

Biomass Conversion to Methanol Integrating Solid Oxide Cells and Two-Stage Gasifier: Effects of Carbon Dioxide Recirculation and Pressurized Operation

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Synthesis of biofuels is an important step in the phase out of fossil fuels in the transportation sector, especially in long-distance sea, air and road transport where direct electrification seems unfeasible. Integration of renewable electricity enables efficient electricity storage as well as an increased utilization of the biomass carbon, which lowers the biomass demand. This paper presents a flexible system for the conversion of biomass and electricity to methanol. The system is based on the deep integration of a Two-Stage gasifier and solid oxide cells (SOC). The integration enables efficient production of a nitrogen-free high-quality syngas, suitable for methanol production. This study focuses on the system in electrolysis mode, and analyzes the effects of recirculating CO₂ from the gas conditioning and methanol synthesis process back to the SOC, as well as the effects of pressurized operation of the gasifier and increased H₂O content in the gasifier. Thermodynamic modeling shows that CO₂-recirculation allows an increase in conversion of the carbon in the biomass to methanol from 80 % up to 92 %, with an energy efficiency of 71 %. Only a slight pressurization seems feasible, as an increase in pressure beyond ~3 bar results in significant methane formation inside the SOC.

1. Introduction

The phase out of fossil fuels from the transportation sector requires several solutions in order to be cost efficient and technically feasible. Battery electric vehicles are an important part of the solution, especially for cars, but biofuels or electro-fuels are needed for long-distance transports, for example by ships, airplanes and trucks (Mathiesen et al., 2015). Gasification represents a pathway to convert biomass to a syngas suitable for production of biofuels, such as methanol (MeOH), dimethyl ether (DME) or synthetic natural gas (SNG) - all suitable for internal combustion engines. A way to limit the consumption of biomass for biofuels is to mix the biomass syngas with electrolytic H₂. This can approximately double the biofuel output per biomass input (Clausen, 2015). Among the different gasification technologies, the Two-Stage Gasifier developed at the Technical University of Denmark (DTU) has high cold gas efficiency and low tar content of the produced syngas, adopting only a bag-filter for gas cleaning (Gadsbøll et al., 2019). New concepts for the Two-Stage gasifier based on updraft fixed bed pyrolysis and fluid bed char gasification can be scaled to 50-100 MW (Gadsbøll et al., 2019), or even more if pressurized. The integration of Two-Stage gasification and solid oxide cells (SOC) has previously been studied, both for electricity production when operating as solid oxide fuel cells (SOFC) (Bang-Møller et al., 2011) or for biofuel production when operated as solid oxide electrolysis cells (SOEC) (Pozzo et al., 2015). One study has also considered both operating modes of the SOC in a polygeneration plant employing Two-Stage gasification and SOC, converting biomass to SNG (69 % efficiency) or electricity (46 % efficiency), depending on electricity prices (Sigurjonsson and Clausen, 2018). Instead of adding electrolytic hydrogen to the syngas, it is also possible to feed the SOEC directly with syngas, as suggested by (Pozzo et al., 2015). In this way, co-electrolysis is performed directly on the syngas, and it becomes much easier to change operation to SOFC mode, as the syngas flow does not need to be redirected. In this paper, the integration

between gasifier and SOC is increased further by placing the SOC between the pyrolysis reactor and the char gasification reactor of the Two-Stage gasifier. The novel configuration features the operation of the SOC as either SOFC or SOEC, creating a system able to produce a high quality syngas for biofuels production no matter the electricity price. Compared to the paper by (Pozzo et al., 2015), this system has simple oxygen handling, as the gasifier does not need oxygen. The fluid bed char reactor is instead electrically heated with heating elements in the bed. Furthermore, when using electric heating the size of the SOC is reduced. Internal reforming in the SOC of pre-reformed tars also increases efficiency in SOFC mode. This novel concept has been named the Two-Stage Electro-Gasifier. This paper focuses on the operation in SOEC mode, as this is the main mode of operation. The syngas is used for methanol synthesis. The system, shown schematically in Figure 1, is designed and analyzed by thermodynamic modelling in energy and exergy terms. A parametric analysis has the objective of investigating the effect of varying pressure and steam content in the gasifier. An increase in pressure could possibly push towards smaller components, whereas the increase in steam content in the gasifier improves the kinetics of the gasification reactions, making the reactor smaller. A number of cases are evaluated by changing these two parameters. Furthermore, the cases will show the impact of recirculating CO₂ from the acid gas removal (AGR) and the topping column in the methanol synthesis section back to the SOEC.

