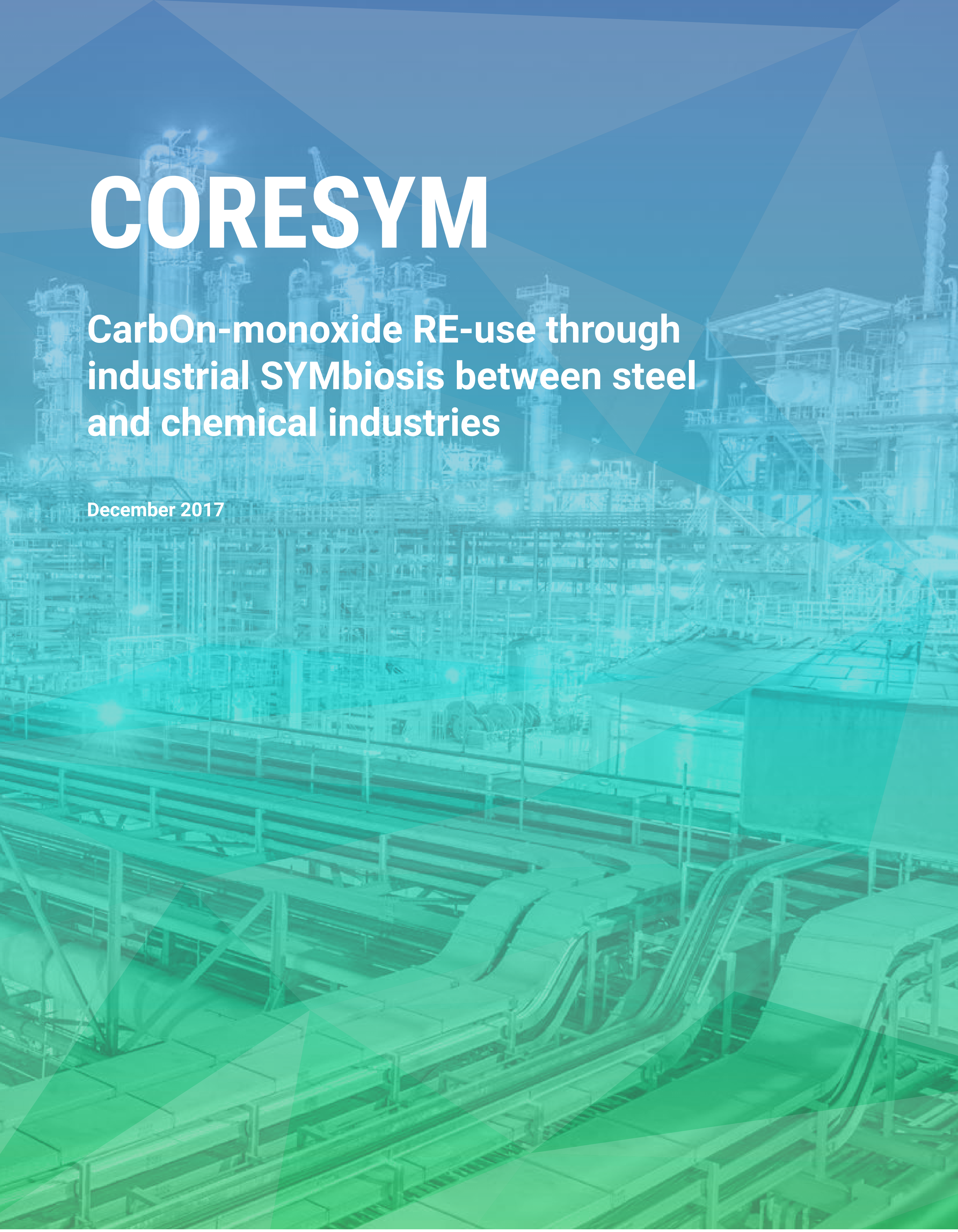

CORESYM

CarbOn-monoxide RE-use through industrial SYMbiosis between steel and chemical industries

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Topsector Energie

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EXECUTIVE SUMMARY

Important shifts are taking place within European industries as companies adopt more efficient technologies, seek low-impact feedstock sources, and adapt to markets and policies which increasingly value efforts towards sustainability. These changes take place within the context of larger societal challenges, including the goals set out in the Paris Agreement to prevent devastating levels of climate change and Europe's goal to reduce climate forcing emissions by 80% by 2050.

One pathway forward, which has gained increasing interest from industry parties, is the recycling of carbon in emissions from industry into products. This allows for mitigating the use of fossil fuels or biomass in production systems, while promoting industrial symbiosis between industries in a step towards a circular economy. However, barriers still exist to realizing these new production systems on the short-term, while the sustainability and systemic implications of a large-scale shift towards waste-gas recycling are still poorly understood.

The steel industry provides a good starting point for understanding the issues around waste gas recycling. The typical carbon content in the waste gas from steel consists of 15 - 25% carbon dioxide (CO_2) and 18 - 30% carbon monoxide (CO). Although chemically the difference between CO and CO_2 is only one oxygen atom, there is a very large difference in the chemical reactivity of the two compounds, which makes CO the first logical option to explore. CO, combined with hydrogen in syngas, is already used on very large scale in many industrial processes, including in the synthesis of methanol, ammonia, or synthetic fuels (with the Fischer-Tropsch process). In addition to having a high concentration of CO, steel mill waste gases also contain a small amount of hydrogen, which makes these gases even more valuable as a potential feedstock.

At the moment, this potential as a feedstock is being lost as these waste gases are used in energy generation or flared. An alternative route (visualized in Figure S1) is to treat the gases and convert them to products which can extend the life-cycle of the carbon, for example by producing feedstocks for plastics or organic chemicals. Within the steel industry, this could even be envisaged as part of a larger circular value chain, if products can be used at the end of their useful lifespan as a replacement carbon source in steel production.

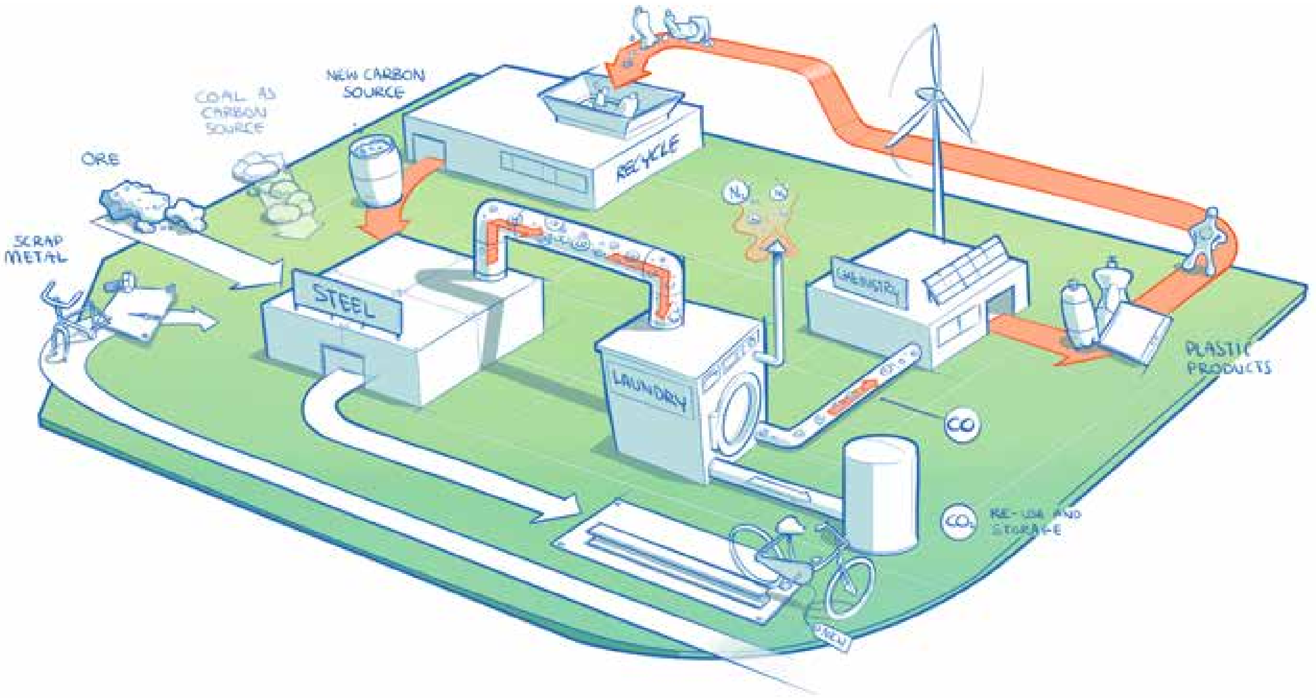


Figure S1. *Outlook for a circular carbon chain around steel mill waste gases*

The study "CORESYM: CarbOn monoxide RE-use through industrial SYMbiosis between chemical and steel industries" was carried out with the purpose of understanding the potential opportunities and impacts of CO recycling in current and future value chains between steel and chemical industries. In the study, an overview of chemical products that can be produced from CO is given. To match the scale of the steel sector a selection of the options was made, narrowing this long list down to products that currently are used in industry on a comparable bulk scale - limiting the products studied in detail to methanol, ethanol, and synthetic fuels, as well as a route to produce bulk hydrogen. An overview of these routes is shown in Figure S2.

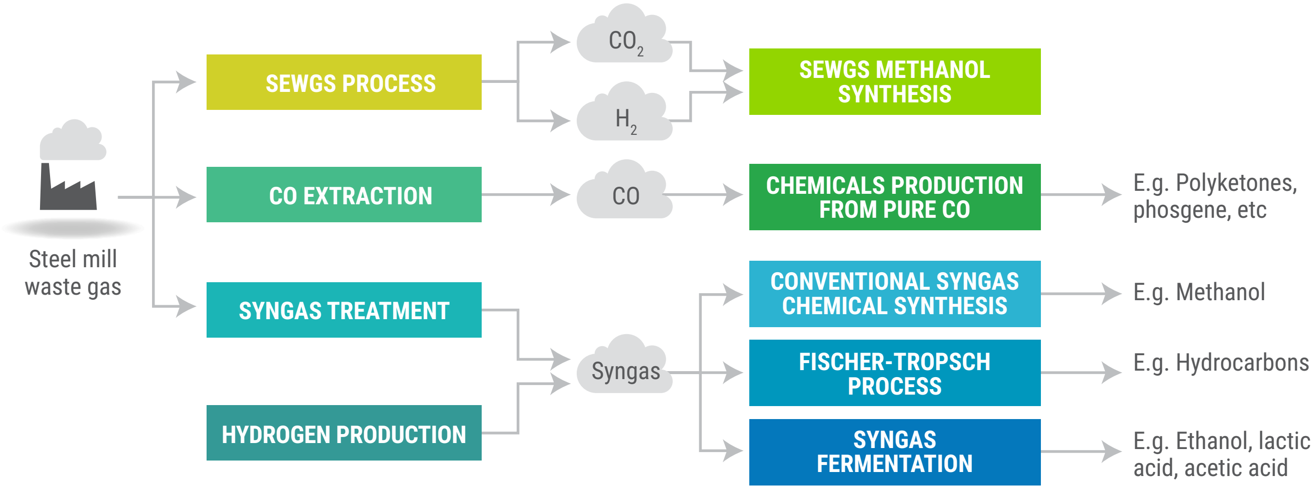


Figure S2. *Main process routes and product types from steel mill waste gases*

For this limited set of products, a techno-economic assessment was done to better understand the technical readiness of the routes and determine the economic potential. The key benefits of fixing CO into products, however, are the potential for carbon emissions reduction and the replacement of traditional fossil feedstocks. The second part of the study was therefore an environmental assessment of both CO_2 emission and other impacts. The assessment was then extended to understand the maximum implications, when these routes for CO recycling are adopted on a European scale. Finally, we examined the primary barriers to implementing waste gas recycling and explored some of the trends taking place or expected in the future, to understand the outlook for waste gas recycling on the long-term.

In this summary, we present the key takeaways from the CORESYM study with our recommendations for the industry sectors and policy makers. The full CORESYM report is available online at http://www.ispt.eu/. Please contact us at info@ISPT.EU if you would like to request a printed copy of the full report or summary.

KEY TAKEAWAYS

Carbon in steel mill waste gases currently represents a missed opportunity for circularity.

In Europe, around 170 million tonnes of steel is produced yearly. The majority of this steel is produced using the integrated production route, which results in concentrated emissions from the coke oven, blast furnace, and basic oxygen furnace which are used in different steps of the steelmaking process. In total, there are nearly 2 tonnes of waste gases (of which 1,3 - 1,5 t CO_2e) produced directly per tonne of steel. These waste gases include high concentrations of valuable components, such as carbon monoxide (CO) and hydrogen (H_2).

The majority of this waste gas is currently used in energy generation, while the remaining gases are flared. This results in a major loss of potential value from a circular economy standpoint; one would ideally preserve the valuable components of the gas, rather than dispersing them in the environment in a non-recoverable form. Alongside the production of one tonne of steel it is possible to co-produce 340 kg methanol, 118 kg of ethanol, or 90 kg of hydrocarbons (eventually producing around 22 kg of ethylene for the route to polyethylene based plastic products) with the waste gases.

CO-rich waste gases can be converted into products with a reduction of CO_2 emissions and other negative impacts.

Using waste gases as a feedstock, instead of for energy, can result in emission reductions from the production of energy and products of up to 21-34% compared to the baseline. In addition, the process of cleaning up waste gases for use as a feedstock also results in a concentrated stream of CO_2, which lends itself to Carbon Capture and Storage (CCS). While roughly a third of the direct emissions from waste gases can be mitigated through use as a feedstock, an additional third is made capture ready in the process. If CCS is implemented alongside waste gas recycling at a European scale, this could result in a reduction of up to 3% of European CO_2 emissions. In addition to reducing CO_2 emissions, when substituting waste gases for biobased feedstocks, water demands, wastewater production, and land use can be reduced, with positive implications for biodiversity.

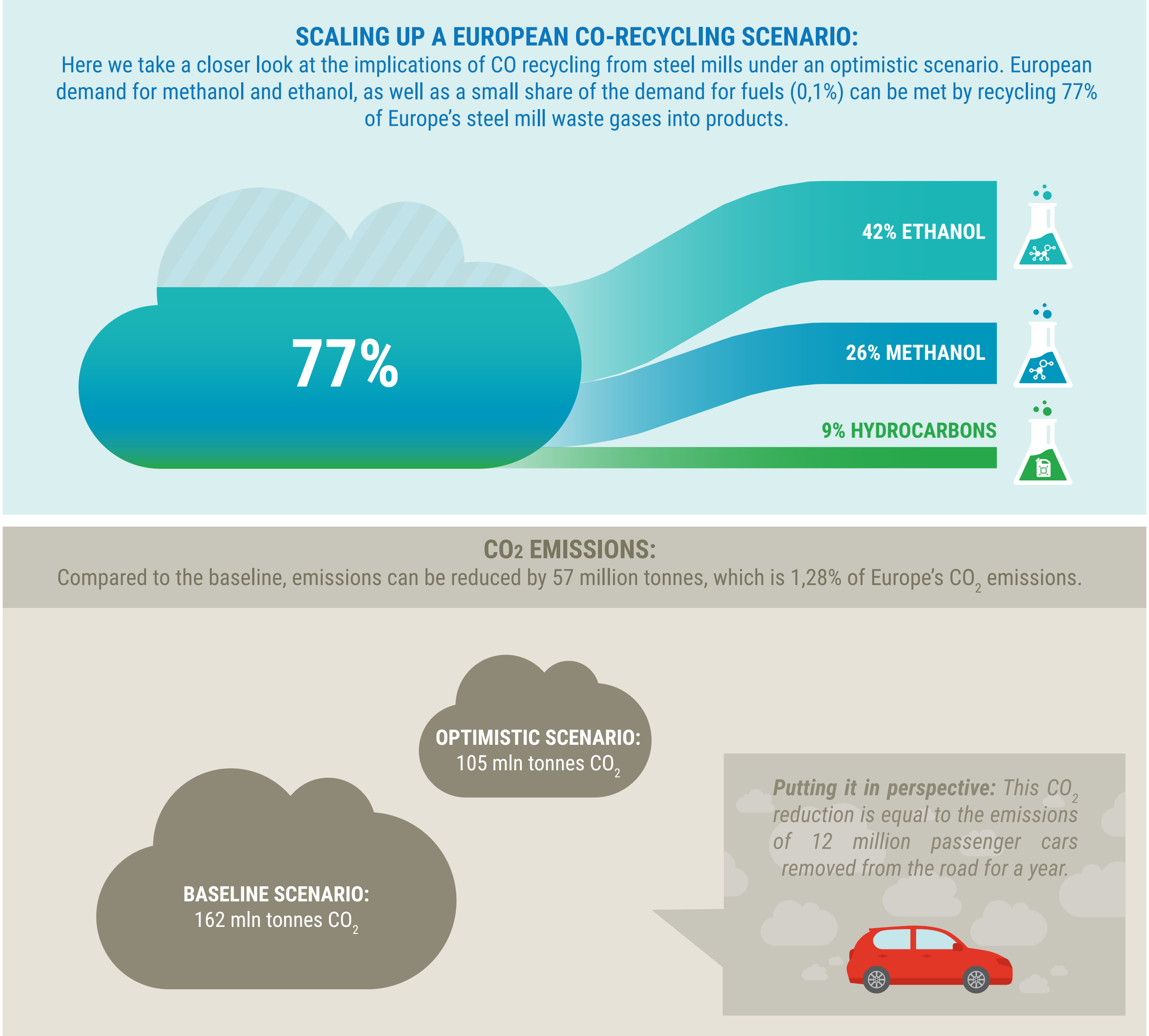
European demand for ethanol and methanol, as well as 0,1% of European fuels could be produced with just over 77% of European steel waste gases. Under an optimistic scenario (with renewable H_2 and energy for waste gas recycling), this scenario could result in a reduction of 57 million tonnes of CO_2 (1,3% of European emissions, Figure S3), before we even consider the additional benefits of CO_2 capture and storage alongside gas recycling. Besides the considerable CO_2 reductions, waste gas recycling can reduce additional pressures caused by other feedstocks. Replacing biobased ethanol with waste gas fermentation, for example, can reduce the embodied land footprint of ethanol by 2 million hectares, reducing pressures on biodiversity in and outside of Europe.

CO-recycling has systemic implications for steel, chemicals, and energy sectors and can be a stepping stone to carbon recycling on the long term.

If waste gas recycling is done on a large scale, this could have big implications for markets and for the sectors involved in this value chain. The scale of potential chemicals production from steel waste gases is significant, far exceeding the current market volumes used in Europe in some cases. If a promising option (such as the SEWGS to methanol route) is fully exploited, this could mean significant changes for the chemicals sector, such as an increasing dominance of methanol as a platform chemical for other products (for example with the methanol to olefins (MTO) route).

Within a CO-recycling value chain, there will be unique opportunities and challenges for industrial symbiosis. H_2 production through electrolysis, for example, also results in a large stream of oxygen as a byproduct, which the steel industry (as the largest oxygen consumer) can make use of. H_2 can also be produced as a means for using excess renewable energy production in peak periods. This highlights an important logistical challenge; chemical synthesis requires a steady flow of feedstocks, while both H_2 and waste gas production is intermittent. CO recycling will result in logistical and operational implications for the steel, energy, and chemicals sectors and require a redesign of major parts of operations.

Finally, an important systemic issue around waste gas recycling is the creation of new dependencies between the steel, energy, and chemical sectors, which poses a risk of technological lock-in (for example delaying a shift to H_2-based steelmaking). However, the expectation is the waste-gas pathway will be feasible at the required scale sooner than direct air capture (DAC) plants. This route offers a transition route that enables a circular carbon value chain on the shorter term. With new technologies for CO_2 conversion to CO and atmospheric CO_2 capture becoming available in the future, a long-term transition towards this route could fill the gap as the steel industry shifts towards lower emission steelmaking processes.



SCALING UP A EUROPEAN CO-RECYCLING SCENARIO:
Here we take a closer look at the implications of CO recycling from steel mills under an optimistic scenario. European demand for methanol and ethanol, as well as a small share of the demand for fuels (0,1%) can be met by recycling 77% of Europe's steel mill waste gases into products.

CO_2 EMISSIONS:
Compared to the baseline, emissions can be reduced by 57 million tonnes, which is 1,28% of Europe's CO_2 emissions.

***Putting it in perspective:** This CO_2 reduction is equal to the emissions of 12 million passenger cars removed from the road for a year.*

Figure S3. *Large-scale sustainability implications of European steel mill waste gas diversion scenario*

Current developments provide an optimistic outlook for gas recycling profitability. However, most low-impact technologies for CO-recycling are not yet profitable on their own.

To make waste gas recycling possible, large investments are required. For a steel mill of roughly the size of Tata Steel's plant in IJmuiden (producing around 7 Mt of steel per year), an investment of around 1-2 billion euros would be required. Including Carbon Capture and Storage (CCS), this scale could enable around 5 Mt of CO_2 mitigation (around 2,6% of Dutch emissions). By comparison, we can consider that the Netherlands currently supports the burning of biomass in coal power plants with around 3,6 billion euros, which accounts for around 40% of the sustainable energy subsidies (Fluxenergie, 2017). According to our assessment, investments in waste gas recycling will only be possible on the short term with financial incentives in place, though LanzaTech claims a positive business case for fermentation with a short payback period of 3-5 years. On the longer term, the very promising SEWGS route will become available on a commercial scale. Currently this route is at a Technology Readiness Level (TRL) of around 6 or 7. The SEWGS route is shown to be profitable, with a payback period of 8 years for the production of methanol and 2 years for the production of hydrogen using this route. However, one downside of this process is that the total potential CO_2 reductions will be lower than the other routes.

Development is required to scale existing technologies and find new options for remaining technical challenges.

Scaling up the SEWGS process (currently at pilot scale, Figure S4), is one important advancement which can enable profitable waste gas recycling, however the technical challenges around gas separation present another opportunity for further development. Steel mill waste gases contain a very large share of nitrogen. When left in the gas stream, nearly twice the volume of gas must be processed, compressed, heated, etc. Separation of nitrogen from CO is technically challenging because the molecules are very similar (e.g. same boiling point, molecular weight and size). This is where the SEWGS process has an advantage; CO is converted to CO_2, which makes N_2 separation simple. If other alternative options for nitrogen separation become attractive, the efficiency of other process routes can be improved.

Affordable low impact hydrogen and renewable energy are key to short term costs.

