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From Residual Steel gases to Methanol: The FReSMe project

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Abstract

With several carbon capture and storage (CCS) pilot and demonstration units deployed worldwide, the complementary approach of carbon dioxide use to increase the unitization of fossil carbon is being suggested. Conversion of CO₂ can lead to useful product. Methanol is a high volume platform chemical of universal use in chemical industry as well as applicable for fueling internal combustion engines. FReSMe project will demonstrate the production of Methanol (MeOH) using as feedstock CO₂ from Blast Furnace Gas (BFG). This paper presents the process modelling of the FReSMe concept and compares it with a standard methanol synthesis plant with Natural Gas as feedstock. The production of methanol based on the concept proposed in the FReSMe project requires higher energy, but lead to a reduction of about 1036 kg_{CO2}/t_{MeOH}.

Keywords: CCUS; CO₂ utilization; Methanol; SEWGS; Blast furnace gases, CO₂ footprint

1. Introduction

With several carbon capture and storage (CCS) pilot and demonstration units deployed worldwide (the largest one being the Boundary Dam Integrated Carbon Capture and Storage Project [1]), the complementary approach of carbon dioxide use to increase the unitization of fossil carbon is being suggested. In these terms, the current most pressing challenge consist of:

- (i) the utilization of the captured CO₂ (CCU) as a feedstock for the process industry on one hand,
- (ii) the production of high-volume value-added products as a commodity chemical, with a reduced carbon footprint

Chemical conversions of CO₂ can be performed at moderately high temperatures and pressures by taking advantage of knowledge already known in the (petro)-chemical industry. A central challenge here can be found in the utilization of low-cost low-carbon electricity that will be intermittently available for the production of hydrogen.

Methanol is a high volume platform chemical of universal use in chemical industry as well as applicable for fueling internal combustion engines. As such, it provides a promising pathway for the large scale re-use of CO₂ to decarbonize the transportation and chemical sectors in Europe and decrease the dependence on fossil fuel imports. Production of

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methanol from CO₂ offers the unique combination of scale, efficiency and economic value necessary to achieve large-scale carbon reduction targets. Currently, a first demonstration plant is being operated by CRI in Iceland using CO₂ originating from geothermal sources [2], and a pilot is being constructed in Germany on the basis of CO₂ coming from a coal fired power plant in MefCO2 project [3].

In this context, the FReSMe project will demonstrate the production of Methanol (MeOH) using as CO₂ from blast furnace gases (BFG) in the iron and steel industry. The sector is responsible for 7% of world CO₂ emissions. BFG consist of ~50% N₂ and equal parts of CO and CO₂ with further minor amounts of H₂. The energetic content is commonly used for local heat and power production, but can also be converted into a highly versatile fuel and chemical, increasing the utilization the fossil fuel which is necessarily used in this sector.

Methanol is a high volume platform chemical of universal use in chemical industry as well as applicable for fueling internal combustion engines. As such it provides a promising pathway for the large scale re-use of CO₂ to decarbonize the transportation and chemical sectors in Europe and decrease the dependence on fossil fuel imports. Production of methanol from CO₂ offers the unique combination of scale, efficiency and economic value necessary to achieve large-scale carbon reduction targets.

In this paper, we will present the process modelling of the FReSMe concept and compares it with a standard methanol synthesis plant with Natural Gas as feedstock.

2. FReSMe Project

FReSMe project [4] will demonstrate the production of Methanol (MeOH) using as feedstock CO₂ from Blast Furnace Gas (BFG) at TRL6 under industrially relevant process conditions and using all the relevant sequential process steps simultaneously. This will be achieved by a consortium consisting of the whole value chain from technology developer and provider, material manufacturers, through engineering to end users. Additionally, the flexible concept will allow supplemental MeOH production with H₂ derived from an electrolyser and provides a route to commercialization for both near-term and future-term implementations that can scale with the increasing availability of low carbon H₂.

FReSMe joins facilities and expertise from two existing pilot sites which are co-funded by the Horizon 2020 program; BFG upgrading equipment available from the STEPWISE project; and MeOH Synthesis equipment available from the MefCO2 project. Today's integrated steel mill is normally a net electricity exporter; by coupling these two highly efficient systems together, the excess energy that is normally only for power production, can be used for the production of a highly versatile fuel and chemical, increasing the utilization of the CO₂ and the fossil fuel from which it is necessarily derived.