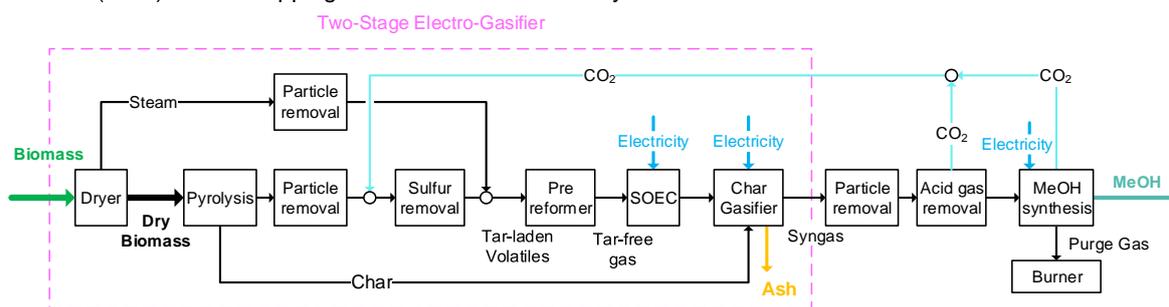


Figure 1: Schematic view of the plant for biomass conversion to methanol, when the SOC operates as SOEC. CO₂ recirculation, not adopted in the base case, is also shown.

2. Methods

The thermodynamic modeling is carried out using the software Dynamic Network Analysis (DNA) (Elmegeard, 1999) for the gasification section and AspenPlus from AspenTech® for the methanol synthesis plant, where PR-BM equations of states are used for the syngas processing and SR-POLAR equations of states are used for the methanol synthesis and distillation and for the recirculation (Clausen, 2015).

2.1 Plant description and modelling

Wet wood chips are dried using superheated steam in an updraft fixed bed. The generated steam is cleaned for particles and added to the gas downstream to provide the H₂O for both electrolysis and the gasification reactions. The dry biomass from the dryer undergoes pyrolysis and is cleaned for particles and sulfur before mixing with steam. To avoid tar condensation in the tar-laden volatiles exiting the pyrolysis, temperature is kept above 250 °C. Sulfur removal is important to preserve the lifetime of the pre-reformer and the SOEC, as both are very sensitive to sulfur poisoning. To effectively remove sulfur, present as H₂S, COS and sulfur-containing organic molecules, the combined effects of Zinc-oxide- and Copper-oxide-bed technologies can be applied (Haldor Topsøe, 2019). Furthermore, the pre-reformer will act as a secondary guard bed for the SOEC, lowering sulfur levels to sub ppm levels. Before sending the gas to the SOEC, the adiabatic pre-reformer converts tar compounds and higher hydrocarbons to methane, to prevent a fast decay of the SOEC lifetime. In the SOEC, the gas is reduced, and the methane in the gas is reformed to H₂ and CO. The gas then enters the electrically heated fluid bed char gasifier, where char is gasified by the steam and CO₂ content in the gas. After particle removal the syngas goes to acid gas removal (AGR) carried out by an amine wash. Dry CO₂-lean syngas is compressed and sent to the methanol synthesis loop. The methanol reactor is cooled with boiling water at ~255 °C. The produced steam condenses at around the same temperature releasing heat primarily to the steam superheater in the steam dryer section. Methanol and water are condensed from the methanol reactor product gas. Most of the residual gas is recirculated to the methanol reactor (97 %). The purged gas is burned to provide high temperature heat to other sections of the plant. The liquid stream is sent to distillation, consisting of a topping column for removal of absorbed gasses, and a distillation column at atmospheric pressure for separation of methanol and water. Table 1 shows all the process parameters used to model the system. The pyrolysis process has been modeled as a balanced reaction (neither exothermic or endothermic), and an "equivalent gas

composition” has been calculated based on this and a normal mass (H,C,O etc.) and energy balance. The SOEC has been modeled as described in (Butera et al., 2019).