Carbon monoxide recycling typically requires additional hydrogen (around 0,1 - 0,4 kg/kg product) and additional energy. In the CORESYM study, we have shown that under a conservative scenario (producing energy and hydrogen from natural gas), waste gas recycling can

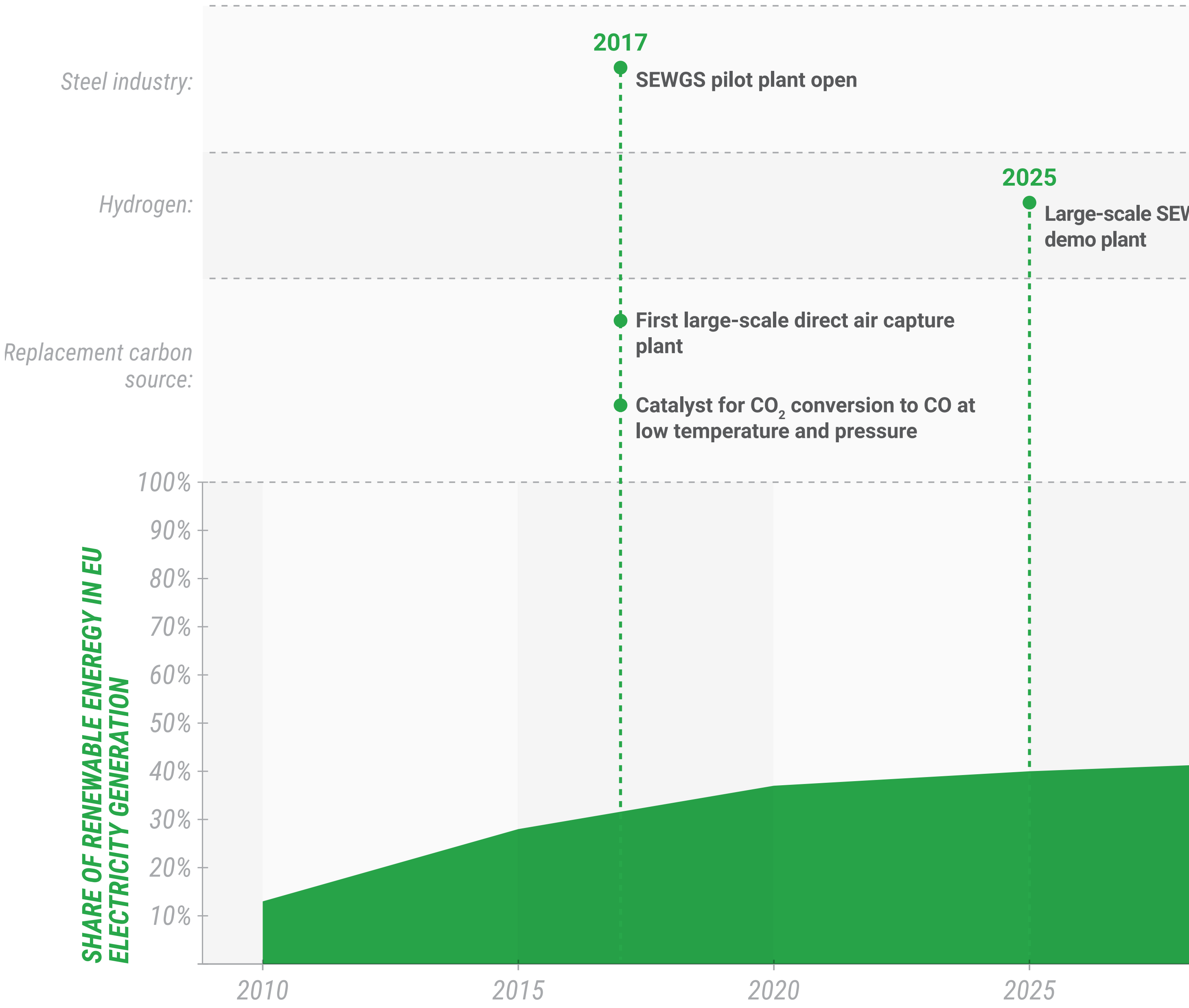
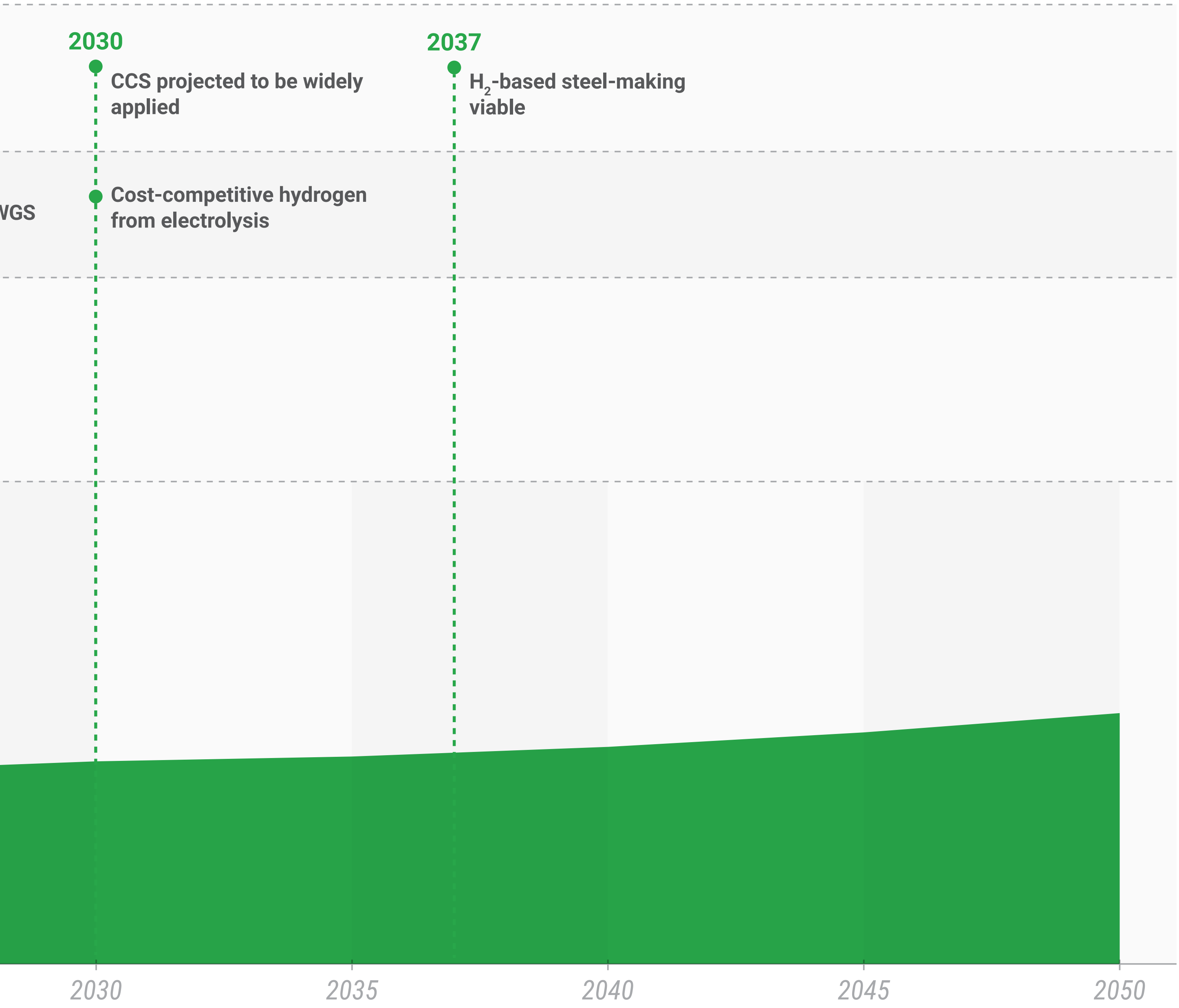


Figure S4. *Timeline of projected trends around CO-recycling* potentially result in CO_2 increases, so we must ensure this route does not occur. While it may be possible to produce ethanol using only the small amount of hydrogen present in the waste gases or to make use of stranded hydrogen that is currently produced as a byproduct, the profitability of low-impact waste gas recycling will largely depend on the price of renewable energy and hydrogen.

The current price of hydrogen from electrolysis is more than 2,9 - 3,8 euros/kg, though will likely reach the 2 euros/kg price relatively quickly. At this price, CO_2 abatement costs range between 46 and 157 euros/tonne for the current options of methanol, ethanol, or Fischer-Tropsch hydrocarbons production. If we assume a hydrogen price approaching zero (either due to the use of stranded hydrogen, extremely low-cost hydrogen from renewable water electrolysis, or in the case that H_2 is not required for effective fermentation) then the CO_2 reductions could occur alongside a profit for methanol and ethanol and at a cost of 31 euros per tonne CO_2 for Fischer-Tropsch hydrocarbons. To put this into perspective, we can consider that CO_2 abatement from renewable energy production has also been estimated in the range of 32 euros/tonne in Germany (McKinsey & Company, 2007).



RECOMMENDATIONS FOR POLICY MAKERS

Positive support of policy measures can quickly become a key driver to adopt the waste-gas re-use technologies, supporting both technological progress and market development. In particular attention is asked for supporting policy measures that address the following:

Incentive structures must be established which work for, not against waste gas recycling.

Achieving the potential impact of CO recycling will not come easily and materializing these routes with a high public value requires clear support of policy measures. For one, the use of waste gases in energy production is currently incentivized by policy, while support for the production of value-added products is not. Support for other alternative industrial feedstocks, such as primary biomass, also creates an uneven playing field for the use of waste gases - even though the environmental footprint of biomass production puts more pressure on the environment than that of waste gas recycling.

Smart carbon pricing can push waste gas recycling into profitable areas, but must also ensure a level playing field.

Carbon taxation can accelerate the development and implementation of waste gas re-use, but only if an international level playing field is warranted - within Europe and with border-tax adjustments between the EU and the rest of the world. At a carbon price of around 60 euros per tonne of CO_2, some of the routes for carbon monoxide recycling already become profitable, even with high costs for energy and hydrogen.

Support must continue for renewables, low-impact H_2 production, and CCS technologies, which affect the prospects for waste gas recycling indirectly.

If large-scale H_2 production from electrolysis with renewable energy becomes affordable in the coming ten years, then the business case outlook for CO recycling becomes much more positive. Policy support for speeding up this development is highly recommended (both in ramping up renewable energy production and in scaling-up H_2 production) to support waste gas recycling. Support for implementation of CCS should extend to CCS alongside steel mill gas valorization.

Additional support is required to research or scale up novel new technologies for waste gas recycling.

There are still technological barriers to overcome to mature necessary technologies to the correct scale. Supporting policies that speed up innovation pathways and support scale-up and demonstration experiments are needed to de-risk the required development trajectories. In particular, support should be put into place for innovation (from research to large-scale demonstration plants) of gas upgrading technologies, such as technologies to separate N_2 from CO-rich waste gases, and for exploring alternative processes and finding economic and environmental optimizations at different scales and with different process setups.

RECOMMENDATIONS FOR INDUSTRY

Industry leaders must take initiative in establishing a feasible transition strategy to waste gas recycling. In addition to remaining informed of developments in this field and working to adopt waste gas recycling when financially feasible, industry should actively work to secure the future of circular carbon recycling in the following ways:

The steel and chemicals sector should lead the way in maturing technologies required in CO recycling.

There needs to be a push from industry to mature technologies around CO recycling such as the SEWGS process, CO-N_2 gas separation technologies, and syngas fermentation. Looking toward the future, in addition to continuing work on these technologies, research and innovation should be pursued for new routes of waste carbon recycling. Industry should be actively seeking new routes for exploration.

The energy sector should move quickly to scale up low-impact H_2 production and increase total renewable energy capacity.

Affordable H_2 from electrolysis and renewable energy are key to the costs of waste gas recycling. Scaling up these parallel developments is necessary to enable waste gas recycling. We have seen that these developments are not happening at a fast enough pace. Additional efforts should be made on the part of the energy sector to ensure a timely shift to renewables.

The steel, chemicals, and energy sectors will need to work together to enable circular carbon value chains and should already be exploring the possibilities now.

Waste gas recycling requires a joint effort of industries, with many implications for infrastructure, operations, and partnerships. There are also many new opportunities for synergies between industries which are associated with waste gas recycling. These opportunities for industrial symbiosis should already be explored now, while technological and policy developments are taking place.

01

INTRODUCTION

WHY CONSIDER CARBON MONOXIDE RECYCLING?

In this study we aim to understand the potential implications of carbon monoxide recycling, which we see as one potentiial pathway for reducing CO_2 emissions in an effective way. However, we must first begin by understanding the context of the problem.

Climate change has been broadly recognized as one of the most significant threats to the continued stability of our planet's biosphere through its potential to trigger systemic changes in key Earth systems. One of the major challenges we face this century is to find ways of rapidly reducing emissions of greenhouse gasses (GHGs), like CO_2, known to contribute to this problem. This already challenging task is further complicated by the fact that we would like to achieve this reduction without causing new forms of negative economic, social, or environmental impacts through our actions. For example, we would like to preserve the function of industries - the provision of goods we use in our daily lives - while reducing our impacts to within safe boundaries.

Most climate change mitigation strategies thus far focus primarily on preventing emissions from occurring in the first place. While this is a logical approach that should be pursued to its fullest extent, it often faces practical and economic challenges stemming from our economy's structural dependency on carbon. Modern humans have arguably only been able to thrive because of our access to extremely abundant and concentrated sources of carbon in the form of fossil fuel deposits. Every single second we consume the fossil-fuel equivalent of all of the biomass that grows on the planet in a year (Dukes, 2003).

A second approach to mitigating GHG emissions, aside from avoiding emissions altogether, is to capture or utilize the gasses that are released as a result of fossil fuel combustion, ideally making beneficial use of the released carbon. One option in this regard is to capture and store the emissions deep underground in perpetuity (carbon capture and storage, or CCS). A second option is to capture and utilize the emissions (carbon capture and utilization, or CCU), for example by producing new products or by using the CO_2 to enhance plant growth in greenhouse production systems.

Though this second approach towards emissions management - carbon capture and utilization - has been criticized by some as an "end-of-pipe" solution that may provide a false excuse for Business As Usual to continue, it is in fact an important complementary pathway to explore for climate change mitigation. In particular, the utilization of emitted carbon as an input for new products is in line with the objectives of a circular economy, and can potentially deliver multiple benefits simultaneously by replacing fossil or biobased feedstocks in production systems. In particular, the capture and utilization of carbon monoxide is promising. While CO_2 can also be utilized as a feedstock, it is often first converted to CO prior to utilization.

At the moment however, the implications of carbon capture and utilization are poorly understood. It is unclear which products or technologies are the most promising or how economic these solutions are. At the same time, we must understand the potential positive or negative environmental impacts of carbon utilization. Beyond this, there are important systemic implications to be considered; the use of CO in products can result in market shifts and restructuring of sectors. Clarifying many of these issues for policy makers and industry leaders is the purpose of this report.

The steel industry is the largest producer of the most concentrated sources of carbon monoxide, and is looking for higher-value uses of these gasses (as an alternative to energy generation). The chemical and energy sectors are the current or potential future users of the waste gases from industry. For this reason, this research is enabled by the collaboration of industry leaders in the steel sector (ArcelorMittal and Tata Steel) and the chemicals and energy production sectors (AkzoNobel, DOW Chemicals, and Nuon).

CHAPTER GUIDE

The rest of this chapter provides an introduction to the context of carbon monoxide recycling, followed by Chapter 2: Our Approach, which briefly explains our methods for evaluating options for CO recycling.

Chapter 3: Promising CO-recycling Products and Processes describes the results of a techno-economic and environmental assessment, which provides the basis for understanding the size of potential impacts and under which conditions carbon monoxide gas recycling results in benefits. In Chapter 4: Large-scale Implications of Process Adoption, we take a look at some of the implications of adoption at a European level and evaluate whether large-scale adoption would lead to positive or negative systemic impacts (e.g. on the demand for fossil fuels, market structure, etc).

In Chapter 5: Barriers and Outlook, we describe some of the issues around feasibility now and in the future, which provides the basis for providing final recommendations for industry leaders and policy makers in Chapter 6: Conclusions and Next Steps.

UNDERSTANDING THE CONTEXT

SOURCES OF CARBON MONOXIDE

Globally, around 2,86 billion tonnes of CO are emitted, with the majority of these emissions coming from anthropogenic sources (IPCC, 2007). As a pollutant, carbon monoxide is problematic due to its direct impact on human health (it is toxic to animals in high concentrations) and through its indirect contributions to climate change. In urban areas, carbon monoxide emissions are usually strictly controlled and monitored for CO-producing industries, commercial vehicles, and private cars.

Carbon monoxide is typically an unwanted byproduct in the incomplete combustion of carbon in solid, liquid, and gaseous fuels. Emissions from vehicle exhaust contribute more than half of all CO emissions globally, though from this source it is too dispersed to effectively recover.

Other sources of CO emissions include industrial processes and fuel combustion in boilers and incinerators. In an industrial setting, carbon monoxide must be incinerated (with or without energy recovery) to prevent health risks. Unlike dispersed sources of CO such as vehicles, industrial activities result in single points of gas emission which makes gas recovery technologically feasible. Of these industrial sources, the steel industry is the leading source of concentrated carbon monoxide emissions.

CARBON MONOXIDE FORMATION IN THE STEEL INDUSTRY

In steel production, iron ore is reduced to hot metal in a blast furnace (BF), usually with coke. To make steel the excess carbon is removed with oxygen in the basic oxygen furnace (BOF). The coke required for steel production is produced in coke ovens, where coal is converted to coke. This process is illustrated in Figure 1.1. While alternative steel production routes exist, around 1,1 billion tonnes of the 1,5 billion tonnes of steel produced globally (around 73%) are produced using this method (Handler et al., 2016).

In this steel production process three main off-gases are available and can be considered for use: the Blast Furnace Gas (BFG), the Coke-Oven Gas (COG), and the Basic Oxygen Furnace Gas (BOFG) (Figure 1.1).

Each stream exhibits specific characteristics in terms of flow and composition (see Table 1.1). The gases contain a significant amount of CO, CH_4, and H_2 typically used for electricity or heat generation, which can also be used in the production of hydrocarbons, chemicals, and materials. Prior to the synthesis of high-added value products, these gases typically require pretreatment (separation and reactive processes) to reach the composition required for synthesis into products (Bermúdez, 2013; Saima, 2013; Uribe-Soto, 2017), which varies per process. For more detailed information on the waste gases, please see the text box on the following page.

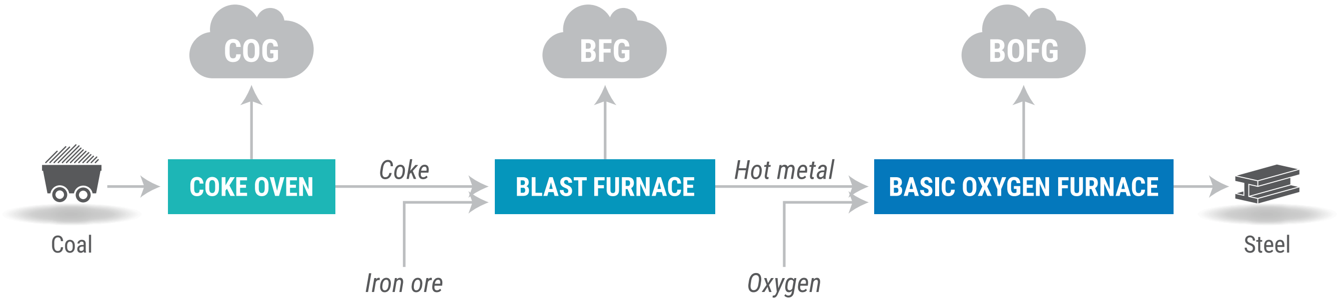


Figure 1.1. *The basic processes in steel production and the gas types emitted at each step. COG: coke oven gas, BFG: blast furnace gas, BOFG: basic oxygen furnace gas.*

Table 1.1. *Typical European steelwork off-gases properties.*

	COKE OVEN GAS	BLAST FURNACE GAS	BASIC OXYGEN FURNACE GAS	MIX
H_2 [%]	58 - 65%	2 - 4%	1 - 2%	15 - 18%
N_2 [%]	~10%	50 - 60%	15 - 30%	39 - 47%
CO [%]	4,8 -6,8%	20 - 35%	50 - 70%	18 - 30%
CO_2 [%]	1,5 - 2,5%	20 - 30%	10 - 20%	15 - 23%
CH_4 [%]	24 - 33%	-	-	6 - 8%

FURTHER INFORMATION ON STEEL MILL WASTE GASES

Types of gases from steelmaking process:

- **Coke oven gas (COG):** Considering the different stages of the steelmaking process in Figure 1.1, the first generated gas is the COG, which is produced in the production of coke in coke ovens by pyrolysis of coal. Coke is a primary raw material in the production of steel, used as fuel to increase the BF temperature, but also as a reducing agent of the iron ore (von Bogdandy and Engell, 2013; Xenidis et al., 2011). The COG is the most valuable gas, due to the large share of H_2, which can react with CO_2 and CO to generate a high value added product.
- **Blast furnace gas (BFG):** The second gas generated is the BFG, corresponding to the output stream of the blast furnace. It contains a large amount of N_2 (because air is used as an oxidant) and contains a small amount of hydrogen. Other compounds contained in this stream, CO_2 and CO, are generated by the combustion of the coke with oxygen to increase the furnace temperature and to reduce the iron ore. Most of the carbon present in the waste gases results from the blast furnace.
- **Basic Oxygen Furnace Gas (BOFG):** The third gas produced is the BOFG. It is generated in the basic oxygen furnace, where the molten iron from the BF is introduced. Oxygen is injected to burn the carbon in the iron and then to produce molten steel. The major component in this stream is CO.

Composition of gases:

- **Nitrogen (N_2):** Considering the overall availability of each compound, N_2 is the most important component at 43,3% on an overall molar fraction basis. The inert character of N_2 may render carbon use difficult, since this compound should be removed in order to avoid excessive compression costs and capital costs. A similar situation occurs with argon and oxygen, but the quantities of these compounds are low.
- **Carbon monoxide and carbon dioxide (CO and CO_2):** The next two compounds, in order of decreasing quantity, are CO and CO_2. They are more or less in the same proportion at 23,9% and 20,5% respectively on a molar fraction basis. From a chemical point of view, the CO_2 reactivity is always lower than that of the CO.
- **Hydrogen (H_2):** The fourth compound to be considered is H_2, which is a key component since it can reduce CO_2 and CO to produce a high value added product. Unfortunately, its quantity is not very large, 6,5% on a molar fraction basis, compared to the amount of CO_2 and CO. Regarding their overall availability, CH_4 and other hydrocarbons are placed in the last position among the valuable compounds at 1,2% on a molar fraction basis.
- **Water (H_2O):** Another consideration is the water content. Indeed, the three streams are saturated with water, 4% on a basis molar fraction basis. This water content will be important in the definition of process diagrams for the use of steelwork off-gases, especially in the compression stages in which water can condense and damage the compressor. These cases will require a multistage compression, removing water between compressor stages.
- **Other compounds:** Finally, the steelwork off-gases have other undesirable compounds that do not appear in Table 1.1. In particular, the presence of dust in the BFG and BOFG, aromatics compounds, and H_2S and HCN in the COG. Since most of these compounds are catalyst poisons, the integration of gas treatment stages should be considered in a potential valorisation process.

CURRENT USE OF STEEL MILL WASTE GASES

Most of the steel mill waste gases produced globally are flared and lost, while in Europe a large share is being used for heat or power generation. Estimates for how much is used in electricity production range from around around 25% for all steel waste gases (Handler et al., 2016) to 50% of all blast furnace gas (Ecofys, 2009), though this share may be even higher.

The waste gases of Tata Steel and ArcelorMittal are used internally and externally (for example by Nuon) to generate heat and power. The export of gases as a waste product currently results in relatively low value to the steel industry. Moreover, both the flaring of steel mill waste gases and the production of energy from the gases are not ideal from the perspective of green chemistry and circular economy principles; ideally the chemical complexity of the materials would be preserved before defaulting to energy generation.

Blast furnace gases are not a very valuable energy source compared to natural gas. While use of the waste gases as an energy source is certainly preferable to their complete loss (the emissions are the same in either case), virtually all other sources of energy, including coal, are preferable energy sources in terms of greenhouse gas emissions (see figure 1.2).