The pilot testing of FReSMe will be implemented at one of the world's few facilities that is specifically designed to supply up to 2500 m³/hr BFG from an integrated iron and steel mill to an experimental hall capable of housing large pilot installations, to produce in excess of 50 kg methanol per hour, an appropriate scale for TRL6. Existing processes will be optimized towards the most effective MeOH production process at the lowest cost and smallest energy penalty for the steel industry.

The FReSMe concept takes advantage of the Sorption Enhanced Water Gas Shift (SEWGS) [5] technology for converting the CO with steam into CO₂ and H₂ and simultaneously separating the CO₂ from the hydrogen in the steel off-gases.

Methanol is produced in a highly-flexible unit designed (i) for testing in an operation environment subject to variation due to the availability of fuel to variation due to the availability of feedstock and changes in feedstock composition and (ii) for producing 1 ton/day methanol at fuel grade standard suitable for use in end-user demonstration.

Because of the high CO₂ to H₂ ratio in the steel-plant off gases, additional H₂ produced from an electrolyzer will be used. In an alternative implementation the excess CO₂ can be sequestered. The concept is depicted in Fig. 1.

Nomenclature

CCS	Carbon Capture and storage
CCUS	Carbon Capture Utilization and storage
BFG	Blast Furnace Gases
MeOH	Methanol
SEWGS	Sorption Enhanced Water Gas Shift

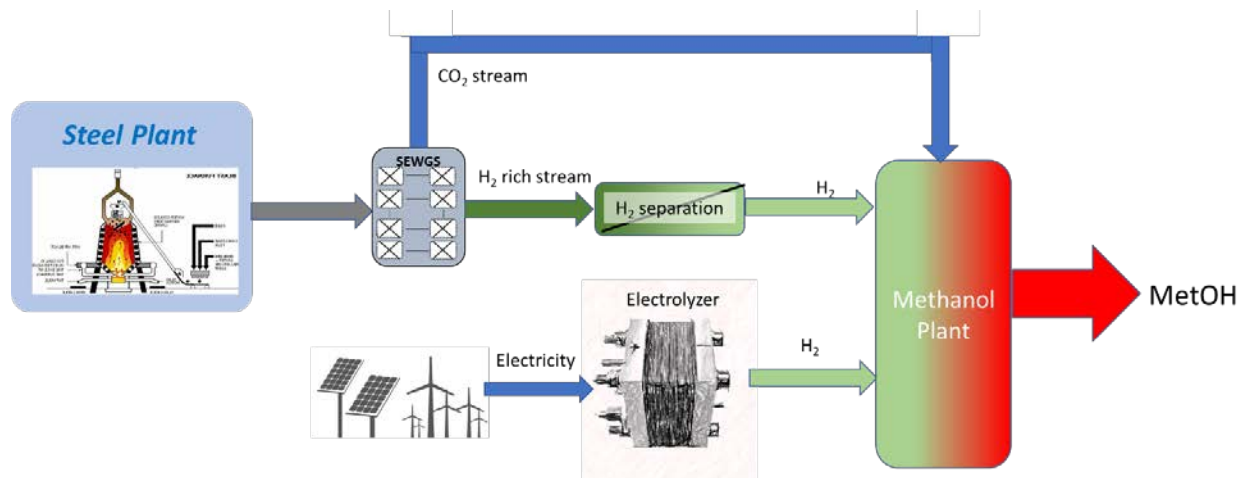


Fig. 1 FReSMe concept

3. Processes Simulations

The plants are simulated with the software Aspen Plus. For the standard synthesis of MeOH three main steps are considered: (i) gas pre-treatments, (ii) natural gas reforming, (iii) methanol production and purification. Energy and mass balances are calculated and detailed. These steps are represented in Fig. 2.