2.2 Parametric analysis

Besides the modeling and analysis of a base case, a parametric analysis is performed to evaluate the effects on the system by 1) including CO₂ recirculation from the AGR and the topping column, 2) increasing the steam content at the outlet of the char gasifier (10-20 mol. %) and 3) increasing the pressure. The change in pressure is done indirectly by changing the maximum allowable methane content in the syngas. The methane content will be determined by the SOEC, as the nickel containing fuel electrode catalyzes methane synthesis (and reforming). An increase in methane content will therefore correspond to an increase in pressure. Grand Composite Curves are built for each case to assess whether an external heat source is needed.

Table 1: Process design parameters for the biomass to methanol conversion plant.

Component	Parameters		
Woody Biomass feed	Dry composition [wt %]: C 48.1, O 44.8, H 6.4, N 0.081, ash 0.619.		
Beech wood chips (Gadsbøll et al., 2019)	Biomass in [MW _{th,dry}]=100 $T_{biomass,in}$ [°C]=25	LHV [kJ/kg]=18280	$C_{p,dry\ biomass}$ [kJ/kg·K]=1.35
Steam Dryer	$T_{inlet,steam}$ [°C]=250 $T_{out,steam,high\ pressure}$ [°C]=170	$T_{out,steam,atm\ pressure}$ [°C]=120 Moisture out [wt %]=2	$T_{out,biomass}$ [°C]=240 $\Delta p_{steam\ dryer}$ [mbar]=30
Pyrolysis reactor (updraft fixed bed)	Char Composition [wt %]: C 90.7, O 4.5, H 2.1, N 0.2, ash 2.5.		
	$C_{p,char}$ [kJ/kg·K]=1.276 LHV [kJ/kg]=33130 $T_{out,char}$ [°C]=740	$m_{char}/m_{biomass,dry}$ [-]=0.25 $T_{in,recirculated\ volatiles}$ [°C]=750 $\Delta p_{pyrolysis}$ [mbar]=30	heat loss [MW]=1 $T_{out,volatiles}$ [°C]=250
Gas Cleaning	$\Delta p_{particle\ removal}$ [mbar]=5	$\Delta p_{sulfur\ removal}$ [mbar]=20	
Compressors, Blowers and Ejector	$\eta_{is,compressor}$ [-]=0.8 $\eta_{is,blower}$ [-]=0.4	$\eta_{is,turbine}$ [-]=0.85 $\eta_{el-mech}$ [-]=0.95;	$\eta_{is,compressor\ part-load}$ [-]=0.4 $\eta_{ejector}$ [-]=0.20*
Solid Oxide Cell	ASR _{cell} = 0.2** $T_{fuel\ gas,in}$ [°C]=750 $T_{air,out}$ [°C]=750 Chemical equilibrium at the fuel outlet.	i_{SOEC} [A/cm ²]=-1 $T_{fuel\ gas,out}$ [°C]=750 no heat loss	$x_{O_2,air,out}$ [mol. %] = 50 $T_{air,in}$ [°C]=700 Δp_{SOEC} [mbar]=30
Char Gasifier (fluid bed)	C conversion*** [-]=0.95 $T_{ash,out}$ [°C]=850 WGS at equilibrium at the outlet (CH ₄ inert).	heat loss [MW]=1 $T_{ash,out}$ [°C]=850	$T_{syngas,out}$ [°C]=850 $\Delta p_{gasifier}$ [mbar]=150
Methanol synthesis	Based on (Clausen, 2015).		
Acid Gas Removal	Heat [MJ/kg _{CO₂,removed}]=3.8 $X_{H_2O,syngas\ out}$ [mol. %] =0	$T_{heat\ for\ stripping\ column}$ [°C]=120 Δp_{AGR} [mbar]=50	$x_{CO_2,syngas\ out}$ [mol. %] =1.2
Heat exchangers	$\Delta T/2_{evap-cond}$ [°C]=2.5 $\Delta T/2_{MeOH\ reactor}$ [°C]=5 $\Delta p_{HE,int.\ pressure}$ [mbar]=100	$\Delta T/2_{gas}$ [°C]=25 $\Delta T/2_{steam\ heater}$ [°C]=5 $\Delta p_{HE,high\ pressure}$ [mbar]=800	$\Delta T/2_{syngas-H_2O-condensing}$ [°C]=5 $\Delta p_{HE,gasif.\ section}$ [mbar]=10
Burner	$x_{O_2,exhausts\ out}$ [mol. %] = 16	Δp_{burner} [mbar]=10	

*Value from (Wendel et al., 2016).