This is an important point, because if steel mill waste gases are diverted to the production of chemicals or hydrocarbons, this energy will need to be replaced. We can see that for any energy source which replaces the waste gases, the CO_2 emissions per unit of electricity will be reduced. This means that even if the overall emissions from the production of chemicals and hydrocarbons from waste gases is higher than using virgin fossil fuels there may still be a strong case for doing so when considering the complete picture. Examining the trade-offs between the two parallel process chains: electricity and chemical or hydrocarbon production, is the main goal of the environmental assessment.

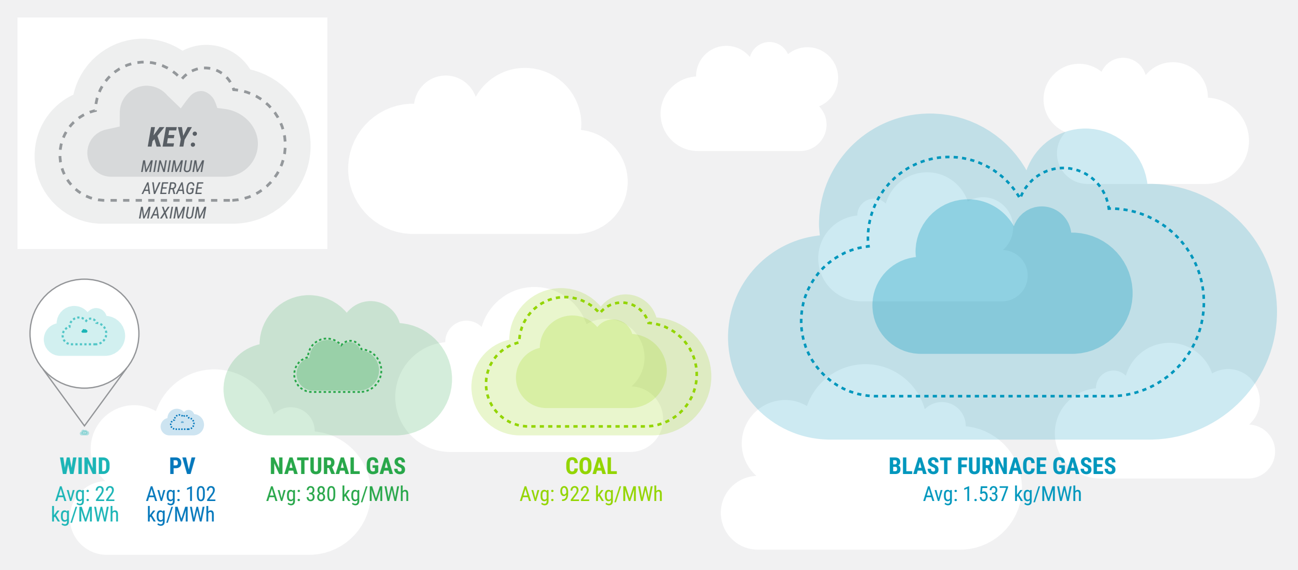


Figure 1.2. Overview of CO_2e emissions for electricity from different sources. *The inner and outer boundaries signify the lower and upper bounds of emissions per MWh, while the dotted line represents the average emissions.*

USING STEEL MILL WASTE GASES AS A FEEDSTOCK

The chemicals sector is shifting towards cleaner process technologies and trying to identify low-impact feedstock sources for chemicals production. There is a shift away from the fossil fuel feedstocks that have formed the basis for the organic chemicals sector until recently.

Most of the focus for alternative feedstocks has been on identifying biobased alternatives. However, our natural systems are already under tremendous pressure. Currently, agriculture occupies around half of the plant-habitable surface of the planet (FAO, 2015), while food production will need to increase by an estimated 25-70% by 2050 (Hunter et al, 2017). Increasing demands for biomass further can contribute to additional biodiversity loss and environmental degradation.

For this reason, companies are starting to look at second and third generation feedstocks, which can reduce the pressures on natural land. Second generation production implies the use of crop or forest residues or non-food crops, while third generation refers to production that does not require arable land (e.g. algae production or post-consumer wastes). One example of this is a project AkzoNobel is working on, which aims to convert mixed municipal solid wastes to syngas, which will be used in methanol production in Rotterdam.

Steel mill waste gases fit into the bigger picture of shifting demands to low-impact feedstock sources, utilization of waste streams, and the implementation of industrial symbiosis to realize a more circular economy within industry.

The steelwork waste gases consist of multi component mixtures containing carbon monoxide, hydrogen, nitrogen, carbon dioxide, methane, and/or moisture. Nitrogen and sulfur containing components are also present, for example NO_x, HCN and H_2S, COS, respectively. These are quite problematic for chemicals production and present a downside for the use of waste gases when compared to syngas from natural gas.

For this reason, the purification processes for steel mill waste gases are one of the key issues for the environmental and economic outcomes for the process. Two main options exist for converting the waste gases to a usable feedstock: purification to remove the impurities (retaining the CO and H_2 as well as non-problematic gases) or separation of only the CO. The former has the main drawback of larger volumes of gas (mainly N_2), for which larger infrastructure is required, while the latter is more expensive and does not retain the H_2, which is also valuable. For further details on the gas purification and separation, please see the text box “Gas purification and separation options”.

There are five high-level process routes which can be distinguished for converting carbon monoxide from steel mill waste gases to chemicals or hydrocarbons, which are shown in the overview in Figure 1.3 and described briefly here.

Firstly, one option is the Sorption Enhanced Water-Gas Shift (SEWGS) process, in which CO is converted to H_2 and CO_2. The hydrogen can be considered the final product or the H_2 and CO_2 can be used in methanol production.

Secondly, CO can be separated from steel mill waste gases as a standalone feedstock for chemicals production. For any chemicals produced with pure CO, the environmental and economic differences between the waste-gas and conventional routes will only come from the CO extraction process. The rest of the chemicals production chain will remain the same.

Finally, steel mill waste gases containing both carbon monoxide and hydrogen can be utilized as a syngas in a wide variety of different production practices. These routes will likely require additional hydrogen inputs.

- When waste gas is used to produce methanol, the differences in performance will result only from the upstream effects of syngas production. The rest of the production chain remains the same, whether you are considering methanol production or production of one of the many derivatives of methanol.
- The Fischer-Tropsch process converts syngas to liquid synthetic hydrocarbons. This entire process chain differs considerably from the conventional petroleum-based production chain and we can expect many different tradeoffs which will need to be evaluated for these products.
- Lastly, syngas can be used in fermentation processes to produce chemicals or fuels such as ethanol. Again, this is a significantly different process than the conventional processes of either petroleum refining or biomass fermentation which this could replace.

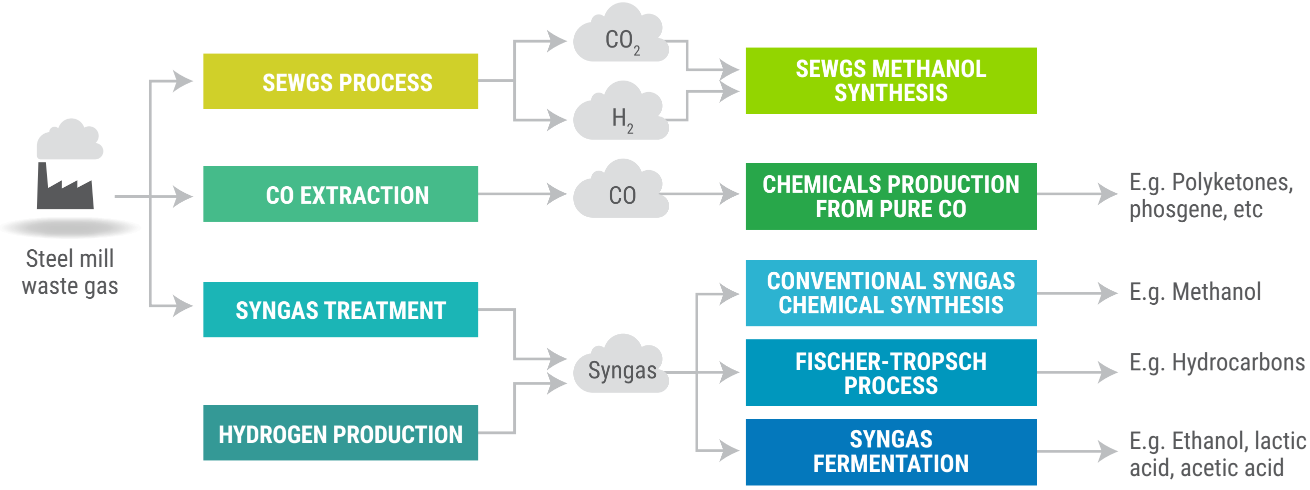


Figure 1.3. *Main process routes and product types from steel mill waste gases*

GAS PURIFICATION AND SEPARATION OPTIONS

Gas purification

Any particulate material can be removed from the gas stream using physical separation methods, such as cyclones, if needed in combination with candle filters or moving bed filters. If, prior to any catalytic conversion, a CO_2 removal step is applied with the preferred amine absorption technology, then hazardous nitrogen and sulfur component are also removed along with the CO_2.

Sulfur components, H_2S and COS, can be removed selectively using metal oxide based adsorption. Well known for this purpose is the use of zinc oxide. Previously, zinc oxide was only used as a non regenerable guard bed for example to protect the catalysts from poisoning in thermo-catalytic conversions. Nowadays, interest is shifting to regenerable utilization of zinc oxide adsorption beds, or beds containing a combination of metal oxides. Oxidative regeneration of spent adsorbent material results in a highly concentrated sulfur oxide side stream for further processing.

CO separation

Cryogenic processes: Cryogenic processes essentially consist of liquefaction of part of the gas stream, followed by a phase separation and distillation of the remaining liquid components. In general cryogenic processes are suitable for large capacity high purity CO installations where the nitrogen content of the purified CO stream is tolerated by the downstream application. This method is the oldest, and various operation schemes have been developed depending on the required purity. Without any special measures, the nitrogen present in the feed largely remains in the final feedstock. Removal of nitrogen from the CO stream requires an additional column and cryogenic distillation step. Generally, the separation of nitrogen and CO by cryogenic process is difficult as the difference in their boiling point is only 6°C.

Adsorption processes: Adsorption process are operated as vacuum swing adsorption (VSA), pressure swing adsorption (PSA), and thermal swing adsorption (TSA). Generally, adsorption processes are suited to the production of high purity product with a high yield of CO. In the process CO is adsorbed onto a solid (the adsorbent). The adsorption is favored by high pressures and low temperatures. Typically, a minimum of three adsorptive beds are used, as the process involves three cyclical steps: production (selective adsorption), regeneration of the adsorber (evacuation of the adsorbed gas), and repressurization of the bed with a portion of the purified stream. The number of beds is increased for higher flow rates or higher CO recovery rates. CO-selective absorbents are generally available to a very limited extent. Sodium-type mordenite active-carbon-supported carbon and activated carbon are the most common absorbents. Active carbon copper is a chemical absorbent based on the selective binding capability of Cu+ to CO. Several adsorbents consisting of porous carriers, such as activated carbon or zeolite, and supported Cu+ , have been developed for CO adsorption. These adsorbents exhibit selectivity for CO; however, their adsorption capacities and selectivity depends significantly on the properties of the carrier.

Membrane processes: Membrane gas separation is a pressure-driven process which entails several advantages compared to other technologies, i.e. easy operation, low capital and operating costs and low-energy requirements (Bernardo, 2009). In a membrane separation process, a gaseous mixture at high pressure is forced to pass through the surface of a membrane which is selectively permeable to one or more of the gas components. As a result, the permeate, the stream obtained after it has passed through the membrane, can be enriched in these components while the retentate, the stream that does not pass through the membrane, is therefore enriched in the rest of the components.

Liquid adsorption processes: Liquid absorption processes are based on the selective and reversible complexation of CO with metal-based complexing compounds in a liquid solution. Liquid absorption processes include: ammonia copper liquor process:

$$CO + Cu(NH_3)_2{}^{+} \text{<-->} CU(NH_3)_2(CO)^{+}$$

COSORB process:

$$CO + Ar - X \text{<-->} CO - X + Ar$$

where ArX=copper(I)tetrachloroaluminate(III) aromatic solution (benzene or toluene).

Other gases, such as hydrogen, carbon dioxide, methane, and nitrogen are chemically inert to this solvent, but are slightly soluble in benzene or toluene. Water, ammonia, hydrogen sulfide, sulfur dioxides, and oxides of nitrogen are poisons to the complex, and therefore must be removed in a pretreatment step (ie, molecular sieve adsorption system). The COSORB process works well to produce high-purity CO from a variety of gas mixtures, including a nitrogen-rich feed. Separation of nitrogen from CO by the COSORB process is easier and more economical that by cryogenic distillation. In a typical process, CO produced by COSORB technology is 99% pure with a 99% yield. COSORB is also less capital intensive than the ammonia copper liquor process. However, due to degradation of the absorbent in the COSORB process, this process is seldom used. New CO-complexing compounds have been studied for liquid absorption applications, including iron complexes, palladium complexes, selenium, and secondary amine systems.

TECHNO-ECONOMIC CONTEXT

While the technologies for treating and utilizing syngas from the steel industry are fairly new, the utilization of syngas from other sources (for example in methanol production) is far more advanced, and the main issue is in handling new sources of syngas. For steel mill gases, new technologies for cleaning the syngas and converting it into products are being explored increasingly in pilot projects and research trajectories. One notable example of a new technology is Lanzatech's syngas fermentation process for the production of fuels. Lanzatech has scaled up in the past ten years from small pilot projects to large-scale recovery and utilization of steel mill waste gases, including a partnership with ArcelorMittal. One example of a large research trajectory for carbon monoxide recycling from the steel industry is the German Carbon2Chem project, which is supported with 50 million euros per year by the Ministry for Science and Education.

Outside of technological developments specifically for utilizing waste gases from steel, other developments contribute to the feasibility and sustainability impacts of potential steel gas production systems. On one hand, the price and adoption of renewable energy production will play a large role in determining the attractiveness of these new process technologies. On the other hand, the developments in hydrogen production will also steer the trajectory of steel waste gas utilization, as hydrogen will be a necessary addition to the steel mill syngas.

Currently the only cost-effective and most widely applied means of producing hydrogen is from steam reforming of natural gas, which results in high CO_2 emissions. In the coming 10-15 years, most industry partners are expecting water-based electrolysis will become cost competitive and replace steam reforming with a far lower environmental impact profile. However, electrolysis is more energy intensive than steam reforming. A low impact profile can therefore only be achieved by the combination of electrolysis and renewable energy sources. Nuon, among others, is exploring options for not only using renewables in hydrogen production, but also in using the renewable energy when there is an overcapacity of energy generated as a means to handle supply fluctuations and store energy.

POLITICAL CONTEXT

With the adoption of the Paris Agreement, the European Union has a renewed sense of urgency to reduce CO_2 emissions, and this may be the driving force behind upcoming legislation that could incentivize or disincentivize technologies and partnerships for recycling carbon monoxide. Reducing CO_2 emissions by 80% by 2050 compared to 1990 will not be an easy task. In the past, the European Union and individual countries have established opportunities for renewable energy investments, biobased initiatives, and circular economy projects, while also pushing for the adoption of carbon capture and storage (CCS) and implementing carbon allowances programs. All of these current and upcoming programs and policies define the political climate in which decision-making on carbon monoxide recycling will take place.

The programs that have already been implemented have had mixed success. Attempts to promote carbon capture and storage (CCS) have, so far, been a failure according to the European Commission (2017a). Due to the financial crash in 2008, the market has had an excess of carbon allowances, which has meant that the price of the allowances has not increased (European Commission, 2017b). This economic circumstance also disincentivizes the implementation of CCS technologies. In the future, carbon allowances will likely be decreased, increasing the price of carbon, and making CCS or CCU technologies more attractive options (European Commission, 2017c). At the same time, if the cost of carbon is too high, industries such as the steel industry may not be able to operate profitably in Europe.

However, there are some incentives which may lead to increased interest in carbon monoxide recycling, including recognition of products made from carbon dioxide as waste-based, low-carbon, or circular, which would mean additional support for new initiatives. In this paper, we explore the current economic feasibility of carbon monoxide recycling and discuss what types of incentives would be required to achieve new carbon monoxide recycling programs (or CO_2 recycling initiatives) on a larger scale.

02

OUR APPROACH

Based on a first quickscan of all of the options for CO recycling, the project consortium made a first selection of the most promising product routes for further evaluation. These options were explored in a techno-economic assessment and an environmental assessment. The criteria used in these assessments are described briefly here. For more information on data and literature used and assumptions, please see the appendices V and VI.

TECHNO-ECONOMIC ASSESSMENT

The selected routes for chemicals production from steelworks off-gases are compared by focusing on a set of key criteria such as technological maturity, potential revenue generation, level of investment needed to achieve commercialization, potential total scale of production, and the applicability to the European economic environment.

Technology maturity

The technologies for the manufacture of chemicals are at varying stages of development and maturity. The highest level includes mature technologies of chemicals that are already in full commercial use. Often licensors can provide production facilities using proprietary off-the-shelf technology. Another category consists of routes that are considered to be promising technologies ready for commercialization. A last category of methods for converting carbon monoxide into chemicals are considered to be promising technologies at a conceptual stage that need to be proven further through technical pilots and/or demonstration plants.

Scale-up potential

The scale up potential looks at the total demand that can be expected to arise from a technology or from the products obtained. This also touches on the estimated amount of CO_2 emission that is avoided by applying the technology. Geographical considerations may be applicable here, for example because of high logistical efforts to reach distributed markets.

Value for money

The potential for revenue generation depends on the price of the chemical that is produced and the volume to be produced. An important aspect is the market size, or the potential market size. With an increasing scale of production capacity of a chemical, the revenue can increase due to the increasing selling volume, but revenues can drop due to decreasing market prices.

Level of investment

The level of investment required to advance a specific carbon monoxide to chemicals route to a demonstration scale or even a commercial operation varies significantly from millions to billions of euros. Often the publicly available information regarding the level of investment required to bring a technology to a certain level of maturity is limited.

Economic Feasibility

The economic feasibility in general studies the revenues and costs of the operation, and balances the net value for example by considering the overall revenues or the income per unit of product. Here, we look at the feasibility from an overall energy balance point of view. For example to estimate the amount of energy of the input flows into the process as compared to the energy of the product flows.

ENVIRONMENTAL AND SYSTEMIC ASSESSMENT

Each scenario explored in the environmental assessment includes two parallel process chains: both electricity production (either from steel mill waste gases or from natural gas as a replacement) and production of a chemical or hydrocarbons (either from steel mill waste gases or from the conventional feedstock). As such, in the assessment, we use the waste gases resulting from the production of one tonne of steel as the functional unit and compare the outcomes for using this unit of gases in either electricity production or chemicals production to derive secondary functional units for energy or chemicals.

For each baseline and alternative production scenario, we looked at a set of indicators, based on Metabolic's holistic circularity assessment framework (Figure 2.1). These indicators are described briefly on the following pages.

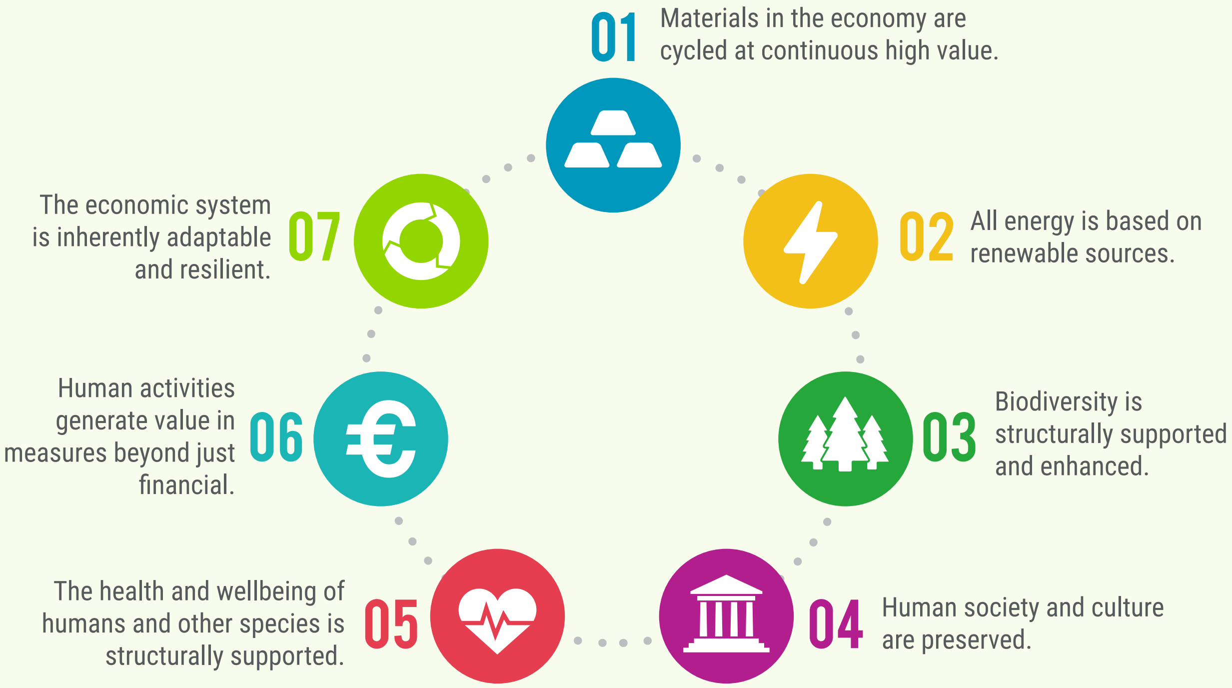


Figure 2.1. *Seven Pillars Circularity Assessment Framework*

01 MATERIALS

- **Solid wastes generation and hotspots:** total expected direct solid wastes resulting from the process chains. Here we define wastes as materials with no or negative economic value (cost to dispose of). We mark qualitatively the lost opportunities for reusing materials in further process, effectively making these wastes instead of byproducts (at a high value, potential for use as source of energy, material input, etc.).
- **Total water inputs:** total consumptive water inputs required for the full process chains.
- **Wastewater generation and hotspots:** a qualitative look at the prospects for reuse of wastewater (level of toxicity, potential for purification and reuse).
- **Carbon efficiency factor:** The carbon efficiency metric is a calculation of the share of carbon inputs which end up in the final product, which serves as a proxy for the overall efficiency of the process.

02 ENERGY

- **Total (net) energy inputs:** total energy inputs associated with the process chains. While this includes energy for consumptive inputs (e.g. natural gas or biomass), it does not include energy for producing capital goods such as the chemical production or energy generation installations.

03 BIODIVERSITY

- **CO_2 emissions:** total CO_2 emissions associated with the process chains.
- **Other atmospheric/air emissions:** emissions of SOx, NOx, $PM_{2.5}$, and VOCs associated resulting from the process chains.
- **Inputs of materials associated with ecotoxicity issues:** We look qualitatively at ecotoxicity issues associated with inputs such as catalysts and solvents for the scenarios. Chemical toxicity was screened with the Column Model for Chemical Substitution by The Institute for Occupational Safety (IFA) of the Social Accident Insurance. This provides a pathway to categorically estimate risks of acute and chronic health hazards as well as environmental hazards based on Chemical Safety Data Sheets specified in the EU REACH Regulation.