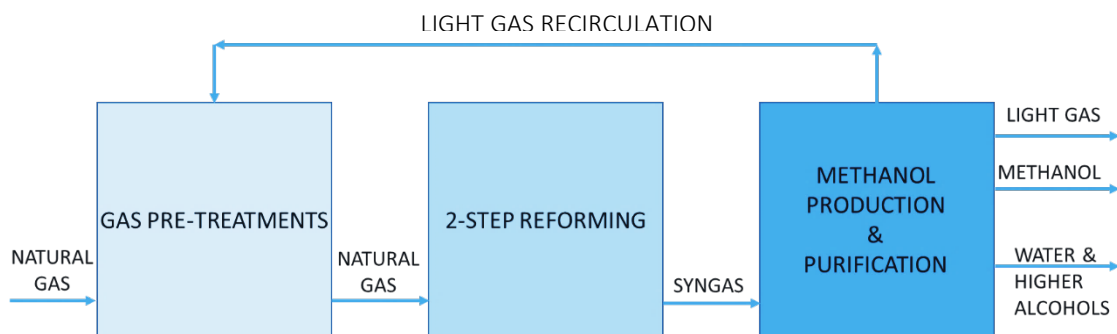


Fig. 2 Flowsheet of methanol production from natural gas

For the synthesis with the gas coming from the SEWGS the main steps are two: (i) gas pre-treatments, (ii) methanol production and purification. The gas pre-treatments are not the same.

The first and second sections represented in Figure 2 are simulated with the Peng-Robinson equation of state, while the third with the NRTL-RK (Non-Random-Two-Liquid/Redlich-Kwong) thermodynamic model.

3.1. Methanol production with natural gas

The gas pre-treatment section is shown in Fig. 3. Natural gas is fed to the plant and is split into two streams. A small fraction is burnt in a combustion chamber and the flue gas is cooled down to 700°C. Part of the heat is exchanged with the natural gas that is compressed.

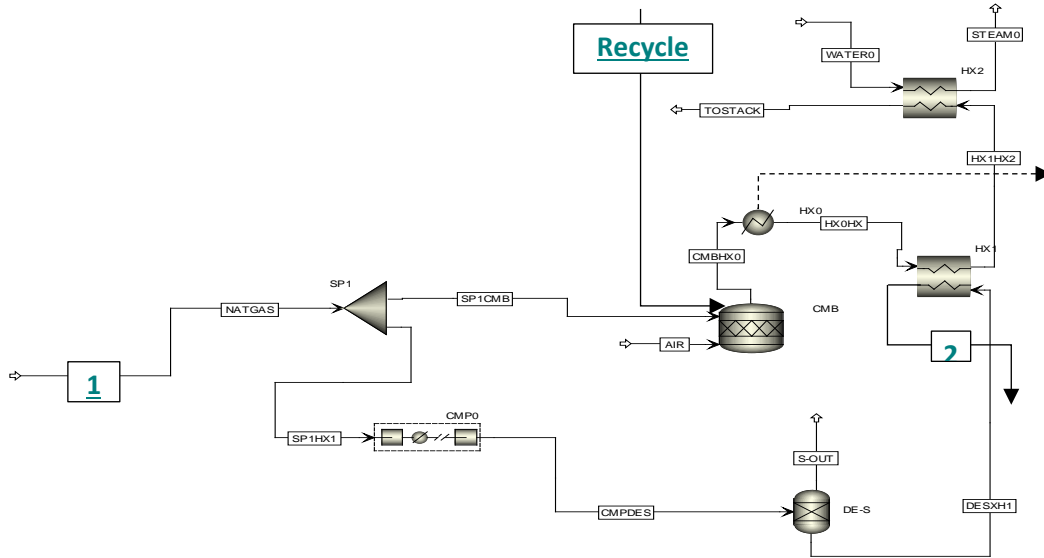
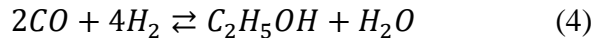
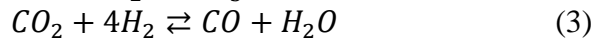
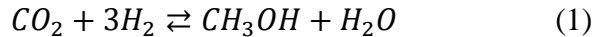


Fig. 3 Gas pre-treatment step for methanol production with natural gas. Stream "1" indicates the natural gas fed to the plant; stream "2" indicates the compressed natural gas fed to the pre-reformer.

The compressed gas enters into a pre-reformer where steam is added in order to obtain a steam to carbon ratio equal to 1.8. The pre-reformer works at temperature of 485°C and 30 bar. The pre-reformed gas enters in the first and second reformer: the first one has an equilibrium temperature of 694°C while the second reaches the temperature of 972°C due to the introduction of O₂ at 95% that allows partial oxidation of the reactants and final methane conversion to hydrogen at high temperature. The reformed syngas is then cooled recovering heat at a useful temperature. The syngas is then compressed to be delivered to the methanol reactor. This step is shown in Fig. 4.