**Value from (Noponen et al., 2014). ASR = ASR_{cell} + ASR_{interconnects}. ASR_{interconnects} is deliberately increased to provide heat for the electrolysis and reforming reactions. The value of ASR_{interconnects} is an output of the model.

***Considering the combined process of pyrolysis and gasification.

3. Results and discussion

The full plant is shown in Figure 2 for the base case, where the gasification section operates at atmospheric pressure and the steam content at the outlet of the gasifier is set to 10 mol %. CO₂ recirculation is not used but shown in light grey to clarify how CO₂ recirculation is incorporated in the other cases.

The exergy analysis performed on the base case, drawn in Figure 3, shows an exergy efficiency of 74.5 %. The analysis shows that the least efficient process from an exergetic point of view is heat transfer (10.2 %, ~11 MW). The temperature difference between fluids is the major responsible for this phenomenon and its reduction could improve the exergy efficiency. Nevertheless, larger-area and more expensive heat exchangers would be required. Table 2 includes the inputs and results from all the cases studied. At 1 and 2 mol. % CH₄ content at the outlet of the SOEC, the pressure in the gasification section increases from atmospheric conditions to 2-6 bar. Furthermore, at constant CH₄ molar fraction (cases B or C), it is seen that an increase in H₂O content results

in an increase in gasifier pressure, as higher steam content inhibits CH_4 formation. An increase in pressure from atmospheric up to 6.3 bar (case C.3), results in approx. 6 times smaller components for the gasification section, which becomes attractive when pushing towards large-scale plants of 100 MW_{th} or more of dry biomass input. The pressure increase also reduces compressor cost and power, from 14 MW_{el} (case A.3) to 7 MW_{el} (case C.3). The CO_2 -recirculation only slightly increases efficiency (70.0 % to 70.6 %) but instead increases overall carbon conversion to methanol from 79.7 % to 92.2 %. Efficiency is reduced when increasing the methane content above 1 %, as inert methane builds up in the methanol synthesis loop, leading to a higher purge gas loss.