04 HUMAN SOCIETY AND CULTURE

- **Will not be considered for this analysis as it is more context-dependent than process-dependent.**

05 HEALTH AND WELLBEING

- **Inputs of materials associated with human health and safety issues:** We will look qualitatively at hotspots for human health and safety associated with specific material inputs.

06 MULTIPLE FORMS OF VALUE

- **Useful byproducts:** we look qualitatively at the potential for use of other byproducts.

07 ADAPTIVITY AND RESILIENCE

- **Non-renewable/non-recoverable resource inputs:** As dependence on non-renewable or non-recoverable resource inputs represents a risk, we estimate the amount of these inputs in each scenario as a measure of resilience.

The results of this assessment are given in Chapter 3. Following the results of the detailed environmental assessment, we look at systemic consequences of large-scale adoption of the technologies in Chapter 4. In this section, we discuss issues such as technological lock-in, market shifts, and production system shifting that could result from scaling up the short-listed processes, based on both the environmental and techno-economic assessment results.

LIMITATIONS OF THE ANALYSIS

Considering that many of the technologies relevant for waste-gas recycling are relatively new, it is difficult to find quantitative data on many technologies which are relevant. Much of the data that would be beneficial for this study is still private intellectual property of the technology providers. Even though our industry partners in this study are involved in projects with these technology providers, they are not able to share their data.

For this reason, proxy data must often be used. For example, while the Fischer-Tropsch process which we explore is well developed and documented, the data available is often from coal gasification. In order to use this data to evaluate the gas cleanup steps, we must adapt existing data or assume it is a reasonable proxy for the situation with waste gases from the steel industry.

For the environmental assessment, the baseline or conventional processes are well documented, with abundant life cycle assessment data available. Data for processes such as methanol production from natural gas are quite complete, with data for all inputs and outputs of the process, such as catalysts, emissions of metals, and waste streams produced. While it is possible to derive basic data on energy, emissions, and water inputs and outputs for the alternative processes from literature sources, more detailed information is missing. One of the largest gaps in the environmental assessment, for example, is the mass of solvents and catalysts used in the alternative processes. This makes it difficult to provide a quantitative assessment of ecotoxicity and human health impacts associated with the production scenarios and makes a full life cycle assessment impossible.

An additional limitation of the environmental assessment is that lacking thorough data on the processes for waste gas to products means that data must be derived from a variety of sources. This makes the comparability of information difficult, as the values correspond to different process setups explored in different studies. Ideally, we would start with a single process setup, and have detailed data for the entire process chain. This means that the environmental assessment can only provide an indication of the total scope of impacts with these technologies for a reference unit of product, and we cannot comment on the full impact of specific process chains.

03

RESULTS:

Promising CO-recycling products and processes

OVERVIEW OF CO-RECYCLING OPTIONS

This section provides a short inventory of the available options for CO recycling (see Figure 3.1). The purpose of this section is to provide some quick insights into some of the options for those unfamiliar with the possibilities. Please see Appendix IV for some further details on these options. This overview also provides the basis for understanding our process selection; why we selected some routes for further exploration.

After explaining the selection of technologies and products, we present the results of the techno-economic assessment and the environmental assessment of the selected routes in the following sections of the chapter.

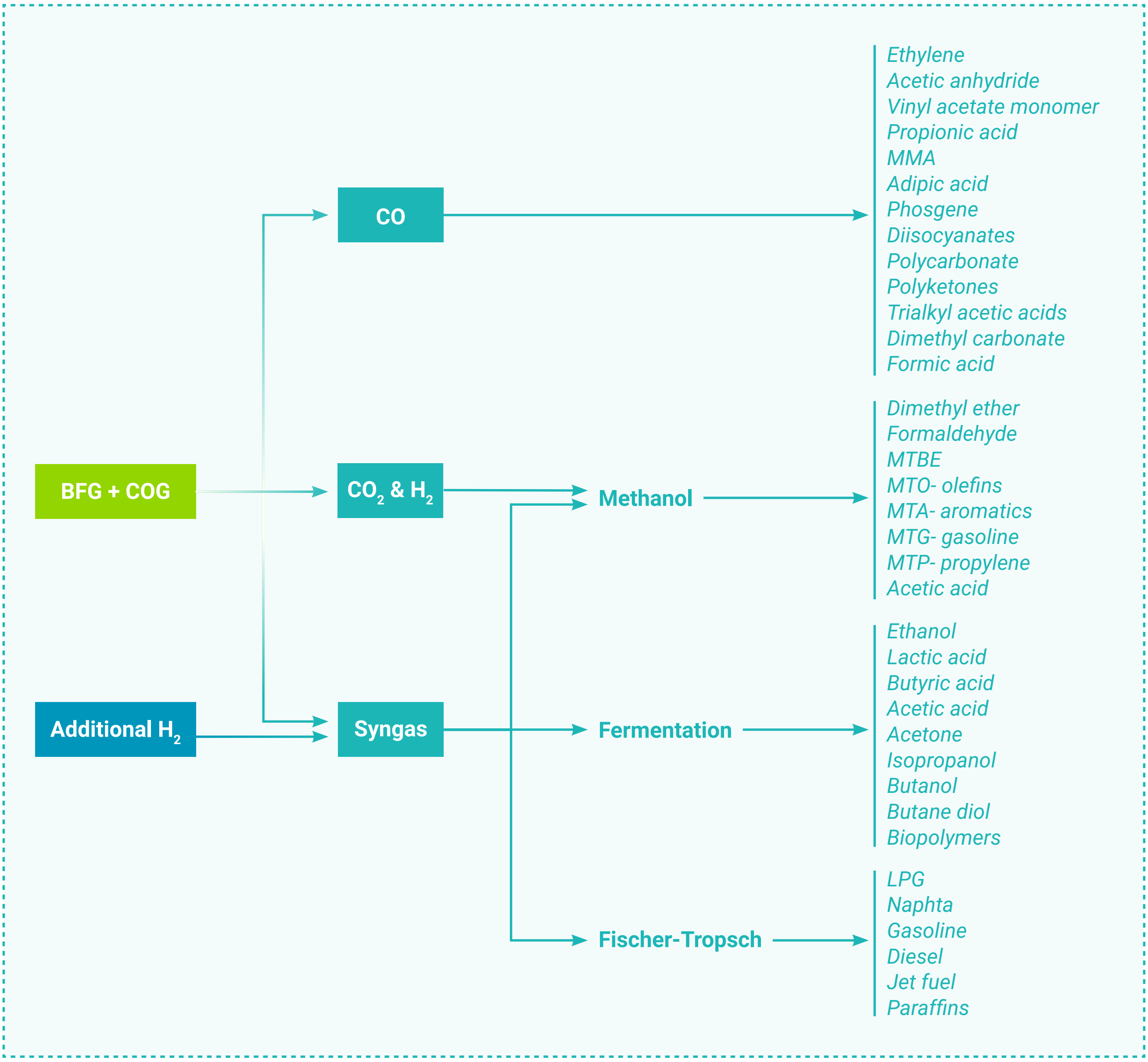


Figure 3.1. *Long list of CO recycling options*

PURE CO USE IN PRODUCTION

Many conventional chemical synthesis processes utilize carbon monoxide as feedstock. 90% of carbon monoxide is used as a mixture with hydrogen for the production of chemicals such as methanol. Other processes, such as the production of phosgene, acetic and propionic acids, and others, require using purified carbon monoxide (IHS Markit, 2016).

There are a number of methods for industrial production of pure carbon monoxide for use in chemicals which are simple and well-established. As such, CO separation from industrial waste gases will have difficulty competing with these processes. Many of the products conventionally produced from pure CO also have a limited market size, which makes them less attractive options for large-scale production from waste gases.

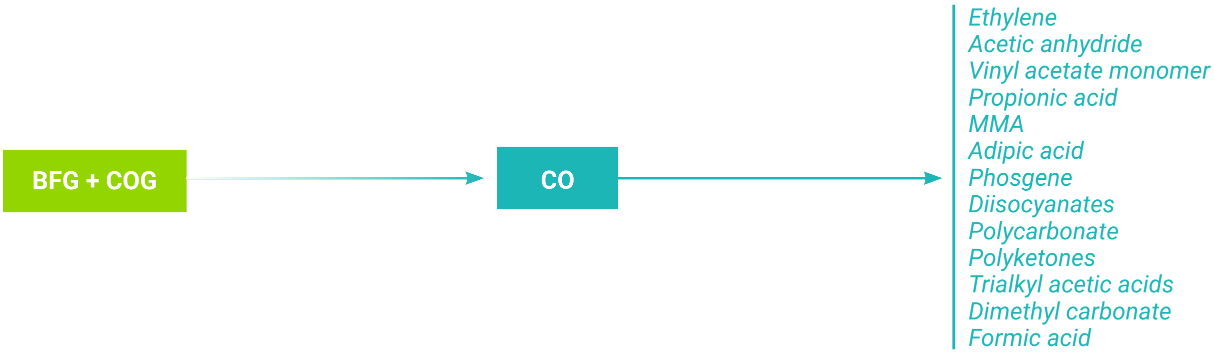
PRODUCT	GLOBAL DEMAND	PRICE	TECHNO-ECONOMIC CONSIDERATIONS
Ethylene	140 Mtpa	1020 €/tonne	- Production from CO: immature technology
Acetic anhydride	2,5 Mtpa	1063 €/tonne	- Limited market size
Vinyl acetate monomer (VAM)	6,5 Mtpa	1020 €/tonne	- Limited market size
Propionic acid	500 ktpa	2210 €/tonne	- Limited market size
Methyl methacrylate (MMA)	4,5 Mtpa	1275 €/tonne	- Limited market size
Adipic acid	3 Mtpa	1700 €/tonne	- Limited market size
Phosgene ($COCl_2$)	only on-site production		- Limited market size, logistical problems
Diisocyanates			- Limited market size
Polycarbonate	4 Mtpa		- Limited market size
Polyketones	≈ 60 ktpa		- Limited market size
Trialkyl acetic acids	small specialized market		- Limited market size
Dimethyl carbonate (DMC)	500 ktpa	748 €/tonne	- Limited market size
Formic acid	≈ 1 Mtpa	510 – 1020 €/t	- Limited market size

SYNGAS FERMENTATION

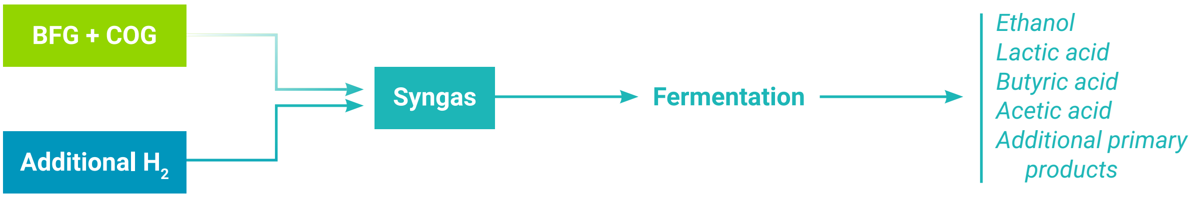
Syngas fermentation is an innovative method for the production of fuels and chemicals. Ethanol is the most important product produced from fermentation, although other chemicals are obtained as co-products from the same process and fermentation has been used to produce additional primary products, some of which are shown in Figure 3.1.

Low gas solubility has been a major technological barrier, but due to recent advances in reactor and fermentation technology, this is becoming less of a barrier to achieving higher carbon conversion efficiencies.

PRODUCT	GLOBAL DEMAND	PRICE	TECHNO-ECONOMIC CONSIDERATIONS
Ethanol	70 Mtpa	404 €/tonne	+ • Current industrial markets are mature. • Demands for fuels still increasing
Lactic acid	≈0.9 Mtpa	Other components, mainly carboxylic acids, are co-produced in minor amounts during syngas fermentation for ethanol	
Butyric acid	≈ 0.8 Mtpa		
Acetic acid	15 Mtpa		
Additional primary products		A number of other primary products can be produced through fermentation	



ENERGY CONSUMPTION	WATER CONSUMPTION	OVERALL ENVIRONMENTAL CONSIDERATIONS
Processes like partial oxidation, steam reforming, and cracking, are used commercially to produce pure carbon monoxide. Depending on feedstock and process, syngas of different compositions are produced at different energy costs. For example, energy balance for steam reforming of natural gas and methanol cracking are around 0,8 and 1,3 Nm^3 methane / Nm^3 CO, respectively (Stoll & Linde, 2000). With waste gases, use of fossil feedstocks can be avoided, but energy for isolating pure CO will still be high.	Wastewater from the processes of cleaning the steel mill gases (cooling, cleaning, etc) might be polluted with chromates, phosphonates, polyacrylates, zinc, and other highly biotoxic chemicals, as well as metals leaching from piping and solder. The prognosis for wastewater contamination will be similar or worse for production from waste gases, compared to conventional processes from natural gas, given the contaminants in waste gas.	Depending on which baseline CO production process is compared to that from steel mill waste gases, there may be an improvement or a higher impact profile. Phosgene production and the product itself are associated with high toxicity and environmental concerns, leading many to seek alternatives. For this reason, phosgene would not be an ideal chemical to produce from CO, even if the process from waste gases would result in an improvement over conventional routes.



ENERGY CONSUMPTION	WATER CONSUMPTION	OVERALL ENVIRONMENTAL CONSIDERATIONS
Energy consumption is very low in a biobased ethanol production process (<2 MJ/kg), while syngas fermentation (excluding hydrogen production and syngas treatment) requires around 8 MJ/kg.	Compared to biobased fermentation, water consumption is considerably lower in a syngas fermentation alternative, due to the high demands for water in biomass production (for example in the production of sugarcane or wheat).	With a potentially higher energy demand, renewable energy will be necessary to keep the CO_2 footprint of syngas fermentation low. However, the fermentation processes come with many additional benefits compared to the biobased baseline, including a reduction in land footprint and pressures on biodiversity due to agricultural production.

METHANOL PRODUCTION

Conventional methanol production utilizes syngas as a feedstock. This syngas comes predominantly from natural gas through steam methane reforming, while syngas can also be produced from biomass or solid wastes. It is possible to produce methanol either from the CO and H_2 from the waste gas in a conventional methanol route (with additional H_2 inputs), or through the SEWGS route, by shifting the CO to CO_2 and H_2 and then producing methanol. The first option comes with a major drawback in that the inert N_2 in the gas poses a technical barrier.

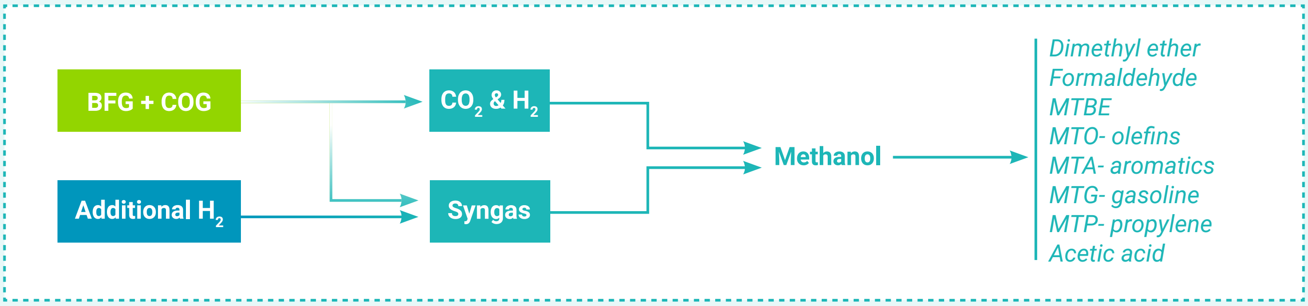
From a techno-economic viewpoint, methanol, or products produced from methanol are attractive options, as the market for these products is large and the technologies well developed.

PRODUCT	GLOBAL DEMAND	PRICE	TECHNO-ECONOMIC CONSIDERATIONS	
Methanol	80 Mtpa	323 €/tonne	+	Mature technology, growing demand
Dimethyl ether (DME)	9 Mtpa	357 €/tonne	+/-	Limited but growing market as LGP replacement
Formaldehyde (FA)	27 Mtpa	298 €/tonne	+/-	Mature technology, fragmented market
Methyl tert-butyl ether (MTBE)	10 Mtpa		-	Gasoline additive, long term future uncertain
MTO methanol to olefins	>10 Mtpa	1020 €/tonne	+/-	Technology demonstrated, economic case for coal based feedstock
MTA methanol to aromatics	>1Mtpa	850 €/tonne	-	Technology demonstrated
MTG gasoline	>1 Mtpa	680 €/tonne	-	Under development
MTP propylene	>1 Mtpa	1105 €/tonne	-	Under development
Acetic acid	15 Mtpa	595 €/tonne	+	Mature technology, growing market size

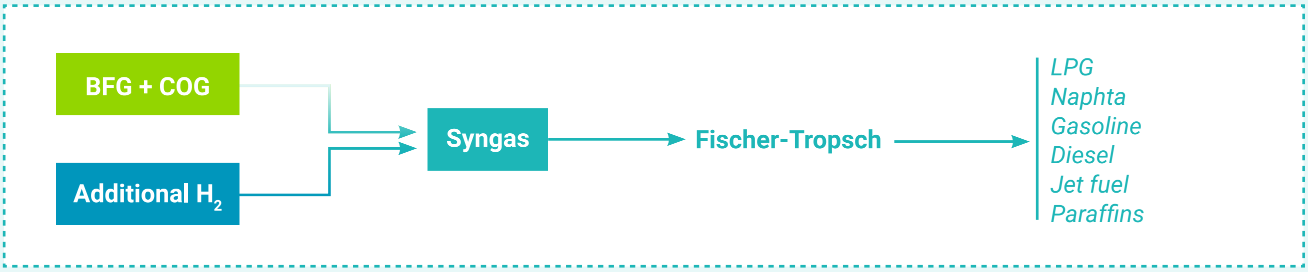
FISCHER-TROPSCH PROCESS

While conventional petroleum refining is associated with a host of issues, it has been developed into a highly efficient process, which synthetic fuels have a difficult time competing with. At the same time, the Fischer-Tropsch process is widely applied and tested as a means to produce fuels in regions without access to petroleum (particularly areas with large supplies of natural gas). As with methanol, the high share of N_2 present in waste gases poses a technical barrier.

PRODUCT	GLOBAL DEMAND	PRICE	TECHNO-ECONOMIC CONSIDERATIONS	
LPG	10 Mbbl/d	638 €/tonne	+	• Fischer-Tropsch synthesis is a mature technology. • Well developed trade and logistic infrastructure. • Naphtha for chemicals and diesel/jet fuel for heavy/air transport expected to stabilize. • Gasoline expected to decrease in the long run.
Naphtha		638 €/tonne		
Gasoline	23 Mbbl/d	680 €/tonne		
Diesel	28 Mbbl/d	680 €/tonne		
Jet fuel	6 Mbbl/d	680 €/tonne		
Paraffins, waxes		850 €/tonne		



ENERGY CONSUMPTION	WATER CONSUMPTION	OVERALL ENVIRONMENTAL CONSIDERATIONNS
Conventional methanol production from natural gas requires around 2 MJ electricity per kg methanol, while the waste gas syngas route requires more, mainly due to H_2 production: around 3,52 MJ electricity per kg when steam methane reforming is used, or 17,9 MJ when electrolysis is used to produce hydrogen. Production of methanol derivatives will have the same environmental performance as the conventional processes, with the differences in the methanol production being the determining factor.	Water consumption is 9 kg/kg methanol with the conventional process and 12,6-19,8 kg/kg methanol from waste gases. Additional water consumption results mostly from hydrogen production, with the higher end of the range corresponding with hydrogen from water electrolysis.	The conventional processes start with natural gas as a feedstock, while in a new scenario the carbon monoxide and some of the hydrogen comes from waste gases, preventing the use of natural gas as a feedstock. As long as hydrogen production and energy replacement do not come from fossil sources, this can result in large CO_2 decreases.



ENERGY CONSUMPTION	WATER CONSUMPTION	OVERALL ENVIRONMENTAL CONSIDERATIONS
Conventional petroleum refining is a relatively energy efficient process for producing hydrocarbons. While the Fischer-Tropsch process has a similar electricity demand, the high demands of electricity for hydrogen production and even the syngas treatment makes waste gas recycling relatively energy intensive compared to petroleum refining.	The Fischer-Tropsch process on its own requires around the same amount of water input per kg of product as petroleum refining (roughly 5 kg of water). However, the other processes required for preparing the syngas for FT (waste gas treatment, hydrogen production), also require water, resulting in an overall water demand of more than 18 kg/kg hydrocarbon.	As the Fischer-Tropsch process requires a large amount of energy, the environmental performance will be, for a large share, determined by the source of energy. In particular, the high purity of gases required for the FT, and additional H_2 demands will affect the environmental outlook for FT.

PROCESS SELECTION

Out of the CO-recycling options, a selection was made for further assessment based on the following criteria:

- Ensuring significantly different types of routes are evaluated in order to explore tradeoffs associated with vastly different process technologies.
- Market size compared to the expected scale of production from steel mill waste gases. Specialty chemicals with small markets were not considered as they could quickly become saturated at this scale.
- The availability or expected availability of technologies and inputs required for production at the correct scale and Technology Readiness Level (TRL).
- Additional benefits of technologies or products (e.g. high CO_2 reduction, ease of preprocessing of gases required in order to use in a given process).

The most important factors for the evaluation of the long-list of options proved to be the market size and the technology maturity.

Often, the demand or market size is not large enough to be able to accommodate an increase in production capacity that corresponds to the use of a significant part of the carbon exhaust from a large steel mill (in the order of several million tonnes per year (Mtpa)), without major price changes. For these products, the scale of production potential is also too low to produce considerable environmental benefits. Therefore, the markets of products with an annual demand of less than 10 Mtpa are considered too small.

Technology maturity causes the overall techno-economic conclusion to be negative if the proposed route, although promising, is still in a conceptual phase and not demonstrated on an at least demonstration plant scale. Only process routes with Technology Readiness Levels (TRL) of 7 and above can be considered feasible at the required industrial scale in the coming decade.

Following the initial quickscan assessment, the following routes were selected for further evaluation:

Methanol through conventional syngas route or SEWGS process

- Methanol is a base chemical with large demand and many high-value derivative products. Due to the large demand, there is low chance of market saturation with the addition of large-scale methanol production.
- For methanol, the syngas route is the conventional production route (with natural gas); the technologies are well developed. Other feedstocks for methanol are already being explored, including the waste to methanol project AkzoNobel is working on with a consortium.
- The SEWGS process is only at a pilot stage, but already has proven to be very promising for further exploration. This process can be used in the production of hydrogen as well as for synthesis of methanol.

FT to produce hydrocarbons

- The Fischer-Tropsch process is a unique production route for producing liquid hydrocarbons. The process can be selective for naphtha production. Naphtha can serve as a feedstock for the production of plastics, which results in longer carbon storage than fuels.
- Large-scale facilities already make use of coal to produce hydrocarbons, so the technologies are already well understood. Alternative feedstocks (e.g. gasified biomass and CO_2) are well researched.
- As the demand for liquid hydrocarbons is very large, production of additional fuels is unlikely to have market effects.
- Fischer-Tropsch is an interesting alternative to petroleum cracking in the absence of fossil fuels.