The methanol reactor converts hydrogen and carbon oxides to methanol. The reactor is a catalytic packed-bed type cooled (methanol reaction is exothermic) generating steam used for the reforming reaction. The reactor is simulated by specifying the reactions involved in the methanol reactor; they are reported in equation (1)-(4):



The main impurities of the MeOH are the gases dissolved in the liquid phase and the by-products such as higher alcohols and especially ethanol [6]. The products at the reactor outlet are flashed to separate the light gases from the liquid (raw methanol). The light gases are mainly recycled to the methanol reactor, while a small fraction is sent to a membrane separator that routes the H₂ to the methanol reactor and the remaining part to the combustion chamber. The raw methanol is processed in a first distillation column designed to separate the residual light gases from the liquid phase. The second column purifies the methanol at Grade AA, which is obtained from the top of the column. The first and second columns' pressure at the bottom is respectively around 2 bar and 1.5 bar. The second column is the one

with the highest heat duty, because of the high reflux ratio. Key operating parameters are given in Tab. 1 and main stream compositions in Tab. 2. Tab. 5 summarizes the overall CO₂ and energy performance for methanol production.

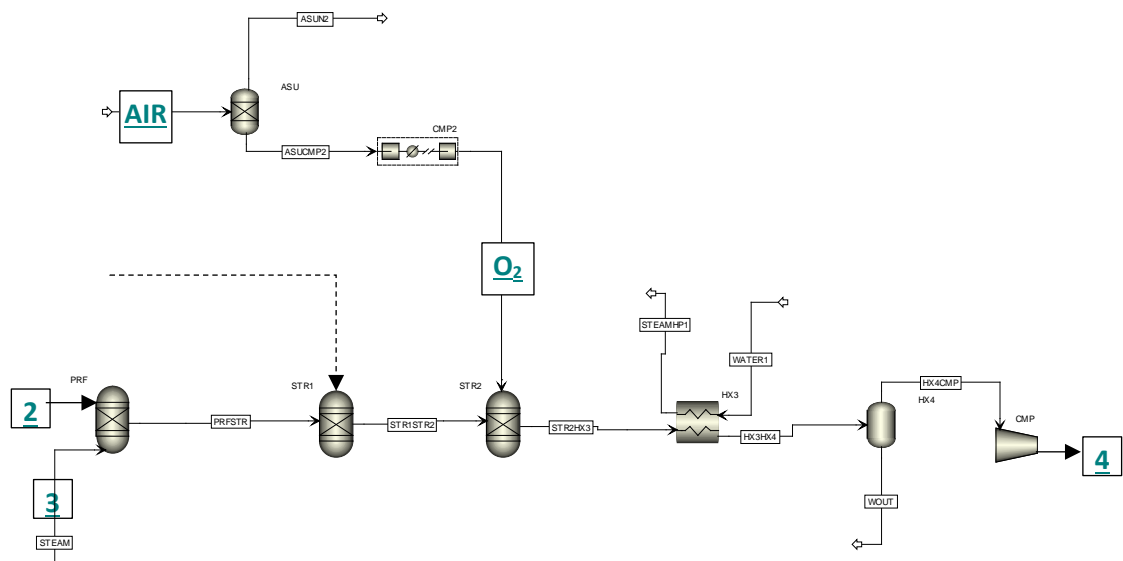


Fig. 4 2-steps reforming step. Stream “2” indicates the compressed natural gas; stream “3” indicates the steam fed to the plant; stream “4” indicates the compressed syngas fed to the methanol reactor.

Tab. 1 Key operating parameters of methanol plant

S/C at reformed inlet	1.8
Process steam consumption	1.09 t _{H2O} /t _{CH3OH}
Overall Natural Gas consumption	0.65 t _{NG} / t _{CH3OH}
$\frac{H_2-CO_2}{CO+CO_2}$ at methanol reactor inlet	3.59
Availability	98%
Nominal capacity for standard plant	2500 t/d CH ₃ OH

