INITIATE
A STEPWISE PROJECT

PUBLIC

DELIVERABLE 5.5

OPPORTUNITIES FOR OTHER INDUSTRIAL SYMBIOTIC SYSTEMS

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Version Management

VERSION	DETAILS
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Disclaimer

Executive Summary

Steelmaking is a major contributor to industrial green-house-gas emissions and is considered a hard-to-abate sector as the potential for use of renewable feedstocks and energy is limited. The INITIATE project proposes a novel symbiotic process that produces urea from steel residual gases. This strategy reduces steelmaking CO_2 emissions and creates a more efficient use of the extracted fossil carbon. The INITIATE project aims to demonstrate reductions in primary energy intensity of 30%; carbon footprint of 95%; raw material intensity of 40%; and waste production of 90%. Within the INITIATE process concept, a N_2-H_2 mixture is produced from residual steel gases, while simultaneously capturing CO_2, by Sorption Enhanced Water Gas Shift (SEWGS) technology. Specifically, two residual steel gases, the Blast Furnace Gas (BFG) and the Basic Oxygen Furnace Gas (BOFG) are considered. These gases represents more than 80% of the overall emissions of steelmaking via the Blast Furnace (BF) route. The basic configuration of the symbiotic system includes the use of the produced H_2 as feedstock for urea production, together with a fraction of the CO_2 product.

A techno-economic evaluation of the INITIATE concept is performed by comparing individual steel and urea production roues with the INITIATE symbiotic coupling and alternative CO_2 capture routes. See public deliverable D 5.3 for further details. The current public deliverable D5.5, however, aims to expand the evaluation of the INTIATE technology, proposing modifications to its application in three domains:

- **Additional symbiotic H_2/N_2 use cases**: to assess the production of alternative symbiotic 'secondary products' next to Urea.
- **Steelmaking with CCS (without symbiosis)**: to assess the use of the INTIATE gas conditioning technology to apply CCS to pure steelmaking, considering alternative steelmaking routes.
- **CO_2 Mineralization for CCS**: to assess the use of alternative options to underground pressurized CO_2 storage.

The main results of these three studies are summarised within the paragraphs below.

Additional symbiotic H_2/N_2 use cases

Next to urea production, the INTIATE concept has the potential to create more symbiotic systems. Within this deliverable report, additional symbiotic systems with the INITIATE gas conditioning technology are evaluated in terms or primary energy consumption (PEC) and carbon avoidance (CA). This is done to provide a first analysis of the environmental benefits of different symbiotic configurations. Four symbiotic uses of the H_2/N_2 product are evaluated, considering a Blast Furnace based steel plant of 3.16 Million Tonnes of Hot Rolled Coil (HRC) per year:

- Urea production (Urea case, 513 $kton_{Urea}$/yr)
- Methanol production (MeOH case, 595 $kton_{MeOH}$/yr)
- Addition steel production via Direct Reduction Process (BF-2-DRP case, additional 2.03 $Mton_{HRC\text{-}DR}$/yr)
- Dispatchable power generation via Ammonia (A-2-P case, 550 GWhr/yr).

Material and energy balances of these four cases are calculated via computer simulations. The results indicate that all four cases lead to a reduction of CO_2 emissions. The relative carbon avoidance are found to range from 49% to 63%. Conversely, the PEC is found to increase across all cases. Relative energy penalties range between 19% and 33%. These energy penalties are caused by a larger consumption of natural gas to generate heat and power. These heat and power inputs are mainly required to run the INITIATE process and to replace the use of the residual steel gases within the BF plant. The use of low carbon power, instead of natural gas, is found to effectively reduce the PEC of the symbiotic systems. Illustratively, for the BF-2-DRP case, relative carbon avoidance of 63% and specific PEC per avoided carbon (SPECCA) of 3.75 $GJ/ton_{HRC\text{-}BF}$ are achieved by using natural gas derived electricity (350 kg_{CO2}/MWh_{el}). When carbon neutral power is used (0 kg_{CO2}/MWh_{el}), these values improve to ~80% and 0.75 $GJ/ton_{HRC\text{-}BF}$, respectively. This approach can also lead to negative primary energy penalties, or primary energy savings. For instance, the Urea case achieves a relative carbon avoidance of ~80% and a (negative) SPECCA of -0.3 $GJ/ton_{HRC\text{-}BF}$. This negative SPECCA corresponds to a 1.6% reduction of the primary energy consumption. These improvements are also expected to further grow when process heating is also decoupled from fossil resources, and fractional use of the produced H_2 as heating source is optimized. Finally, the valorisation of the N_2 excess that comes with processing BFG, or its reduction, would also significantly reduce the energy penalties of the symbiotic systems.

Steelmaking with CCS (without symbiosis)

This second part of this work focuses on evaluating the INITIATE hybrid steelmaking concept (BF-2-DRP) with some of the other available options to produce low carbon steel. Four steelmaking configurations are considered, hereby assuming an overall steel production of 5.19 $Mton_{HRC}$/yr as basis:

- Stand-alone Blast Furnace Process (BF case)
- Stand Alone Natural gas driven Direct Reduction Process (DRP case)
- The proposed hybrid (or symbiotic) steelmaking concept (BF-2-DRP)
- Stand Alone Natural gas driven Direct Reduction Process with carbon capture and storage via SEWGS technology (DRP-CCS)

The results indicate that steelmaking can be effectively decarbonized by integrating BF and DR plants via the INITIATE capture technology, or by applying the same technology to standalone plants. The BF-2-DRP and DRP-CCS cases achieve respective emissions intensities of 0.59 and 0.49 ton_{CO2}/ton_{HRC}. These are 71% and 76% lower than state-of-the art steelmaking via the BF route. When carbon neutral power is used, these values can improve to ~0.30 ton_{CO2}/ton_{HRC} and ~0.20 ton_{CO2}/ton_{HRC}, respectively. Additionally, the adoption of the DR process contributes to reduce the energy penalties. The DRP-CCS case does in fact reduce the PEC by 19% (i.e. -19% relative energy penalty). The BF-2-DRP has an energy penalty of 9%, and a positive SPECCA of 1.41 GJ/ton_{CO2}. However, it is possible to achieve a negative SPECCA in the BF-2-DRP case by considering carbon neutral alternatives to natural gas as mean to generate heat and power. Future study should further focus on evaluating the low carbon power and heat requirements of different options, and what option would achieve the greatest CO_2 reduction potential for different techno-economic constraints (e.g. availability of regional CO_2 storage and potential to generate renewable power). It is likely that the availability (or scarcity) of carbon neutral fuels and power, next to the availability of viable CO_2 storage options, will be important parameters, leading to different local environmental and economic performance of the considered options.

CO_2 Mineralization for CCS

A third and last part of this work evaluates the process of CO_2 mineralization as an alternative to underground CO_2 storage. Specifically, two mineralization approaches are considered:

- Olivine
- Basic Oxygen Furnace (BOF) slag

It is found that both these approaches maintain similar carbon avoidances compared to underground pressurized CO_2 storage as reference case. BOF slag mineralization appears to be the best performing case with a relative carbon avoidance of 47%. This is only 2% lower than the underground CO_2 storage and 5% higher than mineralization with olivine. Additionally, its SPECCA is larger than the conventional case by 1.02 GJ/ton_{CO2}. This is lower than for olivine, which shows an increase of the SPECCA by 4.11 GJ/ton_{CO2} relative to the reference case. Future studies are recommended to evaluate the economic performance of mineralization, especially considering different transport distances to underground storage for the reference case, and including in more details the process requirements to purify the CO_2 product. Mineralization is expected to have less stringent requirements, thereby reducing such purification costs and energy penalties.

Contents

List of abbreviations

A-2-P	Ammonia to Power
BF	Blast Furnace
BFG	Blast Furnace Gas
BFP	Blast Furnace Plant/Process
BFP-CCS	Blast Furnace Plant/Process with Carbon Capture adn Storage
BF-2-DRP	Blast Furnace to Direct Reduction Plant
BOF	Basic Oxygen Furnace
BOFG	Basic Oxygen Furnace Gas
CA	Carbon Avoidance
CA'	Relative Carbon Avoidance
CCS	Carbon Capture and Storage
COG	Coke Oven Gas
DR	Direct Reduction
DRI	Direct Reduced Iron
DRP	Direct Reduction Plant/Process
DRP-CCS	Direct Reduction Plant/Process with Carbon Capture and Storage
EAF	Electric Arc Furnace
FU	Functional Unit
HRC	Hot Rolled Coil
KPI	Key Performance Indicator
LHV	Lower Heating Value
MeOH	Methanol
MM	Methanol Module
PEC	Primary Energy Consumption
SPECCA	Specific Primary Energy Consumption per Carbon avoided
TPG	Top Gas from Direct Reduction Shaft Furnace

1. Objectives and Scope

1.1. Project background

This deliverable is part of the INITIATE (Innovative Industrial Transformation of the steel and chemical industries of Europe) project. The INITIATE project proposes a novel symbiotic process to produce urea from steel residual gases. The project aims to demonstrate a reduction in primary energy intensity of 30%, carbon footprint of 95%, raw material intensity of 40%, and waste production of 90%. Additional to this level of reduction, the concept represents a positive business case.

INITIATE will demonstrate operating reliability and technology-based innovations in a real industrial setting at TRL7 by producing ammonia from steel residual gases as part of three test campaigns spanning six weeks each. The reduction in primary energy intensity, carbon footprint, raw material intensity and waste production will be assessed and verified on a regional and European level by advanced dynamic modelling and Life Cycle Assessment commiserated with ISO 14404 guidelines.

The project will develop a commercial implementation roadmap for immediate deployment of INITIATE after project conclusion and for ensuring roll-out of INITIATE and similar symbiotic systems. Designing a robust and bankable first-of-a-kind commercial plant to produce urea from residual steel gases will allow implementation after project conclusion.

Long term roll-out will be enabled by defining collaborative strategy for stakeholders alignment to implement INITIATE and similar symbiotic systems. Finally, effective and inclusive communication and dissemination of project results are maximized by organizing summer schools and creation of Massive Open Online Course. INITIATE will take advantage of a consortium spanning the full value chain, including major steel and urea industrial players (Arcelor Mittal, SSAB, Stamicarbon, NextChem), functional material suppliers (Johnson Matthey, Kisuma Chemicals), multidisciplinary researchers (TNO, POLIMI, Radboud University) and experienced promoters of CCUS, circularity and symbiosis topics to public (CO_2 Value Europe).

1.2. Objectives

The main objectives of this work are to evaluate the potential Carbon Avoidance (CA) and Primary Energy Consumption (PEC) of:

1) Three additional symbiotic use cases of the INITIATE H_2/N_2 product next to urea production.
2) A symbiotic Blast Furnace (BF) / Direct Reduction (DR) hybrid steelmaking process.
3) Two CO_2 mineralization approaches as an alternative to conventional gaseous storage.

This analysis thereby aims to provide a preliminary case for the adoption of additional business strategies to achieve a reduction of carbon emissions next to urea manufacturing. The results from this study can be the basis for future techno-economic assessments, or scenario analysis, that are not among the objectives of this deliverable.

1.3. Scope

Following the abovementioned objectives, the scope of the deliverable is divided into three parts:

- Additional symbiotic H_2/N_2 use cases.
- Steelmaking with CCS.
- CO_2 Mineralization for CCS.

Key Performance Indicators (KPIs), system boundaries and Functional Unit (FU) are fixed for all these three parts. Additionally, reference systems are defined, as outlined in Methodology and Assumptions chapter. The various cases for each part are described in the following paragraphs.

Additional Symbiotic H_2/N_2 Use Cases

This first activity investigates the alternative use cases of the INITIATE H_2/N_2 product. The INITIATE concept proposes the generation of urea, via ammonia, by converting the H_2/N_2 product stream that is obtained from the main residual steel gases of Blast Furnace (BF) based steelmaking, namely the Basic Oxygen Furnace Gas (BOFG) and the Blas Furnace Gas (BFG). The Sorption Enhanced Water Gas Shift (SEWGS) technology enables the conversion of these gases to two gaseous products, respectively a H_2/N_2 and a CO_2 product. SEWGS is the key gas conditioning technology of INITIATE. Its H_2/N_2 product is then made available to

generate low-carbon heat & power, or to synthetize low-carbon chemicals and fuels. In this work, four alternative uses of the H_2/N_2 stream are considered:

1) **Production of Urea (Urea case):** this is the reference INITIATE approach. Urea is produced by using the H_2/N_2 product stream that is derived from the BOFG and BFG. A fraction of the captured CO_2 is not stored, but it is used as feedstock for urea production.
2) **Production of Methanol (MeOH case):** the H_2/N_2 stream obtained from the BFG and BOFG is used to generate methanol in this case, by also taking a fraction of the captured CO_2 as feedstock of the methanol plant.
3) **Production of additional steel via Natural Gas driven Direct Reduction Process (BF-2-DRP case):** in this case, part of the H_2/N_2 product stream is used to fuel the reformer of a Natural Gas driven DR steelmaking plant.
4) **Production of dispatchable grid power via Ammonia (Ammonia-to-Power, A-2-P case):** Similarly to the Urea case, the H_2/N_2 product stream is used to make Ammonia, which is in this case stored and use to run an ammonia drive turbine to generate dispatchable power.

Steelmaking with CCS

Generally, there are two possible routes to produce steel, namely the Blast Furnace / Basic Oxygen Furnace route and the Direct Reduction / Electric Arc Furnace route. This activity explores how the proposed Hybrid steelmaking concept of the previous task **(BF-2-DRP case)** compares with:

1) the conventional steelmaking processes **(BF and DRP cases)**
2) a stand-alone DRP with CCS by SEWGS technology **(DRP-CCS case)**.

In the BF-2-DRP case, the natural gas fuel of a NG-DR reformer is replaced with the H_2/N_2 mixture that is produced from the BF-BOF residual gases using SEWGS. In the DRP-CCS case, SEWGS is integrated into a standalone natural gas driven DRP by producing a H_2/N_2 reforming fuel from the shaft Top-Gas (TPG).

CO_2 Mineralization for CCS

Two CO_2 mineralization approaches are evaluated as an alternative to conventional CO_2 gaseous storage. Specifically:

1) Olivine mineralization **(Olivine case)**.
2) Slag mineralization **(Slag case)**.

The H_2/N_2 methanol use case with gaseous storage is taken as reference case to evaluate these alternative CO_2 storage options.

2. Evaluation Basis

2.1. Block Schemes and System Boundaries

Additional H_2/N_2 Use Cases

Concerning the Additional H_2/N_2 Use Cases, the reference system is illustrated in Figure 1. A BF steelmaking plant is included in the system, being its core process. The plant primary energy consumption is essentially fully covered by coal import, when very efficiency plants are considered. This coal acts both as feedstock and fuel. As feedstock, the coal acts both as carburization and reduction agent, enabling the conversion of iron oxide to steel (i.e. a mixture of reduced iron and carbon). Additionally, coal oxidation provides thermal energy. However, the residual gases from the steelmaking process retain a significant fraction of the coal chemical energy. These gases are the already mentioned BFG and BOFG, and the Coke Oven Gas (COG). About ~80% of the residual thermal energy is embedded in the BFG and BOFG. All three gases are partially lost to flare. Some losses are unavoidable due to the intermittent and batchwise nature of the steelmaking process. However, efficient plants can lose as little as ~4% of the gases' chemical energy. The rest is used to supply heat and power, enabling to run the plant autonomously from external energy inputs. More than 95% of the direct CO_2 emissions of the steel plant are caused by the combustion of the residual steel gases to generate heat and power. Additional direct emissions occur from handling and processing the solid feedstocks (e.g. due to lime production). An off-site secondary plant is included next to this BF steelmaking process to complete the reference system. This secondary plant produces the intended symbiotic product at the same throughput. The nature of this plant varies across the investigated cases. Urea (Urea Case), Methanol (MeOH Case), Electricity via Ammonia (A-2-P case) or Steel via Direct Reduction Process (BF-2-DRP Case) are the considered secondary products. These are produced by using Natural Gas as fuel and feedstock. Natural Gas is also used to generate the required power to produce these products via a natural-gas-combined-cycle plant (NGCC). Concerning the A-2-P case, the NGCC is defined not to supply power to the secondary plant, but to the grid, being electricity the selected secondary product for this case.

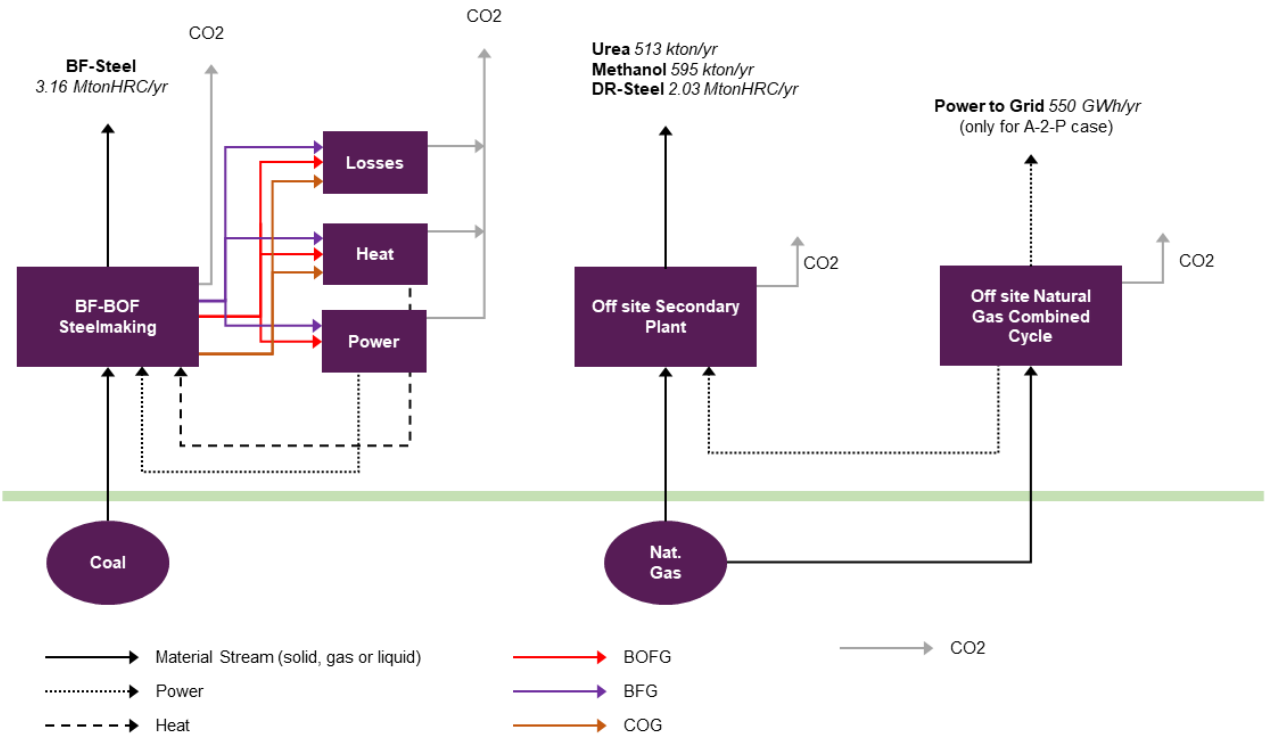


Figure 1. Reference Systems for the evaluation of alternative symbiotic uses of the H_2/N_2 product stream.

The symbiotic H_2/N_2 use systems are illustrated in Figure 2. Differently from the reference system, all the available BFG and BOFG are processed via the INTITIATE gas conditioning technology, SEWGS. Both BOFG and BFG are then converted to a H_2/N_2 stream and a CO_2 stream. The first product is available for producing heat & power, or to be supplied as feedstock to the secondary plant, thereby replacing natural gas. Importantly, when the chemical energy is used to generate a symbiotic product, the heat and power demand of the steelmaking process still needs to be fulfilled. In these cases, it is chosen to replace these demands by burning natural gas directly for heat or in a NGCC for power generation. The SEWGS CO_2 product is compressed to 110 bar and stored underground. Part of the CO_2 product is also used as chemical feedstock, specifically for the production of methanol and urea. Natural gas feedstock is completely replaced in case of methanol, urea or ammonia production by the H_2/N_2 stream. However, in case of the DRP some natural gas is still needed to provide sufficient reducing and carburization gas to the DR shaft furnace. Concerning the A-2-P case, the ammonia is directly combusted in a gas turbine to provide the final electricity product to the grid. As for the other cases, local power demand is met by mean of an off-site NGCC plant (i.e. not the grid). Only for the Urea and BF-2-DRP cases, additional scenarios with power import from the grid are considered. These scenarios are calculated to evaluate the impact of using low to zero carbon power. It is also important to mention that given the size of the secondary plants, different amounts of the H_2/N_2 products are used as feedstock. While the methanol plant uses all the available H_2/N_2 stream to produce the final product, the urea, BF-2-DRP and A-2-P cases use only a fraction of it. The residual H_2/N_2 is used to supply process heat to the INITIATE process and/or the BF steelmaking plant.

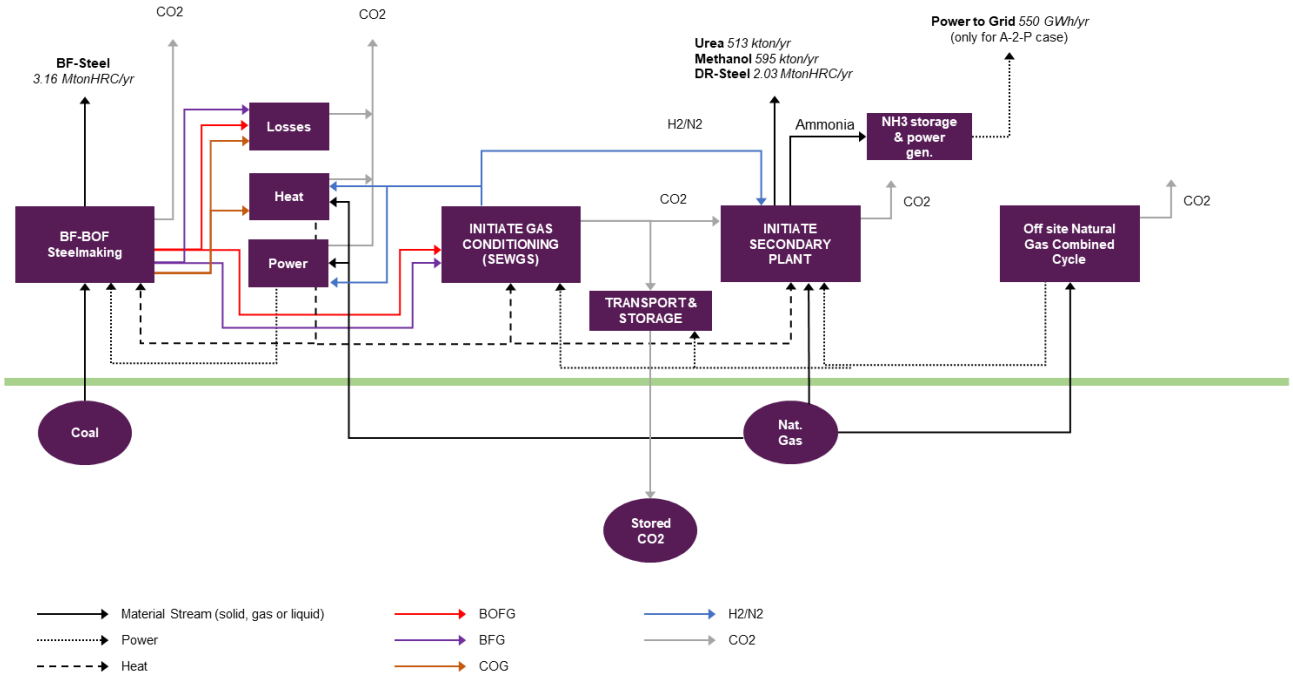


Figure 2. INITIATE symbiotic systems for the evaluation of alternative symbiotic uses of the H_2/N_2 product stream from SEWGS.