Syngas fermentation to ethanol

- Fermentation of syngas, currently being implemented at multiple locations for large scale commercialization, is an important biotechnological alternative to conventional thermo-catalytic conversion processes.
- While it is possible to produce many different products from syngas fermentation, ethanol has a large market that will not be saturated by large-scale production.
- Syngas fermentation has additional benefits:
  - Biocatalysts have higher specificity and spare the use of expensive metal catalysts.
  - Microorganisms can tolerate higher amounts of impurities, reducing gas treatment requirements.
  - CO_2 in the syngas can also be converted to product through a biological reaction (Molitor et al., 2016).
  - While additional H_2 results in higher carbon conversion efficiency, a specific ratio of $CO:H_2$ is not required for the process.

Other processes explored

In addition to exploring these three routes, understanding the gas separation and purification processes as well as the hydrogen production options, is key (see Figure 3.2), as these have large implications for the economic and environmental outcomes.

While gas composition requirements vary by route, additional hydrogen is typically required, or at least improves the carbon conversion efficiency of the process. Hydrogen production can be considered as a separate production process. For this reason, different options for hydrogen production are considered in the techno-economic assessment, while the environmental assessment considers two different hydrogen production scenarios.

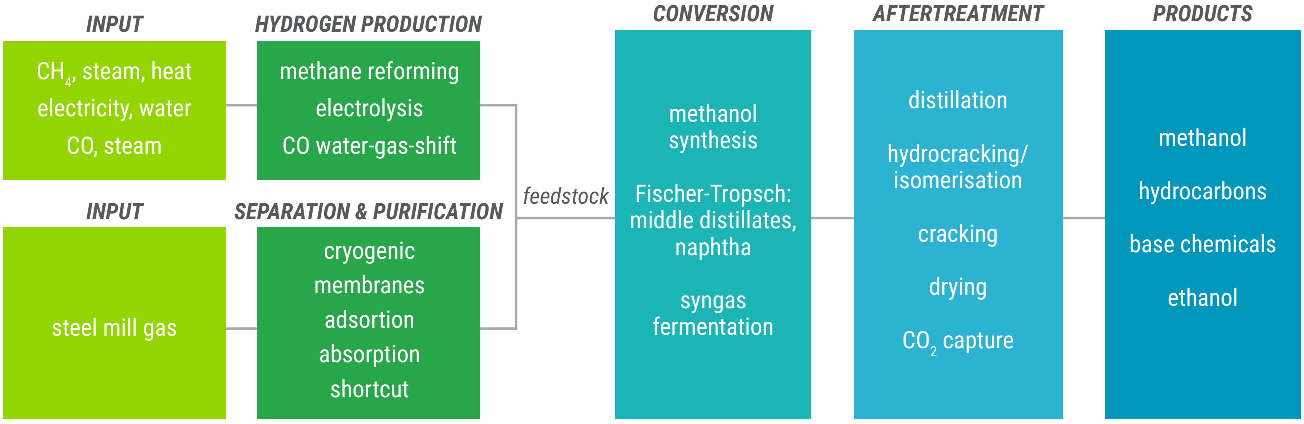


Figure 3.2. *Short list options for reuse of steel production off gases.*

TECHNO-ECONOMIC ASSESSMENT

HYDROGEN PRODUCTION

Both methanol and naphtha synthesis from CO require the production of additional hydrogen, while the carbon conversion efficiency of syngas fermentation from ethanol will be higher with additional hydrogen inputs. This makes hydrogen a key molecule for waste gas valorization and how this hydrogen is produced will be a determining factor in the environmental and economic results. The options for producing this H_2 are described briefly here.

Understanding the options

Steam methane reforming (SMR) is the most well-established method both for the production of hydrogen as well as syngas. In steam methane reforming, the reaction of CH_4 with H_2O produces CO and H_2. The process is usually performed at temperatures of 800–900 °C and moderate pressure (around 30 bar) with a nickel based catalyst. The reaction is endothermic, so an external source of energy is needed.

In a first instance, the product is syngas with a H_2:CO molar ratio close to 3. If the desired product is H_2 instead of syngas, then the CO can be shifted with steam to obtain more H_2. In a subsequent treatment step, CO_2 can be separated using pressure swing adsorption (PSA) to obtain high purity H_2 gas. Similarly, CO in waste gases, rather than from natural gas, may also be shifted to produce hydrogen. The drawback in this case is that CO is converted to CO_2. However, as CO_2 is easier to separate from the problematic N_2 present in steel mill gases, this may also present an opportunity when the goal is to obtain a pure CO_2 stream. The Sorption Enhanced Water-Gas Shift (SEWGS) technology is one promising option for doing this with steel mill waste gas.

Partial oxidation (POX) occurs when sub-stoichiometric fuel-oxygen mixtures are partially combusted in a high temperature reformer of 1200-1500 °C. As the reaction is exothermic no extra energy supply is needed. The H_2 yield is lower than with SMR and oxidation requires a supply of pure oxygen. The use of catalytic partial oxidation (CPOX) lowers the required reaction temperature to around 800-900 °C. In the CPOX reaction, methane is converted with oxygen over metal catalysts to syngas in a single step process.

In auto-thermal reforming (ATR) methane is mixed at high temperature with a mixture of oxygen and steam and ignited in a combustion chamber where partial oxidation occurs at ≈1925 °C. In a subsequent zone reforming reactions take place. The exothermic oxidation can provide for the energy needed with the endothermic reforming reactions. The H_2/CO ratio can vary from 1 to 2, dependent on the amounts of steam and oxygen.

Table 3.1. *Comparison of syngas and hydrogen generation technologies*

TECHNOLOGY	ADVANTAGES	DISADVANTAGES
Methane reforming SMR	Most extensive industrial experience. Oxygen not required, lowest process operating temperature. Highest H_2/CO ratio.	Highest emissions of CO_2. More expensive than POX and autothermal reformers.
CO shifting	Exothermic.	CO is consumed and converted to CO_2.
Methane reforming POX	Feedstock desulfurization not required.	Very high process operating temperature. Usually requires oxygen plant.
Methane reforming ATR	Lower process temperature requirement than POX. Syngas methane content can be tailored by adjusting reformer outlet temperature.	Limited commercial experience. Usually requires oxygen plant.
Methane reforming DMR	Greenhouse gas CO_2 can be consumed instead of releasing into atmosphere. Almost 100% of CO_2 conversion.	Formation of coke on catalyst. Additional heat is required as the reaction takes place at 873 K.
Methane reforming CSDR	Best H_2/CO ratio for production of liquid fuels. Coke deposition drastically reduced.	Separation of unreacted methane from SMR syngas. Project installation cost.
Electrolysis	Clean, can use renewable non-fossil electricity.	Currently high investment costs.

Dry reforming of methane (DMR) is a process that uses carbon dioxide to produce syngas from natural gas. The reaction is more endothermic than SMR and therefore needs more energy input. The H_2/CO ratio is low, of the order of 1. The presence of CO_2 gives rise to an increased danger of carbon formation on catalyst surface. A combination of technologies results in Combined Steam and Dry Reforming (CSDR).

A comparison of syngas generation technologies using natural gas as feed is shown in Table 3.1. Steam reforming is the most widely used reforming process of methane, mainly because it has the largest H_2/CO ratio. Since this requires additional external energy input, depending on the scale of the operation and the energy prices, other types of reforming can be more profitable alternatives. The choice of process type for reforming of methane must also take into consideration the application of the syngas, i.e. the H_2/CO ratio.

The final option for hydrogen production is the electrochemical conversion of water to hydrogen and oxygen through a process known as water electrolysis. Theoretically, the energy needed for the production of hydrogen amounts to 286 kJ/mol or 40 kWh/kg H2. Commercially available electrolysers are currently of the proton exchange membrane (PEM) type or alkaline type. These operate at low temperatures (40-90 °C). From a sustainability viewpoint, electrolysis is the best option, as it can be done with virtually zero emissions.

Techno- economic considerations

Recently, Rabobank has drawn up a financial model to assess the financial feasibility for the construction and operation of two electrolysis plants (and two biomass gasification plants) each of 500 MW (Van Wijk, 2017). Based on an electricity price of €25/MWh and a 70% electrolysis efficiency a hydrogen price of €2,60/kg H_2 was obtained. This amount consisted of electricity costs at €1,4/kg H_2 and capex, opex, transport, financing and other costs at €1,2/kg H_2 in total. The total price mentioned here does not include any credits that can be obtained from useful application of the oxygen coproduced with the hydrogen electrolysis, where the oxygen production rate is 8 kg O_2/kg H_2.

Also recently, Dechema published a report on low carbon energy (Bazzanella et al., 2017). This study presented a comparison of electrolysis and reforming performances and costs, see Table 3.2. This study shows that the costs of electrolytic hydrogen increase strongly at low operating hours of the installation, especially below 4000 h/a, because of the high investment costs. A strategy to use cheap electricity, e.g. during periods of surplus renewable electricity supply, would lead to a significantly low utilisation of the assets with detrimental effects on the economics.

In general, large amounts of electricity are needed to produce a relevant amount of hydrogen, matching with the scale of waste gas production. For example, with the hydrogen obtained from a 1,2 GW electrolysis plant 1,2 Mt/a of CO can be converted to 1,35 Mt/a of methanol (at 8000 h/a), assuming the hydrogen is exclusively used to convert CO into methanol. Along with the hydrogen, pure oxygen is obtained at a rate of 120.000 Nm^3/h.

From a comparison of the available technologies to obtain pure hydrogen the most economic choice at the moment appears to be conventional steam reforming combined with shifting of the CO and separation of the CO_2. For each mole of methane four moles of hydrogen can be obtained. The feedstock, natural gas, is cheap and with CCS in place the CO_2 that is produced can be handled safely. The technology is fully matured and commercially applied on a large scale. However, in the future when the equipment costs have decreased due to increased production volumes the use of electrolysis (esp. SOE) can become attractive.

Table 3.2. *Electrolyser technologies key data*

	ALKALINE	PEM	SOE	SMR(¹)
Investment costs (€/kW)	1000-1200	1900-2300	>2000	500-800
OPEX	2-5% of CAPEX	2-5% of CAPEX	2-5% of CAPEX	
System size (Nm^3 H_2/h)	760	240	40	
System size (MW)	5,3	1,15	0,1	150-300
Efficiency kWh/kg H_2	50-75	50-75	37	Effciency 70-85% (LHV)
costs (€/kg H_2)	2,9 (at 4 €/MWhel)	3,8 (at 4 €/MWhel)		2,0 (at 4 €/MWhth)

(¹) SMR - steam methane reforming, for comparison.

METHANOL SYNTHESIS

The industrial production of methanol requires:

- Production and conditioning of the syngas ($CO+CO_2+H_2$);
- Conversion of syngas into methanol in the synthesis loop;
- Purification of the methanol, usually via distillation.

In the conventional route, methanol is produced from natural gas, which contains both the carbon and the hydrogen required for synthesis. With the carbon monoxide present in steel mill waste gases, there are two options for synthesis. Either full CO conversion can be achieved with the input of additional hydrogen, or the CO can be shifted to produce hydrogen and CO_2 which can be used in methanol synthesis. Details of the methanol reactor and syngas recirculation can be found in Appendix VII.

Understanding the options

The manufacturing and purification of syngas is the starting point of methanol production. Traditional plants for methanol synthesis require natural gas reforming, which takes up half or more the total investment. Production based on steel mill gas does not require reforming, but presents an advantage only when an external source of hydrogen, such as electrolysis, can be secured.

Methanol synthesis is an equilibrium reaction, thus recycling of unconverted reactants is necessary. To avoid accumulation of inerts, a purge stream is required, resulting in some loss of reactants. So there is a trade-off between the concentration of inert gases and the production cost that must be optimized.

Additionally, if the inert gas levels are high (as in gas from steel mills, see Table 1.1), the purge and recycled ratios increase, which implies a loss of reagents and an increase in capital cost (larger compressors and reactors) and operational cost (compression power). In some cases the H_2 contained in the purge is recovered by a membrane separation unit, a cryogenic separation unit, or a PSA unit. In practice, often the purge gas is used as fuel.

Due to the trade-offs between inert concentration and production costs, we first explored two options; using the steel mill gas as-is, including inert compounds and removing the inerts and surplus CO_2.

In the first option steel mill gas is cleaned of catalyst poisons, mainly sulphurous components. The resulting gas is supplemented with additional hydrogen to obtain a correct stoichiometric ratio. The make-up gas obtained this way contains 12% CO, 10% CO_2, 55% H_2 and 23% inerts (mainly N_2). It was found that this type of operation results in very high concentrations of inerts in the synthesis recycle loop and therefore very large volumetric gas flows. In conclusion, the excessive equipment sizes and compressor capacities make this a unfeasible option under current circumstances.

Therefore, the second option for methanol synthesis was considered in more detail. In this option, after sulfur removal from the steel mill gas, the H_2 and CO are recovered while CO_2 and inerts are removed. These separations are accomplished using well-known techniques such as PSA and gas scrubbers. Complete CO_2 removal is not required, as methanol synthesis requires a concentration of 6-10% CO_2. With the addition of external H_2, a gas composition of 22% CO, 8% CO_2 and 69% H_2 and a minor amount (1%) of inert can be obtained. This option is depicted in Figure 3.3.

Separation of N_2 from the CO present in the waste gas presents a technical challenge as the molecules are very similar. Current separation technologies result in large losses of CO. For this reason, we also considered a third option: complete shifting of CO in the steel mill gas, and production of methanol from the resulting hydrogen combined with carbon dioxide.

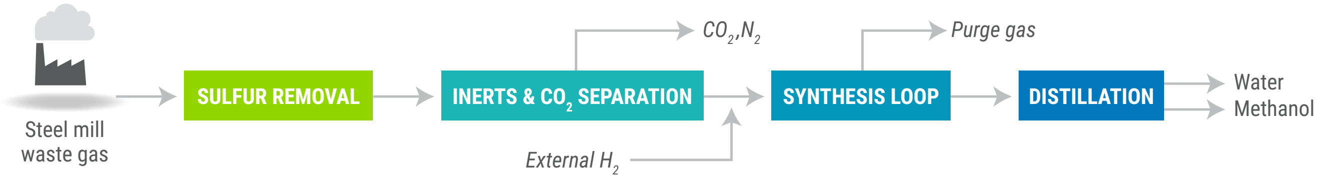


Figure 3.3. *Process scheme for methanol from steel mill gas.*

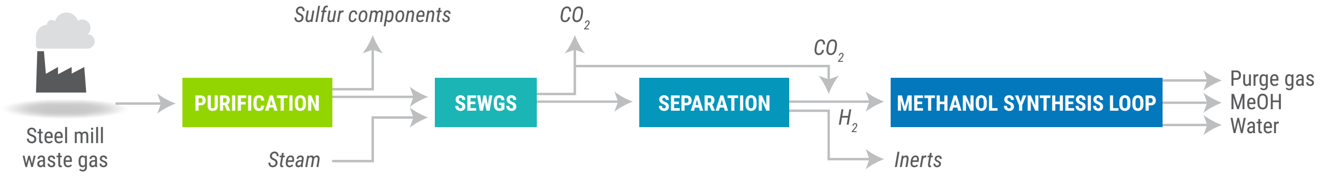


Figure 3.4. *Process layout for methanol from steel mill gas without removal of inerts*

Again, first the steel mill gas is cleaned of catalyst poisons. Via the so-called water-gas-shift reaction, or shift reaction, CO and H_2O in the form of additional steam are converted to CO_2 and H_2. Surplus CO_2 and inerts, mainly N_2, are removed. The resulting hydrogen stream is used with some of the purified CO_2 for methanol synthesis.

ECN has developed a technology based on sorption enhanced water gas shift (SEWGS) that combines, in a single step, the shifting reaction and the CO_2 capture plant. The thermodynamic limitation of the conversion at high temperature is resolved by simultaneously adsorbing the formed CO_2. Being a reactive PSA, the SEWGS step requires multiple columns: at least five. Polytechnico de Milano has concluded that this is the most cost-efficient approach for CO_2 capture in the steel industry (Jansen et al., 2013).

The process scheme envisaged for the work-up of steel mill gas using the SEWGS technology, nitrogen separation, and methanol production from CO_2 and H_2 is shown in Figure 3.4.

Techno- economic considerations

For the techno-economic analysis, we considered a scenario of a steel mill with a production of 7 million tonnes of steel per year (roughly the size of Tata Steel's production in the Netherlands), in order to estimate the appropriate scale of production. We assume a carbon conversion efficiency of 83% for the conventional syngas route, resulting in a total potential production of 2,36 million tonnes per year. For the SEWGS route, it has been estimated that 1,5 million tonnes of methanol could be produced per year.

The full results of the techno-economic analysis is given at the end of the chapter in Table 3.6, while a quick overview of some of the key conclusions is given in Table 3.3. For detailed information on gas upgrading, methanol synthesis, capital and operating costs, and pricing assumptions, please see Appendix V.

Table 3.3. Key techno-economic conclusions for methanol synthesis

CRITERION	COMMENTS
Technology maturity	The main technology concerns steel mill gas purification and syngas conditioning, methanol synthesis and product separation, and methanol distillation. These technologies are commercially available. The main technological barrier for the conventional route is in N_2 separation, which is at a TRL level of only around 6-7. Likewise, the SEWGS technology is at a TRL of around 6 or 7 and requires scaling up.
Scale up potential	The global market size is at 80-90 Mt/a and demand is expected to increase with 1-3% annually. In Europe most of the methanol is imported from overseas: the demand for methanol is around 7.5 Mt/a, also growing, while production is around 2,3 Mt/a.
Value for money	The potential market size for methanol can go well beyond current uses due to increasing use as a fuel additive and new technologies for the production of base chemicals such as olefins and aromatics.
Level of investment	The R&D efforts and the level of investment required to bring the CO to methanol route to commercial operation is limited.
Economic feasibility	Considering the energy flows of the first two options considered for methanol synthesis from steel mill gases then some 70-75% of the energy content of the feed streams is recovered in the methanol product stream. Investments costs for methanol synthesis are considerable. Operational costs depend on the availability of utilities, especially the availability of waste heat at the site of a steel mill for use in gas separation and product distillation. If selecting a route where additional hydrogen is required, the price of hydrogen will be a determining factor in operational costs. Methanol prices are relatively high at around €323/tonne. However prices have fluctuated considerably in the past years.
Investment (CAPEX)	1,5 billion € for syngas route, 1,4 billion € for SEWGS route
CO_2 avoided	4,9 million tonne for syngas route, 2,1 million tonne for SEWGS route
CO_2 avoidance costs	45,9 €/tonne for syngas route (at a hydrogen cost of 1700 €/tonne), -13,6 €/tonne for SEWGS route

FISCHER-TROPSCH HYDROCARBONS

A wide variety of liquid hydrocarbon fuels and various other chemical products can be produced from syngas via the Fischer- Tropsch (FT) process. The FT process yields a mix of products, rather than a single product. Depending on the process conditions and catalysts used, the process can be tailored to produce a higher share of certain products. Tailoring the process for the production of naphtha is particularly interesting as this product can be used in plastics production, with the prospect of longer-term carbon storage.

Understanding the options

The Fischer-Tropsch process consists of a syngas preparation section, a synthesis reactor loop and a product work-up section (see Figure 3.5).

The main steps in syngas preparation include feedstock production, syngas cleanup and conditioning, and sulfur recovery. In traditional FT installations, the syngas preparation and conditioning section takes between one half and two thirds of the total capital costs (De Klerk, 2011; Steynberg, 2004).

Carbon monoxide from the steel mill gases has to be cleaned and separated from the other gases. Also inerts (N_2) have to be removed, otherwise these end up in downstream processing, increasing production costs, and in all the product streams obtained, especially the light weight, gaseous products.

The clean syngas is sent onto the FT reactor (synthesis loop) where it is converted into a series of hydrocarbons. FT synthesis co-produces large amounts of water. The products are recovered and wax, if present, is usually sent to a hydrocracking unit, where it is split into smaller molecular weight hydrocarbon liquids. The reaction products are fractionated into the final products, depending on the desired product mix.

The distribution of the hydrocarbon product mix is key, as it determines the amounts of the products obtained. The product distribution is often given in terms of the weight fraction of hydrocarbons of a certain chain length. The product distribution, is determined to a large extent by the catalyst type and the process conditions such as temperature, partial pressures and residence time.

The FT process operates at temperatures of approximately 200-350 °C and pressures in the range of 10-35 bar. The operating conditions, together with the catalyst choice, determine the product distribution. Higher temperatures lead to higher reaction rates and thus to higher conversions. At the same time, higher temperatures tend to yield, on average, products of lower molecular weight. For example, the amount of naphtha typically is double the amount of diesel at high temperatures; at lower temperatures the situation is reversed and the amount of diesel typically is double the amount of naphtha. Increasing the pressure of the FT reactors leads to higher conversion rates and also in the formation of long chain hydrocarbons.

The catalysts used for FT synthesis are typically iron based catalyst, that can operate at both higher and lower temperatures, and cobalt-based catalysts that are more active and operate at the lower temperatures.

It turns out that in order to maximize the naphtha output it is best to use an iron catalyst at high temperature in a fixed bed reactor. If a high diesel/jet fuel fraction is desired, a slurry reactor with cobalt catalyst is the best choice. Slurry reactors offer better temperature control: a crucial advantage because the FT reactions are highly exothermic.

From separation of the reactor exit flow, the unconverted syngas together with the methane fraction are obtained. A considerable amount of water is coproduced in the reactor, in weight its amount is larger than the weight of hydrocarbons. Other fractions are forwarded to product work-up sections, while the heavy hydrocarbons of the wax fraction are first broken into smaller components using a so-called hydrocracking process.

If the product distribution is optimized for the yield of the naphtha fraction, the process conditions and catalyst are adjusted by operating a fixed bed reactor with iron catalyst at high temperatures (250-300 °C) and low pressures (10-20 bar). Per pass conversion of CO is in the range of 80-90%.

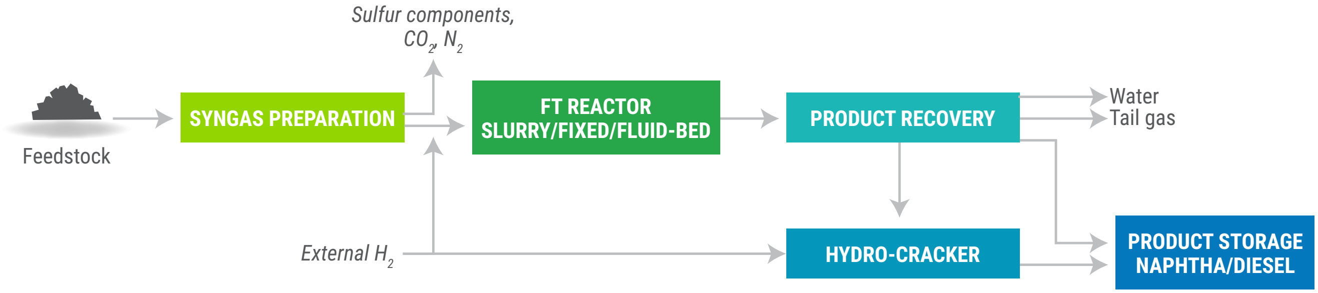


Figure 3.5. *Block scheme of FT hydrocarbon synthesis*

Techno- economic considerations

The techno-economic conclusions are provided in Table 3.4. The option considered here in the production of hydrocarbons from steel mill gas using Fischer-Tropsch synthesis in more detail, is the optimization for naphtha production. An overview of the energy flows and carbon mass flows can be found in the appendices.

For the techno-economic analysis, we considered a scenario of a steel mill with a production of 7 million tonnes of steel per year (roughly the size of Tata Steel's production in the Netherlands), in order to estimate the appropriate scale of production. We assume a carbon conversion efficiency of 75% for the Fischer-Tropsch route, resulting in a total potential production of 930 kt of naphtha per year.

