms of bio-SNG efficiency as compared to the reference case (scenario I). It can be readily perceived that the exergy in the biomass that is retained in the final gas fuel significantly improves by the integration of the MCEC unit, by over 32 units (scenarios II and III) and by over 36 units (scenarios IV and V). In fact, SNG efficiency could be higher than 100% depending on the scenario (Table 8). SNG efficiency greater than 100% does not mean all the chemical energy in biomass is recovered, but it shows that significant part of the hydrogen used in the synthesis is derived from steam during electrolysis process. The underlying assumption for such comparison is that the electricity required to drive the MCEC unit is acquired from power generation units during periods when the produced electricity would have been necessarily wasted.

In terms of electricity equivalents (referring Table 8), scenario I resulted in higher electricity efficiency as compared to the integrated cases, by about 10 percent-units (scenarios II and III) and 7 percent-units (scenarios IV and V). This is an indication that the DC power required to drive the MCEC needs to be obtained inexpensively, for instance, from intermittent resources during periods of excess power generation.

Table 7: Energy input.

	Input (GWh/year)					
	GoBiGas actual [9]	Scenario I	Scenario II	Scenario III	Scenario IV	Scenario V
Wood pellets	256.000	256.000	256.000	256.000	256.000	256.000
RME (bio-oil)	4.000	4.000	4.000	4.000	0.000	0.000
Compressor power	NA	20.944	17.872	17.872	17.680	17.680
Gasification power	NA	5.920	5.920	5.920	5.920	5.920
Total el. input	24.000	26.864	23.792	23.792	23.600	23.600
DC power MCEC	0.000	0.000	99.520	99.520	103.520	103.520

Table 8: Energy output.

	Output (GWh/year)					
	GoBiGas actual [9]	Scenario I	Scenario II	Scenario III	Scenario IV	Scenario V
SNG	160.000	161.920	245.205	245.205	260.743	260.743
Net CHP power	0.000	13.120	11.520	16.272	10.240	14.240
District heating(DH)	25.000	17.500	20.000	2.500	17.500	5.000
El. Equivalency (%)	66.5	71.6	62.2	62.3	65.0	65.3
SNG efficiency (%)	62.5	63.3	95.8	95.8	101.9	101.9

Looking at the difference between the electricity input to the process (Table 7) and the net power output from the CHP system (Table 8), it becomes clear that all the scenarios require external electricity supply for internal operations. However, the magnitude of this external electricity demand differs depending on the process configuration. It is apparent from the the results that scenario III requires the lowest external power input (about 31% of the actual plant) followed by scenario V (about 39 % of the actual plant). It should be noted that both scenarios III and V employ condensing turbine, increasing their respective power outputs. Though, scenario III resulted in the highest net power generation because the scrubbed tar and BTX is utilized in a combustor boosting the amount of steam generation for the CHP system.

4.4. Economic performance

Fig. 7 presents the IO potential as function of MCEC power cost with and without incentive for DH. Accordingly, all the scenarios start to have positive IO index for MCEC power prices in the range 30 to 40 €/MWh (the lower end belonging to cases without internal reforming), Fig. 7a. The MCEC with internal reforming case coupled to the CHP system with DH option (scenario IV) resulted in the highest IO index, with only marginal difference compared to scenario V. The reason is that scenario IV has higher yield of both SNG and DH. However, in places where there is no incentive for DH, scenario V becomes most attractive option, Fig. 7b.

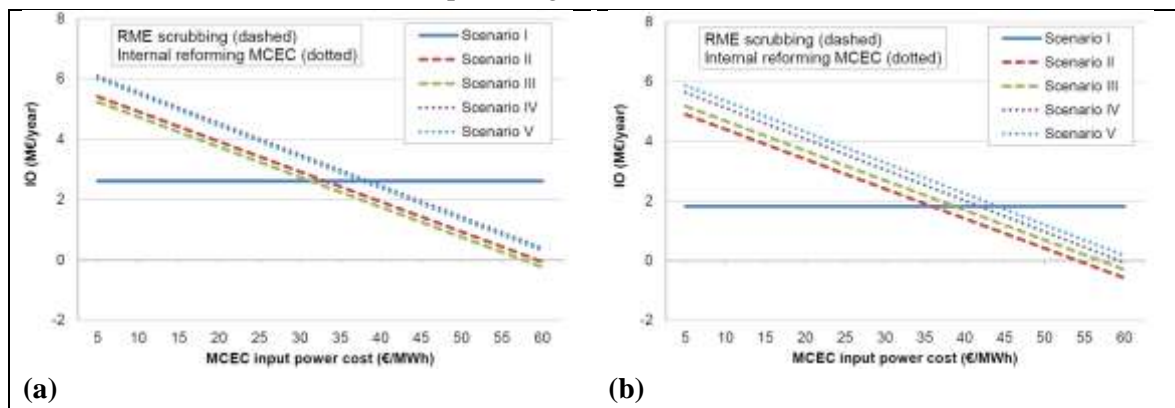


Fig. 7. IO as function renewable electricity price: (a) with, (b) without incentive for DH.