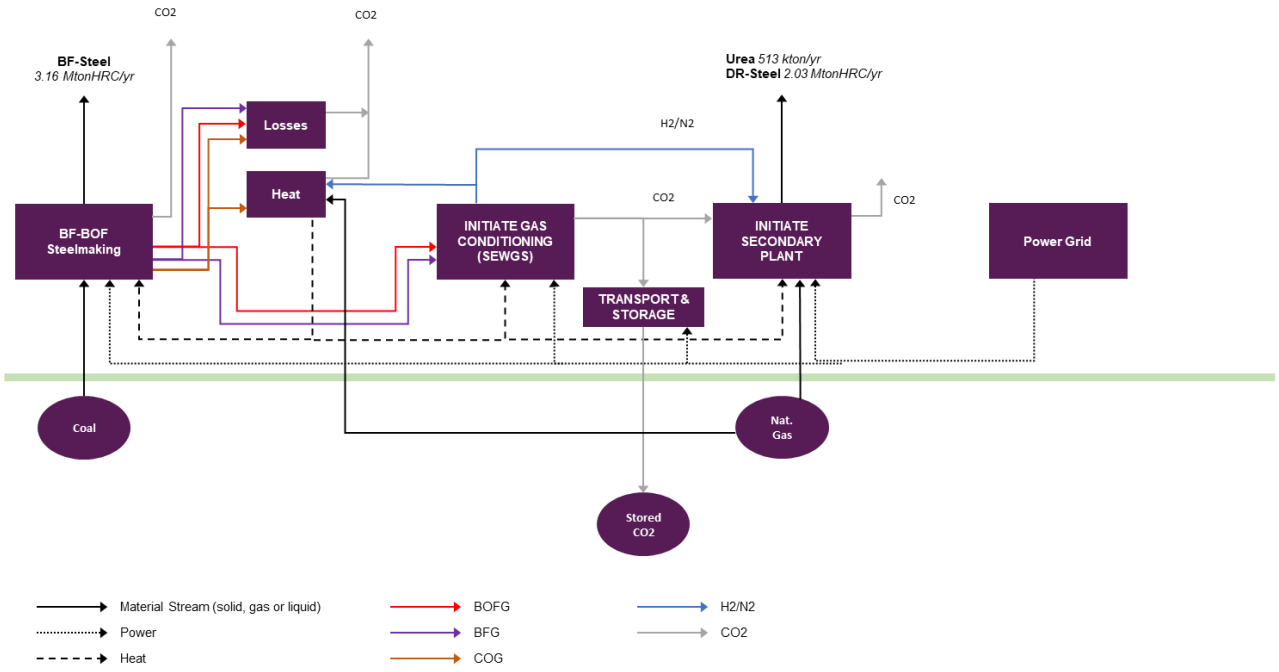


Figure 3. INITIATE symbiotic systems for the evaluation of alternative symbiotic uses of the H_2/N_2 product stream from SEWGS, with power import from the grid to replace power generation from residual steel gases and NGCC plant.

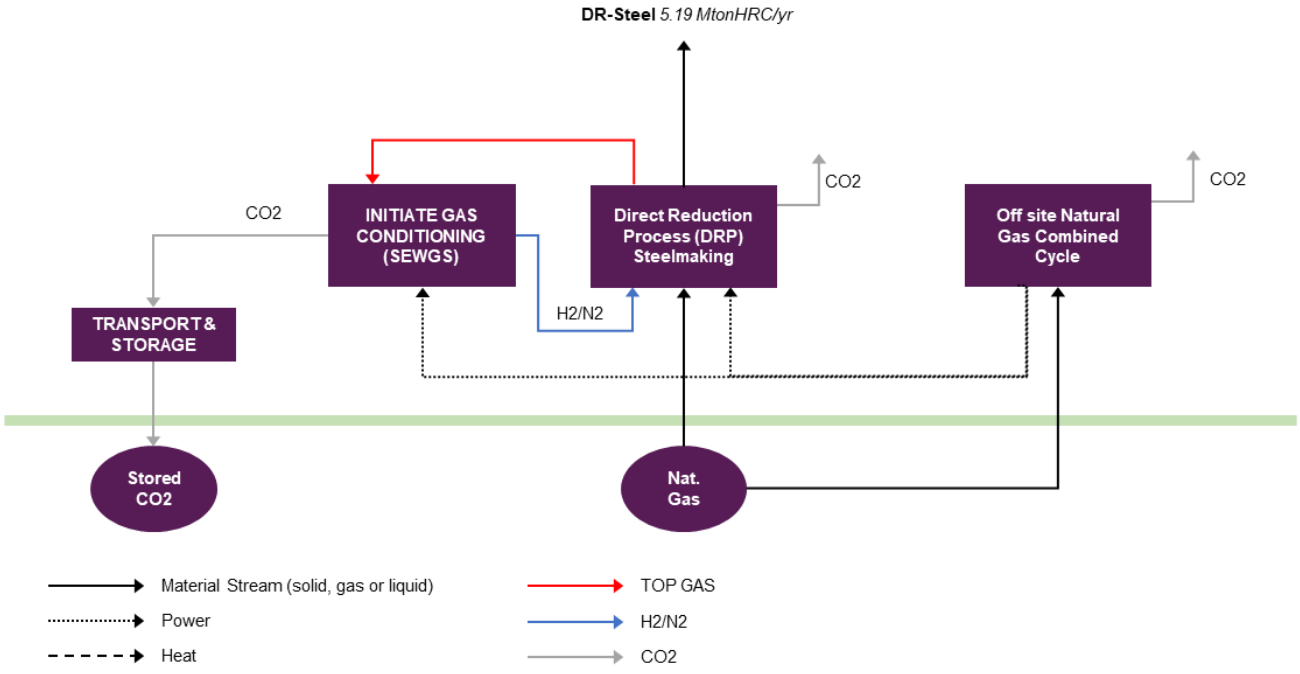


Figure 4. Block scheme of the DRP-CCS case with power import from a NGCC plant. A fraction of the DR shaft Top Gas is processed to produce H_2/N_2 reforming fuel gas.

Steelmaking with CCS

The reference blast furnace steelmaking plant boundaries are the same that are shown in Figure 1. Similarly, the reference direct reduction steelmaking process follows the secondary plant scheme in Figure 1. The BF-2-DRP case block is scheme shown in Figure 2. The DRP-CCS case includes a stand-alone DRP with a SEWGS set-up to process the shaft Top-Gas. The produced H_2/N_2 is used as reformer fuel, while the CO_2 is captured and stored at high pressure. The block scheme for this case is shown in Figure 4. In this case, the required power is generated by mean of NGCC plant. An alternative system is also considered whereby power is imported from the grid (Figure 5).

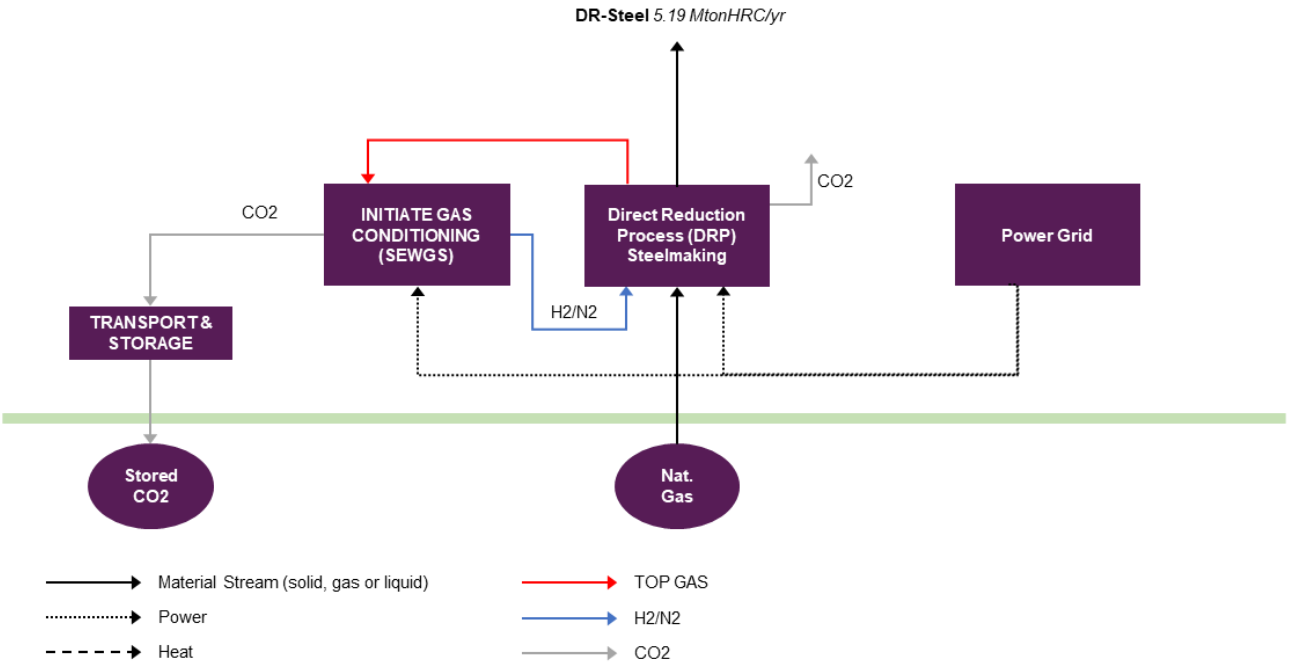


Figure 5. Block scheme of the DRP-CCS case with power import from the grid. A fraction of the DR shaft Top Gas is processed to produce H_2/N_2 reforming fuel gas.

CO_2 Mineralization for CCS

CO_2 mineralization is considered as an alternative to gaseous pressurized storage. Both reference gaseous storage and CO_2 mineralization cases are illustrated in Figure 6. In both cases, power and heat demand are met by using natural gas as primary energy source. Wastewater treatment is considered outside the boundaries for the CO_2 mineralization case.

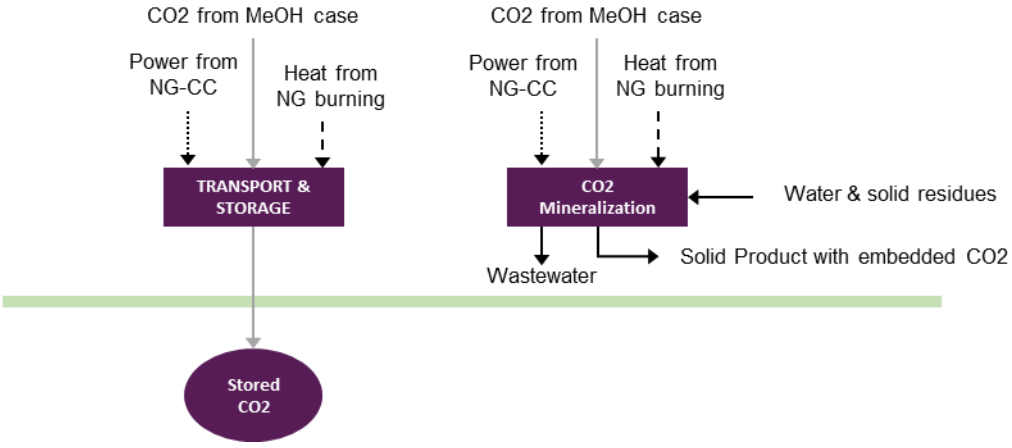


Figure 6. Reference pressurised gaseous CO_2 storage (left) and CO_2 mineralization alternative case (right). In both cases 4.8 MtonCO_2/yr are processed, assuming 8200 hr/yr.

2.2. Functional Units

The main assumption of this study is the product amounts that are fixed as basis of each one of the three studies (i.e. H_2/N_2 symbiotic use cases, Hybrid steelmaking and CO_2 mineralization). These amounts of products are named Functional Unit (FU). Specifically, the total amount of product that is manufactured over 1 year is fixed as FU in every study. Different products and respectively different annual amounts are fixed for the three parts of this study, as illustrated in Table 1.

Starting from the H_2/N_2 use cases, all systems are sized on the basis of a **3.16 $Mton_{HRC\text{-}BF}$/yr** BF steelmaking capacity. Additionally, secondary product capacities are fixed as illustrated in Table 2. Specifically, urea production is chosen to match a typical large scale fertilizer plant, i.e. **1,500 Tonnes Urea per Day**. This plant size leaves an excess of H_2/N_2 product that is used to supply process heat. The Methanol plant is conversely sized to maximize use of the available H_2/N_2 as feedstock. This corresponds to **1,742 Tonnes Methanol per Day**. In this case, the 100% of the available H_2 is used to synthetize the chemical, and process heat and power demands are met through natural gas consumption, both for the INTIATE process and the BF steelmaking plant. Moving to the A-2-P case, **550 GWhr/yr** are fixed. This amount corresponds to the equivalent ammonia production that is needed to synthetize 1500 Tonnes Urea per day. Finally, concerning the BF-2-DRP case, the secondary unit is fixed at a typical DR steelmaking plant size of **2.03 $Mton_{HRC\text{-}DR}$/yr**. A large part of the H_2/N_2 is used to generate heat for the reformer in this case. The residual product is returned to the BF steelmaking plant.

In the Hybrid steelmaking study, four steelmaking routes are compared. These are all fixed at a capacity of **5.19 $Mton_{HRC}$/yr**. In this study, the whole production of steel is considered as basis for the comparison. However, calculations are actually computed at different capacities, due to time limitation to perform the study. In principles, all plant sizes shall be fixed at 5.19 $Mton_{HRC}$/yr, namely for the reference BF and DRP cases, as well as for the BF-2-DRP and the DRP-CCS cases. This is needed to guarantee that comparable plants are evaluated. Plant efficiencies are indeed bound to be scale dependent, for instance due to heat integration and optimization of equipment sizing (e.g. it is quite common that large scale chemical plants present higher efficiency than smaller scale ones). However, scale differences are neglected in this (first) study and it is assumed that heat integration and equipment performance are the same between different steel production capacities from 2.03 to 5.19 $Mton_{HRC}$/yr, whatever the amount of respective processed gas through the INITIATE process.

Concerning CO_2 mineralization, both olivine and slag cases are based on a CO_2 input of **14,114 Tonnes CO_2 per day.**

Table 1. Functional Units of the three parts of this study.

	Ref. Unit Definition	Metric	Value
H_2/N_2 use cases	BF steelmaking production capacity	$Mton_{HRC\text{-}BF}$/yr	3.16
BF-DRP Hybrid steelmaking with CCS	Total steelmaking production capacity	$Mton_{HRC}$/yr	5.19*
CO_2 mineralization for CCS	CO_2 available to be stored	$Mton_{CO2}$/yr	4.81

***Note:** Scale differences are neglected in this (first) study. Actual plant sizes are: 1) Ref.BF = 3.16 $Mton_{HRC}$/yr; 2) Ref. DRP = 2.03 $Mton_{HRC}$/yr; 3) DRP-CCS = 2.03 $Mton_{HRC}$/yr; 4) BF-2-DRP = 5.19 $Mton_{HRC}$/yr.

Table 2. Secondary product units and fractional H_2/N_2 use, for the H_2/N_2 use cases study.

Case	Secondary Product Unit	Metric	Value	Fractional use of the SEWGS produced H_2 (%mol)
Urea	Urea production capacity	kton/yr	513	44% to Urea synthesis (66% to heating)
MeOH	Methanol production capacity	kton/yr	595	100% to Methanol synthesis (0% to heating)
BF-2-DRP	DR-Steel production capacity	$Mton_{HRC\text{-}DR}$/yr	2.03	No chemical synthesis (100% to heating)
A-2-P	Generated annual average power	GWh/yr	550	44% to Ammonia synthesis (66% to heating)

2.3. Basic Assumption and Data

- Plants uptime: this is fixed for all processes at 8200 hours per year.
- Reference BF steelmaking power and heat input is fully fulfilled by residual steel gases (BFG,BOFG and COG).
- NGCC is used as reference for power generation.
- Grid power is used for scenario analysis in the following cases:
  - Urea
  - BF-2-DRP
  - DRP-CCS
- Residual steel gases compositions are taken as reported in Table 3.
- Used Emission Intensity and Primary Energy Consumption data of conventional routes are reported respectively in Table 4 and Table 5.
- As product use it is outside the boundaries of these studies, all emissions that are related to product use are neglected (these are often referred as scope 3 emissions). This is true for all products: BF-steel, DR-steel, Urea, Methanol and electricity.
- Heat generation from natural gas is computed assuming a natural gas to heat efficiency of 92%.
- NGCC power generation efficiency is assumed to be 60%.

Table 3. Composition and flowrates of BFG, BOF, COG and TPG that are used in this work.

	Name	BFG	BOFG	COG	DR-TPG
H_2	vol%	2.4	3.3	59.5	40.8
N_2	vol%	53.5	18.8	5.8	1.6
O_2	vol%	0.0	0.0	0.2	0
CO	vol%	22.7	56.4	3.8	18.7
CO_2	vol%	21.4	20.8	1.0	17.0
CH_4	vol%	0.0	0.0	23.0	2.5
Ar	vol%	0.0	0.6	0.0	0
H_2O	vol%	0.0	0.0	4.0	19.5
Other HC	vol%	0.0	0.0	2.7	0
Total	vol%	100.0	100.0	100.0	100
Reference steel mill size for flow values (excluding losses to flare)		3.16 MtonHRC/yr			2.03 MtonHRC/yr
Flow	kmol/hr	33,017	1,466	2,695	21,690

Table 4. CO_2 Emission Intensity of Conventional Production Routes

Product	Conventional Production	Emission Intensity
Urea	Natural gas based urea at large scale (1,500 TPD)	0.33 ton_{CO2}/ton_{Urea}
Steel	Steel Produced via BFG-BOF Route	2.05 ton_{CO2}/ton_{HRC}
Methanol	Methanol produced from natural gas	0.5 ton_{CO2}/ton_{MeOH}
Electricity	Electricity from zero carbon grid scenario (Hydro, Solar, Wind, nuclear, etc…).	0.00 ton_{CO2}/MWh_{el}
Electricity	Electricity from low carbon grid	0.25 ton_{CO2}/MWh_{el}
Electricity	Electricity from combined cycle with 60% efficiency	0.35 ton_{CO2}/MWh_{el}

Table 5. Primary Energy Consumptions of Conventional Production Routes

Product	Conventional Production	Fossil Primary Energy Consumption
Urea	Natural gas based urea at large scale (1500 TPD)	19.64 GJ/ton_{urea}
Steel	Steel Produced via BFG-BOF Route	21.93 GJ/ton_{hrc}
Methanol	Methanol produced from natural gas	30 GJ/ton_{MeOH}
Electricity	Electricity from fossil free grid (Hydro, Solar, Wind).	0.00 GJ/GJ_{el}
Electricity	Electricity from combined cycle with 60% efficiency	1.67 GJ/GJ_{el}

2.4. Main Key Performance Indicators (KPIs)

Definitions of the KPIs of the comparisons are here reported. In this preliminary work only primary energy consumption and emission intensities are considered so to have a first assessment of the environmental benefits of the proposed concepts. GHG emission intensity are expressed in terms of annual amount of CO_2 equivalent emissions. Primary energy consumptions include all the consumptions of fossil resources in terms of GJ per year, thereby including both fossil feedstocks and fuels.

GHG Emission Intensity

$$Symbiotic\ System\ Emissions\ Intensity: e_{SS}\left[\frac{ton_{CO_2,eq}/yr}{FU}\right] = e_{IN,SM} + e_{IN,P} + e_{T\&S} + e_{RP} \quad \text{Equation 1}$$

$$Reference\ System\ Emissions\ Intensity: e_{RS}\left[\frac{ton_{CO_2,eq}/yr}{FU}\right] = e_{RSM} + e_{SP} \quad \text{Equation 2}$$

$$Carbon\ Avoidance: CA' = e_{SS} - e_{RS} \quad \text{Equation 3}$$

$$Relative\ Carbon\ Avoidance: CA = \frac{CA'}{e_{RS}} \quad \text{Equation 4}$$

Detailed symbols:

- FU: Functional Unit, this is different per study as presented in Table 1.
- $e_{IN,SM}$: emission intensity INITIATE steelmaking
- $e_{IN,P}$: emission intensity INITIATE process
- $e_{T\&S}$: emission intensity CO_2 transport & storage
- e_{RP}: emission intensity heat & power replacement of BOFG & BFG in BF steelmaking
- e_{RSM}: emission intensity reference steelmaking
- e_{SP}: emission intensity secondary product

Primary Energy Consumption

$$Symbiotic\ System\ PEC: PEC_{ss}\left[\frac{GJ/yr}{FU}\right] = PEC_{IN,SM} + PEC_{T\&S} + PEC_{RP} \quad \text{Equation 5}$$

$$Reference\ System: PEC_{RS}\left[\frac{GJ/yr}{FU}\right] = PEC_{RSM} + PEC_{SP} \quad \text{Equation 6}$$

$$Energy\ Penalty: EP' = PEC_{SS} - PEC_{RS} \quad \text{Equation 7}$$

$$Relative\ Energy\ Penalty: EP = \frac{EP'}{PEC_{RS}} \quad \text{Equation 8}$$

$$Specific\ PEC\ per\ Carbon\ Avoided: SPECCA = \frac{EP'}{CA'} \quad \text{Equation 9}$$

Detailed symbols:

- $PEC_{IN,SM}$: primary energy consumption INITIATE steelmaking & process
- $PEC_{T\&S}$: primary energy consumption for CO_2 transport & storage
- PEC_{RP}: primary energy consumption heat & power replacement of BOFG & BFG in BF steelmaking
- PEC_{RSM}: primary energy consumption reference steelmaking
- PEC_{SP}: primary energy consumption secondary product

3. Process Modelling

3.1. Reference Blast Furnace Steelmaking

The block diagram of the reference Blast Furnace Plant (BFP) is shown in Figure 7. The calculated heating and power demands for a 3.16 $Mton_{HRC-BF}$/yr plant are presented in Figure 8. Overall, 1,035 MW_{th} are available through the three residual steel gases of the process, namely the Coke Oven Gas (COG), the Blast Furnace Gas (BFG) and the Basic Oxygen Furnace Gas (BOFG). These are used to produce 668 MW_{th} of heat (assuming 92% fuel to heat efficiency) and 159 MW_{el} (assuming 51% fuel to power efficiency). Generally, the overall BFP can be roughly divided into 4 sections:

- Raw material preparation;
- Ironmaking;
- Steelmaking;
- Casting & rolling.