Tab. 2 Thermodynamic conditions, flowrates and compositions of the main streams shown in Fig. 3, Fig. 4, Fig. 5. *includes NG to distillation, not shown in Fig. 5

point	T	p	m	Molar composition (%)												
				CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂	CO ₂	CO	CH ₃ OH	C ₂ H ₅ OH	H ₂ O	H ₂	N ₂	
1*	20.0	1.00	18.87	83.9	9.2	3.3	1.2	0.2	1.8	0	0	0	0	0	0	0.4
2	716.1	30.00	15.87	83.9	9.2	3.3	1.2	0.2	1.8	0	0	0	0	0	0	0.4
3	450.0	50.00	31.72	0	0	0	0	0	0	0	0	0	100	0	0	0
4	51.3	80.00	80.25	32.8	0	0	0	0	6.9	0.8	0.9	0	0.1	55.3	3.1	0
5	50.0	79.00	35.15	1	0	0	0	0	1.5	0	75.1	0.2	22	0.2	0	0
6	50.0	79.00	81.06	32.8	0	0	0	0	6.9	0.8	0.9	0	0.1	55.3	3.1	0
7	30.4	1.30	1.01	36.2	0	0	0	0	42.3	0.2	13.1	0	0.7	6	1.5	0
8	77.9	1.57	29.09	0	0	0	0	0	0.3	0	76.9	0.2	22.6	0	0	0

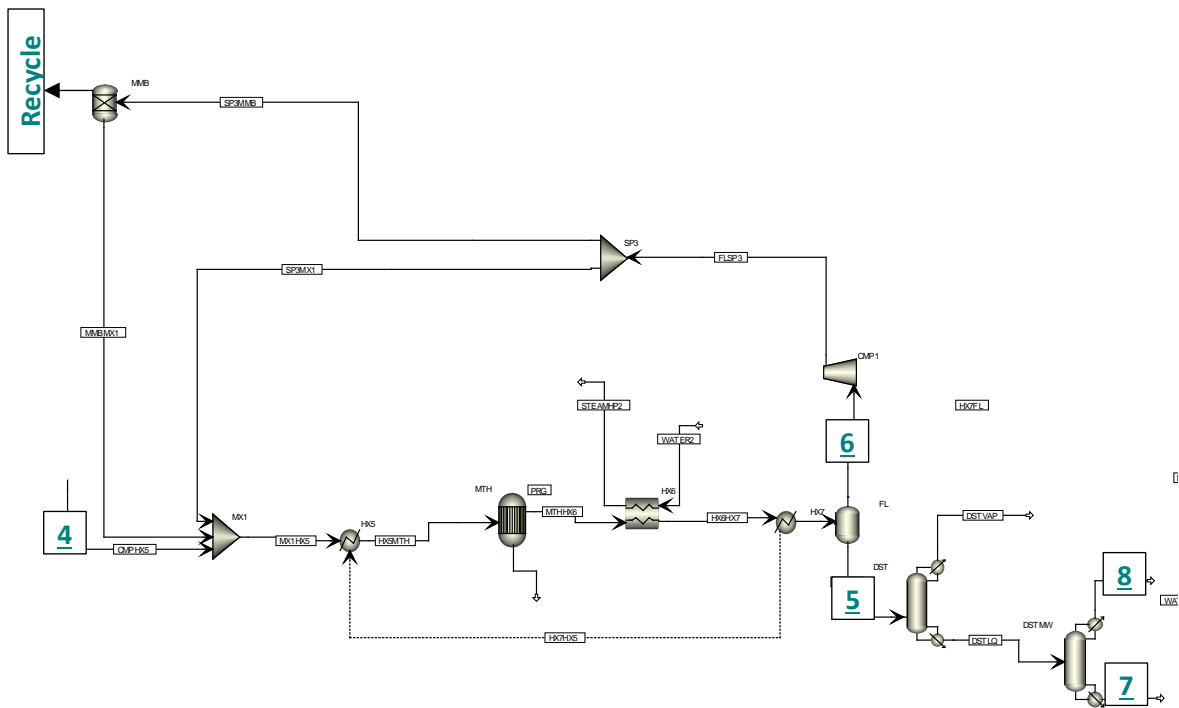


Fig. 5 methanol production and purification step. Stream “4” indicates the compressed syngas; stream “5” indicates the raw methanol production; stream “6” indicates the light gases separated from the raw methanol production; stream “7” indicates the high-boiling component of the raw methanol; stream “8” indicates the grade AA methanol production.