The IO indicates that the RE input to the MCEC needs to be acquired from low cost sources, e.g. from intermittent RE at times when the supply exceeds demand. When renewable intermittent power production, such as wind, solar and wave power, increases the need for electricity storage increases to be able to fully utilize the potential. This is no problem as long as the intermittent energy sources account for a minor share of the energy supply. However, when the intermittent power capacity is significantly increased, there will be times with a large surplus of electricity. MCEC could help to take advantage of this surplus and reduce the need for electricity storage. In so doing the targeted benefit is twofold. Firstly, MCEC adds flexibility to energy production and use by linking naturally with the synthesis of gaseous fuels and electrical energy forms. Secondly, the intermittency of RE and subsequently its storage issue can be addressed with appropriated SNG buffers.

4.4.1. Sensitivity analysis

In order to assess the response of the IO potential towards the most influential resource or product market values, a sensitivity analysis is carried out by varying the price of a selected commodity while the rest are held at their base value, as reported in Table 4.

The price of biomass feedstock has great impact on the economic viability of the integrated configurations. Fig. 8a shows wood pellets prices above 26 €/MWh would result in negative IO for the reference case (scenario I) and in a very marginal IO potential for the integrated scenarios for low price of MCEC power input. Raising the MCEC power price to electricity grid value would require biomass prices lower than 17 €/MWh to get positive IO, Fig. 8b.

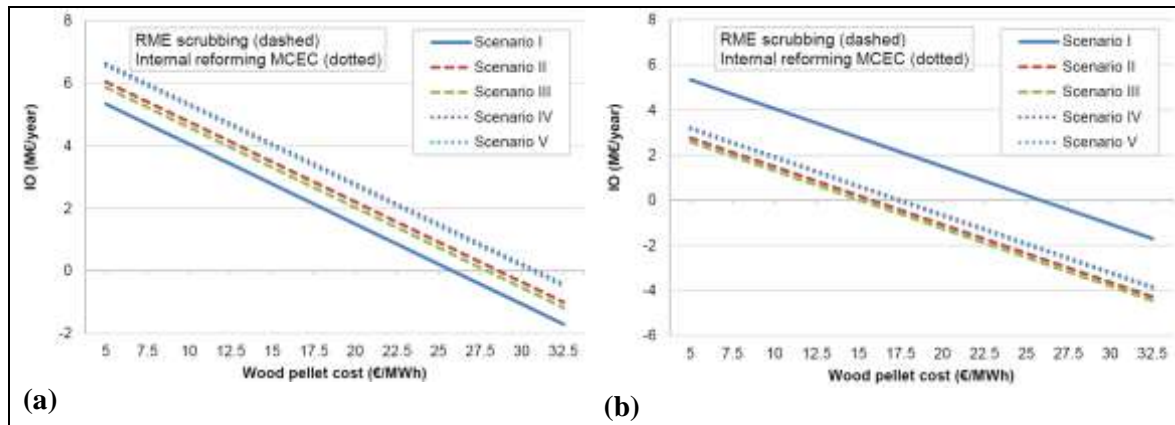


Fig. 8. Sensitivity of IO to biomass price for MCEC power prices of: (a) 26 €/MWh, (b) same as grid price.

Another important parameter is the market price of natural gas which the final product of the integrated process is expected to compute with. Hence, the sensitivity of IO towards natural gas price is investigated and the results are summarized in Fig. 9. According to Fig. 9a, the integrated cases result in wider IO margins compared to the reference scenario for natural gas market prices of at least 30 €/MWh (scenarios IV and V) and 35 €/MWh (scenarios II and III). If the MCEC input power price is same as grid, the integrated scenarios display lower IO margin in reference to scenario I for natural gas prices lower than 65 €/MWh (scenarios IV and V) and 73 €/MWh (scenarios II and III).