The main raw materials for iron and steelmaking are: 1) Coal: to provide a reducing and carburization agent, next to be an energy source, 2) Iron ore: to provide the main component of the final steel product, 3) Lime (CaO): a fluxing agent that is needed in steelmaking to enhance the incoming iron slag more fluidity. The raw materials preparation typically includes the coke, sintering and lime production plants. In the coke plant, coal is converted to coke via a pyrolysis like process in an oxygen-free environment. The process releases a H_2 rich gas, the Coke Oven Gas (COG). This represents approximately 28% of the total available thermal energy within the residual steel gases. The process of providing energy to the coke ovens is typically called 'underfired heating' and it requires 184 MW_{th} of gaseous fuel. This demand is mainly met by the COG itself and part of BFG. Due to its H_2 richness, the COG can deliver a higher flame temperature than the BFG. When BFG is mixed with COG, the BFG fuel quality is so increased. The energy that is required for the sintering and lime production steps is also supplied by the COG, due to its superior quality. Within the lime production step, calcium carbonate is heated to high temperature to form lime (CaO). This conversion also releases CO_2 as by-product, directly contribution to the plant's emissions. Approximately 32 MW_{th} of COG are used for this step. Finally, coke, lime and iron ore fines are agglomerated into a suiTable product for ironmaking, within the sintering step. 8 MW_{th} of COG are used to provide the required thermal energy for this step.

Following solids handling and pre-processing, the next plant section is ironmaking. The blast furnace is the key equipment of ironmaking. In the blast furnace, raw materials are converted to an iron melt that is suiTable for steelmaking. The blast furnace is fed from the top with sintered agglomerates, coke and other additives in series. As the solid mixture travels to the bottom the iron ore is reduced to metallic iron. A hot blast is fed into the blast furnace at approximately 1/3 of its height. This hot blast includes preheated enriched air. In addition, pulverised coal is also injected in the blast furnace to generate heat through oxidation. The iron reduction reaction occurs within the agglomerates, among the iron and sintered coke, as well as between the loaded coke and iron layers. Coke also provides the carbon content of the melt product, which is between 3.5% and 4.5% on a mass basis. This final product is collected at the bottom of the blast furnace in the form of hot liquid metal. The blast furnace produces BFG as by product. This is the largest residual gas stream in an integrated iron and steel plant (652 MW_{th}, ~63% of the total available gaseous energy). The BFG is almost entirely responsible for power generation on site. Additionally, it contributes both to coke oven underfired heating and heating the hot blast air within the hot stoves that are placed next to the blast furnace.

Following ironmaking, the iron is converted to steel. This is achieved by driving off the carbon to reach <1.5% carbon content in the metal. This is done in the basic oxygen furnace. Here, oxygen is introduced to convert and separate the carbon excess. The process results in the production of basic oxygen furnace gas (BOFG), the third and last residual gas stream of an integrated steel plant (96 MW_{th}, approximately 9% of the total available energy). The BOFG is richer in CO compared to the BFG, but has still double the N_2 content than the COG. The BOFG is manly used to provide heat to the steel finishing step and generate power.

The liquid steel that is produced is sent to the last section, namely casting & rolling. Where the liquid steel is formed into standard product shapes and further processed into a variety of products. Depending on the type of steel product additional additives and treatments are also introduced either after steel making in the BOF or after the steel is cast. Overall reheating and rolling require 153 MW_{th}, which are mainly met by COG combustion, due to the higher energy content and flame temperature of this gas. In this study, the final product is assumed to be hot rolled coils (HRC). It is important to highlight that every integrated BF steel plant is unique in the way its residual gas streams are integrated, and the described energy flows are only representative of integrated plants with overall losses to flare of 44 MW_{th} (~4.3% of the total available gaseous energy).

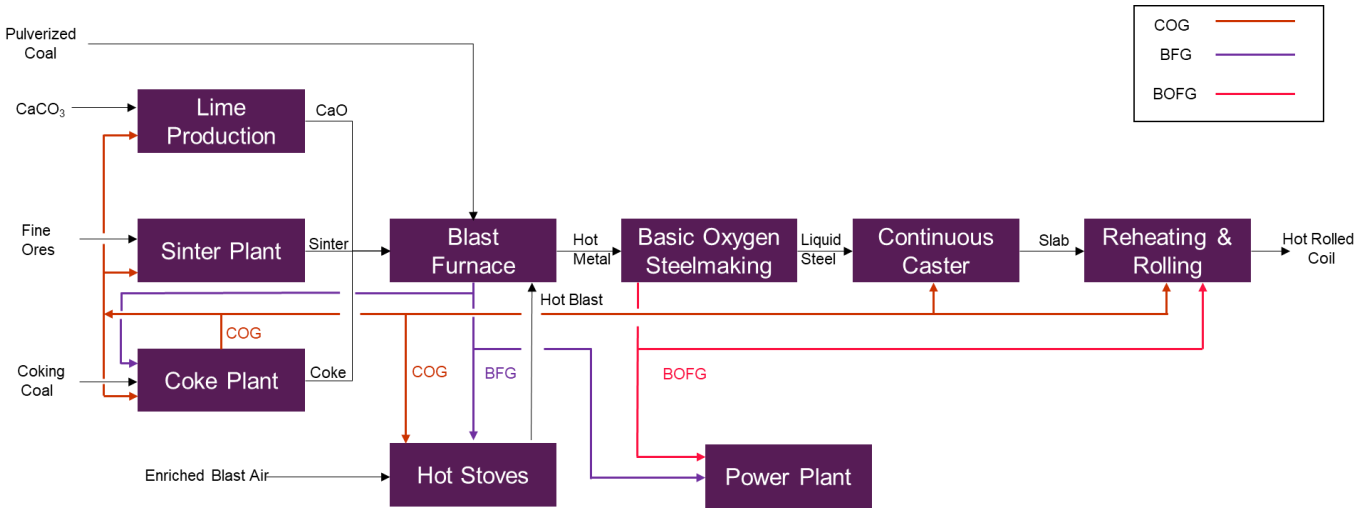
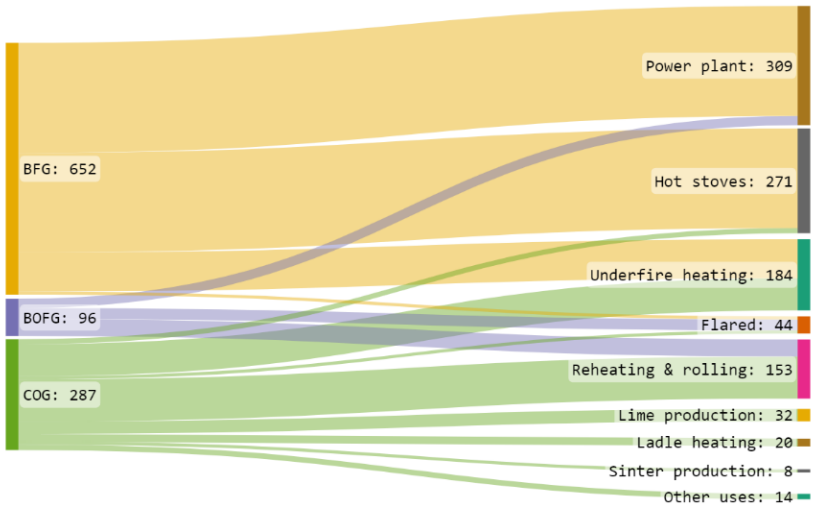


Figure 7. Block Diagram of Reference Blast Furnace Steelmaking Plant (BFP).

Values in MW_{th}, valid for a 3.16 MtonHRC/yr plant:



Coke Plant	14.80	[kWh/t_{HRC}]
Sinter Plant	36.84	[kWh/t_{HRC}]
Iron Making	101.52	[kWh/t_{HRC}]
Steelmaking	50.50	[kWh/t_{HRC}]
Continuous Casting	11.28	[kWh/t_{HRC}]
Reheating & Rolling	108.98	[kWh/t_{HRC}]
Lime Production	2.69	[kWh/t_{HRC}]
ASU - HP Oxygen	69.13	[kWh/t_{HRC}]
Ancillary	4.97	[kWh/t_{HRC}]
Off Site users	13.35	[kWh/t_{HRC}]
Total	414.07	[kWh/t_{HRC}]
Total Electrical Energy Demand	159	[MW_{el}]

Figure 8. Sankey Diagram of modelled thermal energy flows in the reference BF plant. On the left, the respective electrical energy demands are reported. It is assumed that 309 MW_{th} are used to generate 159 MW_{el}, with an efficiency of 51% thereby matching the total electrical energy demand.

3.2. INITIATE Gas Conditioning by SEWGS

The INITIATE gas conditioning step is used to process the BOFG and BFG. The conditioning delivers a H_2/N_2 high pressure product that retains the feedstocks' energy content while being carbon free. The conditioning step occurs at high pressure and temperature (15-25 bara and 400 ºC). It combines water gas shift conversion of CO and H_2O, respectively to H_2 and CO_2, as well as CO_2 separation. The process includes auxiliary equipment to provide steam, heat and increase the feedstock's pressure. The core units are a WGS reactor to pre-adjust the CO content, and the SEWGS multi-columns set-up, whereby additional CO conversion and CO_2 separation are achieved by mean of adsorption-reactive operations. The SEWGS is a gas adsorption technology and it is operated in pressure swing mode.

SEWGS modelling and simulations are executed with TNO's proprietary MATLAB based model, starting from the pre-shifted BFG, BOFG and TPG depending on the case study. This is a 1D SEWGS column model, which is able to reproduce temperature, composition and pressure profiles across the SEWGS sorbent bed. A programming routine ensures that all adsorption cycle steps are simulated, so that the overall cycle material and energy balance can be derived by mean of time integration.

Overall, three SEWGS set ups are simulated, based on three different feedstock mixtures that results from the 5 investigated cases (Table 7). Specifically, three cases are based on the processing of a BFG/BOFG mixture (i.e. Urea, A-2-P and MeOH), one case is based on a mixture of BFG/BOFG and DR top gas (BF-2-DRP case), finally one case is based on the pure treatment of DR top gas (DRP-CCS). Pre-shifted feedstock mixtures are reported in Table 6.

All designs recover more than 95% of the theoretical H_2 potential, with CCR and CP respectively greater than 92% and 97%. Hydrogen production capacity ranges from 99 to 297 kNm^3/hr, while CO_2 capture capacity from ~1 to almost 6.7 $MtonCO_2/yr$, which are very large gas processing plant sizes compared to state-of-the-art equivalent in industrial gas processing plants (e.g. methane reforming plants). Two SEWGS cycles are designed, respectively with 15 (Figure 9) and 20 columns (Figure 10). The 20 columns option is used for the stand alone DRP-CCS design. The increased number of columns is needed to efficiently process the pure TPG, which shows a significant change in composition with lower carbon concentration and higher hydrogen content.

Table 6. Composition and conditions at SEWGS inlet.

	Name	BFG & BOFG mix	BFG & BOFG & TPG mix	TPG
H_2	vol%	16.4	20.1	46.7
N_2	vol%	37.9	33.3	1.4
O_2	vol%	0.0	0.0	0.0
CO	vol%	2.9	5.4	5.4
CO_2	vol%	30.2	28.7	25.9
CH_4	vol%	0.0	0.4	2.2
Ar	vol%	0.0	0.0	0.0
H_2O	vol%	12.6	12.1	18.4
Total	vol%	100.0	100.0	100.0

Table 7. SEWGS design for the 5 considered applications. Three designs are reported. Different designs are due to the different feedstock compositions across some cases.

Use-Case		Urea, MeOH, A-2-P	BF-2-DRP	DRP-CCS
Feed gas type		BFG, BOFG	BFG, BOFG, TPG	TPG
Feed Flow Rate	kNm^3/hr	1,074	1,596	201
Feed Pressure	bara	17	17	18
Feed Temperature	ºC	400	400	400
CO_2 capture capacity	$MtonCO_2/y$	5.74	6.68	0.95
Hydrogen capacity	Nm^3/hr	198,185	297,801	99,236
H_2 Recovery Factor	%	95.20%	95.21%	95.36%
CCR	%	97.30%	96.30%	92.10%
CP	%	97.80%	98.60%	98.85%
Number of modules	dim.less	6	6	2
Number of columns per module	dim.less	15	15	20
Internal Diameter	meters	3.95	3.95	2.77
Internal Bed height	meters	7.34	7.75	7.44
S/C Rinse	mol_{H2O}/mol_C	0.55	0.49	0.29
S/C Purge	mol_{H2O}/mol_C	1.00	1.20	0.80
Cycle Time	sec	225	225	260

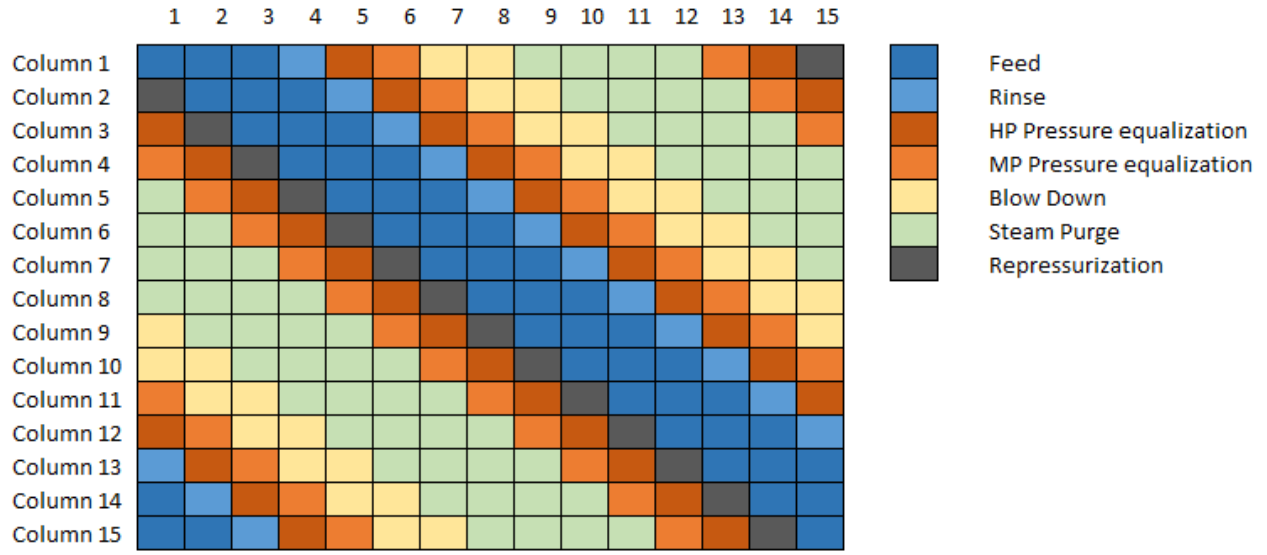


Figure 9. Cycle design with 15 columns for the Urea, MeOH, A-2-P and BF-2-DRP cases.

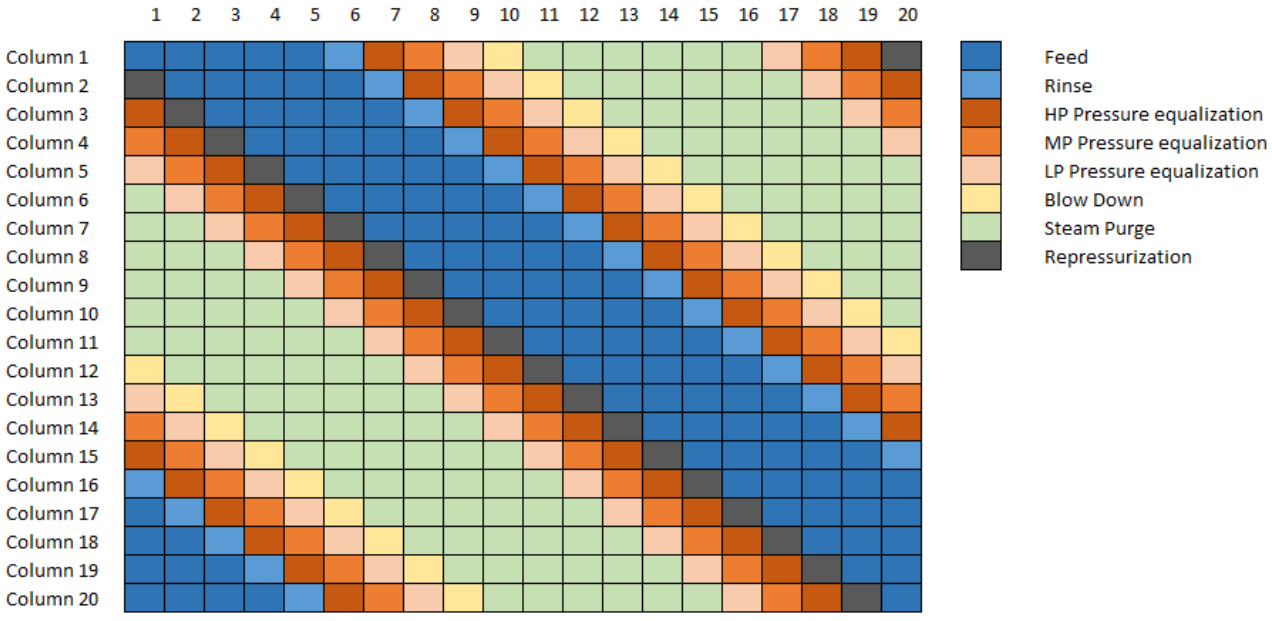


Figure 10. Cycle design with 20 columns for the stand alone DRP-CCS case.

3.3. Methanol Synthesis

In this section, the alternative application of using SEWGS coupled with steelmaking residual gases for methanol production is modelled. According to the scheme below, all the available BFG and BOFG are used to produce Methanol Grade AA (higher commercial purity grade). The electricity and heat that are needed by the steel plant, previously covered by the combustion of residual gases, are replaced using NGCC electricity and natural gas combustion, respectively. The process is simulated on Aspen Plus V11 flowsheeting software. Feedstocks' compositions are taken from the simulated SEWGS outputs. The simulated process scheme for methanol synthesis is illustrated in Figure 11. The two gas streams coming from the SEWGS (H_2-IN and CO_2-IN) are first purified to recover pure carbon dioxide and hydrogen, respectively. Especially, the H_2 stream is purified by mean of pressure swing adsorption (PSA), as the H_2-IN stream contains ~35%vol H_2 and 65%vol N_2 on a dry basis. After mixing the two streams and bringing them to the operating conditions of the methanol synthesis reactor, the unconverted gaseous fraction is recycled to the reactor inlet, while the liquid phase is sent to the final separation. A fraction of the unconverted gases is purged rather than being recirculated, to avoid accumulation of inert components. This stream is fed to a separator (PSA), with the goal of recovering as much hydrogen as possible to be recycled back to the process, achieving an increased conversion. The separation and purification of methanol is designed with two distillation columns, aiming to obtain a methanol stream that satisfies the required purity (Methanol grade AA: Methanol content > 99.85 %wt).

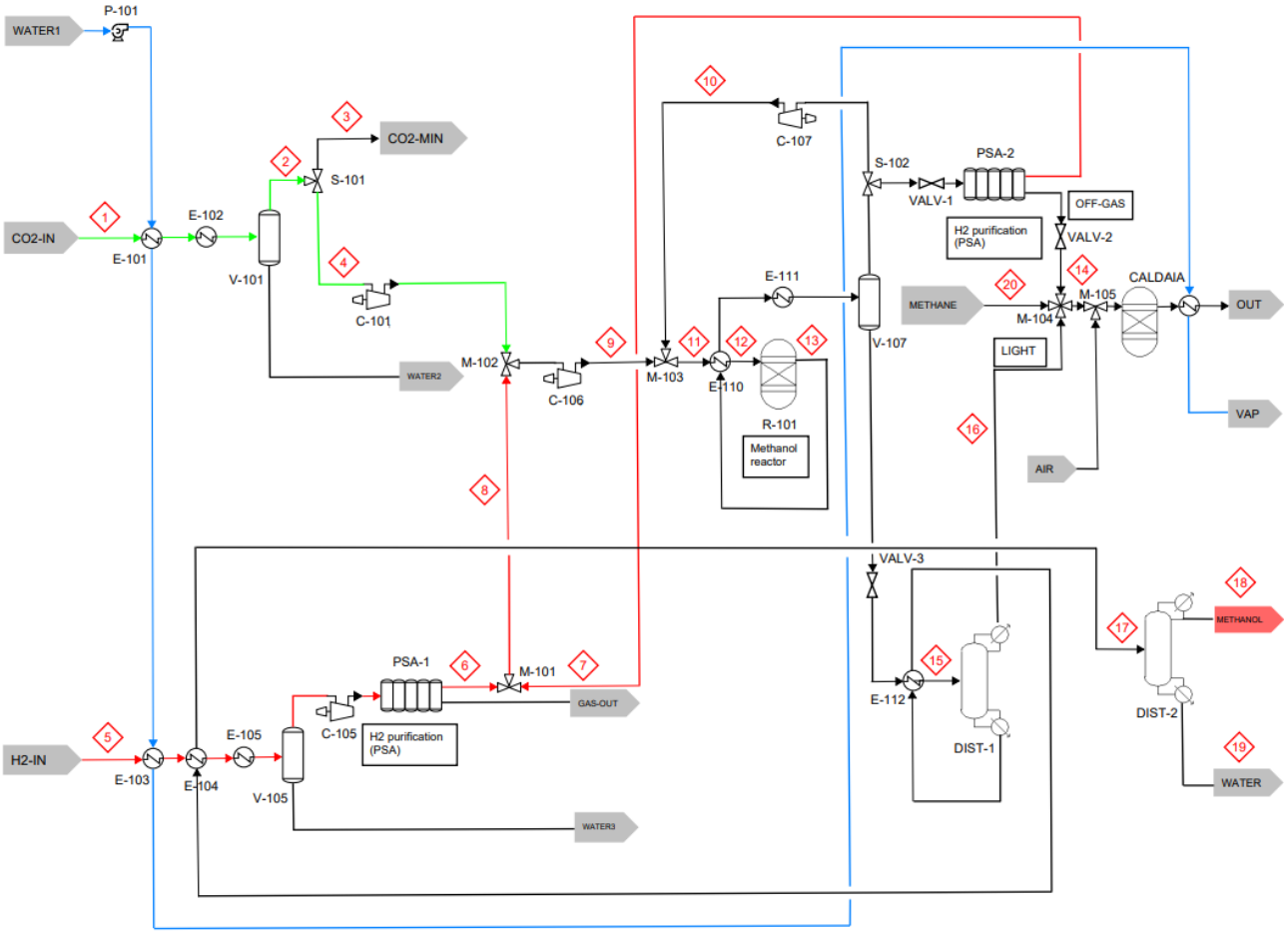
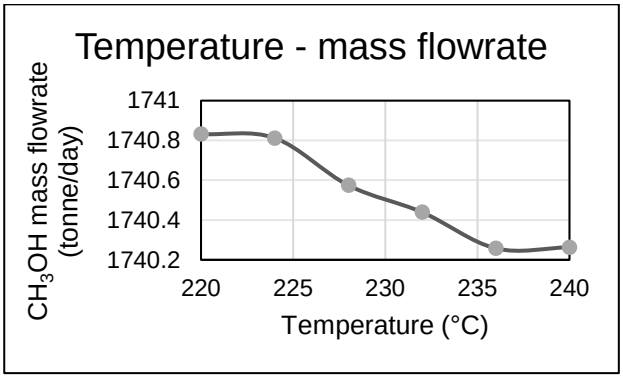


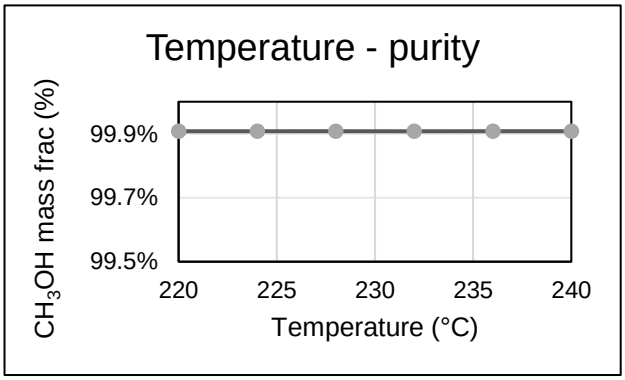
Figure 11. Process Flow Diagram of the Methanol Synthesis Plant.