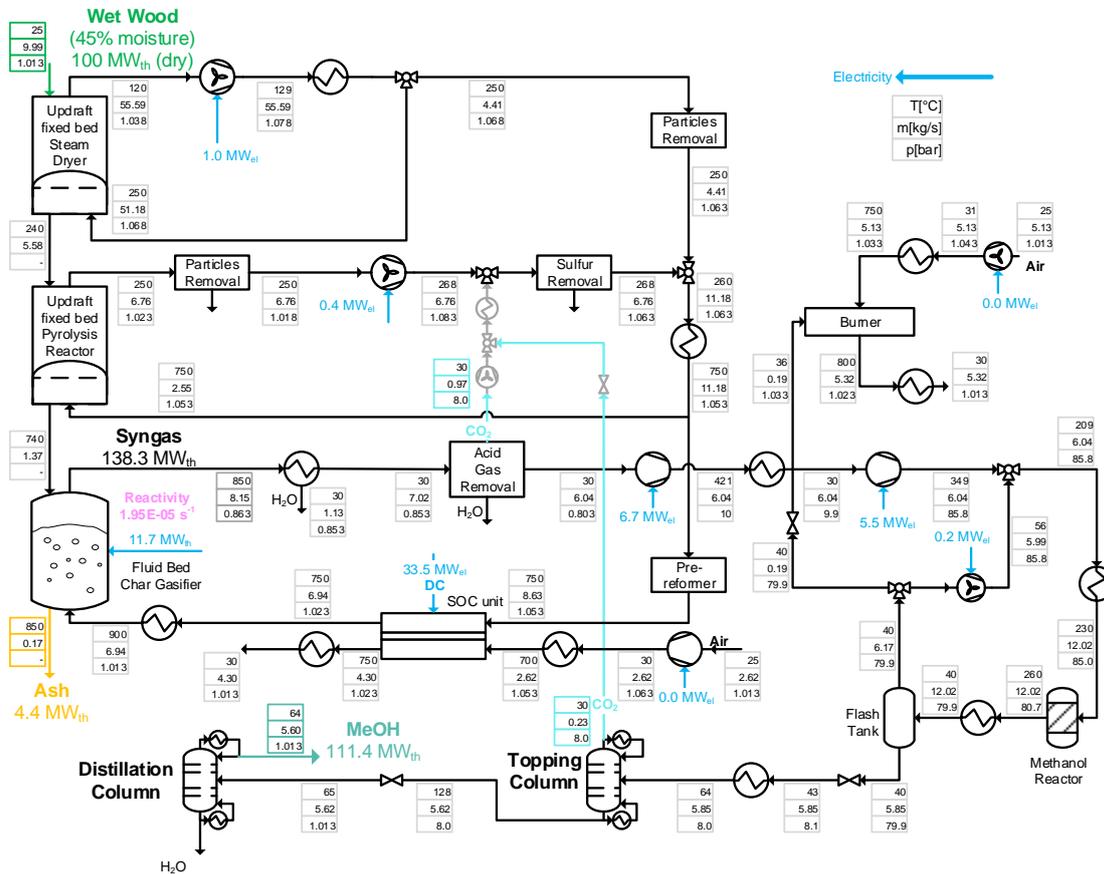


Figure 2: Full plant for the conversion of woody biomass to methanol. Data refers to the base case. (note: components in grey are not used in the base case). Note: the reactivity in the char gasifier is calculated by the method explained in (Gøbel, 1999).

A high H_2O content (20 %) also has a negative impact on efficiency, as there is not enough waste heat to cover the needed heat for steam drying, AGR and the distillation column reboiler. This can also be seen on the Grand Composite Curve for case B.3 (Figure 4). Here a maximum external heat source of 7.97 MW is needed to satisfy the thermal energy demand of the process. The need for an external heat source is detrimental for the efficiency of the system, as the heat is assumed to be provided by electric heating. A solution is to use a heat pump to cover the distillation column heat demand by using excess low temperature heat from the plant. This could considerably decrease the demand for external heat. When AGR heat is supplied through electric heating, the use of a high temperature heat pump to cover the AGR heat demand would improve the energy efficiency of the process even further. Table 2 also reports the char gasifier reactivity evaluated at the outlet of the gasifier. By changing the steam content from 10 mol. % to 20 mol. % the reactivity increases by ~140 %, indicating the potential size reduction of the fluid bed char gasifier. The specific size of the methanol reactor is indirectly shown by the ratio between the molar flow rate of gas at the inlet of the methanol reactor divided by the molar flow rate of product methanol. Adding CO_2 recirculation does not change this ratio, as the increase in gas flow to the methanol reactor is compensated by an increase in methanol production. When increasing the CH_4 content to 1-2 %, the reactor size is increased by 66 % (case C.3), as the methane builds up in the methanol synthesis loop.

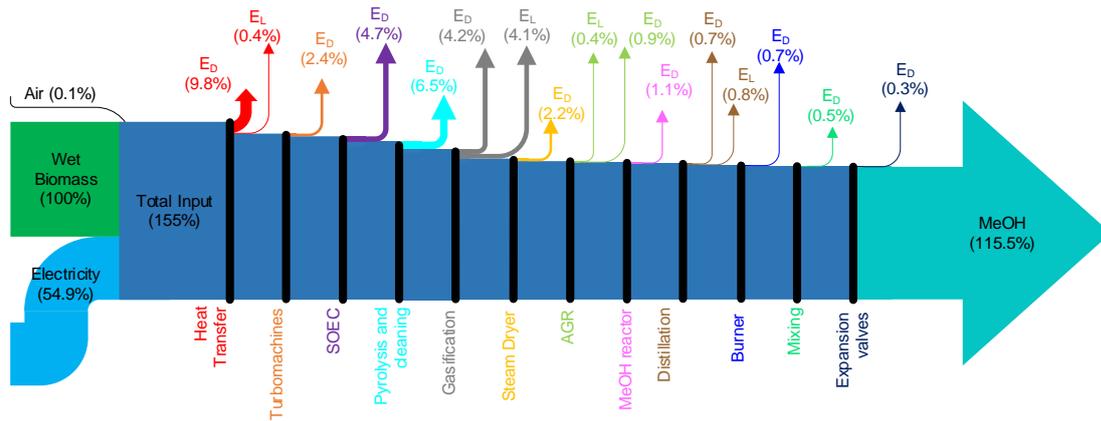


Figure 3: Exergy analysis for the base case. Reference temperature T_0 and pressure p_0 are set respectively to 25 °C and 1.013 bar. Reference environment for the chemical exergy is the Model II, Appendix C from (Bejan et al. 1999). ED and EL stand for exergy destruction and exergy loss in each process.