The full results of the techno-economic analysis is given at the end of the chapter in Table 3.6, while a quick overview of some of the key conclusions is given in Table 3.4. For detailed information on gas upgrading, the Fischer-Tropsch route, capital and operating costs, and pricing assumptions, please see Appendix V.

Table 3.4. *Key techno-economic conclusions for Fischer-Tropsch hydrocarbons*

CRITERION	COMMENTS
Technology maturity	Fischer-Tropsch synthesis consists of many individual processes, but each of these are well known operations. Also the combination of upstream gas conditioning, the synthesis loop with recycling, and downstream product separation and processing is commercially applied. The main technological barrier for the conventional route is in N_2 separation, which is at a TRL level of only around 6-7.
Scale up potential	The EU-28 annual consumption of LPG, gasoline and diesel amounts 4157 TWh/a (Eurostat) or about 450 Mt/a. At this scale, the production of an additional amount, even several Mt/a, can easily be absorbed by the market.
Value for money	The potential for revenue generation exists due to the large market size. But the product pricing varies with the crude oil price which entails the risk of a price drop over time. Under the assumptions we have taken, the route is not currently profitable.
Level of investment	The R&D efforts and the level of investment required to bring the Fischer-Tropsch synthesis route to commercial operation is limited.
Economic feasibility	Investments costs for Fischer-Tropsch are high. In Fischer-Tropsch the downstream processing consists of a series of separations and reactions. The gases have to be separated using cryogenic distillation. The waxes are treated with hydrocracking. Considerable amounts of methane are always produced, and have to be recycled and reformed back to syngas. As additional hydrogen is required, the price of hydrogen will be a determining factor in operational costs.
Investment (CAPEX)	1,4 billion €
CO_2 avoided	3,5 million tonnes
CO_2 avoidance costs	157,3 €/tonne (at a hydrogen cost of 1700 €/tonne)

FERMENTATION TO ETHANOL

Steel mill waste gases can be converted to ethanol in fermentation by micro-organisms (see Figure 3.6). This is a route being explored by LanzaTech, among others, and comes with some advantages over other routes in the case of steel mill waste gases.

Understanding the options

The general principle of syngas fermentation is that micro-organisms fix gaseous carbon by reducing CO and/or CO_2 to liquid products such as ethanol. Acetogens are particularly attractive for commercialized gas fermentation due to their ability to synthesize useful products such as alcohols and diols and the fact that they are anaerobes. Anaerobic conditions avoid flammability issues working with combustible gases and also makes biological contamination less likely in a sugar and oxygen-free atmosphere.

Technical advantages (Michael et al., 2011; Mohammadi et al., 2011) claimed for fermentation technology (as compared to thermo catalytic conversion) are:

- capable of taking in low H_2/CO ratios
- irreversible product formation
- high product selectivity, i.e. low amounts by-products are formed
- the biocatalysts are less susceptible to poisoning by sulfur, chlorine and tars

To fix the oxidized carbon contained in the various syngas sources, the micro-organisms require reducing equivalents in the form of electrons to reduce the carbon to the central building block acetyl-CoA and further to reduced products such as alcohols. CO and H_2 present in the syngas itself can provide these reducing equivalents by oxidation to CO_2 and water, respectively. During gas fermentation using CO only, a portion of the CO substrate pool must be converted to CO_2 to provide necessary reducing equivalents for fixing the gaseous carbon. Some of this CO_2 is not fixed and instead emitted from the cell, lowering the yield of carbon substrate fixed. The highest gas fermentation ethanol yields and selectivities have been demonstrated with CO-rich feedstocks (i.e. low on CO_2) (Gaddy et al.,2007),

The acetogens are have a particularly effective carbon fixation mechanism. In short, CO_2 is enzymatically reduced over a series of steps to a methyl group and then fused to a CO molecule and converted to ethanol. In case the CO_2 required for these steps is not present in the substrate the organism produces its own CO_2 via an enzyme catalyzed water-gas shift reaction. Similarly, if no CO is present in the feed then the acetogens produce CO internally via the reverse watergas shift reaction (Abubackar et al., 2011)

Usually, the micro-organisms employed for syngas fermentation are mesophilic, therefore their optimum operation temperature is in the range of 30 to 37°C. The volumetric ethanol production rates that can be found in the open literature vary, with values of 195 g/L/d (Molitor, 2016) and 360 g/L/d at elevated pressures (Gaddy et al., 2007).

The advantages of syngas fermentation have led to scaling up for commercial scale production. Three companies, Coskata, INEOS Bio, and LanzaTech have operated pilot and demonstration plants for extended periods of time. Coskata's technology has not been been scaled up further. LanzaTech, on the other hand, is currently scaling up their processes to commercial scale with facilities built or being built at a scale of roughly 25-50 kt/a of ethanol (Lane, 2015a,b)

The syngas fermentation process consists of three steps:

- syngas pretreatment and conditioning
- the actual fermentation of the syngas in a bioreactor
- product separation and work-up

The tolerance of the micro-organisms used for syngas fermentation to various contaminants in the syngas is subject of ongoing research. It appears that microorganisms are able to grow in the presence of limited levels of H_2S and COS. However, NO_x and HCN are considered particularly troublesome and need to be removed to low levels from the feed gas. The presence of (organic) contaminants also has to be considered regarding the final product quality.

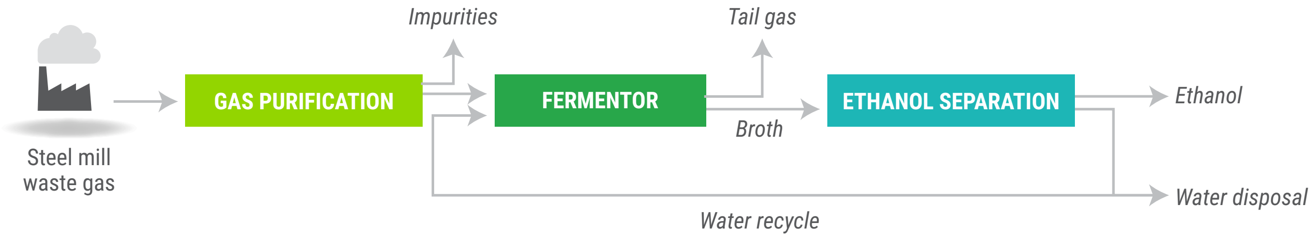


Figure 3.6. *Block scheme of ethanol fermentation*

Bioreactors appear to be operated at elevated pressures. The fermentation depends on a number of operation variables. Bioreactor design, agitation, gas composition and supply rate, pH, temperature, headspace pressure, oxidation-reduction potential (ORP), nutrients, and amount of foaming in the bioreactor all can contribute to the goal of improving selectivity and yield of the desired product. A high product concentration is beneficial for separation, but micro-organism activity is inhibited with product concentration, limiting productivity. One major obstacle immediately present in gas fermentation is the low solubility of the gaseous substrates and combined with an efficient transfer of their masses into the liquid media. CO, H_2, and CO_2 are soluble to approximately 28 mg/L, 1,6 mg/L, and 1,7 g/L (293 K, 1 atm), respectively.

The bioreactors themselves are of the bubble column type, rather than the stirred fermentor types often used in the laboratory, because of the much lower power requirements. The N_2 can be kept in the gas stream as it provides mechanical energy that is used to mix the biorector by bubbling.

Product separation is required to separate ethanol from the fermentation broth. Distillation systems are common to separate lower boiling point products such as ethanol, but this is energy-intensive especially for low concentration products. Other extraction technologies include gas stripping, adsorption, pertraction, pervaporation, and vacuum distillation. Each of these separation technologies has their own benefits and drawbacks, including potential fouling of membranes (perstraction and pervaporation) and substrate removal (gas stripping and liquid-liquid extraction).

For the product separation step the concentration or product accumulation is an important factor, where higher product concentrations facilitate easy separation. On the other hand higher product concentrations are negative for fermentation productivity. An optimization is needed here, and can be the objective of future work. The syngas composition is also of influence on the fermentor productivity. Most research thus far has been with CO containing feed streams, where CO acts as both the carbon and energy source to synthesize ethanol. However, in those cases a lot of CO_2 is co-produced.

The matter and energy flows of the main input and output streams of the fermentation operation are shown in Appendix IX.

Techno- economic considerations

The overall techno-economic conclusions are given below in Table 3.6.

For the techno-economic analysis, we considered a scenario of a steel mill with a production of 7 million tonnes of steel per year (roughly the size of Tata Steel's production in the Netherlands), in order to estimate the appropriate scale of production. We assume a carbon conversion efficiency of 40% for ethanol production, resulting in a total potential production of 820 kt/year.

The full results of the techno-economic analysis is given at the end of the chapter in Table 3.6, while a quick overview of some of the key conclusions is given in Table 3.5. For detailed information on gas upgrading, syngas fermentation, capital and operating costs, and pricing assumptions, please see Appendix V.

Fermentation is the newest and least documented process in scientific literature out of the main routes explored, which makes it difficult to properly assess the economics of the process. LanzaTech claims their technology can result in much higher conversion rates, close to that of methanol, while syngas fermentation can also be implemented without additional H_2 inputs. We examined this with an additional sensitivity, including a carbon conversion efficiency of 60% and no additional costs for hydrogen production. Under this scenario, the economic case would turn positive, with a production of 1,25 million tonnes/annum and a net benefit of 10,2 euros/tonne CO_2 avoided.

Table 3.5. *Key techno-economic conclusions for syngas fermentation to ethanol*

CRITERION	COMMENTS
Technology maturity	Ethanol production via fermentation consist of steel mill gas purification, the actual fermentation at high pressure, and the separation and purification of the product. The first and third step are widely commercially available, and the fermentation of syngas is being applied on commercial scale by LanzaTech.
Scale up potential	Global production of ethanol from bioresources is around 75 Mtpa. For Europe the production was estimated at 5,4 Mt for 2016, out of which 4,1 Mt was used for fuel blending. Although an increase in the amount of ethanol for fuel blending can be expected from 2020 onwards, the introduction in the EU of an additional 0,5 to 1,2 Mtpa of ethanol from CO may influence the price development significantly.
Value for money	The potential market size can increase considerably in the future if ethanol is blended with fuels on a larger scale. However, then the revenues from ethanol may become linked to the price of crude oil.
Level of investment	The investment needed to develop the syngas fermentation to ethanol technology to full commercial application depends to a large extent on the outcome of ongoing research. Currently, various demonstration scale projects using the technology are being conducted. If selecting a route where additional hydrogen is used, the price of hydrogen will be a determining factor in operational costs.
Economic feasibility	The investment costs for the fermentation to ethanol route, although still considerable, are lower than the methanol and Fischer Tropsch routes. An important factor are the investments needed for gas clean-up equipment. Less details of the actual conversion process are publicly available resulting in a larger uncertainty of the evaluation as compared to the methanol and FT-routes.
Investment (CAPEX)	1,2 billion €
CO_2 avoided	5,6 million tonnes
CO_2 avoidance costs	96 €/tonne (at a hydrogen cost of 1700 €/tonne)

TECHNO-ECONOMIC CONCLUSIONS

Upgrading the amount of CO contained in steel off-gas into marketable products calls for significant investments. According to the economic analysis performed in this study, most routes cannot currently return revenues to a level that would justify these investments (see Table 3.6 for an overview of the economic analysis), though a number of factors could change this picture. Some of these factors include CO_2 credits, subsidies, opportunities for industrial symbiosis, process optimizations or technological developments in H_2 production, process synthesis, or gas separation technologies. We have considered these factors of the outlook for CO recycling and come to the following conclusions:

Hydrogen production

Currently, H_2 from electrolysis can be produced with a cost as low as 2900 euros per tonne, but this cannot compete with the cost of steam methane reforming at 2000 euros per tonne. Technology and scale developments (e.g. large-scale electrolysis with electricity from wind at sea) are expected to drive renewable hydrogen manufacturing cost levels down to as low as 1700 euros per tonne. The fermentation route has a clear advantage in that it can be implemented without supplementary hydrogen inputs.

Industrial symbiosis

In some cases, “stranded” hydrogen is available as a byproduct from another production process. In this case, the hydrogen may be considered “free” or very low cost. At a hydrogen price of zero, all cases except Fischer-Tropsch naphtha turn positive. Additionally, in the case where hydrogen is produced via electrolysis, the process also results in a large stream of oxygen, which is valuable for the steel industry, while process heat or steam demands for the production routes could be produced as byproducts of other industrial processes. Further exploration into the possibilities for process optimizations is required and may improve the outlook of the routes.

Carbon pricing

Implementation of one of the upgrading technologies would also bring the steel manufacturing industry in a position whereby a significant amount of the CO2 equivalent emissions will be consolidated into an either CO_2 capture ready stream (some 50 – 95% of all off-gas CO_2 equivalents). With CCS in place, this would imply a significant CO_2 emission reduction. With a CO_2 tax applied to direct emissions to air (e.g. 85 euros/tonne) and a CO_2 feed-in tariff of 42,5 euros/tonne of CO_2 turn all cases positive at 850 euros/tonne of Hydrogen.

Process efficiency

While we considered a carbon conversion efficiency of 40% for ethanol production, under a conversion efficiency of 75%, the costs per tonne of CO_2 avoided drop to 34 euros/tonne. For syngas fermentation in particular, the process route is relatively new, and there may be much more to gain in efficiency as the technology improves. LanzaTech claims much higher carbon conversion efficiencies are possible: up to 83% with additional hydrogen inputs.

Gas separation technologies

For the methanol and Fischer-Tropsch cases, gas separation is a major barrier. The CO has to be purified and separated from the large amount of inert N_2. Although technically feasible, it is costly and needs further development from the current estimated Technology Readiness Leve (TRL) of around 6-7. Further developments in the separation technologies could improve the techno-economic outlook for these routes.

SEWGS technology

Currently the most promising option from an economic viewpoint is the SEWGS technology for producing either hydrogen or methanol. An advantage of this operation is that no external hydrogen is needed. Instead a relatively cheap steam flow is needed for the shift reaction, which is probably available from onsite waste heat at the steel mill. Another advantage is that the difficult separation of CO and N_2 is avoided. Separation of H_2 and N_2 is not difficult and the technology is readily available, for example using pressure swing adsorption. However, the underlying SEWGS technology currently under development by ECN is far from mature. This also applies to the hydrogenation of CO2 into methanol. Technology Readiness Levels (TRL) are probably around 6 or 7. Both options show positive revenues under the assumptions made, with one poor (methanol option) and one interesting (hydrogen option) payback time of 8 and 2 years respectively. Both SEWGS options would deliver a benefit of some 12,8 and 76,5 euros per tonne of CO_2 avoided (to methanol and to hydrogen, respectively).

Overall, the main conclusion of the techno-economic analysis is that the technologies which are currently mature enough for the appropriate scale of CO recycling could be profitable under shifts in carbon pricing and hydrogen costs. Process optimizations and technological developments that are currently taking place could result in a more positive outlook for all of the routes on the short to medium term.

Table 3.6. *Full overview of techno-economic results*

VALUES	UNIT	METHANOL	SEWGS & METHANOL	SEWGS FOR HYDROGEN	FT NAPHTHA	ETHANOL
Capex CO_2 capture	mln €	246,5	510	510	246,5	246,5
Capex N_2 rejection	mln €	208,3	85	127,5	208,3	208,3
Capex Syngas conversion	mln €	1020	782		909,5	735,3
Total Capex	mln €	1474,8	1377	637,5	1364,3	1190
Volume	mln t/a	2,36	1,5	0,325	0,95	0,82
Pricing	€/tonne	297,5	297,5	1700	382,5	425
Income	mln €/a	704	446,3	552,6	361,3	349,4
Value off-gas (3,4 €/MMBTU)	mln €/a	198,9	198,9	198,9	198,9	198,9
H_2 feed costs (renewable, 3400 €/tonne)	mln €/a	880,6			880,6	880,6
Opex CO_2 capture	mln €/a	40,4	25,5	25,5	40,4	40,4
Opex N_2 rejection	mln €/a	42,5	0	0	42,5	42,5
Opex Syngas Conversion[1]	mln €/a	0	0	0	0	0
CO_2eq CO_2 capture unit	mln t/a	4,7	7,3	9,4	4,7	4,7
CO_2eq N_2 rejection unit	mln t/a	0,8	0,5	0,5	0,8	0,8
CO_2eq Syngas conversion	mln t/a	1,3	0,1	0	1,6	3,0
Total CO_2 eq.	mln t/a	6,8	7,9	9,9	7,2	8,5
Costs CO_2 -emissions	mln €/a	0	0	0	0	0
Fixed Costs (4% of Capex)	mln €/a	59	55,1	25,5	54,6	47,6
Net revenues	mln €/a	-518,5	167,5	302,6	-855,1	-860,2
Simple Pay-Back time	years	N/A	8,2	2,1	N/A	N/A
TAC CO_2 avoidance[2]	mln €/a	665,6	-29,4	-239,2	990,7	979
CO_2 avoided	mln t CO_2/a	4,9	2,1	3,2	3,5	5,6
Specific CO_2 avoidance cost (@ 3400 €/t H_2)	€/tonne CO_2 avoided	136	-13,6	-75,7	283,1	175,1
Specific CO_2 avoidance cost (@ 1700 €/t H_2)	€/tonne CO_2 avoided	45,9	-13,6	-75,7	157,3	96
CO_2eq in product (t/a)	mln t/a	3,2	2,1	0	3,0	1,6
Carbon efficiency	-	0,83			0,75	0,4
Heat Content offgas (4,4 GJ/t)	GJ/tonne	4,4	4,4	4,4	4,4	4,4

1 Opex set at 0 as all related utility costs have been assumed to be included in the carbon efficiency
2 Total Annualised Costs for CO2 avoidance, defined as all annual expenses plus 10% capital depreciation and corrected for the off-gas upgrade from caloric value to product value

ENVIRONMENTAL ASSESSMENT RESULTS

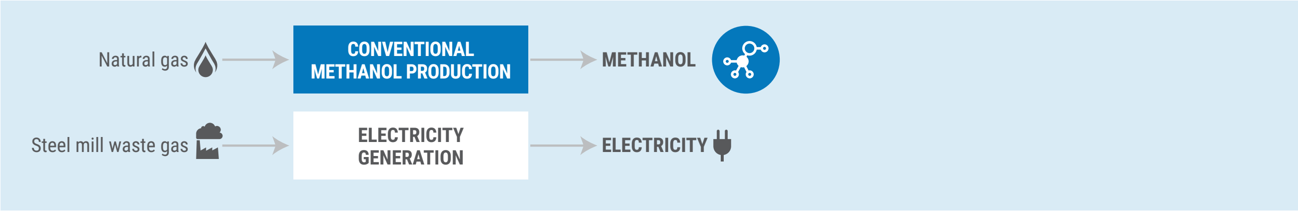
In this section, we present the results of the environmental assessment by route, first introducing the scenarios we evaluated along with some key facts, showing the results of the two scenarios in a side by side comparison, and finally presenting our key conclusions for each product route. At the end follows an overview and a reflection on the implications of different technologies selected on the environmental outcomes and opportunities for additional improvements in environmental performance.

METHANOL SYNTHESIS

For the environmental assessment of methanol, we consider a case of production of 340 kg of methanol and 965 kWh of electricity, which could be produced with the blast furnace and coke oven gases associated with one tonne of steel production. For further details and results of the environmental assessment, see Appendix VI.

Baseline Methanol Scenario:

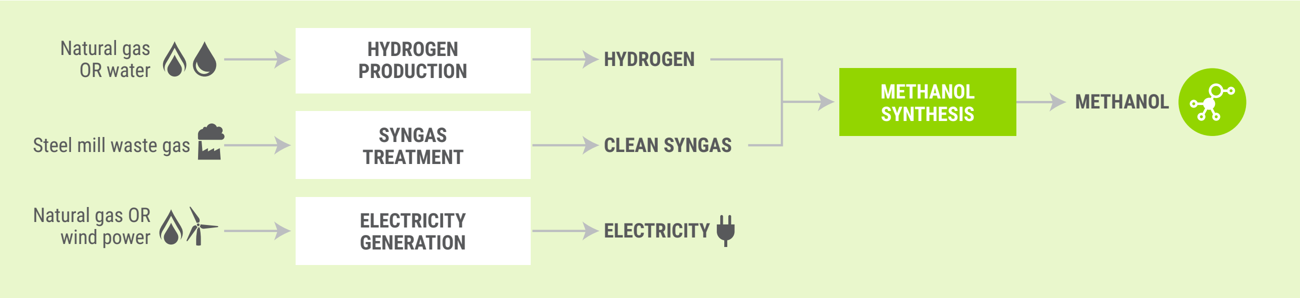
In the methanol baseline scenario, we consider the conventional production of methanol from natural gas and electricity generation from the waste gases of the steel industry. This scenario results in a relatively high consumption of natural gas and requires material inputs with high impact profiles.



- **Non-renewable resource consumption:** 223 kg natural gas (189 for methanol production and 34 for electricity generation).
- **Byproducts:** No notable byproducts.
- **Wastes and wastewater:** Nearly 2.000 kg wastewater from methanol production (additional wastewater from operations associated with electricity generation).
- **Ecotoxicity and human health & safety:** Several of the inputs commonly used in conventional methanol production include ones with chronic or acute health hazards, including aluminum oxide, nickel, and zinc. Additionally, molybdenum is associated with high physico-chemical hazards, while zinc is also associated with potentially high environmental hazards.

Alternative methanol scenarios:

We consider two alternative methanol production scenarios: a conservative scenario, where hydrogen is produced by steam reforming of natural gas and electricity demands are met with natural gas and an optimistic scenario where hydrogen is produced with electrolysis and electricity demands are met with wind power.



- **Carbon efficiency:** 83%
- **Non-renewable resource consumption:** Increase in natural gas consumption in the conservative scenario: 195 kg natural gas for electricity replacement, 135 kg natural gas for hydrogen production, and 15 kg for energy in syngas treatment.
- **Byproducts:** 20 kg elemental sulfur from syngas cleanup.
- **Wastes and wastewater:** Close to 2.700 kg wastewater from methanol production, mainly from synthesis, but also from hydrogen production and syngas treatment. Additional wastewater from operations associated with electricity generation.
- **Ecotoxicity and human health & safety:** Dimethyl ethers in Selexol fluid (for syngas cleanup) is associated with high physico-chemical hazards, while zinc oxide is associated with high environmental hazards and relatively high acute health hazards.