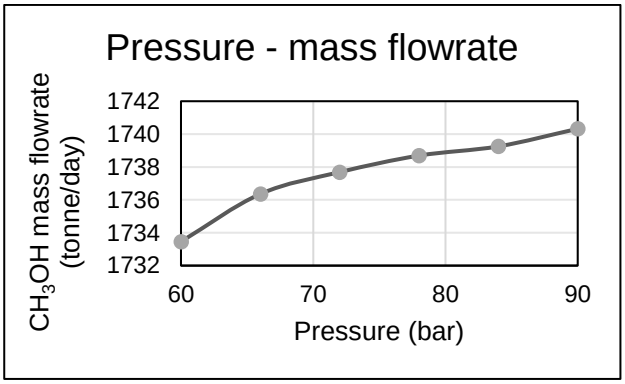
The process is optimized through some preliminary parametric sensitivities. In these sensitivities, temperature, pressure, OFF-GAS split fraction (amount of gas purged from the conversion loop), and methanol module (MM, see definition below), are varied.

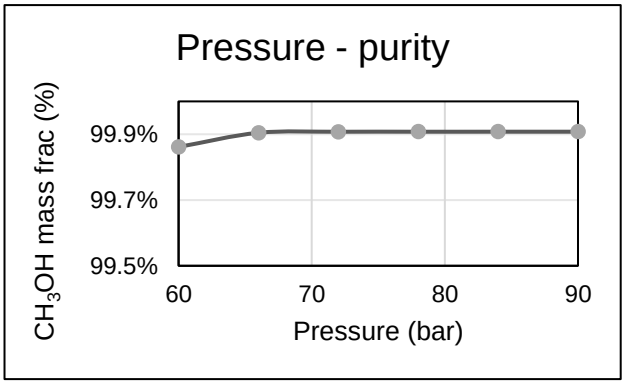
$$MM = \frac{H_2 - CO_2}{CO - CO_2}$$

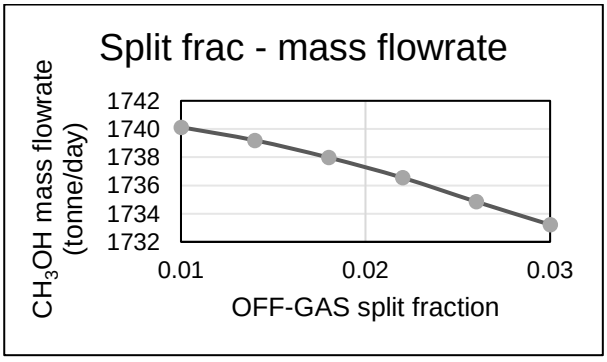
These parameters are varied within pre-defined ranges, specifically 220-240°C for temperature, 60-90 bar for pressure, 0.01-0.03 for split fraction, and 2-2.5 for methanol module. The sensitivities' objective is to maximize methanol productivity (mass flow rate of methanol calculated in ton/day) and its purity (mass fraction). Hence, minimization of resource intensity (e.g. energy consumption) or total costs are not yet considered in these calculations. The results of the analysis are shown below in the form of graphs:

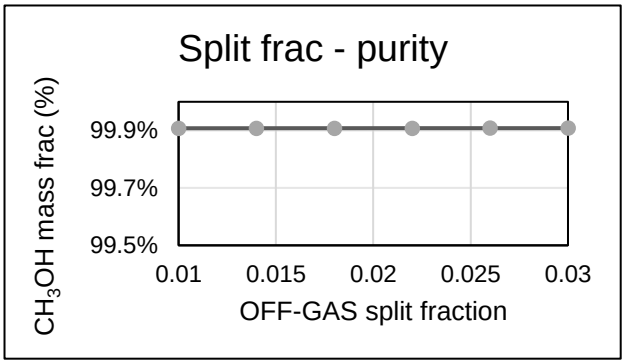


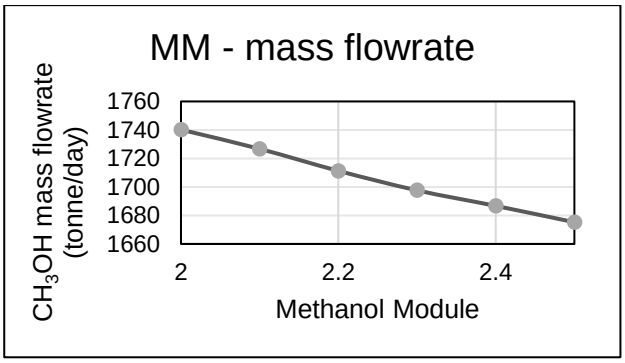


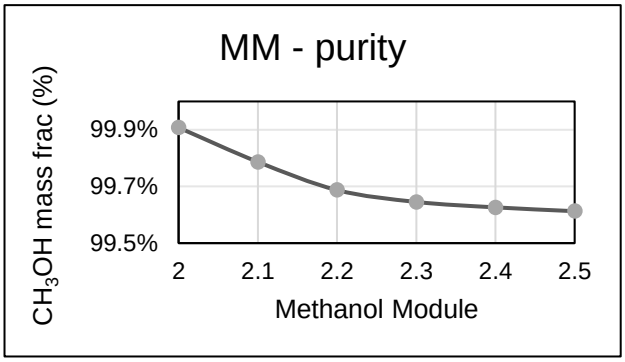












The optimization results in the following optimal operating conditions: T = 220 °C, P = 90 bar, OFF-GAS split fraction = 0.01, MM = 2. Thermal energy recovery is then implemented to improve the energy efficiency of the overall process. The largest residual thermal energy demands are those that are required to produce steam for CO conversion and CO_2 separation, respectively within the WGS and SEWGS units. Steam is generated through an initial preheating of water and partial vaporization by mean of heat recovery. Complete vaporization and superheating up to 400°C are then achieved using a fired steam generator, in which the combustion of the process off-gases (i.e. "LIGHT" and "OFF-GAS") and externally introduced methane takes place. This combustion is assumed to occur with an air-to-fuel ratio of 11.2, so to consider a 15% excess of air. The overall heat and mass balances of the plant are reported in the Table below. This Table shows flow rates and compositions of the main streams that are obtained from the simulation (Table 8). The flow rate of CO_2 that is sent to sequestration, by either CO_2 mineralization or storage (CO2-MIN) is 14,113.51 ton/day, while that which is exploited in the methanol synthesis process is 2,626.06 tonne/day. Thus, it is possible to say that about 84% of the CO_2 flow rate (CO_2-PURE) is sent to sequestration.

Table 8. Streams Table of the MeOH symbiotic use case.

	1: CO2-IN	2: CO2-PURA	5: H2-IN	6: H2MAKEUP	7: H2RECYCL	8: H2-PURO	9: MAKEUP	10: RECYCLE
Temperature (°C)	395.00	32.72	444.88	34.98	30.86	34.84	209.60	36.73
Pressure (bar)	1.30	0.70	16.90	33.90	36.80	33.90	90.20	90.20
Mass flow (tonne/day)	11847.02	8138.98	14216.88	469.26	18.27	487.53	3089.12	24954.06
Components	*Mass fraction (%)*							
CO_2	65.76%	95.71%	0.49%	0.15%	2.86%	0.25%	82.44%	20.73%
CO	0.03%	0.05%	1.44%	0.44%	0.25%	0.43%	0.11%	1.81%
H_2	0.04%	0.06%	2.97%	72.09%	57.78%	71.56%	11.35%	5.24%
N_2	1.25%	1.82%	83.75%	25.37%	9.13%	24.77%	5.47%	66.19%
CH_4	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
AR	0.00%	0.00%	0.06%	1.86%	0.46%	1.81%	0.29%	3.34%
NH_3	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
H_2O	32.92%	2.36%	11.27%	0.04%	0.71%	0.06%	0.17%	0.05%
O_2	0.00%	0.00%	0.00%	0.05%	28.73%	1.12%	0.18%	2.08%
CH_3OH	0.00%	0.00%	0.00%	0.00%	0.08%	0.00%	0.00%	0.55%

	12: REAC-IN	13: REAC-OUT	14: OFF-GAS	15: FEED-1	16: LIGHT	17: FEED-2	18: METHANOL	19: WATER
Temperature (°C)	220.00	250.00	22.62	83.50	67.49	99.67	65.07	113.07
Pressure (bar)	90.00	89.50	2.00	2.80	2.00	2.50	1.00	1.50
Mass flow (tonne/day)	28043.25	28043.25	233.79	2837.12	81.39	2755.73	1744.94	1010.79
Components	*Mass fraction (%)*							
CO_2	27.53%	18.77%	22.13%	1.38%	48.28%	0.00%	0.00%	0.00%
CO	1.62%	1.63%	1.93%	0.00%	0.04%	0.00%	0.00%	0.00%
H_2	5.91%	4.71%	1.13%	0.00%	0.09%	0.00%	0.00%	0.00%
N_2	59.51%	59.51%	70.65%	0.08%	2.77%	0.00%	0.00%	0.00%
CH_4	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
AR	3.01%	3.01%	3.57%	0.01%	0.47%	0.00%	0.00%	0.00%
NH_3	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
H_2O	0.06%	3.65%	0.00%	35.60%	0.39%	36.64%	0.09%	99.74%
O_2	1.87%	1.87%	0.00%	0.01%	0.31%	0.00%	0.00%	0.00%
CH_3OH	0.49%	6.86%	0.59%	62.91%	47.65%	63.36%	99.91%	0.26%

3.4. Power Generation from Ammonia

In this section the possibility to use BFG/BOFG derived ammonia as fuel for power generation is modelled. Ammonia is produced using as feedstock 45% of the H_2/N_2 product that is derived from the whole available BFG and BOFG from a 3.16 $Mton_{HRC}$/yr blast furnace plant. The steel gases are first compressed to 18 bar and then treated in a WGS section, adopting a split configuration sending to the first WGS reactor only 50% of the gas stream coming from the compressor. The steam requirement at the inlet of first WGS reactor is set equal to 3 mol_{H2O}/mol_{CO}, while for the second WGS reactor is 2 mol_{H2O}/mol_{CO}. The resulting overall steam requirement is equal to 1.55 mol_{H2O}/mol_{CO}. The inlet temperature is set to 320°C for both the reactors.

The H_2/N_2 rich stream coming from the SEWGS still contains some CO and CO_2. These are poisonous for the ammonia catalyst. Therefore, CO and CO_2 have to be converted to CH_4 in a methanation reactor. The inlet temperature of the methanator is set to 250°C. Downstream the methanator a membrane system is adopted to remove the nitrogen excess and reach the stoichiometric ratio of 3 between H_2 and N_2 that enables efficient ammonia synthesis. Once this ratio is reached, the gas stream is compressed to 330 bar to produce ammonia. The ammonia loop produces 860 ton_{NH3}/day. A storage of 573.3 ton_{NH3}, equivalent to continuous production over 16 hours is selected. The storage is at pressurized conditions (i.e. at 15 bar) and ambient temperature. The amount of ammonia stored per ton of steel used to build the vessel is estimated to be 2.8 ton_{NH3}/ton_{steel} [1].

An ammonia driven power generation through turbine technology is selected. Power generation is run on part of the produced ammonia, during low power demand period. In these periods, the rest of the ammonia is stored. During peak demand periods, power generation is run on the previously stored ammonia and the continuously produced amount. The selected gas turbine type is the heavy-duty H-25 series produced by Mitsubishi Heavy Industries. The required number of gas turbines is computed supposing to work at full capacity for 8 hours each day. The size of each gas turbine is 40 MW_e with a net efficiency of 36.2% in simple cycle [2]. Although the turbines are designed to work for 8 hours at full capacities, it is possible to operate them at partial load, while increasing the working hours, so that ultimately all the produced ammonia is converted to power and match the annual capacity of 550 GWhr/yr. The analysis is carried out supposing that each gas turbine can work between 60% and full load.

Table 9: Main design parameters of the WGS section and the SEWGS reactor

Parameter	Unit	Value
WGS_1 inlet temperature	[°C]	320
WGS_1 steam consumption	$[mol_{H2O}/mol_{CO}]$	3
WGS_2 inlet temperature	[°C]	328
WGS_2 steam consumption	$[mol_{H2O}/mol_{CO}]$	2
WGS_s overall steam consumption	$[mol_{H2O}/mol_{CO}]$	1.55
SEWGS Inlet pressure	[bar]	18
SEWGS Inlet temperature	[°C]	400
Purge consumption	$[mol_{H2O}/mol_{C)}]$	1.0
Purge pressure	[bar]	1.6
Purge temperature	[°C]	400
Rinse consumption	$[mol_{H2O}/mol_{C}]$	0.55
Rinse pressure	[bar]	18
Rinse temperature	[°C]	400

Table 10: Main design parameters of ammonia storage and power production section

Parameter	Unit	Value
Ammonia from production	[kg/s]	9.95
Storage size	$[t_{NH3}]$	573.3
Storage size	$[m^3]$	2,687
Storage pressure	[bar]	15
Gas turbine size	$[MW_{el}]$	40
Gas turbine efficiency	[%]	36.2

3.5. Direct Reduction Steelmaking

The direct reduction steelmaking process represents an alternative primary steel production route to the traditional BF/BOF route [3]. Solid primary iron (or direct reduced iron) is produced from iron ores through reducing gases in special furnaces, called shaft furnaces. The reducing gases are mainly produced from natural gas or coal reforming, and includes a mixture rich in CO and H_2. The direct reduced iron is then melted in electric arc furnaces to produce steel. Different processes have been developed which mainly differentiate on the basis of the type of furnace adopted. Among all the commercial available processes, the MIDREX represents the one with the largest market share, equal to the 60% in the 2020 [4]. For this reason, this process has been selected and is investigated in this work. For this study the ArcelorMittal Montreal plant, located in Contrecœur (Quebec), Canada, was selected as base case since real plant data are available in literature [5], [6]. The data used in this work are reported in Table 11 and in Table 12. In this work the size of the plant has been increased from 1 $Mton_{DRI}$/yr to 2.5 $Mton_{DRI}$/yr, which matches a hot rolled coil size of 2.03 $Mton_{HRC\text{-}DR}$/yr. Two main emissions points can be identified: the flue gas of the reformer and the electric arc furnace. About the flue gases, emissions are related to the utilization of the top gas as fuel to supply the heat necessary to the reforming reaction. The top-gas contains a relevant amount of CO and CO_2. Furthermore, some additional natural gas is provided as fuel to the reformer. As mentioned above, the other emission point is related to the electric arc furnace where the direct reduced iron is melted and further prepared for steel production. In any case, the main contribution to the direct emissions of the whole process is given by the flue gas of the reformer. The top gas, downstream the scrubber is divided into two streams; the one used as fuel for the reformer is roughly the 33% of the total, while the remaining part is recycled back and mixed with fresh natural gas in order to produce the reducing gases that is necessary for the reduction of the iron ore. The direct reduced iron then is sent to an electric arc furnace to be melted and produce steel.

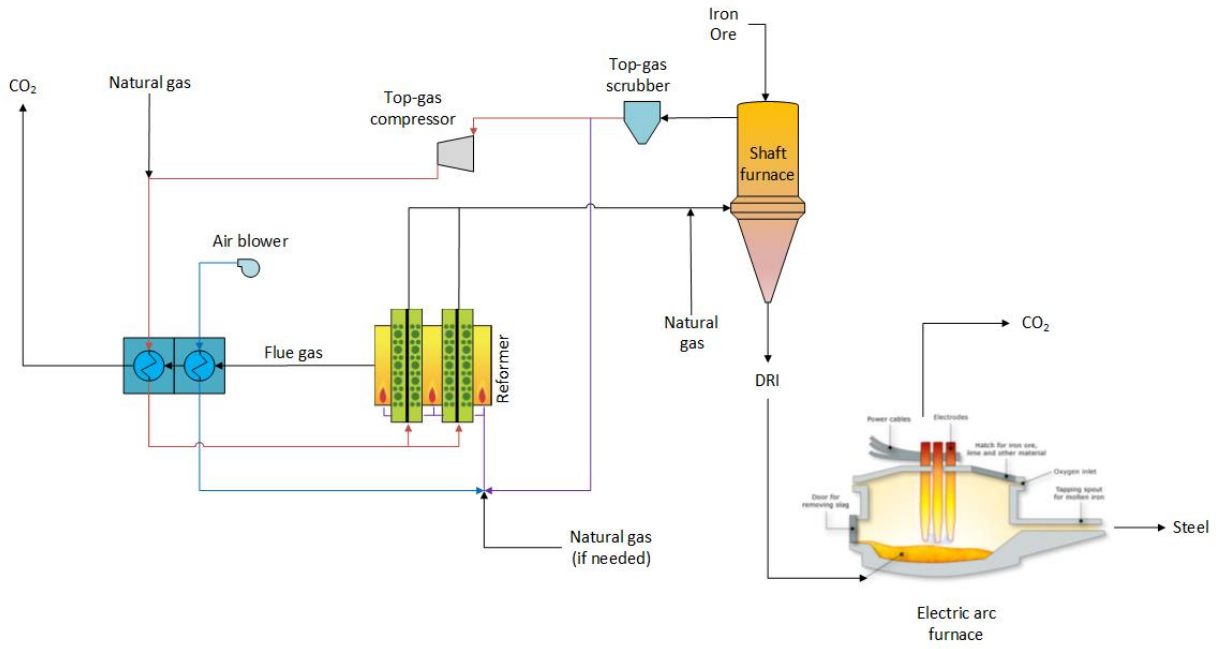


Figure 12. Conventional Direct Reduction (DR) plant scheme with electric arc furnace.

Table 11. Specifications of reducing gas, top gas and cooling gas

Stream	Temperature [°C]	Pressure [bar]	Mole flow rate [kmol/h]	Molar composition [%mol]					
				H_2	N_2	H_2O	CO	CO_2	CH_4
Reducing gas	957	n.a.	19,644	49.66	1.76	4.28	32.71	2.40	9.08
Top gas	285	1.42	21,690	40.28	1.02	19.03	19.58	17.09	2.95
Cooling gas	41	n.a.	4,515	13.42	0.78	3.20	4.30	2.40	75.90

Table 12. Specification of iron ore and bottom product

Stream	Temperature [°C]	Pressure [bar]	Mass flow rate [kg/s]	Mass composition [%]					
				Fe_2O_3	Fe_3O_4	FeO	Fe	C	Gangue
Iron ore	-10	1.013	113.85	96.65	0.00	0.00	0.00	0.00	3.35
DRI	n.a.	n.a.	82.7	0.00	0.00	7.47	85.72	2.00	4.71

3.6. Direct Reduction Steelmaking with CCS (DRP-CCS)

The top gas coming from the shaft furnace and then used as fuel for the reformer contains a high quantity of CO and CO_2. The direct reduction process can be decarbonized by shifting the CO to CO_2 in a WGS section and then capture the CO_2 in the SEWGS carbon capture section. The overall conversion achieved in the two WGS reactors adopted is equal to 68% with an overall steam to CO ratio equal to 1.7. A split configuration is adopted with only 37% of the gas sent to the first WGS reactor. The products of the first reactor are then mixed with the remaining top gas and sent to the following WGS reactor to complete the conversion. The inlet temperature of the first WGS reactor is set to 320°C while at the inlet of the second one is set to 340°C. The CO molar fraction at the inlet of the SEWGS is equal to 5.3% since the WGS reaction take place also in the SEWGS reactor. Before being shifted, the top gases are compressed to the operating pressure of WGS and SEWGS reactors. The SEWGS reactor produces a H_2/N_2 mixture and a high-purity CO_2 stream. The water present in this stream is condensed and then removed. The CO_2-rich stream is compressed up to 78 bar in a multistage compressor, liquefied being cooled to 25°C and pumped to 110 bar for sequestration. The H_2 rich stream is then used as clean fuel in the reformer. The H_2/N_2 mixture before to be sent to the reformer and used as fuel is expanded to a pressure slightly higher than the atmospheric one producing in this way electricity. SEWGS operating conditions, in terms of inlet pressure and temperature, purge and rinse consumption, are summarised in Table 13.

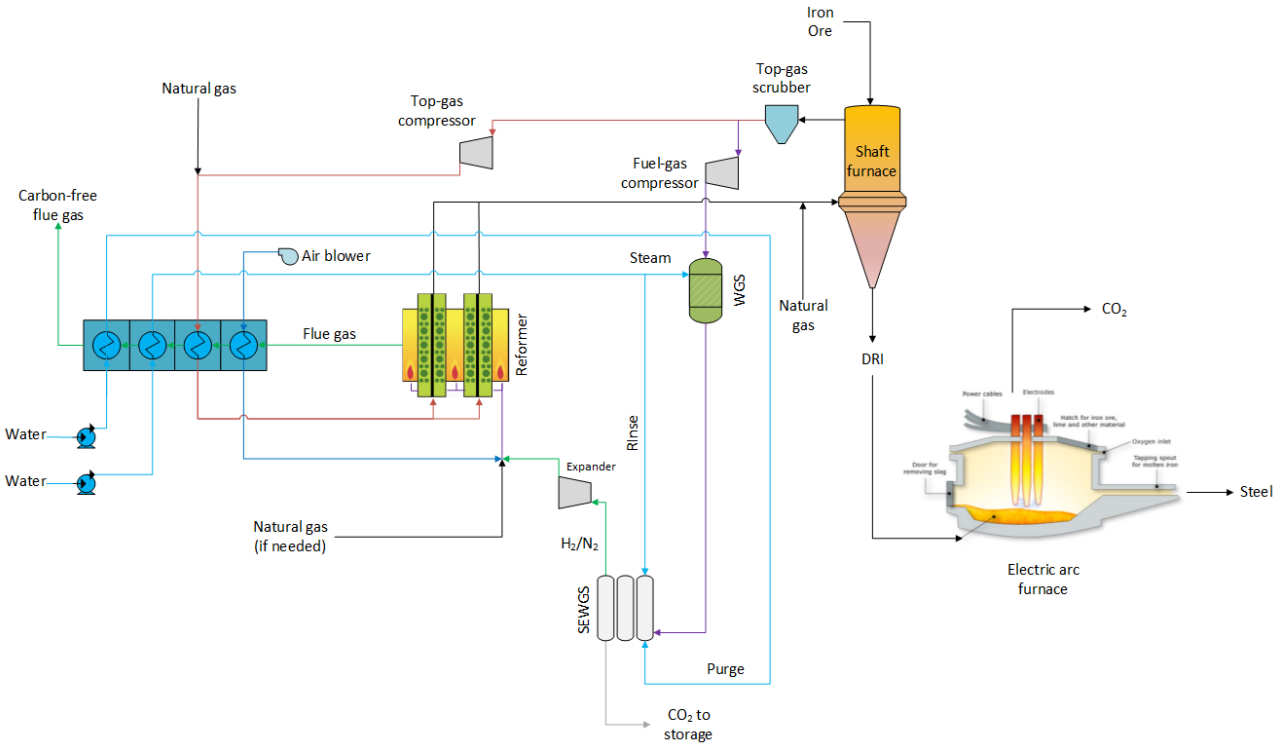


Figure 13. Direct Reduction (DR) plant scheme with SEWGS pre-combustion carbon capture section (DRP-CCS) and electric arc furnace.

Table 13. SEWGS operating conditions for the DRP-CCS case.