3.2. Methanol production with SEWGS gases

The FReSMe plant accounts for the reaction of the CO_2 and H_2 separated from the BFG, by means of SEWGS technology [5], additional H_2 is obtained by the adoption of an electrolyzer. SEWGS, which stands for Sorption Enhanced Water Gas Shift reactor, works at high pressure (20÷30 bar) and combines the shift reaction with the CO_2 adsorption. The sorbent regeneration is performed by reducing the reactor pressure to low pressure. After the SEWGS two main streams are sent to the plant for the methanol production. One is rich in H_2 and the other is rich in CO_2 . The detailed compositions are reported in reported in Tab. 3.

In this work, the amount of the gases available from the blast furnace of the steel plant are the one considered in the STEPWISE Project. Their composition is obtained by applying the SEWGS technology.

Tab. 3 Composition of the gases fed to the plant for the production of methanol

name	T (°C)	P (bar)	M (kg/s)	CO , %	CO_2 , %	H_2 , %	H_2O , %	N_2 , %
H_2 -rich	430	24	89.9	2.2	3.95	33.68	4.64	55.53
CO_2 -rich	411.2	1.2	152.8	0	48.26	0	50.57	1.17

The scheme of plant for methanol production with the gases coming from the steel plant is shown in Fig. 6.

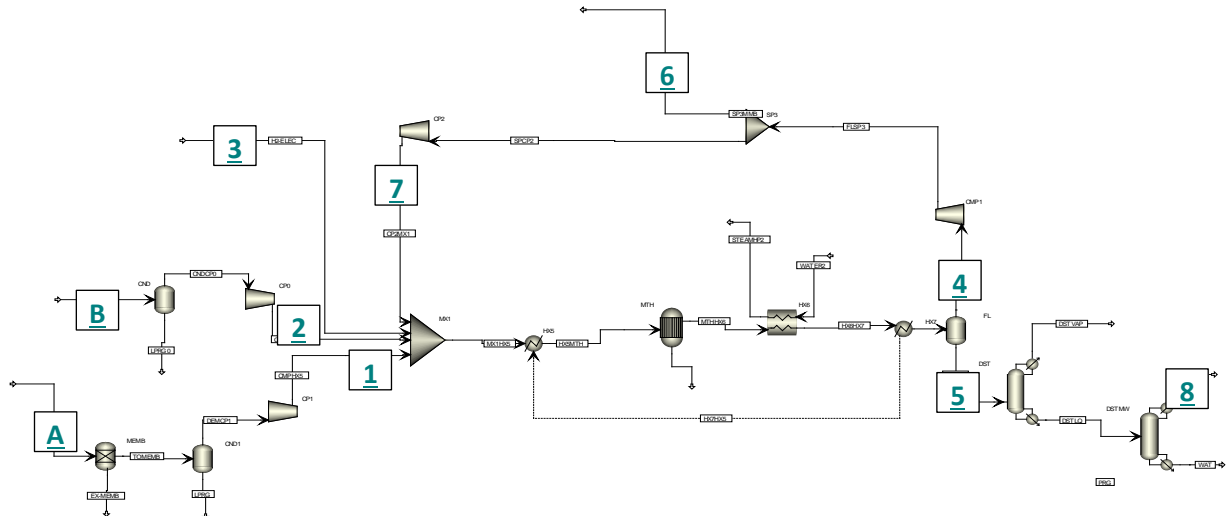


Fig. 6 Scheme of plant for methanol production with gas from SEWGS. Stream “A” indicates the stream H₂-rich fed to the plant, while the “B” indicates the CO₂-rich. The stream “1” indicates the stream rich in H₂ that is sent the methanol reactor; the stream “2” indicates the stream rich in CO₂ that is sent to the methanol reactor. The stream “3” indicates the H₂ added with an electrolyzer; stream “4” indicates the light gases separated from the raw methanol production; stream “5” indicates the raw methanol production; stream “6” indicates the vented light gases; stream “7” indicates the high-boiling component of the raw methanol; stream “8” indicates the grade AA methanol production.