CONSERVATIVE METHANOL SCENARIO:

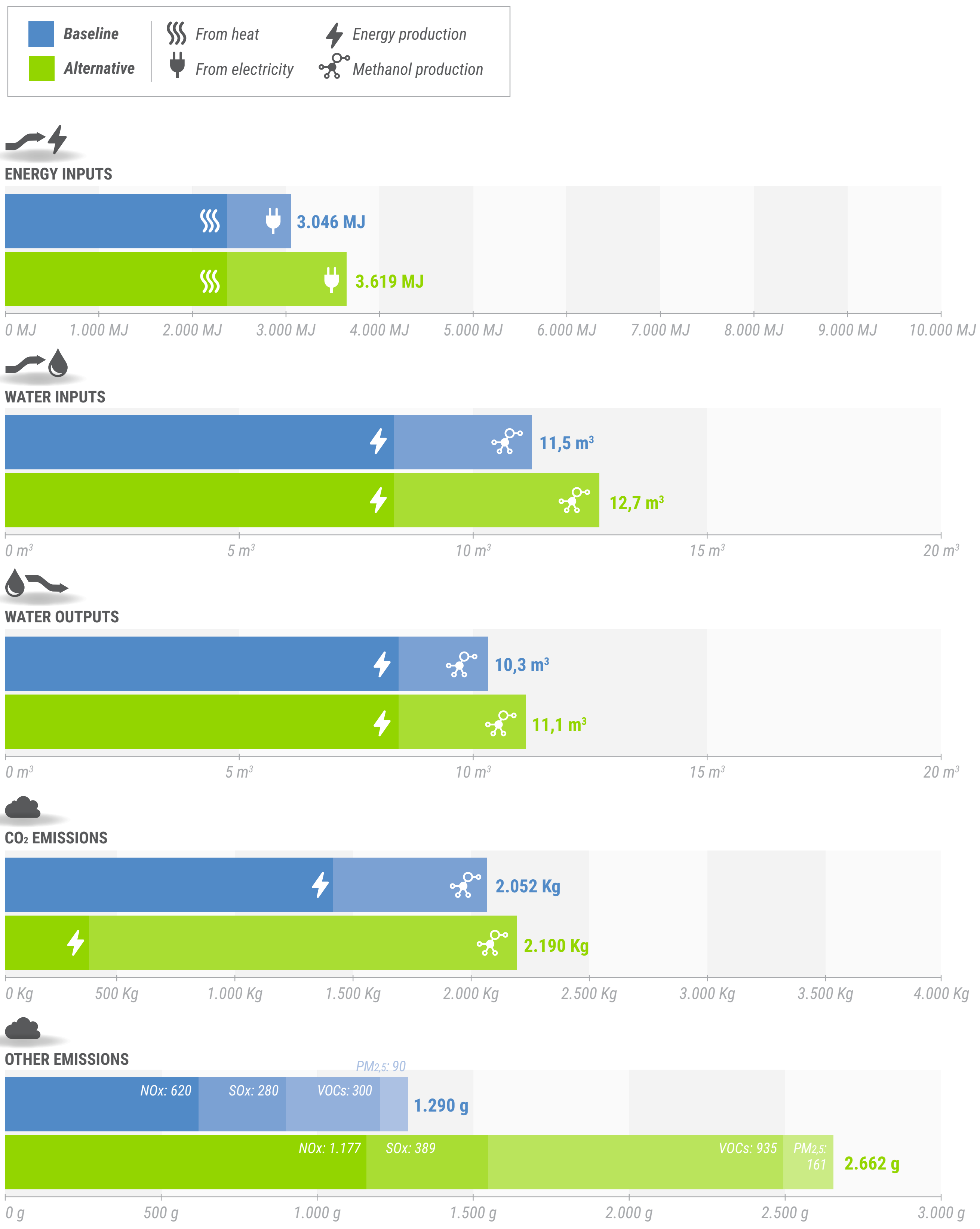


Figure 3.7. *Overview of baseline and alternative methanol scenario performance for conservative scenario*

OPTIMISTIC METHANOL SCENARIO:

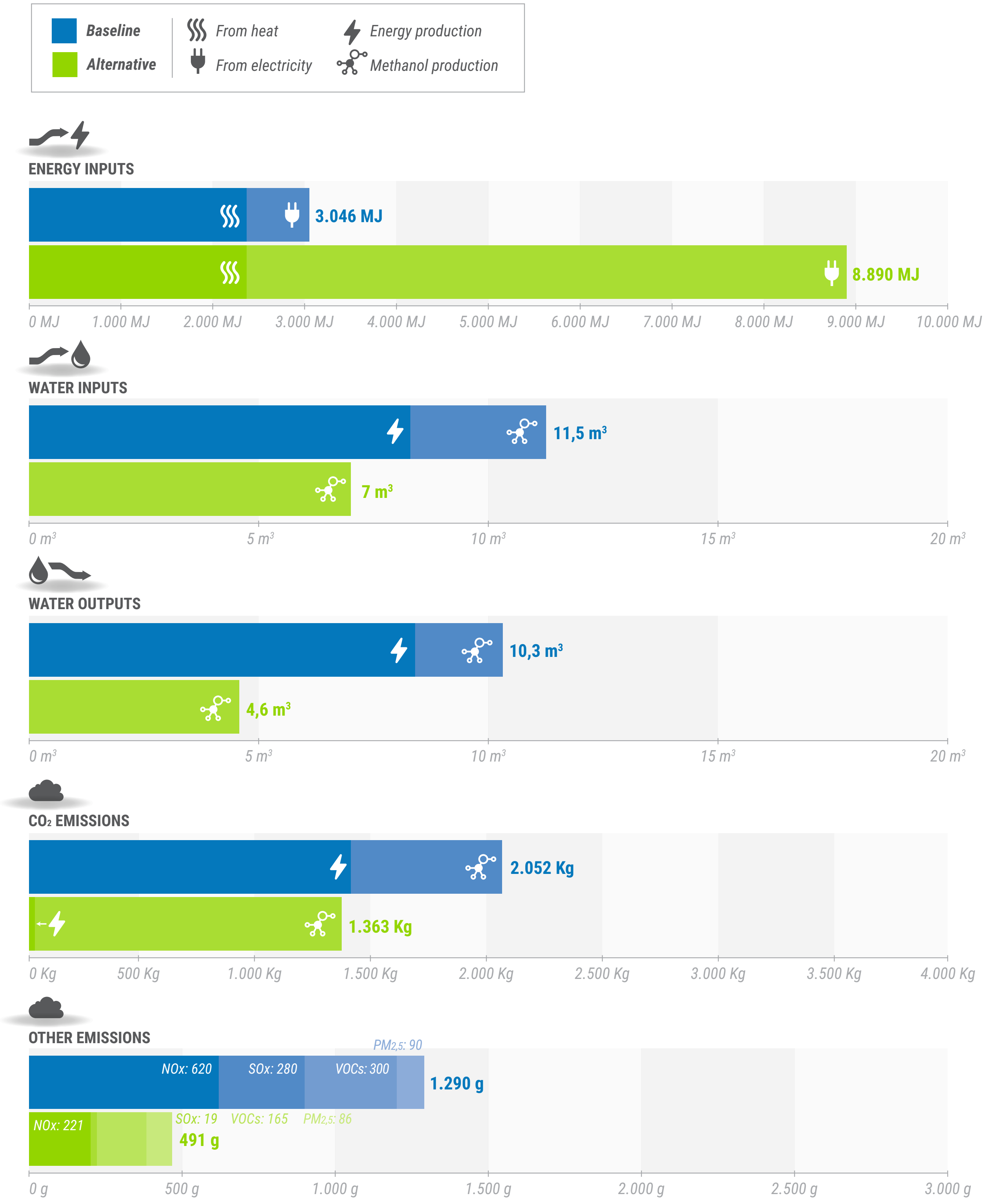


Figure 3.8. *Overview of baseline and alternative methanol scenario performance for optimistic scenario*

Key Takeaways Methanol

Both methanol production scenarios result in a higher energy demand compared to the baseline. For the conservative scenario, this is only a slight increase, while the optimistic scenario results in an increase from around 3.000 MJ to more than 8.000 MJ (due to the high energy demands of electrolysis).

As the reduction in emissions from electricity production in the conservative scenario cannot compensate for higher emissions from methanol production from waste gases, this scenario results in an overall increase of CO_2e emissions of around 6,5%. On the other hand, the optimistic scenario leads to an overall decrease of 33,7% of the CO_2e emissions, mainly due to the large decreases of emissions from hydrogen production (difference of 375 kg CO_2e) and electricity replacement with wind power (345 kg CO_2e).

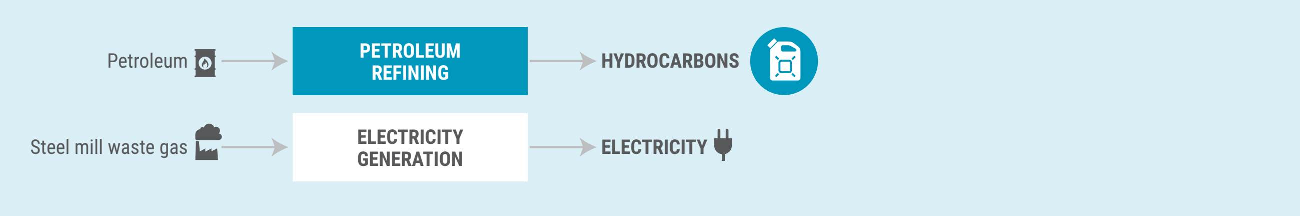
While our scenarios represent the range, or extremes possible, even implementing one of these changes from the conservative scenario results in CO_2e reductions. This also holds true for fossil fuel consumption; the conservative scenario results in a considerable increase of natural gas consumption, but either hydrolysis or renewable energy would results in an overall reduction of gas consumption.

FISCHER-TROPSCH HYDROCARBONS

For the environmental assessment of Fischer-Tropsch hydrocarbons, we consider a case of production of 340 kg of methanol and 965 kWh of electricity, which could be produced with the blast furnace and coke oven gases associated with one tonne of steel production. For further details and results of the assessment, see Appendix VI.

Baseline Hydrocarbons scenario:

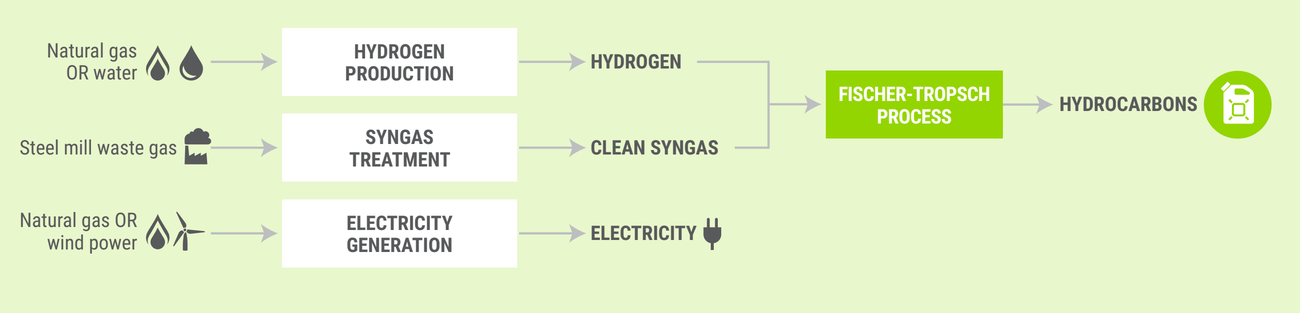
In the baseline hydrocarbons scenario, we consider the case of conventional petroleum refining to produce a mix of hydrocarbons, while electricity is produced from the steel mill waste gases.



- **Non-renewable resource consumption:** 97 kg crude oil (raw material), 84 kg heavy fuel oil (process consumption).
- **Byproducts:** Nearly all of the petroleum is converted to fractions of valuable products, with a small amount of byproduct being diverted to produce electricity directly for the process. Some other products, such as elemental sulfur and spent catalysts will also result as byproducts of refining.
- **Wastes and wastewater:** 426 kg wastewater from hydrocarbons production. Several different types of wastewater streams occur with high levels of contamination and complex treatment is required.
- **Ecotoxicity and human health & safety:** The petroleum cracking process consumes a number of types of catalysts, which are regenerated but eventually removed over time. These spent catalysts are often classified as hazardous waste and will need to be disposed of as such.

Alternative hydrocarbons scenarios:

For the alternative hydrocarbons scenarios, we consider a case of Fischer-Tropsch hydrocarbon production from the steel mill waste gases and replacement of electricity.



- **Carbon efficiency:** 51%
- **Non-renewable resource consumption:** 195 kg natural gas for electricity replacement, 135 kg natural gas for hydrogen production, and 15 kg for energy in syngas cleanup process
- **Byproducts:** 20 kg elemental sulfur from syngas cleanup. In additional to the final product mix, Fischer-Tropsch results in sulfur as a byproduct and hydrocarbons that are unsuitable for use as fuels and are used instead for producing electricity or steam.
- **Wastes and wastewater:** Large amounts of wastewater (1187 kg), from hydrogen production (522), syngas treatment (211), and Fischer-Tropsch processes (454 kg). Wastewater from FT process contains a high concentration of oxygenated byproducts, aldehydes, and hydrocarbons (Wang, 2017).
- **Ecotoxicity and human health & safety:** Cleaning the syngas and the Fischer-Tropsch process in our scenario will require selexol fluid (containing dimethyl ethers, associated with high physico-chemical hazards), zinc oxide, carbonyl sulfate, and/or cobalt catalysts, associated with high chronic and acute health hazards and environmental hazards.

CONSERVATIVE HYDROCARBONS SCENARIO:

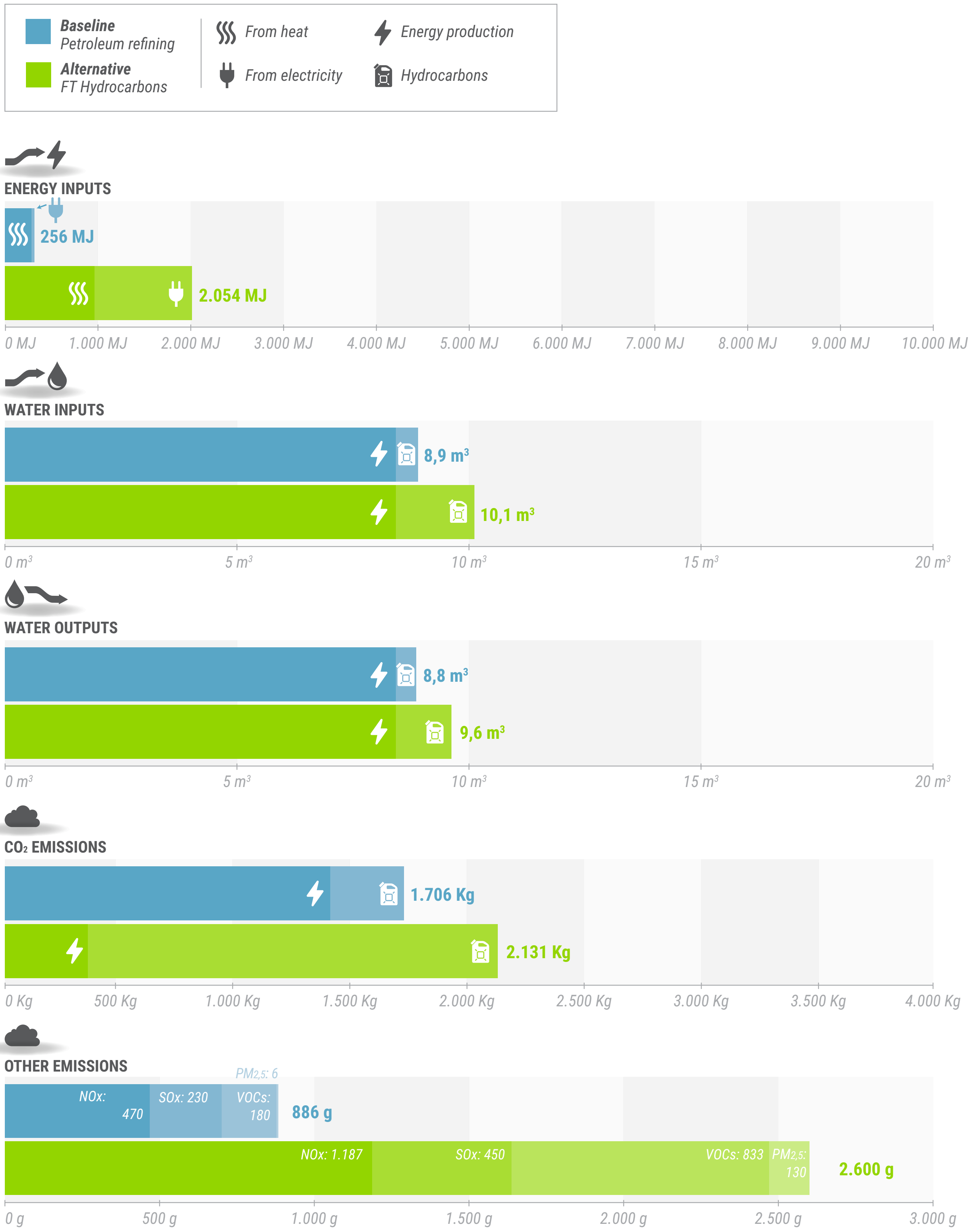


Figure 3.9. *Overview of baseline and alternative FT hydrocarbons scenario performance for conservative scenario*

OPTIMISTIC HYDROCARBONS SCENARIO:

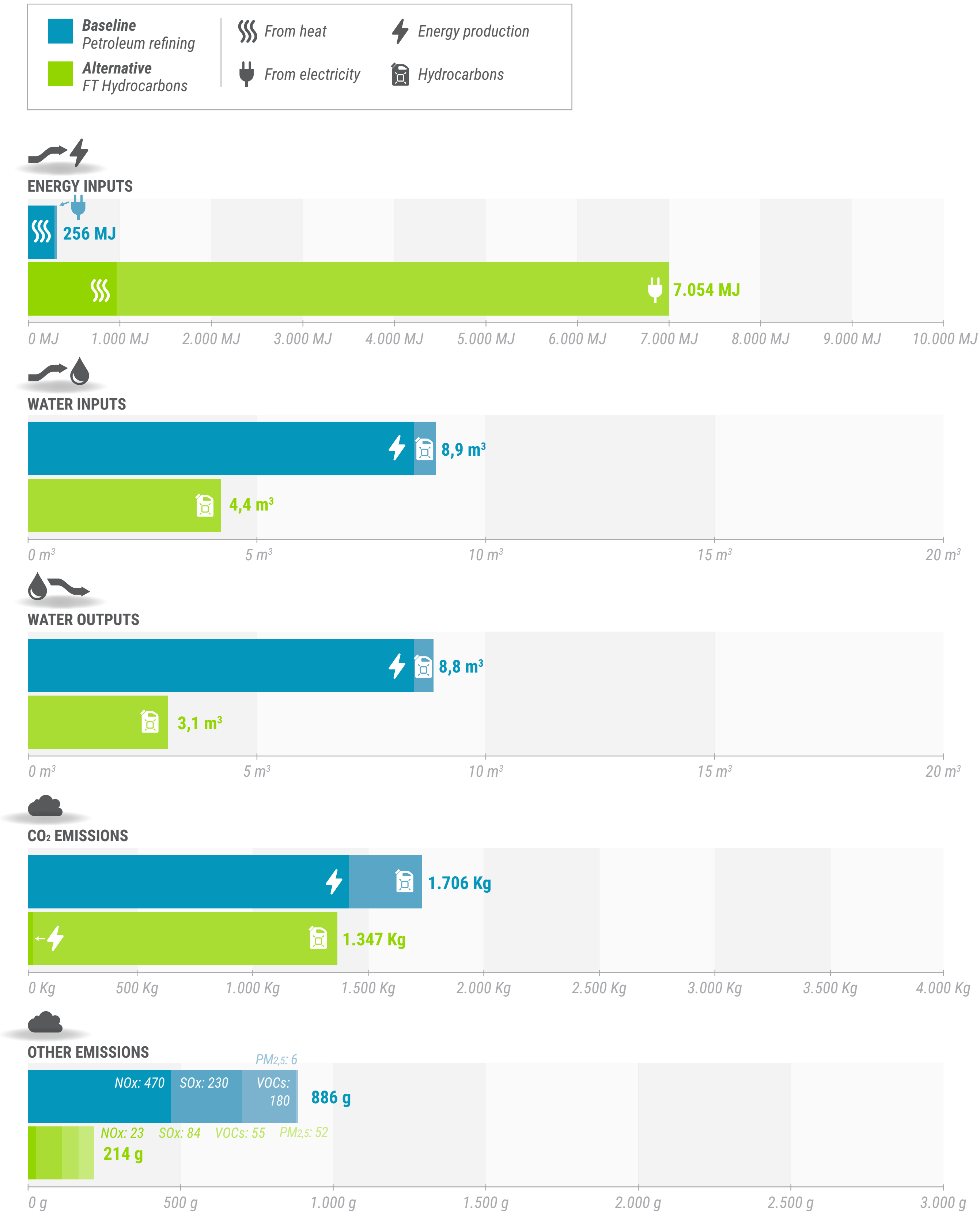


Figure 3.10. *Overview of baseline and alternative FT hydrocarbons scenario performance for optimistic scenario*

Key Takeaways Hydrocarbons

The Fischer-Tropsch process scenario requires a considerably higher energy consumption compared to the conventional petroleum scenario in both the conservative and optimistic scenarios. The conservative scenario also requires more natural gas for energy replacement and hydrogen production, though the consumption of crude oil and heavy fuel oil is avoided. The optimistic scenario results in particularly high energy demands due to the additional demands for electrolysis.

Overall, the conservative scenario results in a higher CO_2 emissions for the Fischer-Tropsch process, mainly due to the emissions from steam methane reforming and the direct emissions due to a relatively low carbon conversion efficiency. On the other hand, the optimistic scenario results are very positive, and show a CO_2 emission decrease of 21,1% compared to the baseline.

Wastewater resulting from both petroleum refining and the Fischer-Tropsch process are particularly problematic and will need to undergo extensive treatment. Water inputs and wastewater production are slightly higher in the Fischer-Tropsch scenarios compared to petroleum refining, due to additional consumption in syngas treatment and hydrogen production as well as in the FT process itself. However, water demand in the optimistic scenario for electricity replacement with wind power are negligible, resulting in an overall decrease of water demand and wastewater production in this scenario.

An additional sustainability consideration for the Fischer-Tropsch process is that the fuels produced are generally meant to be combusted. This means two things: the carbon in the product will be released to the environment on a relatively short timescale and when this happens, the carbon will be lost in a more or less non-recoverable form. From a circularity viewpoint, this is not an ideal situation. An alternative is to tailor the FT process to have a high selectivity for naphtha production. This naphtha can then be used in ethylene production as a feedstock for petrochemicals, and subsequently in products with a longer lifespan and a chance of recycling on the long-term.

To model this, we evaluated the CO_2 outcomes for ethylene production scenarios using the conventional route (frm fossil-based naphtha) and using the FT route (with naphtha selectivity and a carbon conversion efficiency of 66%). With this route, approximately 22 kg of ethylene can be produced per tonne of steel mill waste gas. When looking at the share of emissions allocated to just the ethylene, compared to the baseline we see that the conservative scenario results in an increase of CO_2 by 25%, while the optimistic scenario leads to a reduction of 30,8%. The outcomes are shown below in Figures 3.11 and 3.12.