Parameter	Unit	Value
SEWGS Inlet pressure	[bar]	18
SEWGS Inlet temperature	[°C]	400
Purge consumption	[mol_{H2O}/mol_C]	0.8
Purge pressure	[bar]	1.4
Purge temperature	[°C]	400
Rinse consumption	[mol_{H2O}/mol_C]	0.29
Rinse pressure	[bar]	18
Rinse temperature	[°C]	400

The plant that is described above is simulated in Aspen Plus V11, except for the electric arc furnace whose performances are taken from the literature [7], [8]. The model is calibrated to match the composition and the temperature of the reducing gas at the inlet of the shaft furnace that is available from literature. In addition, the shaft furnace has been modelled to reproduce the conditions of the top-gas as close as possible to the available plant data. The model of the reformer has been built by adopting a RGibbs reactor, to simulate the steam reforming reaction, and a RStoic reactor to simulate the burner. The shaft furnace has been simulated mainly with RGibbs and RStoic reactors in order to mimic the reactions occurring in it. The power consumption of the electric arc furnace and the one of the rolling process considered in this work are taken from literature. The first one is equal to 400 kWh/ton_{HRC} [7] while the latter is equal to 110 kWh/ton_{HRC} [9]. The direct emissions of the electric arc furnace are considered equal to 0.1 ton_{CO2}/ton_{HRC} [8] while the ones related to the iron ore production are computed according to the carbon footprint associated with the electricity production and based on values found in [10]. The primary energy consumption of the pellets production, used to compute the PEC of the whole direct reduction process is equal to 2.58 GJ/ton_{HRC} [7].

Table 14: Assumptions for the thermodynamic assessment

Parameter	Unit	Value
EAF electric consumption	kWh/ton_{HRC}	400
Rolling process electric consumption	kWh/ton_{HRC}	110
EAF direct emissions	ton_{CO2}/ton_{HRC}	0.1
Iron ore production direct emissions ($C.I._{elec}$ = 0.3 kg_{CO2}/kWh)	ton_{CO2}/ton_{HRC}	0.072
Iron ore production direct emissions ($C.I._{elec}$ = 0.9 kg_{CO2}/kWh)	ton_{CO2}/ton_{HRC}	0.129
PEC of pellets production	GJ/ton_{HRC}	2.58

3.7. BF-2-DRP Hybrid Steelmaking with CCS (BF-2-DRP)

In this section the symbiosis between a direct reduction plant and a blast furnace steel mill is described. The residual steel gas, i.e. BOFG and BFG, available from the blast furnace steel mill, are threated in a gas conditioning section (i.e. pre-WGS and SEWGS) in order to produce an H_2 rich stream that can be used both as fuel for the reformer of the direct reduction plant, and to produce the steam necessary for the reaction of WGS and for the carbon capture step that takes place in the SEWGS reactor. Additionally, the H_2/N_2 stream in excess is sent back to the still mill to cover as much as possible the heat demand. The fraction of the shaft furnace top-gases that are normally used as fuel in the reformer, are mixed with the WGS outlet gas stream and sent to the SEWGS reactor, completing the shifting of CO into CO_2 and capturing the CO_2. Two WGS reactors are adopted with the first one treating only 50% of the mixture coming from the blast furnace steel mill. The overall H_2O/CO ratio is equal to 1.55. Since all the available BOFG and BFG are processed by SEWGS, no electricity is produced internally, meaning that all the power necessary to run the blast furnace still mill has to be imported from a NGCC or the grid. Further assumptions regarding the WGS section and the SEWGS reactor are summarised in Table 15.

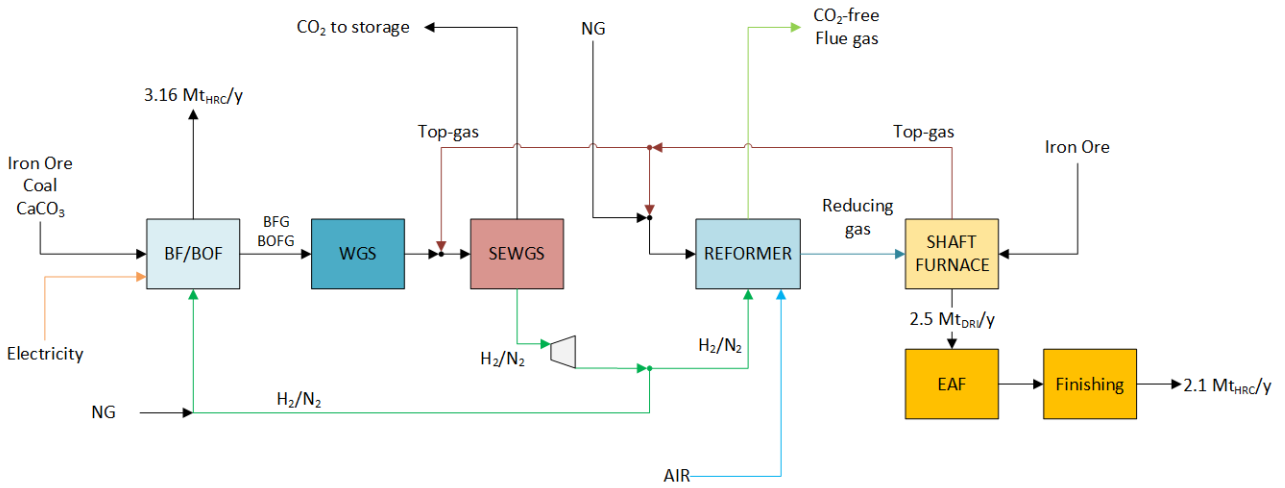


Figure 14. Flowsheet of BF-2-DRP hybrid steelmaking case. H_2/N_2 product is used to replace part of the BFG and BOFG in the BF plant, as well as the totality of the reforming fuel in the DR plant.

The above-described process is simulated in Aspen Plus V11.1 with RKS-BM method, excluding the blast furnace steel mill. The WGS reactors are simulated in Aspen Plus as adiabatic reactors adopting REquil model. The overall CO conversion into CO_2 is 82.5% with a molar concentration of CO in gas stream at the outlet of the second WGS reactor equal to 3%. The inlet temperature of the second WGS reactor is controlled with a heat exchanger that is placed upstream and it is set in order to have a temperature at inlet of the SEWGS equal to 400°C. The SEWGS operation is optimized by using a proprietary cycle model developed by TNO, as described before [11], [12], [13]. These results are then incorporated into Aspen Plus by adopting a calculator and some other native equipment simulating blocks. The CO molar concentration at inlet of the SEWGS is equal to 5.3% since the gas stream from the WGS section is mixed with part of the top-gas from the shaft furnace that contains a certain amount of unreacted CO. Regarding the direct reduction steelmaking section, the assumptions adopted are the ones that are described in previous sections.

Table 15: Main design parameters of the WGS section and the SEWGS reactor

Parameter	Unit	Value
WGS_1 inlet temperature	[°C]	320
WGS_1 steam consumption	[mol_{H2O}/mol_{CO}]	3
WGS_2 inlet temperature	[°C]	328
WGS_2 steam consumption	[mol_{H2O}/mol_{CO}]	2
WGS_s overall steam consumption	[mol_{H2O}/mol_{CO}]	1.55
SEWGS Inlet pressure	[bar]	18
SEWGS Inlet temperature	[°C]	400
Purge consumption	[$mol_{H2O}/mol_{C)}$]	1.2
Purge pressure	[bar]	1.6
Purge temperature	[°C]	400
Rinse consumption	[mol_{H2O}/mol_{C}]	0.49
Rinse pressure	[bar]	18
Rinse temperature	[°C]	400

3.8. CO_2 Mineralization

The mineralization process is an alternative method to classic geological confinement for storing carbon dioxide. Unlike the traditional process, the mineral carbonation is the only known process of permanent storage and the storage capacity of this process is higher. In addition, the produced carbonates are environmentally benign and reusable for many applications, such as building materials, fertilizers, paper and paint industry. The process also has drawbacks, especially the low reaction rate, caused by the formation of carbonates layers and calcium and magnesium depleted silicate zones during the carbonation process, which leads to hinder calcium and magnesium leaching from steel slags and CO_2 diffusion to the surface of unreacted phases. Another negative aspect is represented by the high costs associated with pre-treatments, such as grinding, necessary to reach good results in terms of carbonation efficiency. Also, there is the limitation linked to the ability to separate the products from the unreacted material so that they can be easily exploited for the applications mentioned above. Studies are currently in progress related to this aspect. Mineral carbonation process can be based on both natural minerals and industrial wastes, such as steel mill slags. One the one hand, exploiting residual slags as feed guarantees: low or zero cost availability, since they come directly from industrial emissions, the possibility to reduce grinding, because they are generally characterized by smaller solid particles sizes, and a greater reactivity to less energy-intensive operative conditions. On the other hand, industrial wastes are less available than natural minerals. Among the different options available, it was considered that the most efficient approach was provided by the aqueous phase direct carbonation process, in which both the dissolution step of calcium and magnesium ions in the aqueous medium (leaching step) and the actual precipitation of carbonates (carbonation step) take place in a single reactor. Between the possibility of using a slurry approach, characterized by liquid-to-solid ratios greater than one, and a wet approach, with ratios less than one, the former method was selected, as it seems to be the most complete and the most discussed in the literature. The scheme in Figure 15 was identified as a possible process scheme: A literature study was carried out, and from the various articles reviewed, the results obtained in terms of carbon capture under varying operating conditions and feed material were evaluated. A comparison was also made between a process in which pure CO_2 was used and one in which it was present in a gaseous mixture, with a concentration of 40% to emulate a syngas coming directly from industrial emissions. The achieved results showed that very similar performances were obtained in terms of carbonation degree, suggesting that it is indeed possible to avoid the CO_2 capture step before the process, considering that is very energy intensive. Prominent among the various experimental analyses gathered from literature research is the result derived from the mineralization of the natural minerals olivine, serpentine and wollastonite in a study by O'Connor et al. (2005) [14]. Leaving aside the results obtained for serpentine, as the need for thermal pre-treatment to make it active requires an excessive energy contribution, the information derived for the other two minerals seems promising. Taking as feed to the process an olivine with a composition of 88.7% in Mg2SiO4 and 11.3% in Fe2SiO4, a carbonation degree of 81% was achieved by using the following operating conditions: d_0 (initial solid particle diameter) = 20 mm; d_1 (diameter after grinding) = 0.037 mm; T = 458 K; p_{CO2} = 15 MPa; L/S = 5.7 l/kg; t = 1 h. For the derived carbonation efficiency, it is necessary to introduce to the process an amount of mineral equal to 2.22 ton/ton$_{CO2}$ to be removed. Similar results were obtained with wollastonite, with 100% $CaSiO_3$ composition, with small variations in operating conditions. Taking as reference the articles "*Mineral carbonation and industrial uses of carbon dioxide*" and "*A review on ex situ mineral carbonation*", average process costs were estimated excluding those from CO_2 capture (of which can be assumed a cost of \$15/ton$_{CO2}$ treated to achieve 85% CO_2 purity) [15, 16]. The average economic demand for the case of olivine is around

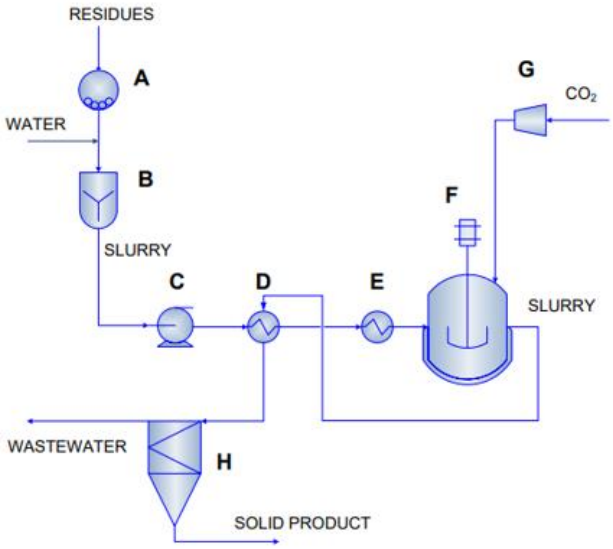


Figure 15. The main operating units are grinding (A), mixing (B), pumping (C), heat recovery (D), heating (E), reactor (F), compression (G), separation (H). [19]

$59/ton$_{CO2}$ removed, increasing to $64/ton$_{CO2}$ in the case of wollastonite. In addition, the energy requirements associated with the processes are about 640 kWh/ton$_{CO2}$ and 430 kWh/ton$_{CO2}$, respectively. Regarding the analyses performed on steel mill slags as material fed to the mineralization process, the present analysys has been focusses on BOF slag, as interesting with respect to the studied cases. Based on the results obtained from the study of Huijen et al. (2005) [17], it is stated that it is possible to achieve a carbonation efficiency of 75.6%, with a residue composition characterized by 56.8% CaSiO3, 7.7% CaCO3 and 35.5% FeO, and using the following operating conditions: d_0 = 20 mm; d_1 = 0.052 mm; T = 423 K; p_{CO2} = 1.9 MPa; L/S = 10 l/kg; t = 0.5 hr. For the derived carbonation efficiency, it is necessary to introduce to the process an amount of mineral equal to 6.143 t/t$_{CO2}$ to be removed. Even in this case, by exploiting the information derived from the articles "*A review on ex situ mineral carbonation*" and "*Development of a new pH-swing CO_2 mineralization process with a recyclable reaction solution*", average process costs and energy requirements were estimated, excluding those from CO_2 capture. Respectively they are $64/ton$_{CO2}$ and about 300 kWh/ton$_{CO2}$ [16, 18]. Taking advantage of the data obtained from the methanol synthesis simulation regarding the amount of CO_2 that must be sent to mineralization (5,479.56 tonne/day), it is possible to identify a material balance of the components involved. The use of olivine as a natural mineral, and BOF slag as a solid waste, are examined as reference cases. Taking into consideration the values associated with the energy required in the process reported earlier from the literature, it is possible to obtain the following results:

Table 16. Material balances of the two CO_2 mineralization processes that are considered.

MASS BALANCE				
Olivine				
d_0 (mm)	d_1 (mm)	T (K)	p_{CO2} (MPa)	L/S (kg/kg)
20	0.037	458	15	5.7
Mineral amount per tons of removed CO_2 (ton/ton$_{CO2}$)	2.22			
CO_2 sent to mineralization (ton$_{CO2}$/hr)	228			
Mineral to mineralization (ton$_{Olivine}$/hr)	507			
Water consumption (ton$_{H2O}$/hr)	2,889			
BOF slag				
d_0 (mm)	d_1 (mm)	T (K)	p_{CO2} (MPa)	L/S (kg/kg)
20	0.052	423	1.9	10
Mineral amount per tons of removed CO_2 (ton/ton$_{CO2}$)	6.14			
CO_2 sent to mineralization (ton$_{CO2}$/h)	228			
Slag to mineralization (ton$_{Slag}$/h)	1,403			
Water consumption (ton$_{H2O}$/h)	14,025			

Table 17. Energy demands of the two CO_2 mineralization approaches.

ENERGY BALANCE	
Olivine	
Required energy per tons of removed CO_2 (kWhr/ton$_{CO2}$)	640
Primary energy consumption (GW_{th})	0.15
BOF slag	
Required energy per tons of removed CO_2 (kWhr/ton$_{CO2}$)	300
Primary energy consumption (GW_{th})	0.07

4. Case Specific Results

4.1. Urea Synthesis

The raw material consumption, the CO_2 emissions, the primary energy consumption and the relative KPIs are reported in Table 18, in Figure 16 and Figure 17. Interestingly, the symbiotic case allows to reduce CO_2 emissions, but increases electricity import from 3 to 383 MW_{el}. To further investigate this trade-off, results are computed for two different scenarios. In the first one, it is assumed to import electricity from the grid with a carbon footprint of 250 kg_{CO2}/MWh. In the second scenario, it is supposed the electricity is generated by emissions free sources, i.e. zero carbon scenario. The PEC related to electricity is considered equal to zero in the zero-carbon scenario since no fossil fuels are consumed. As can be seen from the graphs, the SPECCA of the symbiotic system varies from 2.7 to less than zero. A negative SPECCA is achieved because natural gas consumption is reduced, although the overall electricity import is increased. This increased electricity import occurs because the steel plant power demand is not covered anymore by BFG/BOFG combustion, but also because all the BFG and BOFG available need now to be compressed to the operating pressure of the water gas shift reactor. In addition, the nitrogen present in excess in the BFG contributes to increasing the power consumption of the INITIATE plant, without contributing to the synthesis of ammonia or to other processes. For this reason, when a zero-carbon scenario is considered, having a PEC of electricity equal to zero, the SPECCA of the INITIATE plant becomes negative being the PEC of the INITIATE plants lower than the PEC of the base case. This means that the symbiotic configuration allows to reduce the primary energy consumption (i.e. natural gas) while reducing the CO_2 emissions. The Carbon Avoidance varies from 67%, for the worst case scenario, to 80% for the zero-carbon scenario corresponding to annual saving of 4.40 and 5.21 Mt_{CO2} respectively.

Table 18. Import and export of base case and INITIATE plant

Parameter	Unit	Ref. System	INITIATE symbiotic case
Coal import	ton/day	6,240	6,240
Natural gas import	ton/day	602	553
Electricity import	MW_{el}	3	383
Steel production	ton/day	9,249	9,249
Urea production	ton/day	1,500	1,500

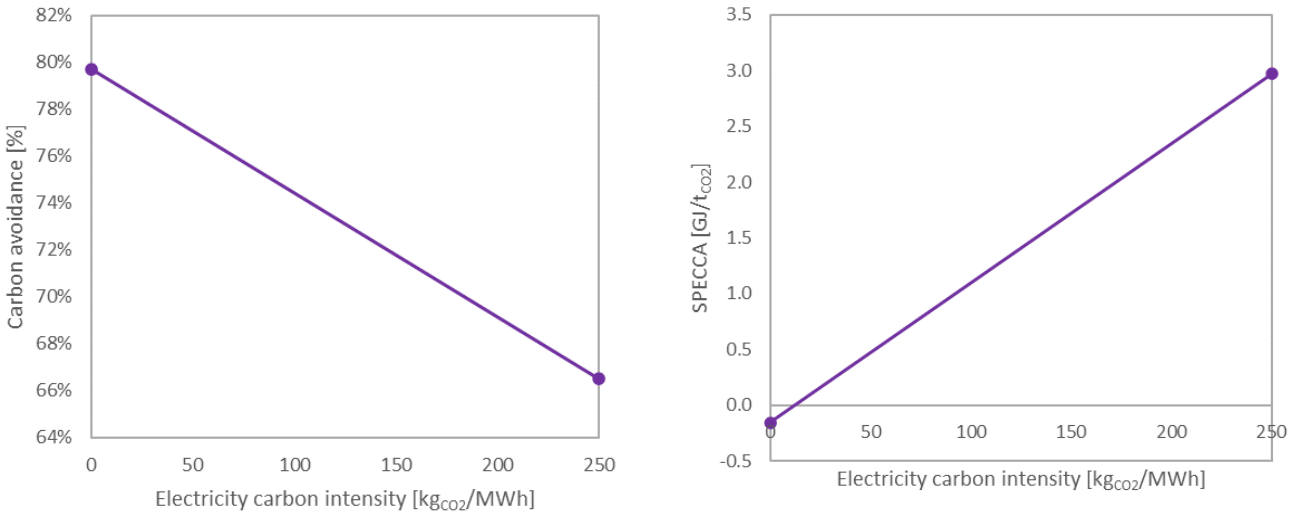


Figure 16. Carbon Avoidance and SPECCA of the Urea H_2/N_2 use case for different values of electricity carbon footprint.

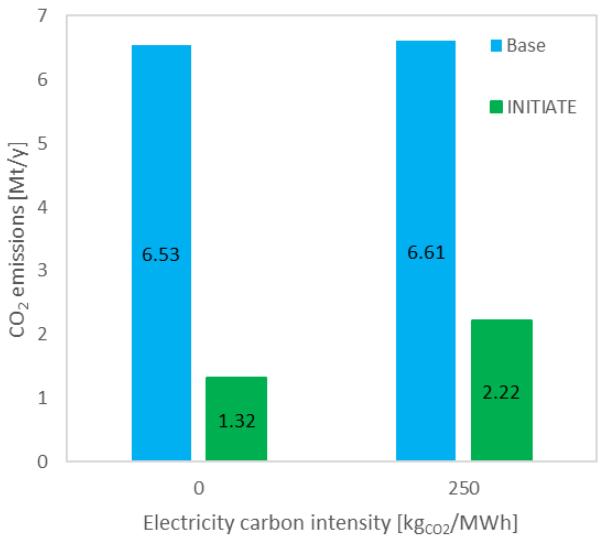


Figure 17. CO_2 annual emissions of the reference system (Base, blue) and the H_2/N_2 Urea symbiotic use case (INITIATE, green). Two scenarios based on importing power from a low-carbon (250 kg_{CO2}/MWh) and zero-carbon (0 kg_{CO2}/MWh) are evaluated.

In addition to the results presented above, the relative carbon emissions and PEC are reported in Table 19. In this case the carbon footprint of the electricity imported from the grid is equal to 350 kg_{CO2}/MWh_e. As can be observed the symbiotic system allow to reduce the emissions by 61.3% while increasing the PEC by 25.13%. The computed SPECCA is then equal to 4.57.

Table 19. KPIs for the Urea synthesis symbiotic H_2/N_2 use case. FU = 3.16 $Mton_{HRC-BF}$/yr.