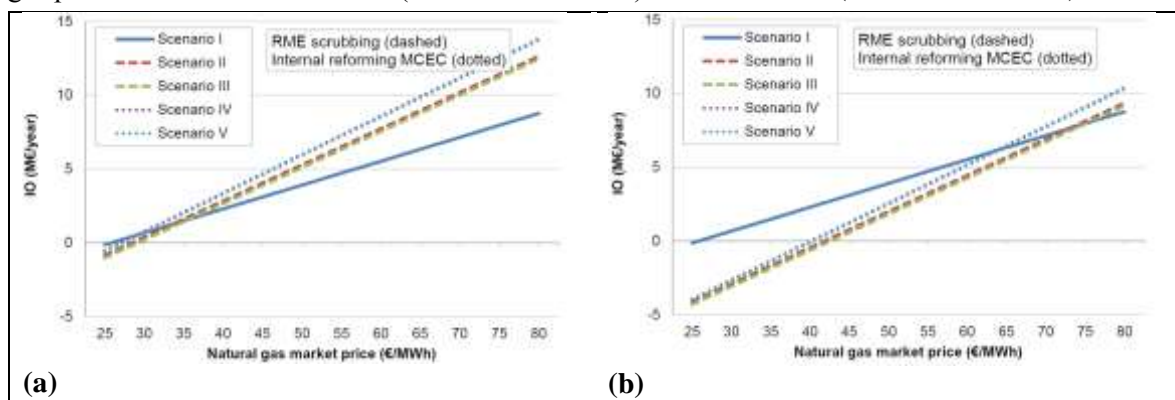


Fig. 9. Sensitivity of IO to natural gas market prices for MCEC power prices of: (a) 26 €/MWh, (b) same as grid price.

Generally, the MCEC cases without internal reforming (scenarios II and III) resulted in lower IO as compared to the cases with internal reforming (scenarios IV and V). These results indicate that, from a pure economic perspective, increasing the yield of SNG with tar and BTX reforming creates wider IO margins as opposed to scrubbing.

5. Concluding remark

The main conclusion of this study is that MCEC integrated with biomass gasification could boost the production of syngas provided that the electricity powering comes from low cost sources.

The mass and energy balance shows that the production of bio-SNG can be boosted by up to 60% (for scenarios assuming internal reforming of tars) without the need of an additional carbon source, i.e. for the same biomass input as in stand-alone operation of the GoBiGas plant.

The economic assessments further revealed the price ranges for biomass, SNG and RE electricity that would allow wider margin in terms of IO index for the process configurations considered, as compared to the standalone SNG plant. Under the assumed economic conditions, RE electricity prices higher than 26 €/MWh would make the integration MCEC infeasible. Moreover, the sensitivity analysis have shown that for RE price 26 €/MWh the biomass feedstock price needs to be below 26 €/MWh and that of natural gas market price above 30 €/MWh in order to get positive IO index for all the scenarios.

The results presented in this work can be considered as a pre-study for a more rigorous techno-economic evaluation of the conceptual process. Particularly, experimental investigations of the MCEC fed with syngas would be necessary in order to justify thermodynamic chemical equilibrium assumption when determining the composition of the process streams, prior as well as after the MCEC. Once experimental investigations are made, the process economics can be performed in a more detailed manner, for instance by considering different indicators such as net present value and internal rate of return, which would further elaborate the feasibility of such configurations.

Acknowledgments

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Nomenclature

CT	Condensing turbine
DH	District heating
GCC	Grand composite curve
IGCC	Integrated grand composite curve
IO	Investment opportunity
MCEC	Molten carbonate electrolysis cell
MCFC	Molten carbonate fuel cell
NG	Natural gas
RE	Renewable electricity
RME	Bio-oil (rapeseed-oil methyl ester scrubbing solvent)
SMR	Steam-methane reformation
SNG	Synthetic natural gas
SOEC	Solid oxide electrolysis cell
WGS	Water gas shift

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APPENDIX 2: RECOMMENDATIONS FOR FUTURE R&D STUDIES

There are a number of anticipated R&D activities to be addressed before utilising the molten carbonate electrochemical cell technology. The activities are briefly described in a proposed timeline below.

BASIC RESEARCH ACTIVITIES

Experimental investigations of the molten carbonate electrolysis cell (MCEC)

The following activities are foreseen:

- Effects of gas phase sulphur compounds on the performance of MCEC deactivation, using a model gas with and without hydrocarbons. Issue to be addressed is S tolerance at different mode of operation.
- Investigating internal reforming of different hydrocarbons in MCEC mode using a model gas.
 - Effects of heavier hydrocarbons: different amounts and types (toluene, naphthalene, methylnaphthalene, etc.).
 - Investigate the possibility of controlling the reforming/decomposition of light hydrocarbons such as methane.
- Investigate alternating between MCEC and molten carbonate fuel cell (MCFC) operational mode using a model gas, containing the main product gas compounds, as well as sulphur compounds and heavier hydrocarbons. Long-term exposure tests will be performed.

Process modelling of integrated MCEC and MCFC

The thermodynamic equilibrium model developed in the pre-study will be verified and refined using results obtained in the experimental investigations. The refined model will be used to investigate the effects of impurities and internal reforming of hydrocarbons. A detailed assessment of the opportunities to interact with the electrical system through the flexibility of switching between power-to-gas and gas-to-power will be performed.

APPLIED RESEARCH ACTIVITIES

After a positive outcome of the basic research activities, MCEC/MCFC technology will be applied in tests using real gas from biomass gasification. The tests will be planned based on results from the basic research activities.

This part also includes a detailed techno-economic feasibility study to establish the basis for a decision to move to demonstration activities.

DEMONSTRATION ACTIVITIES

Results from the applied research activities will be used for the engineering and development of a demonstration unit to be demonstrated in a biomass gasification plant.