Table 2: inputs and relevant outputs of the analyzed cases. Note that pressure is an input at atmospheric pressure when the methane content is not set, but pressure is an output when the methane content is set.

Case	Base	A.1	A.2	A.3	B.1	B.2	B.3	C.1	C.2	C.3
Inputs										
XCH ₄ ,SOEC-outlet [mol. %]	-	-	-	-	1	1	1	2	2	2
XH ₂ O,gasifier-outlet [mol. %]	10	10	15	20	10	15	20	10	15	20
CO ₂ recycle	No	Yes								
pSOEC-outlet [bar]	1.02	1.02	1.02	1.02	2.27	3.08	4.18	3.38	4.60	6.28
Outputs										
Syngas compressors [MW _{el}]	12.1	14.0	14.0	14.0	10.4	9.3	8.4	8.9	8.0	7.1
Total power demand [MW _{el}]	58.8	81.9	82.0	87.8	77.7	77.0	83.1	75.6	74.7	76.9
Methanol output [MW _{th}]	111.4	128.4	128.7	128.9	125.1	124.7	124.1	120.9	119.9	118.8
AGR heat demand [MW _{th}]	2.0	2.3	7.8	12.1	2.2	7.7	11.9	4.1	7.5	11.6
External heat source [MW _{th}]	0.0	0.0	0.0	5.7	0.0	0.3	8.0	0.0	0.0	3.0
Efficiency [%]	69.8	70.5	70.6	68.5	70.4	70.4	67.7	68.7	68.6	67.2
Carbon Conversion to methanol [%]	79.7	91.8	92.1	92.2	89.5	89.2	88.7	86.4	85.8	85.0
Char gasifier reactivity (outlet) · 10 ⁵ [s ⁻¹]	1.95	1.95	3.17	4.62	1.98	3.24	4.76	2.01	3.29	4.82
Eq biomass moisture content [wt. %]	45.3	50.9	54.4	57.9	50.8	54.2	57.7	50.6	53.9	57.4
MeOH reactor size [kmol _{gas} / kmol _{MeOH}]	5.78	5.88	5.74	5.67	7.11	7.27	7.51	8.76	9.13	9.58

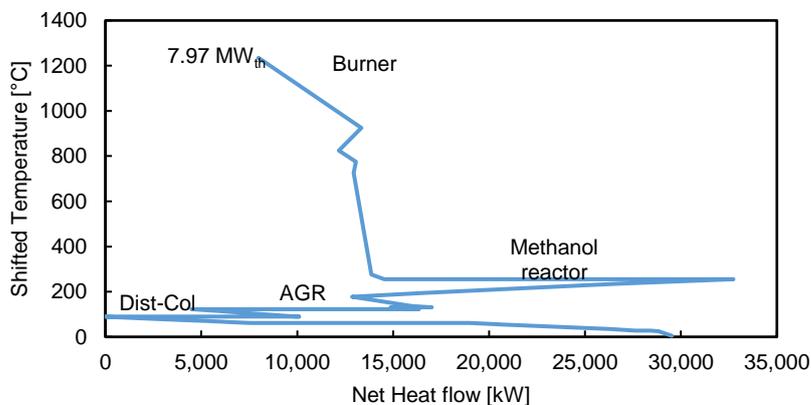


Figure 4: Grand Composite Curve for the case B.3.

4. Conclusion

A novel system integrating a Two-Stage gasifier and solid oxide cells for the conversion of biomass and electricity to methanol has been proposed and analyzed by thermodynamic modelling. The effects of CO₂ recirculation, pressurization and H₂O content in the gasification have been evaluated. In general, the analysis showed that the system overall benefits from CO₂ recirculation, as carbon conversion increases from 80 % up to 92 %, while plant efficiency is stable. The increase in pressure of the Two-Stage Electro-Gasifier decreases component sizes as well as compressor power and cost. Increasing the pressure beyond ~3 bar results in decreased carbon conversion and efficiency and increased size of the MeOH reactor, as methane is formed in the SOEC. Further analysis is needed to assess whether an increase in pressure is beneficial for the economy of the system. Increasing steam content in the char gasifier increases the reactivity, allowing it to be downsized, but when the steam content is increased beyond 15 mol. % the plant efficiency decreases. The decrease in efficiency can almost be offset by integrating a heat pump. Further experimental campaign will also investigate SOC running on pyrolysis gas, to test the SOC operation without use of the pre-reformer.

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