GHG Emission Intensity	Symbol	Value	Unit
Initiate steelmaking emissions	$e_{IN,SM}$	0.26	ton_{CO2}/ton_{HRC-BF}
Initiate process emissions (urea)	$e_{IN,P}$	0.18	ton_{CO2}/ton_{HRC-BF}
Replacements emissions	e_{RP}	0.31	ton_{CO2}/ton_{HRC-BF}
CO_2 storage emissions	$e_{T\&S}$	0.06	ton_{CO2}/ton_{HRC-BF}
Symbiotic system emissions	e_{SS}	0.81	ton_{CO2}/ton_{HRC-BF}
Reference steelmaking emissions	e_{RSM}	2.05	ton_{CO2}/ton_{HRC-BF}
Secondary product emissions	e_{SP}	0.05	ton_{CO2}/ton_{HRC-BF}
Reference system emissions	e_{RS}	2.10	ton_{CO2}/ton_{HRC-BF}
Carbon Avoidance	**CA'**	**1.29**	**ton_{CO2}/ton_{HRC-BF}**
Relative Carbon avoidance	**CA**	**61.30**	**%**
Primary Energy Consumption		**Value**	**Unit**
Initiate process PEC	$PEC_{IN,SM}$	24.59	GJ/ton_{HRC-BF}
Replacements PEC	PEC_{RP}	5.38	GJ/ton_{HRC-BF}
CO_2 transport and storage PEC	$PEC_{T\&S}$	1.05	GJ/ton_{HRC-BF}
Symbiotic system PEC	PEC_{SS}	31.02	GJ/ton_{HRC-BF}
Reference steelmaking PEC	PECRSM	21.93	GJ/ton_{HRC-BF}
Secondary product PEC	PEC_{SP}	3.20	GJ/ton_{HRC-BF}
Reference system PEC	PEC_{RS}	25.13	GJ/ton_{HRC-BF}
Energy penalty	**EP'**	**5.89**	**GJ/ton_{HRC-BF}**
Relative energy penalty	**EP**	**23.4**	**%**
Specific PEC per Carbon Avoided	**SPECCA**	**4.57**	**GJ/ton_{CO2}**

4.2. Methanol Synthesis

In the GHG emission intensity, we considered the contributions that are presented in Equations Equation 1 to Equation 5. All emission rates are computed as annual emission rates and related to the functional unit (3.16 $Mton_{HRC}$/yr) to achieve the emission intensity values '*e*'. The **carbon avoidance (CA')** is computed through the difference between the emission intensity of the symbiotic system (e_{SS}) and the emission intensity of the reference system (e_{RS}). The first term consists of three contributions: the emission intensity that is still related with BF steelmaking in the symbiotic case (e.g. due to losses, COG use and lime processing), which go under the name of initiate steelmaking emissions intensity ($e_{IN,SM}$); the emissions intensity due to CO_2 transport and storage ($e_{T\&S}$); the emissions intensity due to thermal/electric power use in the INITIATE process and those associated with its process effluents, like purged gas ($e_{IN,P}$); the emissions intensity that is associated with the thermal/electric use of natural gas to meet steelmaking demands that were originally met by BFG/BOFG use (e_{RP}). The second term in the CA' definition, namely the emissions intensity of the reference system (e_{RS}) includes two contributions: 1) the emissions intensity from the reference steel mill in the non-symbiotic case (e_{RSM}), and the emissions intensity due to methanol production in the scenario where residual steel mill gases were not reused for its synthesis (e_{SP}). This last emissions are related to the size of the plant under consideration (i.e. 1741.82 ton_{MeOH}/day). The resulting value of the avoided emissions is –1.05 ton_{CO2}/ton_{HRC}. In addition, we determine the **relative carbon avoidance (CA)** as the ratio of carbon avoidance and the emissions intensity of the reference system. The resulting value is 49,30%. A similar procedure is used to calculate the PEC. We assume an efficiency of 60% for the conversion from electrical energy to primary energy, and a combustion efficiency of 92% for the conversion from thermal energy to primary energy. In this case we focus on the calculation of the **energy penalty (EP').** This parameter is derived as the difference between the PEC of the symbiotic system ($PEC_{IN,SM}$) and the PEC of the reference system (PEC_{RS}). The result is 8.87 GJ/ton_{HRC}. Then, the **relative energy penalty (EP)** is obtained as the ratio of the energy penalty and the PEC of the reference system. Its value is equal to 32.16%. Another parameter that is included in this section is the **SPECCA**. This is given by the ratio of the energy penalty and the avoided emissions, and is 8.42 GJ/ton_{CO2}.

Table 20. KPI's for the Methanol synthesis symbiotic H_2/N_2 use case. FU = 3.16 $Mton_{HRC}$-BF/yr.

GHG Emission Intensity	Symbol	Value	Unit
Initiate steelmaking emissions	$e_{IN,SM}$	0.26	ton_{CO2}/ton_{HRC-BF}
Initiate process emissions (methanol)	$e_{IN,P}$	0.42	ton_{CO2}/ton_{HRC-BF}
Replacements emissions	e_{RP}	0.35	ton_{CO2}/ton_{HRC-BF}
CO_2 storage emissions	$e_{T\&S}$	0.05	ton_{CO2}/ton_{HRC-BF}
Symbiotic system emissions	e_{SS}	1.08	ton_{CO2}/ton_{HRC-BF}
Reference steelmaking emissions	e_{RSM}	2.05	ton_{CO2}/ton_{HRC-BF}
Secondary product emissions	e_{SP}	0.09	ton_{CO2}/ton_{HRC-BF}
Reference system emissions	e_{RS}	2.13	ton_{CO2}/ton_{HRC-BF}
Carbon Avoidance	**CA'**	**-1.05**	**ton_{CO2}/ton_{HRC-BF}**
Relative Carbon avoidance	**CA**	**49.30**	**%**
Primary Energy Consumption		**Value**	**Unit**
Initiate process PEC	$PEC_{IN,SM}$	7.28	GJ/ton_{HRC-BF}
Replacements PEC	PEC_{RP}	6.25	GJ/ton_{HRC-BF}
CO_2 transport and storage PEC	$PEC_{T\&S}$	0.99	GJ/ton_{HRC-BF}
Symbiotic system PEC	PEC_{SS}	14.52	GJ/ton_{HRC-BF}
Reference steelmaking PEC	PECRSM	21.93	GJ/ton_{HRC-BF}
Secondary product PEC	PEC_{SP}	5.65	GJ/ton_{HRC-BF}
Reference system PEC	PEC_{RS}	27.58	GJ/ton_{HRC-BF}
Energy penalty	**EP'**	**8.87**	**GJ/ton_{HRC-BF}**
Relative energy penalty	**EP**	**32.16**	**%**
Specific PEC per Carbon Avoided	**SPECCA**	**8.42**	**GJ/ton_{CO2}**

4.3. Power Generation from Ammonia

In this section those results that regard the ammonia to power case are presented. The system have been designed to work at full capacity for 8 hours. The storage can be filled in 16 hours diverting all the ammonia production to the storage.

5 NH_3-fueled gas turbines of 40 MW_e each can be installed. The resulting size of the storage is 573.3 t_{NH3} or 2687 m^3. The estimated construction steel necessary for the storage is 205 ton_{steel}.

The analysis is carried out supposing that each gas turbine can work between 60% and full load. This means that the power produced by the system can vary from 24 MW_e (one turbine working at 60%) to 200 MW_e (all the turbines working at full load).

In the case of producing 200 MW_e, the storage is emptied is 8 hours. Taking into account the 16 hours to fill completely the storage, a complete cycle lasts 24 hours.

Working at partial loads leads to a different duration of a cycle. Indeed if less than 200 MW_e are generated, the storage is emptied in more than 8 hours, increasing the duration of a cycle. This is true till 67 MW_e (i.e. one turbine working at full load and one at 67.5%).

When less than 67 MW_e are generated, the ammonia produced is more than ammonia used to run the turbine(s), meaning that the level in the storage will increase.

The hours to empty the storage, the duration of a complete cycle and the capacity factor are shown in the following figure. The INITIATE capacity factor is defined as the ratio between the working hours and the plant availability in one year (i.e. 8200 h). The lower value represented on x-axis is equal to 80 MW_e in order to appreciate the curves. The closer to 67 MW_e, the higher the number of hours to empty the storage and consequently the higher the duration of a cycle. The capacity factor, as has been defined, will approach the value of 1 when generating 67 MW_e.

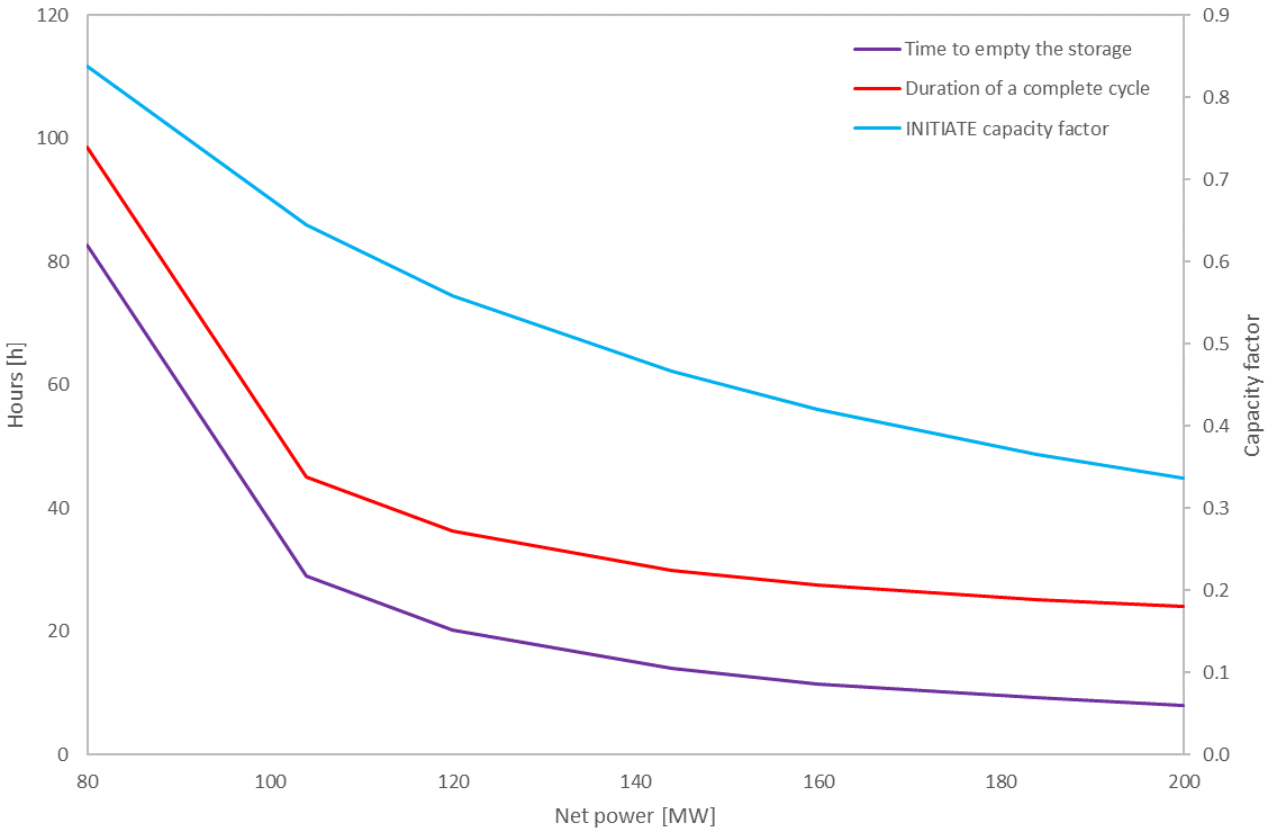


Figure 18. Hours to empty the storage, duration of a complete cycle, capacity factor as function of net power generated

The relative carbon emissions and PEC are reported in Table 21. The power generation from ammonia is compared to a NGCC having a carbon footprint of 350 kg_{CO2}/MWh_{el}. As can be observed the symbiotic system allow to reduce the emissions by 62.4% while increasing of the PEC by 33.3%. The computed SPECCA is then equal to 5.81 GJ/t_{CO2}.

Table 21. KPI's for the A-2-P symbiotic H_2/N_2 use case. FU = 3.16 $Mton_{HRC-BF}$/yr.

GHG Emission Intensity	Symbol	Value	Unit
Initiate steelmaking emissions	$e_{IN,SM}$	0.26	ton_{CO2}/ton_{HRC-BF}
Initiate process emissions (power generation)	$e_{IN,P}$	0.18	ton_{CO2}/ton_{HRC-BF}
Replacements emissions	e_{RP}	0.28	ton_{CO2}/ton_{HRC-BF}
CO_2 storage emissions	$e_{T\&S}$	0.07	ton_{CO2}/ton_{HRC-BF}
Symbiotic system emissions	e_{SS}	0.79	ton_{CO2}/ton_{HRC-BF}
Reference steelmaking emissions	e_{RSM}	2.05	ton_{CO2}/ton_{HRC-BF}
Secondary product emissions	e_{SP}	0.06	ton_{CO2}/ton_{HRC-BF}
Reference system emissions	e_{RS}	2.11	ton_{CO2}/ton_{HRC-BF}
Carbon Avoidance	**CA'**	**1.32**	**ton_{CO2}/ton_{HRC-BF}**
Relative Carbon avoidance	**CA**	**62.4**	**%**
Primary Energy Consumption		**Value**	**Unit**
Initiate process PEC	$PEC_{IN,SM}$	24.58	GJ/ton_{HRC-BF}
Replacements PEC	PEC_{RP}	4.92	GJ/ton_{HRC-BF}
CO_2 transport and storage PEC	$PEC_{T\&S}$	1.13	GJ/ton_{HRC-BF}
Symbiotic system PEC	PEC_{SS}	30.62	GJ/ton_{HRC-BF}
Reference steelmaking PEC	PECRSM	21.93	GJ/ton_{HRC-BF}
Secondary product PEC	PEC_{SP}	1.04	GJ/ton_{HRC-BF}
Reference system PEC	PEC_{RS}	22.97	GJ/ton_{HRC-BF}
Energy penalty	**EP'**	**7.65**	**GJ/ton_{HRC-BF}**
Relative energy penalty	**EP**	**33.3**	**%**
Specific PEC per Carbon Avoided	**SPECCA**	**5.81**	**GJ/ton_{CO2}**

4.4. BF-2-DRP Hybrid Steelmaking with CCS

In this section the computed KPIs are presented. The symbiotic case is compared to the base case, production of steel in separate BF/BOF and DRI/EAF plants. The size of the base BF/BOF steel mill and the base DRI/EAF plant are the same as the symbiotic case making in this way possible the comparison between these solutions. The primary energy consumption, the CO_2 emissions and the relative KPIs are reported in Figure 19. Specific CO_2 emissions, Carbon Avoidance, PEC and SPECCA of the investigated plant solutions for the BF-2-DRP case

. The specific CO_2 emissions take into account the direct and indirect emissions. Indirect emissions of the base case are mainly related to the power consumption of the DR plant since the combined cycle of the integrated steel mill produce enough power to cover the its electricity demand. On the other hand, in the symbiotic case, the import of electricity increase consistently for two reasons: (i) all available BOFG and BFG are no more used in the power plant of the BF/BOF steel mill, meaning that all the electricity necessary to run the plant has to be imported from the grid, (ii) the BFG+BOFG mixture as well as the top-gas from the shaft furnace have to be compressed from almost atmospheric pressure to the working pressure of the gas treatment section (i.e. WGS and SEWGS working pressures). Part of the additional electricity demand is covered by an expander in which the H_2/N_2 mixture is expanded from 17.9 bar to 1.5 bar.
The H_2/N_2 mixture is used as fuel for the reformer in the DR plant but also to produce part of the steam necessary in the plant. The remaining part is used in the integrated steel mill covering 62% of its heat demand. The remainder is covered by additional natural gas to be imported. The LHV of the H_2/N_2 mixture is equal to 5.5 MJ/kg, higher than the one of BFG and BOFG. This is due to the fact that some hydrogen, present in the shaft-furnace top-gas is added upstream the SEWGS reactor.
The PEC of the symbiotic case is, in general, higher than the one of the separate plants due to the above-mentioned higher import of electricity and natural gas. This difference decreases as the carbon intensity related to electricity generation decreases, becoming almost zero when the renewable energy scenario is considered. Indeed, in this case, the PEC associated to electricity generation is considered equal to zero since no fossil fuels are used reflecting on a SPECCA almost equal to zero.
The PEC of the base case is not as sensible to electricity carbon intensity as for the symbiotic case since it affects only DR plant, being the BF/BOF steel mill self-sufficient in terms of electricity generation.
The Carbon Avoidance reaches 80% when electricity carbon intensity is equal to zero, reducing to 41% in the worst scenario.

Table 22. Process carbon intensity and PEC for different values of carbon footprint of electricity from the grid. Both blast furnace process with separate DRP (BFP & DRP) and BF-2 DRP are both computed with grid power input. FU = 5.19 $Mton_{HRC}$/yr of total steel production.

Grid Emissions Intensity		0	300	600	900	[kg_{CO2}/MWh]
Process Carbon Intensity	BFP & DRP	1.488	1.589	1.690	1.791	[ton_{CO2}/ton_{HRC}]
	BF-2-DRP	0.302	0.551	0.799	1.047	[ton_{CO2}/ton_{HRC}]
Carbon Avoidance	BF-2-DRP vs BFP	-1.186	-1.038	-0.891	-0.744	[ton_{CO2}/ton_{HRC}]
Primary Energy Consumption	BFP & DRP	18.71	19.96	20.48	20.85	[GJ/ton_{HRC}]
	BF-2-DRP	19.57	23.34	24.91	26.04	[GJ/ton_{HRC}]
Energy Penalty	BF-2DRP vs BFP	0.86	2.38	4.43	5.19	[GJ/ton_{HRC}]

Table 23. CA and SPECCA for different values of carbon footprint of electricity from the grid, comparing BFP & DRP separate plants with the hybrid BF-2-DRP process. FU= 5.19 $Mton_{HRC}$/yr of total steel production.

Grid Emissions Intensity	0	300	600	900	[kg_{CO2}/MWh]
Relative Carbon Avoidance	79.7	65.3	52.7	41.5	[%]
SPECCA	0.73	3.26	4.98	6.98	[GJ/ton_{CO2}]

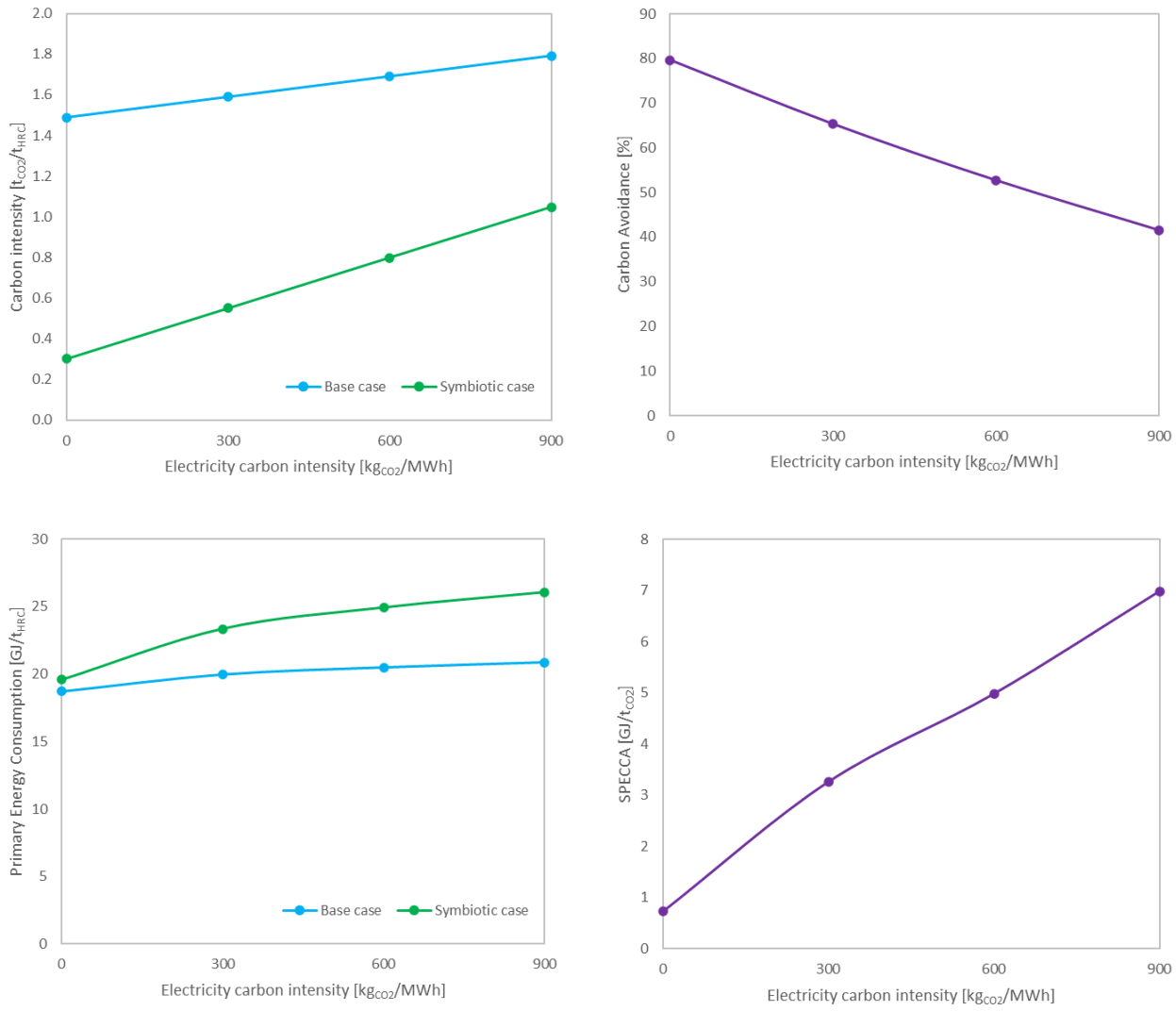


Figure 19. Specific CO_2 emissions, Carbon Avoidance, PEC and SPECCA of the investigated plant solutions for the BF-2-DRP case

In addition to the results presented above, the relative carbon emissions and PEC are reported in Table 24. In this case the carbon footprint of the electricity imported from the grid is equal to 350 kg_{CO2}/MWh_{el}. As can be observed the symbiotic system allow to reduce the emissions by 63.1% while increasing the PEC by 18.9%. The computed SPECCA is then equal to 3.75.

Table 24. KPI's for the BF-2-DRP symbiotic H_2/N_2 use case. FU = 3.16 $Mton_{HRC-BF}/yr$.

GHG Emission Intensity	Symbol	Value	Unit
Initiate steelmaking emissions	$e_{IN,SM}$	0.31	ton_{CO2}/ton_{HRC-BF}
Initiate process emissions (DRP)	$e_{IN,P}$	0.36	ton_{CO2}/ton_{HRC-BF}
Replacements emissions	e_{RP}	0.23	ton_{CO2}/ton_{HRC-BF}
CO_2 storage emissions	$e_{T\&S}$	0.07	ton_{CO2}/ton_{HRC-BF}
Symbiotic system emissions	e_{SS}	0.97	ton_{CO2}/ton_{HRC-BF}
Reference steelmaking emissions	e_{RSM}	2.05	ton_{CO2}/ton_{HRC-BF}
Secondary product emissions	e_{SP}	0.59	ton_{CO2}/ton_{HRC-BF}
Reference system emissions	e_{RS}	2.64	ton_{CO2}/ton_{HRC-BF}
Carbon Avoidance	**CA'**	**1.67**	**ton_{CO2}/ton_{HRC-BF}**
Relative Carbon avoidance	**CA**	**63.1**	**%**
Primary Energy Consumption		**Value**	**Unit**
Initiate steelmaking and process PEC	$PEC_{IN,SM}$	34.19	GJ/ton_{HRC-BF}
Replacements PEC	PEC_{RP}	3.90	GJ/ton_{HRC-BF}
CO_2 transport and storage PEC	$PEC_{T\&S}$	1.31	GJ/ton_{HRC-BF}
Symbiotic system PEC	PEC_{SS}	39.40	GJ/ton_{HRC-BF}
Reference steelmaking PEC	PECRSM	21.93	GJ/ton_{HRC-BF}
Secondary product PEC	PEC_{SP}	11.22	GJ/ton_{HRC-BF}
Reference system PEC	PEC_{RS}	33.15	GJ/ton_{HRC-BF}
Energy penalty	**EP'**	**6.25**	**GJ/ton_{HRC-BF}**
Relative energy penalty	**EP**	**18.9**	**%**
Specific PEC per Carbon Avoided	**SPECCA**	**3.75**	**GJ/ton_{CO2}**

Table 25. KPIs for the BF-2-DRP case for steelmaking with CCS evaluation. FU = 5.19 $Mton_{HRC}$/yr of total steel production.