The stream H₂-rich is fed to the methanol plant and passes through a membrane to increase the H₂ concentration by separating the N₂ that is purged (the high nitrogen content comes from the BFG). The concentrated H₂ is cooled and a liquid purge is separated before to compress the purified stream. In parallel, the stream CO₂-rich is cooled to eliminate the water before the stream compression. The BFG has a very high carbon content with respect to the hydrogen meaning that the amount of H₂ coming from the SEWGS is less than stoichiometric with respect to Eq. (1). To reach the stoichiometric value, there are two options: the first one consists of supplying additional H₂ produced with an electrolyzer, while in the second case, not considered in this work, part of the CO₂ is captured and stored. The main rationale behind this concept is the utilization of green electricity produced from renewable sources- The energy consumption due to the adoption of the electrolyzer is evaluated to be equal to 5 kWh/Nm³ [7]. All these feeding streams are mixed in the methanol reactor. After the mixer, the scheme of plant is the same as the case fed with the natural gas. The main streams composition and thermodynamic conditions are reported in Tab. 4.

Tab. 4 Thermodynamic conditions, flowrates and compositions of the main streams shown in Fig. 6.

point	T °C	p bar	m kg/s	Molar composition											
				CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂	CO ₂	CO	CH ₃ OH	C ₂ H ₅ OH	H ₂ O	H ₂	N ₂
1	207.9	80.0	14.2	0	0	0	0	0	9.9	5.5	0	0	0.5	84.2	0
2	537.3	80.0	152.8	0	0	0	0	0	97.6	0	0	0	0	0	2.4
3	50.0	80.0	18.6	0	0	0	0	0	0	0	0	0	0	100	0
4	50.0	79.0	764.2	0	0	0	0	0	17.9	5	0.6	0	0.1	69.6	6.8
5	50.0	79.0	170.4	0	0	0	0	0	1.4	0	49.5	0.1	49.1	0.1	0
6	50.0	79.0	15.3	0	0	0	0	0	17.9	5	0.6	0	0.1	69.6	6.8
7	51.4	80.0	748.9	0	0	0	0	0	17.9	5	0.6	0	0.1	69.6	6.8
8	64.3	1.0	107.1	0	0	0	0	0	0.3	0	99.4	0	0.2	0	0

4. Results and Discussions

Some performance indexes are defined to evaluate the system performance: specific consumption of feedstock, purity, specific energy demand and specific CO₂ emissions.

The specific consumption of feedstock is referred to the production of one ton of methanol. It is defined for the natural gas and for the electricity:

$$\text{specific consumption of natural gas} = \frac{\text{mass of natural gas [ton]}}{\text{mass of produced MeOH [ton]}}$$

$$\text{specific consumption of electricity} = \frac{\text{energy [kWh]}}{\text{mass of produced MeOH [ton]}}$$

$$\text{Purity} = \frac{\text{mass of pure MeOH [kg]}}{\text{mass of product obtained from the light components distillation [ton]}}$$

The specific energy demand is defined accounting both natural gas and electricity which is reported to the primary energy with a conversion factor of 50%:

$$\text{Specific energy demand} = \frac{\text{energy contained in the consumed feedstock [GJ]}}{\text{mass of produced MeOH [ton]}}$$

The specific CO₂ emissions are defined for the natural and for the electricity with an emission factor of emission factor 460 g/kWh:

$$\text{Specific CO}_2 \text{ emission} = \frac{\text{mass of CO}_2 \text{ contained in the consumed feedstock [kg]}}{\text{mass of product obtained from the light components distillation [ton]}}$$

The results are reported in Tab. 5 for the case with Natural Gas as feedstock, while for the case studied with the concept proposed in the FReSMe Project the results are reported in Tab. 6.

Tab. 5 Summary of energy balance and CO₂ emissions for the plant fed with Natural Gas

	Specific consumption		Specific energy demand		Specific CO ₂ emission	
Natural gas	0.65	t NG/t MeOH	30.40	GJ/t MeOH	1759.9	kg CO ₂ /t MeOH
Electricity	275.3	kWh/t MeOH	2.48	GJ/t MeOH*	126.6	kg CO ₂ /t MeOH
Pure MeOH (purity)	994.5	kg/t MeOH	-19.83	GJ/t MeOH	-1371.6	kg CO ₂ /t MeOH
Net per tonne MeOH			13.05	GJ/t MeOH	515.0	kg CO ₂ /t MeOH

For the conventional way for methanol production the total amount of energy required is about 13 GJ/tMeOH and the specific emission are about 515 kgCO₂/tMeOH.