GHG Emission Intensity	Symbol	Value	Unit
Initiate steelmaking & process emissions	$e_{IN,SM}$	0.40	ton_{CO2}/ton_{HRC}
Replacements emissions	e_{RP}	0.14	ton_{CO2}/ton_{HRC}
CO_2 storage emissions	$e_{T\&S}$	0.05	ton_{CO2}/ton_{HRC}
Symbiotic system emissions	e_{SS}	0.59	ton_{CO2}/ton_{HRC}
Reference steelmaking emissions	e_{RSM}	1.61	ton_{CO2}/ton_{HRC}
Reference system emissions	e_{RS}	1.61	ton_{CO2}/ton_{HRC}
Carbon Avoidance	**CA'**	**1.02**	**ton_{CO2}/ton_{HRC}**
Relative Carbon avoidance	**CA**	**63.1**	**%**
Primary Energy Consumption		**Value**	**Unit**
Initiate steelmaking and process PEC	$PEC_{IN,SM}$	20.80	GJ/ton_{HRC}
Replacements PEC	PEC_{RP}	2.38	GJ/ton_{HRC}
CO_2 transport and storage PEC	$PEC_{T\&S}$	0.79	GJ/ton_{HRC}
INITIATE system PEC	PEC_{SS}	23.97	GJ/ton_{HRC}
Reference steelmaking PEC	PEC_{RSM}	20.16	GJ/ton_{HRC}
Reference system PEC	PEC_{RS}	20.16	GJ/ton_{HRC}
Energy penalty	**EP'**	**3.81**	**GJ/ton_{HRC}**
Relative energy penalty	**EP**	**18.9**	**%**
Specific PEC per Carbon Avoided	**SPECCA**	**3.75**	**GJ/ton_{CO2}**

4.5. Direct Reduction Steelmaking with CCS

The primary energy consumption, the CO_2 emissions and the relative KPIs are reported in Figure 20. The specific CO_2 emissions take into account the direct and indirect emissions of the DRI production and the ones related to the electric arc furnace. The PEC of the direct reduction process increases with the increase of the electricity carbon footprint. Indeed, the primary energy consumption associated to electricity generation is considered equal to zero for a renewable energy scenario (i.e. electricity carbon footprint equal to 0 kg_{CO2}/kWh) since no fossil fuels are consumed but it increases with the electricity carbon footprint. The DRP-CCS plant import the same quantity of natural gas but a higher quantity of electricity with respect to the direct reduction base plant. For this reason, when a full renewable energy grid is considered, and so when the PEC of electricity generation is equal to zero, the PEC of the two plants is the same, reflecting on a SPECCA equal to 0 GJ/t_{CO2}. When a renewable energy scenario is considered the relative carbon avoidance of the DRP-CCS respect to state-of-the-art DRP is 67%. A further decrease of the CO_2 emissions becomes harder since when renewable energy is considered the majority of the emissions are associated to EAF direct emissions and iron ore production.

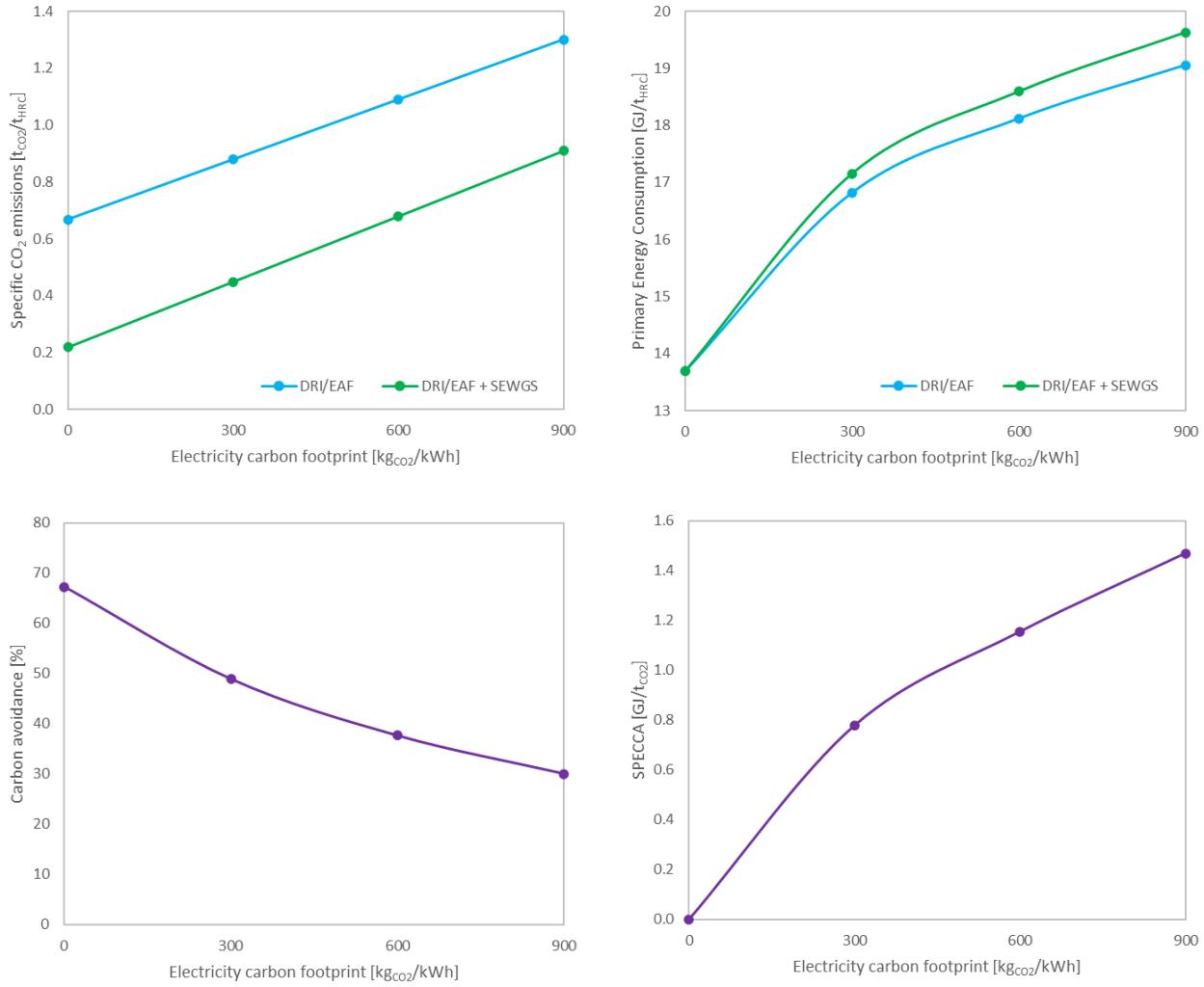


Figure 20. Specific CO_2 emissions, Carbon Avoidance, PEC and SPECCA of the investigated plant solutions with respect to DRP-CCS (DRI/EAF+SEWGS in graphs) case, using a state-of-the-art MIDREX DRP as reference (DRI/EAF).

The results showed in the previous Figure are reported in the following tables, where the KPIs are computed for different values of carbon footprint of electricity imported from the grid.

Table 26. Process carbon intensity and PEC for different values of carbon footprint of electricity from the grid. Both DRP and DRP-CCS cases are computed with grid power input. FU = 5.19 $Mton_{HRC-DR}$/yr.

Grid Emissions Intensity		0	300	600	900	[kg_{CO2}/MWh]
Emissions Intensity	DRP	0.668	0.879	1.090	1.301	[ton_{CO2}/ton_{HRC}]
	DRP-CCS	0.219	0.449	0.679	0.910	[ton_{CO2}/ton_{HRC}]
Carbon Avoidance	DRP-CCS vs DRP	-0.449	-0.430	-0.411	-0.391	[ton_{CO2}/ton_{HRC}]
Primary Energy Consumption	DRP	13.7	16.8	18.1	19.1	[GJ/ton_{HRC}]
	DRP-CCS	13.7	17.1	18.6	19.6	[GJ/ton_{HRC}]
Energy Penalty	DRP-CCS vs DRP	0.0	0.3	0.4	0.5	[GJ/ton_{HRC}]

Table 27. CA and SPECCA for different values of carbon footprint of electricity from the grid for the comparison between DRP and DRP-CCS cases. FU = 5.19 $Mton_{HRC-DR}$/yr.

Grid Emissions Intensity	0	300	600	900	[kg_{CO2}/MWh]
Relative Carbon Avoidance (DRP-CCS vs DRP)	67	49	38	30	[%]
SPECCA (DRP-CCS vs DRP)	0.00	0.78	1.15	1.47	[GJ/ton_{CO2}]

Table 28. KPIs for DRP-CCS case for steelmaking with CCS evaluation, FU = 5.19 $Mton_{HRC}$/yr of total steel production.

GHG Emission Intensity	Symbol	Value	Unit
Initiate steelmaking emissions	$e_{SM,IN}$	0.47	ton_{CO2}/ton_{HRC}
CO_2 storage emissions	$e_{T\&S}$	0.02	ton_{CO2}/ton_{HRC}
INITIATE emissions	e_{SS}	0.49	ton_{CO2}/ton_{HRC}
Reference steelmaking emissions	e_{RSM}	2.05	ton_{CO2}/ton_{HRC}
Reference system emissions	e_{RS}	2.05	ton_{CO2}/ton_{HRC}
Carbon Avoidance	**CA'**	**-1.55**	**ton_{CO2}/ton_{HRC}**
Relative Carbon avoidance	**CA**	**76.1%**	**%**
Primary Energy Consumption	**Symbol**	**Value**	**Unit**
Initiate process PEC	$PEC_{IN,P}$	17.44	GJ/ton_{HRC}
CO_2 transport and storage PEC	$PEC_{T\&S}$	0.29	GJ/ton_{HRC}
Symbiotic system PEC	PEC_{ss}	17.73	GJ/ton_{HRC}
Reference steelmaking PEC	PEC_{RSM}	21.93	GJ/ton_{HRC}
Reference system PEC	PEC_{RS}	21.93	GJ/ton_{HRC}
Energy penalty	**EP'**	**-4.2**	**GJ/ton_{HRC}**
Relative energy penalty	**EP**	**-19.2%**	**%**
Specific PEC per Carbon Avoided	**SPECCA**	**-2.7**	**GJ/ton_{CO2}**

4.6. CO_2 Mineralization for CCS

The results obtained led to common conclusions for both natural minerals and industrial wastes. As a matter of fact, it can be said in both cases that reducing the size of the solid particles increases the reactivity of the material, decreasing the amount required for CO_2 sequestration, but by carrying out a grinding operation that leads to a solid particle size of less than 38 μm, the energy required increases significantly, because another mechanical pre-treatment will have to be provided in that case. In addition, by increasing the partial pressure of carbon dioxide, the total energy requirement decreases, the reactivity of the material increases and thus the amount required for the process decreases. Regarding temperature, it has a dual effect: on the one hand, its increase causes a reduction in the solubility of CO_2, leading to a reduction in the efficiency of the process, but on the other hand it brings a rise in reaction kinetics. For this reason, it is necessary to identify an optimum. Focusing on the liquid-to-solid ratio, an increase in this parameter does not lead to an actual change in the reactivity of the mineral, while it increases the energy requirements (particularly the costs related to pumping, heating, and reaction) due to the increased amount of water to be treated. Following the same procedure mentioned before for the case of the reference CO_2 capture process (storage), a comparison can be made with the approach of olivine mineralization and BOF slag.

Table 29. CO_2 mineralization KPI results.

	Base case	Olivine case	BOF slag case	Unit
Primary Energy Consumption				
INITIATE process PEC (methanol)	7.28	7.28	7.28	$GJ/ton_{HRC\text{-}BF}$
Replacements PEC	6.25	6.25	6.25	$GJ/ton_{HRC\text{-}BF}$
CO_2 storage PEC	0.99	-	-	$GJ/ton_{HRC\text{-}BF}$
Mineralization PEC	-	3.52	1.65	$GJ/ton_{HRC\text{-}BF}$
Symbiotic system PEC	14.52	17.05	15.18	$GJ/ton_{HRC\text{-}BF}$
Reference system PEC	27.58	27.58	27.58	$GJ/ton_{HRC\text{-}BF}$
Energy penalty	**8.87**	**11.40**	**9.53**	**$GJ/ton_{HRC\text{-}BF}$**
Relative energy penalty	**32.16**	**41.33**	**34.55**	**%**
SPECCA	**8.42**	**12.53**	**9.44**	**GJ/ton_{CO2}**
GHG Emission Intensity				
INITIATE steelmaking emissions	0.26	0.26	0.26	$ton_{CO2}/ton_{HRC\text{-}BF}$
INITIATE process emissions (methanol)	0.42	0.42	0.42	$ton_{CO2}/ton_{HRC\text{-}BF}$
Replacements emissions	0.35	0.35	0.35	$ton_{CO2}/ton_{HRC\text{-}BF}$
CO_2 storage emissions	0.05	-	-	$ton_{CO2}/ton_{HRC\text{-}BF}$
Mineralization emissions	-	0.19	0.09	$ton_{CO2}/ton_{HRC\text{-}BF}$
Symbiotic system emissions	1.08	1.22	1.12	$ton_{CO2}/ton_{HRC\text{-}BF}$
Reference system emissions	2.13	2.13	2.13	$ton_{CO2}/ton_{HRC\text{-}BF}$
Avoided emissions	**-1.05**	**-0.91**	**-1.01**	**$ton_{CO2}/ton_{HRC\text{-}BF}$**
Carbon avoidance	**49.30**	**42.72**	**47.42**	**%**

It is proper to make a mention about possible applications of mineral carbonation products in the cement industry. According to the article "*From Unavoidable CO_2 Source to CO_2 Sink? A Cement Industry Based on CO_2 Mineralization*" combining CO_2 mineralization to cement production is possible to reduce the carbon footprint by 44%, or even 85% considering the theoretical potential [19]. Most of the emissions from cement plants are from the production of clinker, the reactive component of cement. One possible solution to this problem may be to replace it with pozzolan, a silica-rich material that, when exposed to water in the presence of calcium, hydrates and exhibits cementitious properties. Materials with pozzolan-like properties can be obtained precisely from mineralization, which also has silicates as products. If a feasible technology for separating the products could be identified, there could be great advantages from this perspective. Another good solution of reusing carbonation products is the possibility of exploiting them as aggregates in concrete synthesis, as shown in the following figure:

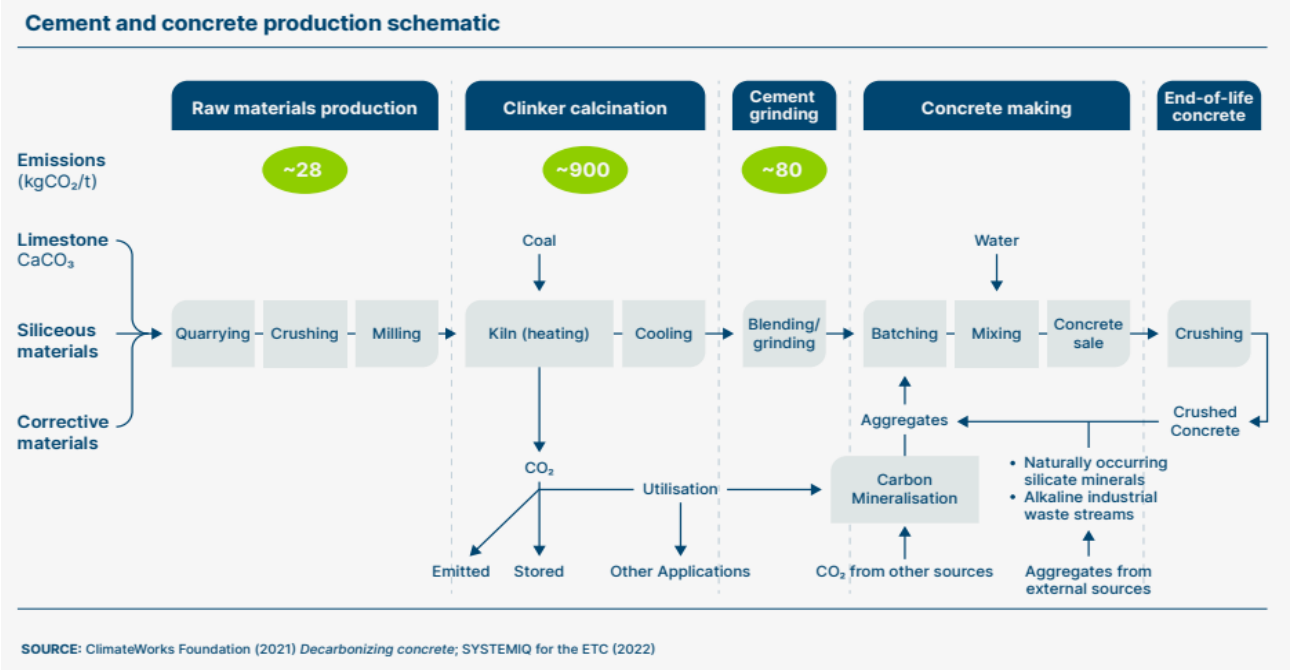


Figure 21: Cement and concrete production

5. Aggregated Results

5.1. Symbiotic H_2/N_2 Use Cases

Emissions Intensity

The emission intensities of the four symbiotic H_2/N_2 use cases are reported in Table 30 and Figure 22. The total specific emissions of the reference systems vary across the four cases. The BF-2-DRP shows the largest emissions with a value of 2.63 $ton_{CO2}/ton_{HRC\text{-}BF}$. This result reflects the largest emission intensity of steelmaking in comparison to chemicals and fuel production. The production of 2.03 $Mton_{HRC}$/yr by DRP does actually lead to 0.59 $ton_{CO2}/ton_{HRC\text{-}BF}$. Urea and methanol productions, respectively of 513 and 595 kton/yr, only lead to 0.05 and 0.09 $ton_{CO2}/ton_{HRC\text{-}BF}$. Looking at the symbiotic systems, the residual use of COG, BF-plant losses and additional emissions contribute to 0.26 $ton_{CO2}/ton_{HRC\text{-}BF}$. These emissions are equal across all cases. CO_2 transport and storage emissions are relatively small, with values between 0.06 and 0.08 $ton_{CO2}/ton_{HRC\text{-}BF}$. The BF-2-DRP and A-2-P cases do not make use of the CO_2 product. Accordingly, their CO_2 emissions for CO_2 transport and storage are larger. The BF-2-DRP case also processes a larger volume of CO_2, since the H_2/N_2 product is only used to replace part of the DR reforming fuel. As natural gas feedstock to the DRP is maintained, the SEWGS plant processes also the natural gas import for fuelling and feeding the DR steelmaking plant. An additional source of CO_2 emissions is the use of natural gas to replace BFG and BOFG within the BF steelmaking plant. This term is a significant fraction of the specific emissions of all studied symbiotic H_2/N_2 uses. The emission intensity due to BFG/BOFG replacement ranges from 0.29 to 0.35 $ton_{CO2}/ton_{HRC\text{-}BF}$. The MeOH case shows a slightly higher value because all the H_2/N_2 product is used as feedstock for MeOH production. Therefore, the natural gas import must balance the whole BFG and BOFG thermal input to the BF steelmaking plant. Minor amounts of H_2/N_2 product are used in the other cases to replace BFG and BOFG, thereby reducing the required natural gas amount. A similar trend can be seen with the INITIATE process emissions term. This term is the largest contributor to the symbiotic systems' emissions. Both Urea and A-2-P show significant lower emissions than the MeOH case, approximately 50% less. This is due to the larger fraction of H_2/N_2 product use to generate process heat. Once again, as the whole H_2/N_2 product is used as feedstock, natural gas import is required to provide process heat to the INTIATE process, thereby increasing the CO_2 emissions. The BF-2-DRP case has also a large emission intensity on this case, namely 0.41 $ton_{CO2}/ton_{HRC\text{-}BF}$, which is linked to the greater primary energy demand that is needed to produce 2.03 $Mton_{HRC}$/yr by DRP than the indicated throughputs of chemicals and power. Overall, all symbiotic systems contribute to reduce CO_2 emissions compared to their respective reference systems, showing carbon avoidance from -1.05 to -1.66 $ton_{CO2}/ton_{HRC\text{-}BF}$. The relative carbon avoidance ranges from 49% to 63%. With the exception of the MeOH case, all relative avoidances are rather close to each other. This is due to the different original emissions of the various reference systems. It points out that the INITIATE process can effectively reduce emissions across all these sectors.

Primary Energy Consumptions

Similarly to CO_2 emissions, primary energy consumption varies across the four reference systems (Figure 23 and Table 31). While the BF steelmaking always consumes 21.93 $GJ/ton_{HRC\text{-}BF}$, the secondary products have different consumptions. The BF-2-DRP case shows the highest consumption with 11.20 $GJ/ton_{HRC\text{-}BF}$. A-2-P cases is the lowest, as power is hereby generated through natural gas combustion. The urea case has then a lower consumption than the methanol case. This is because of the chosen throughputs (513 ton_{Urea}/yr and 595 ton_{MeOH}/yr respectively, Table 2) and higher specific energy consumption of methanol production per ton of product (~19 GJ/ton_{Urea} and 30 GJ/ton_{MeOH} respectively, Table 5). For every case, the symbiotic system requires a larger amount of primary energy than the respective reference system. Most of this additional primary energy is required to replace the BFG and BOFG in the BF steelmaking plant. Additional power and heat are also needed to run the INITIATE plant. Qualitatively speaking, the INTIATE project has additional energy requirements for gas separation. In all cases, CO_2 is deeply removed in the SEWGS. The steam consumption for this separation is an addition to the reference systems. Additionally, the Urea, MeOH and A-2-P requires the removal of a large excess N_2 flow. This N_2 mainly comes from the BFG, and it is also compressed up to the separation and reaction pressures, thereby further increasing the energy consumption compared to the reference system. Finally, CO_2 transport and storage also involve additional consumptions, which are not present in the reference systems as CO_2 is fully emitted. The combination of all, or part of, these energy requirements leads to an energy penalty for every symbiotic system. This penalty ranges from 5.88 to 8.87 $GJ/ton_{HRC\text{-}B}$, leading to relative increases from 19% to 33%. Interestingly, the relative penalty of BF-2-DRP is the lowest. Conversely, the largest penalty stands for the A-2-P case, as an intermediate carbon neutral energy carrier (i.e. NH_3) is here generated to substitute natural gas.

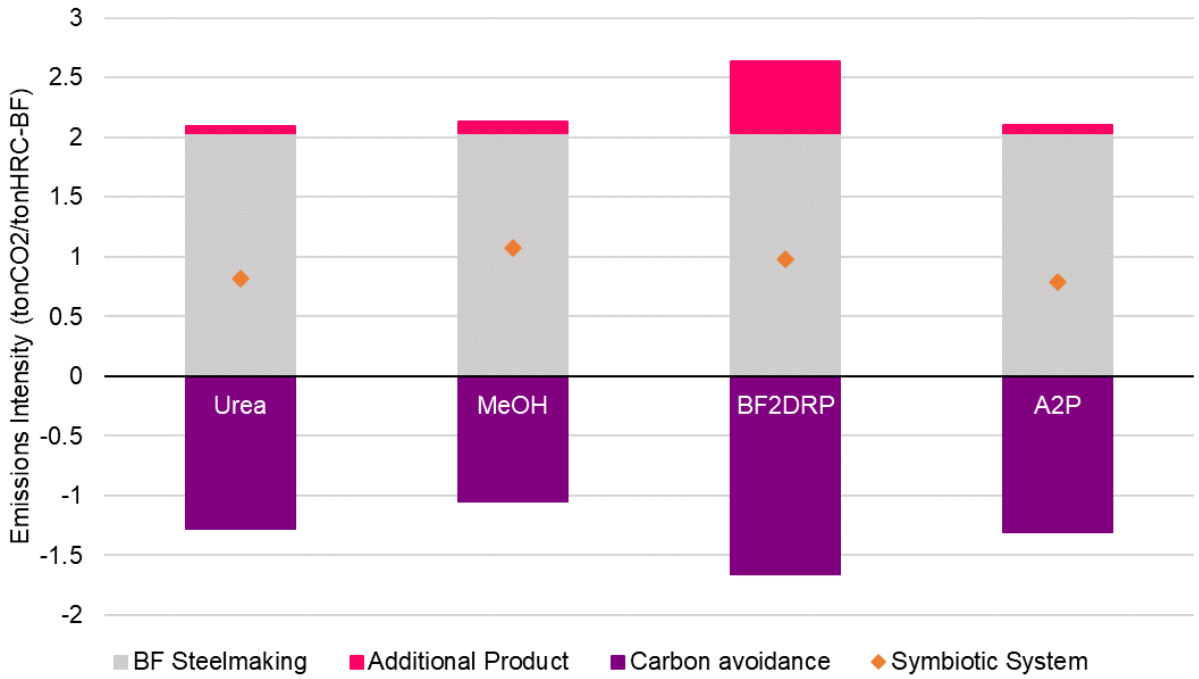


Figure 22. Emissions Intensities of the four H_2/N_2 symbiotic use cases.