Tab. 6 Summary of energy balance and CO₂ emissions for the plant fed with gas from SEWGS

	Specific consumption		Specific energy demand		Specif CO ₂ emission	
Natural gas	0.08	t NG/t MeOH	3.61	GJ/t MeOH	209.2	kg CO ₂ /t MeOH
Electricity	242.8	kWh/t MeOH	2.19	GJ/t MeOH*	111.7	kg CO ₂ /t MeOH
Electricity for the electrolyzer	10229.4	kWh/t MeOH	36.83	GJ/t MeOH	0	kg CO ₂ /t MeOH
Pure MeOH (purity)	994.1	kg/t MeOH	-19.83	GJ/t MeOH	-1371.6	kg CO ₂ /t MeOH
Net per tonne MeOH			22.79	GJ/t MeOH	-1050.7	kg CO ₂ /t MeOH

For the production of methanol with SEWGS gases (as FReSMe concept) the total amount of energy required is about 22.8 GJ/tMeOH and the specific emission computed in this way are negative: about -1050 kgCO₂/tMeOH. There is a small amount of natural gas, it is required for the distillation process.

These values shown that the energy impact of the new plant is higher than the conventional. The higher amount of the energy contribution is due to the electrolyzer. It is worth to highlight that, in the concept of the FReSMe project, the energy required for this component is obtained from renewable sources. The carbon footprint results lower with the new concept proposed in the project. A comparison with dimensionless values of the results, between the two ways of production, is shown in Fig. 7. The case with the conversion of the natural gas is taken as reference. It can be noted that the energy required from the FReSMe concept is about one and half time the energy required by the standard way, whereas the CO₂ emitted for a ton of MeOH is the double for the standard way.

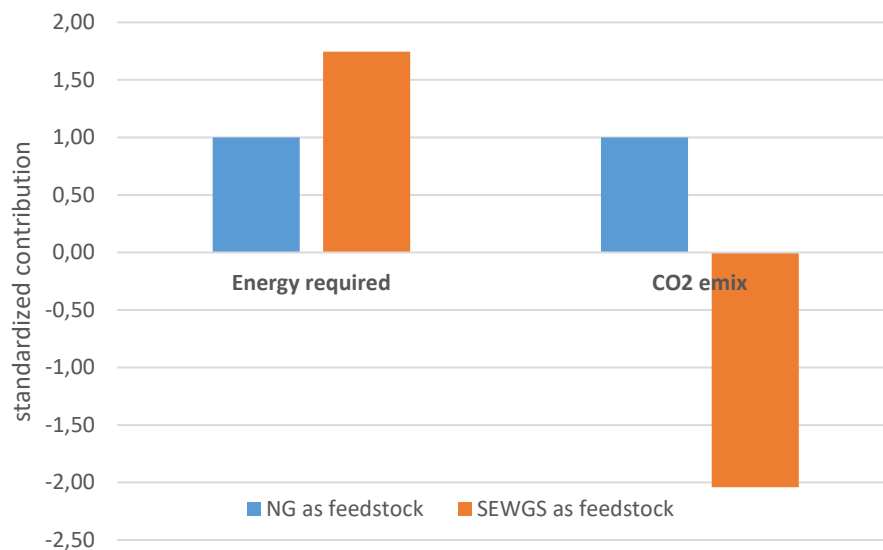


Fig. 7 Comparison of the energy impact for the two ways of methanol production and their CO₂ footprint.

5. Conclusions and future works

This work presented the production of Methanol (MeOH) using as feedstock CO₂ from Blast Furnace Gas (BFG) which is investigated in the FReSMe project. Two ways for the production of methanol are studied: (i) a standard way with the conversion of Natural Gas used as reference and (ii) FReSMe's approach based on the conversion of SEWGS gases from a steel plant. The main results obtained from the two systems allow the evaluation of the CO₂ emitted from the plants and thus the CO₂ avoided with the innovative process.

It can be concluded that:

- The production of methanol based on the SEWGS gases is effective in the CCUS: a CO₂ emission reduction of 1050 kg_{CO2}/t_{MeOH} is assessed.
- The higher energy requirement for the methanol based on the SEWGS gases is due to the consumption required by the electrolyzer, where in the FReSMe approach, is supplied by renewable sources.
- High quality of methanol can be obtained

The carbon footprint is lower in the new concept because NG used in conventional production is replaced by a combination of: 1) CO₂ that would otherwise have been emitted and 2) renewable electricity. Further analysis of environmental impact using LCA and overall techno-economics will be conducted."

Acknowledgements

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