Table 30. Breakdown of the Emissions Intensities of the four H_2/N_2 symbiotic use cases.

FU = 3.16 MtHRC-BF/y Values in ton_{CO2}/ton_{HRC-BF}	Symbol	Urea	MeOH	BF-2-DRP	A2P
Ref. BF steelmaking	e_{RSM}	2.05	2.05	2.05	2.05
Ref. Additional Product	e_{SP}	0.05	0.09	0.59	0.06
Total Reference system	e_{RS}	2.09	2.13	2.63	2.10
INITIATE Steelmaking Residual	$e_{IN,SM}$	0.26	0.26	0.26	0.26
INITIATE Process	$e_{IN,P}$	0.19	0.42	0.41	0.18
Transport & storage	$e_{T\&S}$	0.06	0.05	0.08	0.07
BOFG/BFG Replacement	e_{RP}	0.31	0.35	0.29	0.29
Symbiotic Plant Emissions	e_{SS}	0.81	1.08	0.98	0.79
Carbon Avoidance	CA’	-1.28	-1.05	-1.66	-1.31
Relative Carbon Avoidance	CA	61%	49%	63%	62%

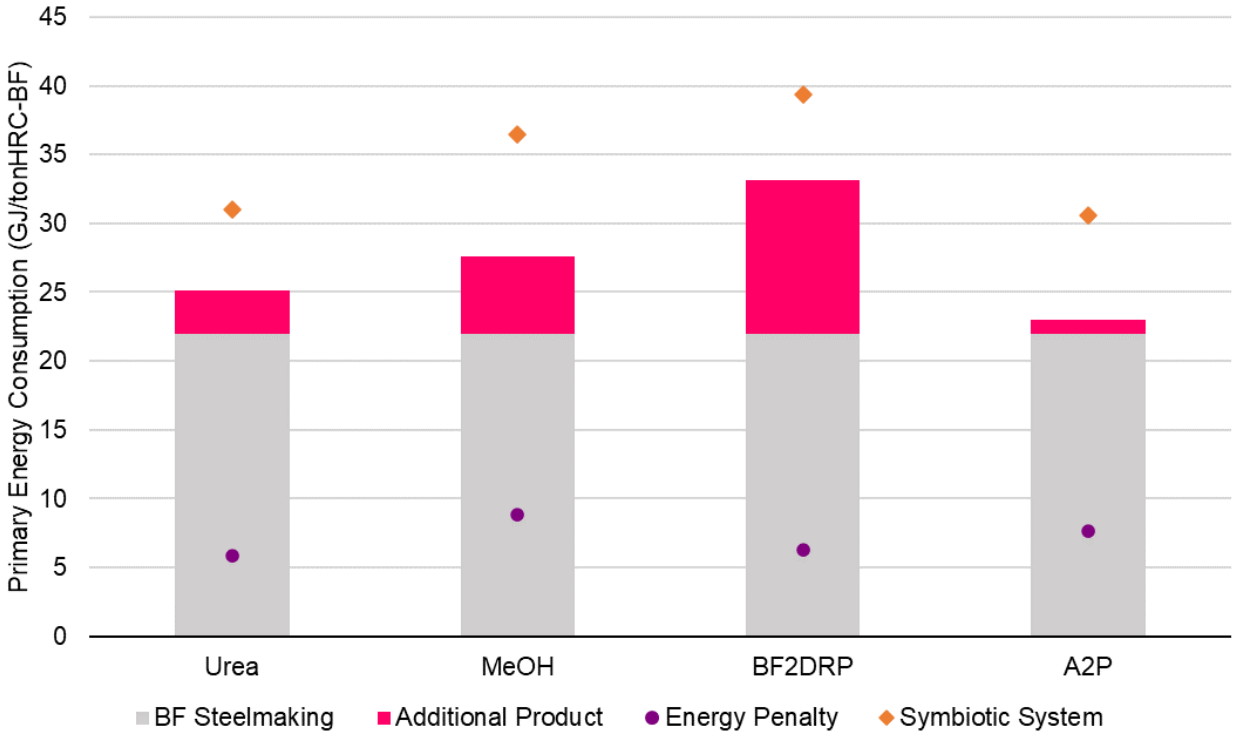


Figure 23. Primary Energy Consumptions of the four H_2/N_2 symbiotic use cases.

Table 31. Break-down of the Primary Energy Consumptions of the four H_2/N_2 symbiotic use cases.

FU = 3.16 Mt_{HRC-BF}/yr Values in GJ/ton_{HRC-BF}	Symbol	Urea	MeOH	BF2DRP	A2P
Ref. BF steelmaking	PEC_{RSM}	21.93	21.93	21.93	21.93
Ref. Additional Product	PEC_{SP}	3.20	5.65	11.20	1.04
Total Reference system	PEC_{RS}	25.13	27.58	33.13	22.97
INITIATE Process & steelmaking	$PEC_{IN\&SM}$	2.66	7.28	12.26	2.65
CO2 Transport & storage	$PEC_{T\&S}$	1.05	0.99	1.31	1.13
BOFG/BFG Replacement	PEC_{RP}	5.37	6.25	3.90	4.91
Total symbiotic	PEC_{SS}	31.01	36.45	39.40	30.62
Energy Penalty	EP’	5.88	8.87	6.27	7.65
Relative Energy Penalty	EP	23%	32%	19%	33%
Specific PEC per Carbon Avoided	SPECCA	4.57	8.42	3.75	5.81

5.2. Steelmaking with CCS

Emissions Intensity

The emissions intensities are reported in Figure 24 and Table 32, for all the considered steelmaking approaches. The reference BF plant presents the highest emissions, with an intensity of 2.05 ton_{CO2}/ton_{HRC} (note that here the total production of HRC is considered as functional unit). The DR plant already brings down these emissions to 0.92 ton_{CO2}/ton_{HRC} , leading to a relative carbon avoidance of 55%. When CCS is added, the carbon footprint is further reduced. The BF-2-DRP approach shows a final emission intensity of 0.59 ton_{CO2}/ton_{HRC}, while the DRP-CCS case stands at 0.49 ton_{CO2}/ton_{HRC}. Interestingly, the steelmaking & initiate process term has lower value in the BF-2-DRP case, as opposed to the DRP-CCS, since the reforming fuel is fully replaced with H_2/N_2. However, the natural gas that is required to compress a larger CO_2 volume, and to replace the BFG/BOFG within the BF plant, leads to the overall larger emissions by 0.10 ton_{CO2}/ton_{HRC} . In any case, both approaches achieve relative carbon avoidance above 70%. The DRP-CCS case stands at the highest relative avoidance of 76%, 5% larger than the BF-2-DRP case.

Primary Energy Consumptions

Primary energy consumptions are presented in Figure 24 and Table 33. BF steelmaking stands at a primary energy consumption of 21.93 GJ/ton_{HRC}. DR steelmaking enables to reduce this value to 17.34 GJ/ton_{HRC}. Accordingly, a negative energy penalty is obtained. This is equal to -4.59 GJ/ton_{HRC}, or -21% in relative terms. DR steelmaking thereby allows to reduce primary energy consumption. The addition of CCS implies a growth of the energy penalty. The BF-2-DRP case stands at 23.96 GJ/ton_{HRC}. This is due to the large amount of compressed and stored CO_2 (0.79 GJ/ton_{HRC}) and natural gas consumption to replace BFG/BOFG (2.37 GJ/ton_{HRC}). The consequent energy penalty is equal to 2.04 GJ/ton_{HRC}, or 9% in relative terms. Interestingly, energy savings, or a negative penalty, is achievable by using carbon neutral electricity. Increasing the fraction of steel that is produced through the DR process, the coal consumption per ton of final product is infact reduced, leading to 20.83 GJ/ton_{HRC} of primary energy demand. Finally, the DRP-CCS consumes 17.73 GJ/ton_{HRC}. This is larger by 0.40 GJ/ton_{HRC} than the DR plant without CCS. However, it is still well below the BF process, leading to a negative penalty of -4.20 GJ/ton_{HRC}, or -19% in relative terms.

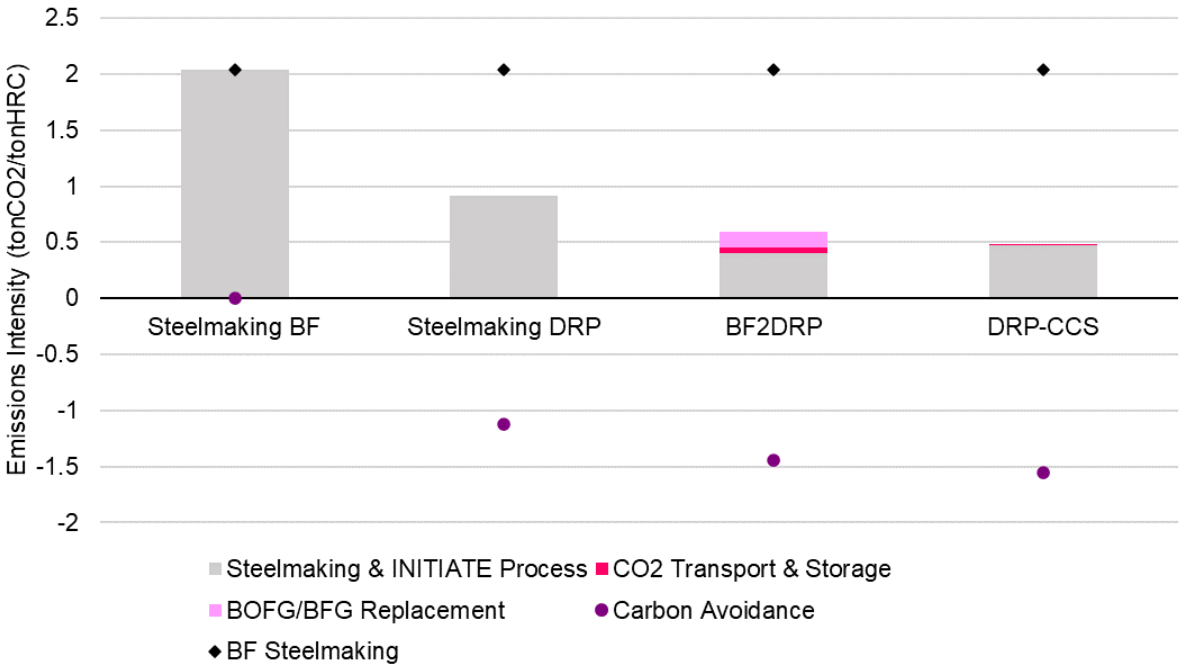


Figure 24. Emissions intensities of various steelmaking approaches with and without CCS.

Table 32. Break-down values of the emissions intensities of various steelmaking approaches with and without CCS.

FU = 5.19 $Mton_{HRC}/yr$ Values in ton_{CO2}/ton_{HRC}	Symbol	Steel-making BF	Steel-making DRP	BF-2-DRP	DRP-CCS
Ref. BF Steelmaking	e_{RSM}	2.05	2.05	2.05	2.05
Steelmaking & INITIATE Process	$e_{IN\&SM}$	2.05	0.92	0.41	0.47
CO_2 Transport & Storage	$e_{T\&S}$			0.05	0.02
BOFG/BFG Replacement	e_{RP}			0.14	
Total INITIATE	e_{IN}	2.05	0.92	0.59	0.49
Carbon Avoidance	CA’		-1.12	-1.45	-1.55
Relative Carbon Avoidance	CA		55%	71%	76%

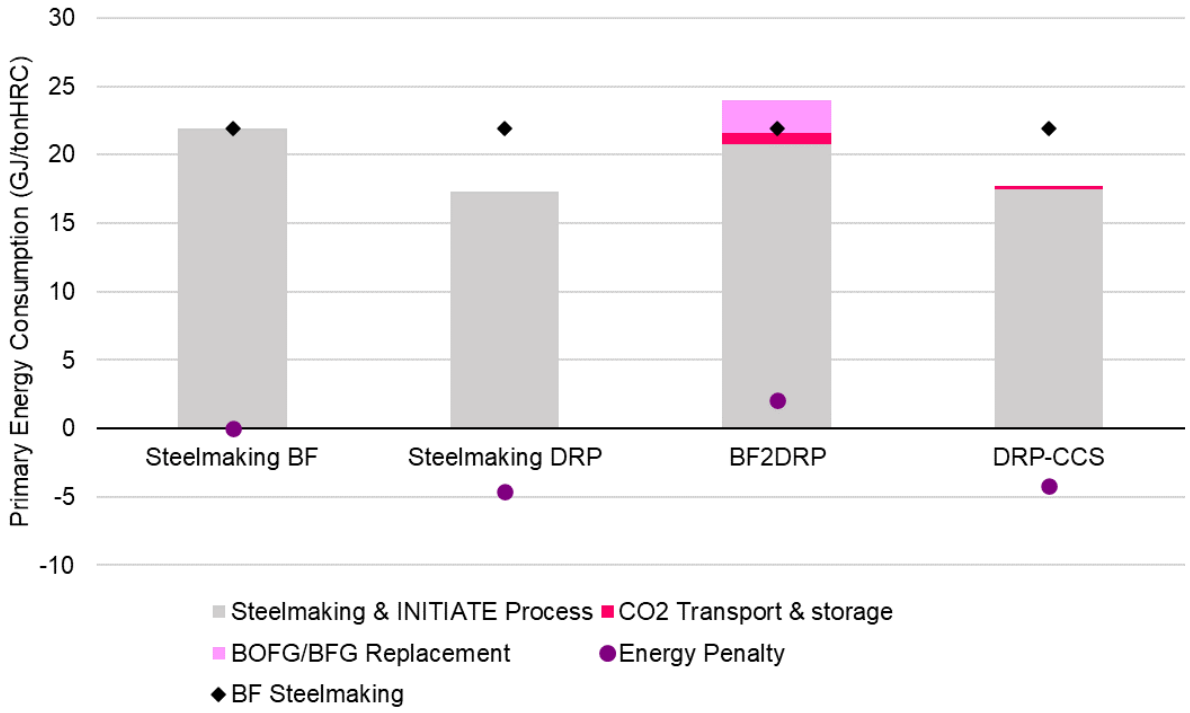


Figure 25. Primary energy consumptions of various steelmaking approaches with and without CCS.

Table 33. Break-down values of the primary energy consumptions of various steelmaking approaches with and without CCS.

FU = 5.19 Mt_{HRC}/yr Values in GJ/ton_{HRC}	Symbol	Steel making BF	Steel making DRP	BF-2-DRP	DRP-CCS
Ref. BF Steelmaking	PEC_{RSM}	21.93	21.93	21.93	21.93
Steelmaking & INITIATE Process	$PEC_{IN\&SM}$	21.93	17.34	20.80	17.44
CO_2 Transport & storage	$PEC_{T\&S}$			0.79	0.29
BOFG/BFG Replacement	PEC_{RP}			2.37	0
Total INITATE	PEC_{IN}	21.93	17.34	23.96	17.73
Energy Penalty	EP’		-4.59	2.04	-4.2
Relative Energy Penalty	EP		-21%	9%	-19%
Specific PEC per Carbon Avoided	SPECCA		-4.09	1.41	-2.7

6. Conclusions and Recommendations

H_2/N_2 Symbiotic use case

All the four H_2/N_2 symbiotic use cases reduce CO_2 emissions. Relative carbon avoidance values range from 49% to 63%. These relative carbon avoidance values are obtained together with relative energy penalties between 19% and 33%. Therefore, the symbiotic systems reduce CO_2 emissions, while increasing primary energy consumptions.

In all cases, the energy penalty is mainly caused by a larger consumption of natural gas, whose purpose is to generate heat and power. These thermal and electrical energy inputs are required to run the INITIATE process, as well as to replace the BFG and BOFG within the BF plant. Only in the BF-2-DRP case, natural gas is also used as feedstock to the DR plant, since the H_2/N_2 product replaces only the reforming fuel.

The use of low carbon power effectively mitigates the primary energy penalty of the symbiotic system, as indicated by preliminary sensitivities on the Urea and BF-2-DRP cases. For instance, relative carbon avoidance of 63% with SPECCA of 3.75 GJ/ton$_{HRC\text{-}BF}$ are achieved by using NGCC electricity (350 kg$_{CO2}$/MWh$_{el}$). When carbon neutral power is used (0 kg$_{CO2}$/MWh$_{el}$), these values improve to ~80% and 0.75 GJ/ton$_{HRC\text{-}BF}$, respectively. This approach can also lead to negative primary energy penalties, or primary energy savings. For instance, the Urea case achieves a relative carbon avoidance of ~80% and SPECCA of -0.3 GJ/ton$_{HRC\text{-}BF}$, or a relative energy penalty of -1.6%.

These improvements are expected to further grow when process heating is also decoupled from fossil resources. This is already apparent when a larger fraction of the H_2/N_2 product is used to produce process heat. For instance, 66% of the produced H_2/N_2 is used to generate heat within the Urea case. Conversely, the full process heat demand is met with natural gas in the MeOH case. This leads the MeOH case to achieve an energy penalty of 7.28 GJ/ton$_{HRC\text{-}BF}$. This penalty is larger by 4.62 GJ/ton$_{HRC\text{-}BF}$ than the Urea case's one. This result is achieved although the same SEWGS configuration is used across the two cases.

All symbiotic systems present inherent additional energy demands for N_2 separation, pressurization and heating. Only in the BF-2-DRP case H_2/N_2 separation is avoided, as H_2 purity is less stringent than what is required to produce methanol or ammonia. Currently, this N_2 excess is vented. Valorisation of this N_2 excess may offset these additional energy consumptions. Progressive decarbonization of BF steelmaking heating (e.g. by electrification or use of low carbon fuels) will additionally unlock the use of COG as carbon neutral H_2 source. This can for instance be used to match part of the BFG N_2 excess. Alternatively, enriched air operations of the BF steel plant could be considered. This is particularly relevant, as the combined theoretical H_2/N_2 ratio of all steel gases is estimated to be ~0.8, thereby limiting the residual steel gases potential to valorise the embedded N_2 to ammonia (which requires a ratio of at least > 2.0, ideally ~3).

Further work needs to focus on simultaneous technical, economic and environmental evaluation of the proposed options. Based on the above conclusions, it is recommended that such future work carefully consider the following key assumptions, as these are going to heavily influence the optimal symbiotic system design:

- Steel plant efficiency;
- Availability of renewable sources (wind and solar);
- Availability of a stable low carbon power mix (e.g. by mixing wind and solar with nuclear, NGCC with CCS, or other non-intermittent power sources);
- Availability of flow carbon fuels as alternative to natural gas;
- Availability and capacity of CO_2 storage;
- Secondary product local demand for low carbon substitute.

Additionally, it is recommended to evaluate and optimize the following key design parameters:

- Ratio between the secondary product throughput and BF-steelmaking throughput;
- Fractional use of H_2/N_2 product as secondary product feedstock or fuel to generate low carbon heat and power;
- Imported amount of (low carbon) power and fuels from outside battery limits;
- Extent of COG use as additional carbon neutral H_2 source (with low N_2 content);
- Use of enriched air to drive the BF steelmaking process (e.g. by air separation or O_2 from water electrolysis).

Steelmaking with CCS

Steelmaking can be effectively decarbonized by integrating BF and DR plants via the INITIATE capture technology, or by applying the same technology to standalone plants. The BF-2-DRP and DRP-CCS cases achieve respective emissions intensity of 0.59 and 0.49 ton$_{CO2}$/ton$_{HRC}$. These are 71% and 76% lower than state-of-the art steelmaking via the BF route. When carbon neutral power is used, these values can improve

to ~0.30 ton_{CO2}/ton_{HRC} and ~0.20 ton_{CO2}/ton_{HRC}, respectively in the BF-2-DRP and DRP-CCS cases. This improvement means the achievement of relative carbon avoidances of 85% and 90%. Further improvements are conceivable when thermal energy consumption is also decarbonized.

Additionally, the adoption of the DR process contributes to reduce the energy penalties. The DR process shows in fact a relative energy penalty of -21%, meaning that the primary energy consumption is reduced by one fifth. Slightly less energy savings are achieved when CCS is added. The DRP-CCS case does in fact stand at -19% relative energy penalty. The BF-2-DRP is the only case with an actual penalty, requiring 9% more primary energy, and leading to a SPECCA of 1.41 GJ/ton_{CO2}. However, it is possible that a negative SPECCA is achieved also within the BF-2-DRP case. This depends on the use of carbon neutral alternatives to generate heat and power, as well as to an increased DR plant throughput.

Interestingly, the BF-2-DRP case achieve comparable emission reduction than the DRP-CCS cost, but at increased primary energy consumption. This means that the BF-2-DRP case can effectively achieve comparable CO_2 emissions reduction in those cases where carbon neutral power is limited. Future study should further focus on evaluate the merit order of renewable power to achieve carbon neutral steelmaking. The choice between BF-2-DRP, BF-CCS or DRP-CCS approaches is likely to depend on the availability (or scarcity) of carbon neutral fuels and power, among other factors that includes above all the availability of carbon storage options. Within future studies, it is then useful to consider not only the primary energy consumption, but also the required amounts of low-carbon thermal and electrical utilities (i.e. power and fuels), which are needed to achieve a certain carbon avoidance. This is to highlight which steelmaking approach is able to achieve the optimal compromise between the use of BF residual steel gases and externally imported carbon neutral power and fuels. Optimal compromise that could be finally measure in terms of carbon avoidance, cost per carbon avoided (CCA), specific primary energy consumption per carbon avoided (SPECCA) and specific consumption of ‘non-fossil’ energy per avoided carbon.

CO_2 Mineralization

The implementation of the INTIATE approach relies on the availability of carbon storage options. This is the case as long as pressurized CO_2 underground storage is considered. CO_2 mineralization can be implemented when underground storage is not available. Applying two CO_2 mineralization approaches to the MeOH H_2/N_2 use case, it is found that both maintain comparable carbon avoidance rate with underground pressurized CO_2 storage. BOF slag mineralization appears the best performing case with a relative carbon avoidance of 47%. This is only 2% lower than the conventional CO_2 storage and 5% higher than mineralization with olivine. Additionally, its SPECCA is larger than the conventional case only by 1.02 GJ/ton_{CO2}. This is still lower than for olivine, which shows a SPECCA larger than the conventional case by 4.11 GJ/ton_{CO2}. It is recommended to add the cost per avoided carbon to complete the comparison and enable a complete techno-economic evaluation, for instance in comparison to distant CO_2 underground storage or with unaddressed emissions at increasing economic penalty. Furthermore, CO_2 purification requirements need to be addressed in more details, as mineralisation could potentially be less stringent than alternatives.

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