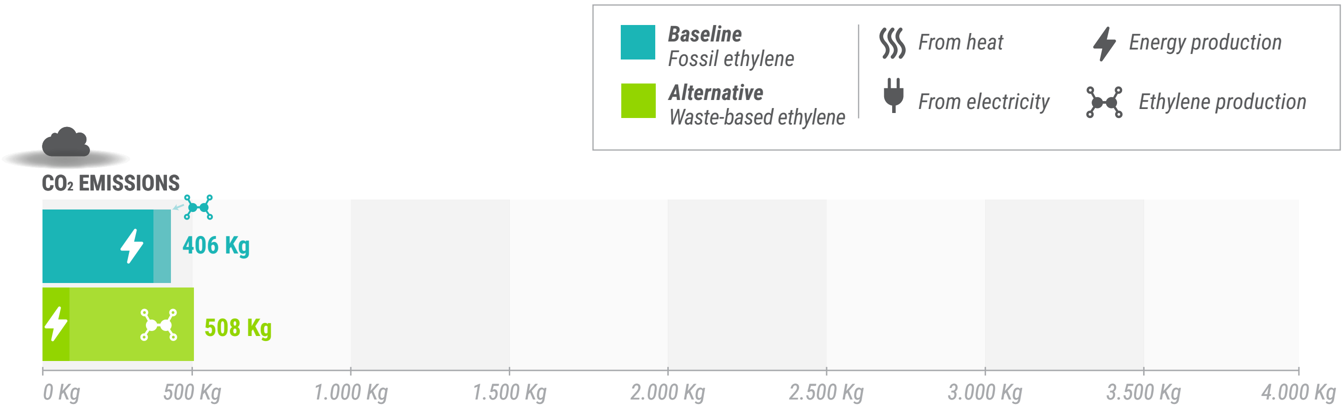


Figure 3.11. *Overview of baseline and alternative ethylene scenario performance for conservative scenario*

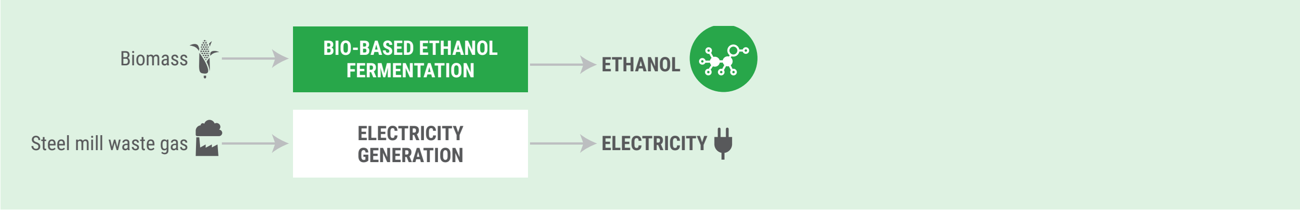
Figure 3.12. *Overview of baseline and alternative ethylene scenario performance for optimistic scenario*

FERMENTATION TO ETHANOL

For the environmental assessment of ethanol, we consider a case of production of 118 kg of ethanol and 965 kWh of electricity, which could be produced with the blast furnace and coke oven gases associated with one tonne of steel production.

Baseline ethanol scenario:

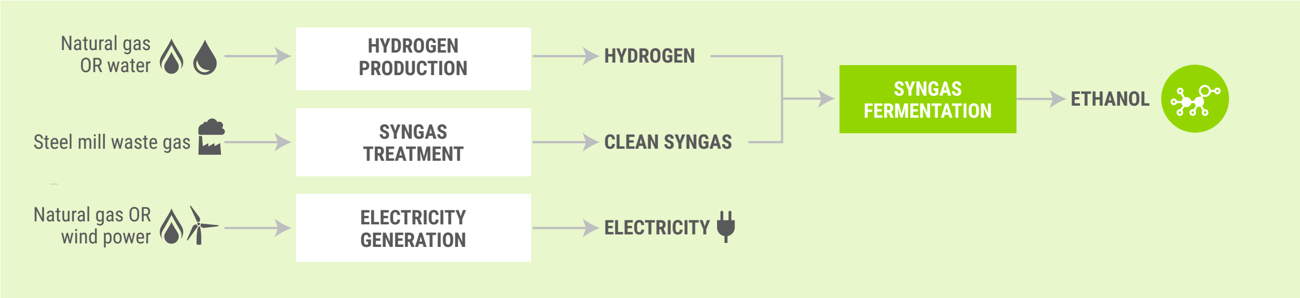
For the baseline ethanol scenario, we consider biobased ethanol fermentation, as this is the most common route for ethanol production. The baseline scenario also includes electricity production from steel mill gases.



- **Non-renewable resource consumption:** 3 kg diesel (for biomass production).
- **Byproducts:** Crop residues and lignocellulosic material will be a byproduct from any biobased production. In our scenario, sugarcane production results in 1.937 kg vinasse, which can be consumed as an energy source or used in other products.
- **Wastes and wastewater:** Nearly 3.670 kg of wastewater with biomass fermentation. This wastewater is rich in salt and typically dehydrated for use in animal feed.
- **Ecotoxicity and human health & safety:** Lime used in biobased ethanol production is associated with relatively high acute health hazards.

Alternative ethanol scenario:

The alternative ethanol scenario includes steel mill waste gas processing to usable syngas and ethanol production through syngas fermentation. We consider a conservative scenario (hydrogen is produced from steam reforming and electricity is supplied by natural gas) and an optimistic scenario (hydrogen from electrolysis and wind power for electricity).



- **Carbon efficiency:** 40% (LanzaTech has demonstrated higher carbon conversion efficiences)
- **Non-renewable resource consumption:** In conservative scenario: 195 kg natural gas for energy replacement and 150 kg in ethanol production (135 kg for hydrogen production and 15 kg for energy in syngas treatment).
- **Byproducts:** 20 kg elemental sulfur from syngas cleanup
- **Wastes and wastewater:** For ethanol production: 885 kg wastewater in conservative scenario and 2.644 kg in optimistic scenario, of which 152 kg salt-rich wastewater from fermentation, which will need to undergo treatment and is not suitable for use in animal feed.
- **Ecotoxicity and human health & safety:** Cleaning the syngas in our scenario will require selexol fluid (containing dimethyl ethers, associated with high physico-chemical hazards), while the process may also require ammonia, which is associated with high acute health, environmental, and physico-chemical hazards.

CONSERVATIVE ETHANOL SCENARIO:

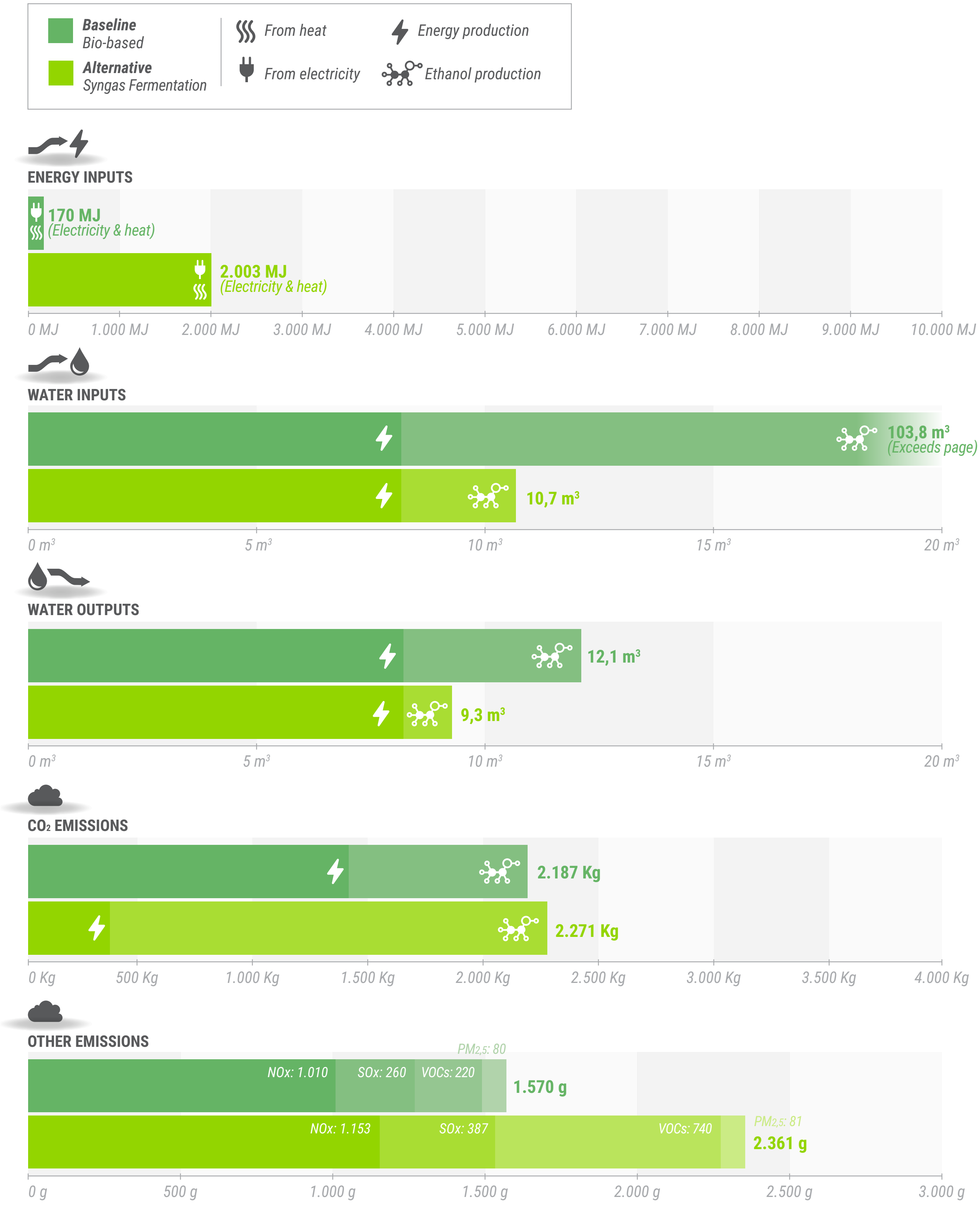


Figure 3.13. *Overview of baseline and alternative ethanol scenario performance for conservative scenario*

OPTIMISTIC ETHANOL SCENARIO:

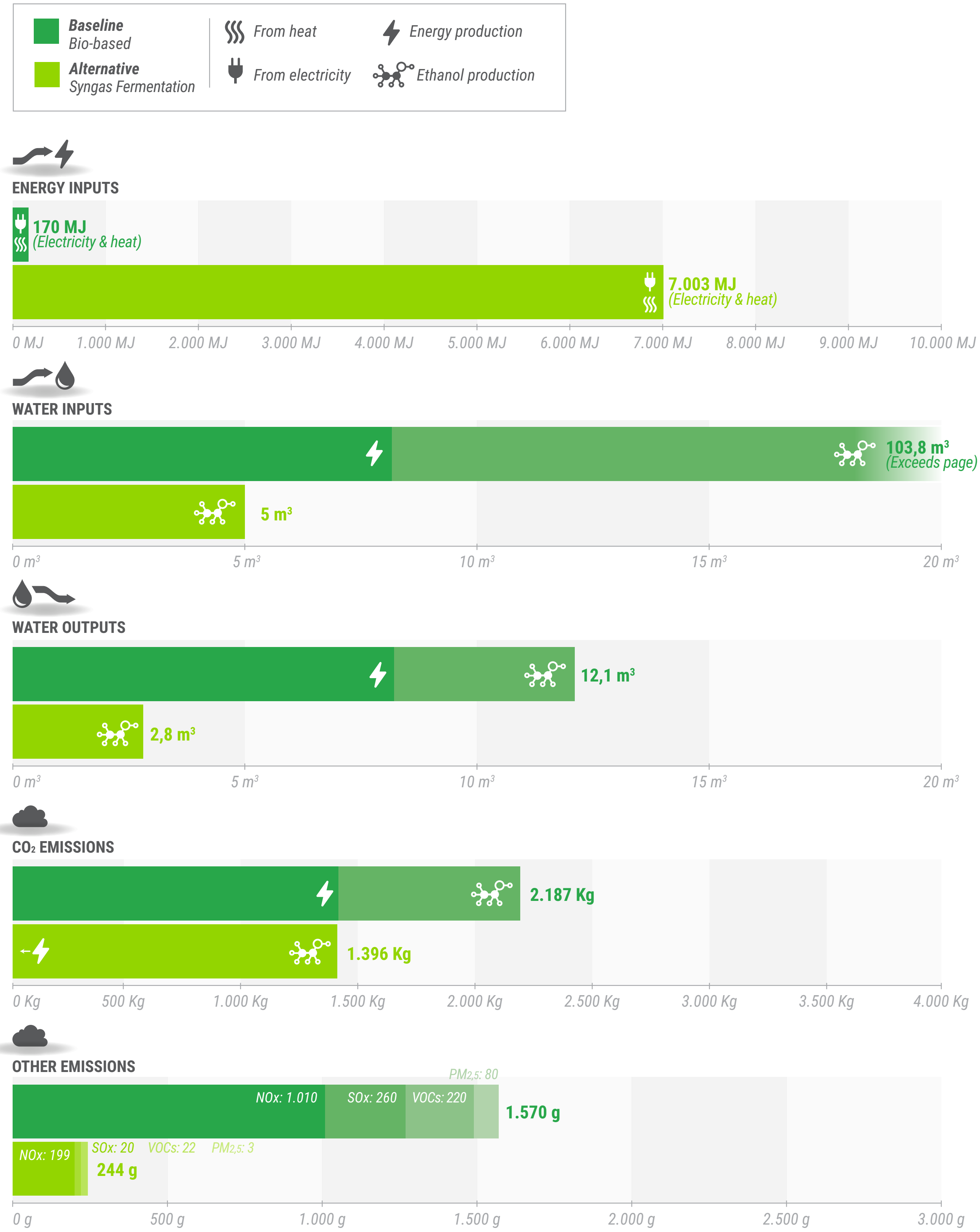


Figure 3.14. *Overview of baseline and alternative ethanol scenario performance for optimistic scenario*

Key Takeaways Ethanol

Electricity demands for syngas fermentation to ethanol are far higher than for the bio-based baseline scenario. Additionally, the conservative scenario results in a considerable increase in natural gas consumption from replacement of the waste gases in electricity generation and hydrogen production.

For the conservative scenario, the additional energy demands result in an overall CO_2 increase of 3,83% for the scenario as a whole. The CO_2 emissions for the optimistic scenario are reduced by 36,16% however, making it the best-performing scenario in terms of CO_2 reductions.

Part of the reason why syngas fermentation performs well in terms of CO_2 is that the process converts some of the CO_2 in the waste gas to product as well, as it is first converted to carbon monoxide through a biological water-gas shift reaction, when there is sufficient hydrogen available. Biomass fermentation, likewise, receives a credit for CO_2 consumption during fermentation. Syngas fermentation can also be implemented without additional hydrogen inputs. In this case, the impacts associated with hydrogen production can be avoided, though less of the CO2 in the gas will be converted to product.

It should be noted that we did not allocate a CO_2 credit for uptake in biomass production in the bio-based scenario, as is common life cycle assessment (LCA) practice. The reason for this is that this would assume that the land on which the biomass was produced would otherwise be bare, which is an unlikely scenario. In terms of water use, the fermentation scenarios are far higher than the fossil-based scenario. The bio-based scenario is particularly high due to the additional water consumption for the biomass feedstock production.

IMPLICATIONS OF NEW TECHNOLOGIES

For the environmental assessment, we had to make decisions on the electricity generation and hydrogen production scenarios, but this choice of scenario has a large impact on the final outcomes, particularly for CO$_2$e emissions (See Figure 3.15 for methanol comparison).

The conservative scenario is a "worst case" scenario, if the cheapest technologies were implemented today. For this reason, we selected natural gas as the replacement for steel mill waste gases in electricity production and steam reforming of natural gas for hydrogen production. Of course, this results in overall CO$_2$ increases and additional consumption of natural gas over the baseline.

The optimistic scenario is a "best case" scenario, based on technologies already available or expected to be available on the short-term. It is clear that the development of affordable electrolysis for H$_2$ production and an increase of renewable energy capacity are key to utilizing waste gases for the reduction of fossil fuel consumption. Industry frontrunners who are exploring CO valorization are anticipating a scenario where the electricity replacement will come from renewables and H$_2$ will be produced using electrolysis and they are actively working on these technologies.

Replacing electricity from steel mill waste gases with wind power instead of natural gas and producing H$_2$ using electrolysis are not the only ways to reduce impacts from the conservative scenario. Table 3.7 gives an overview of the CO$_2$e emissions along each step of the process, and highlights additional opportunities.

Other important ways to reduce emissions could include, for example, improving the syngas treatment steps over the process chain we used data for in the analysis. This process removes a large share of the carbon dioxide and some of the CO and H$_2$ as well, resulting in large direct emissions from carbon not converted into syngas and a need for additional H$_2$.

Another option is improving the carbon conversion efficiency of the processes, so that more of the carbon is converted into products. For the ethanol fermentation in particular, there may be a lot to gain in terms of efficiency with new bio-catalysts.

Finally, capturing carbon which does not end up in the syngas or final chemicals or hydrocarbons and using carbon capture and storage (CCS) is another important option for reducing emissions. In particular, the syngas treatment step goes hand in hand with carbon capture. In this step, more than half of the carbon is removed and the CO$_2$e emissions of this step are 754 kg.

Combining syngas treatment with CO$_2$ capture and storage (CCS) is an attractive option because CCS requires a gas stream of at least 90% CO$_2$. The syngas

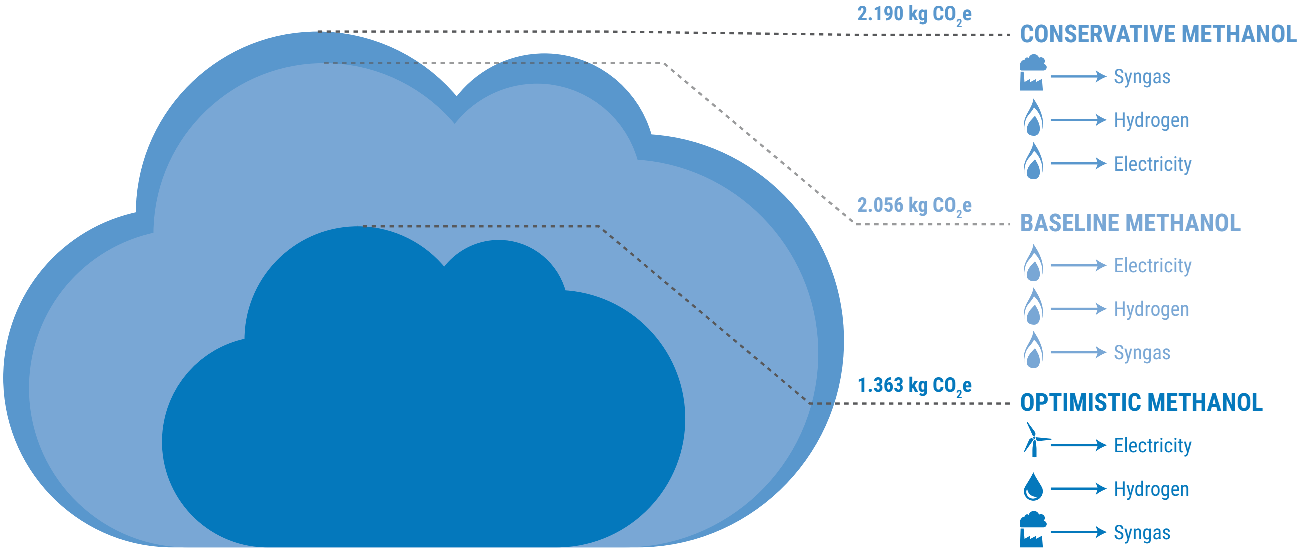


Figure 3.15. *CO$_2$ outcomes for three methanol scenarios*

treatment steps can result in a concentrated CO_2 stream and the additional energy requirements will be low. Looking at one example of CO_2 capture alongside syngas treatment for Fischer-Tropsch (Bibber et al., 2007), only around 229 MJ electricity per tonne of pressurized CO_2 is necessary. Per tonne of steel, this would be an additional 173 MJ. If natural gas were used in electricity generation, this would result in an additional 18 kg of indirect CO_2e.

With CO_2 capture and storage alongside syngas treatment, all of the scenarios would become positive, even the conservative scenarios. As the treatment of waste gases and carbon capture and storage are complementary strategies in this case, improving the performance of one another, these two options should be considered simultaneously.

In addition to CO_2 reduction, the waste gas recycling options come with additional benefits, especially when compared to biobased options. In particular, water demands and wastewater production compared to biobased alternatives can be greatly reduced by using waste gases. On the longer term, when gas recycling can be done profitably with electrolysis and renewable energy, the demand for additional fossil inputs will be reduced with gas recycling.

When making products from waste gases (rather than fuels), the stored carbon can potentially be recovered and used again. One such option for reuse is as a feedstock in steelmaking. Recycled plastics can be used in this way as an alternative carbon source for steel production (Krishnan et al., 2013; Carpenter, 2010). As such, steel gas recycling can form one link in a circular carbon value chain.

Table 3.7: *Overview of CO_2e emissions results per scenario and step. Indirect emissions are from energy demands.*

SCENARIO	PROCESS STEP	METHANOL	HYDROCARBON	ETHYLENE	ETHANOL
Baseline scenario	Biomass production	-	-	-	54
	Biomass fermentation	-	-	-	556
	CO_2 consumption in fermentation	-	-	-	-51
	Natural gas processing	27	-	-	-
	Methanol synthesis	160	-	-	-
	Petroleum refining	-	20	-	-
	Ethylene production	-	-	30	-
	Emissions from product at end of life	467	284	25	225
	Emissions from waste gases (electricity or flaring)	1.402	1.402	351	1.402
	Total	**2.056**	**1.706**	**406**	**2.187**
Alternative scenario: conservative	Syngas treatment (direct emissions)	754	754	188	754
	Syngas treatment (indirect emissions)	31	31	8	31
	Hydrogen production	425	425	106	425
	Direct emissions from synthesis	97	267	55	369
	Indirect emissions from synthesis	50	4	33	100
	Emissions from product at end of life	467	284	25	225
	Emissions from electricity replacement	367	367	92	367
	Total	**2.190**	**2.131**	**508**	**2.271**
	Percentage change compared to baseline	**+6,52%**	**+24,93%**	**+24,95%**	**+3,83%**
Alternative scenario: optimistic	Syngas treatment (direct emissions)	754	754	188	754
	Syngas treatment (indirect emissions)	2	2	.45	2
	Hydrogen production	19	19	5	19
	Direct emissions from synthesis	97	267	55	369
	Indirect emissions from synthesis	3	.21	2	6
	Emissions from product at end of life	467	284	25	225
	Emissions from electricity replacement	21	21	5	21
	Total	**1.363**	**1.347**	**281**	**1.396**
	Percentage change compared to baseline	**-33,71%**	**-21,01%**	**-30,75%**	**-36,16%**

04

LARGE-SCALE IMPLICATIONS OF PROCESS ADOPTION

LARGE-SCALE IMPLICATIONS OF PROCESS ADOPTION

The majority of organic chemicals and fuels are produced from fossil fuels (Rass-Hansen, 2007; Stankiewicz, 2013), with a small share coming from primary biomass, and an even smaller share coming from waste products (Rothermel, 2015; Flach, 2015). If the technologies for conversion of steel mill waste gases are applied on a large scale, this would have larger, systemic effects in terms of impact (reduction), positive and negative effects on the steel, chemical, and energy markets, and implications for the structure of the production systems.

To get a sense of what these effects would look like, we ask the question: ***What would the expected systemic impacts be if all of the steel mill waste gases in Europe were converted to chemicals and hydrocarbons under an optimistic scenario?*** In this section, we discuss what we anticipate the larger scale implications of steel mill waste gas conversion will be in these different areas.

SYSTEMIC ENVIRONMENTAL IMPACTS

In Europe, 100,6 million tonnes of steel are produced with the blast furnace method (World Steel Association, 2016). If all of the waste gases from this steel production were used in energy production, this would mean roughly 97.0977 GWh of energy could be generated, which is around 3,2% of the total electricity produced in Europe (Eurostat, 2017e). As mentioned previously, even though the use of the waste gases in energy production is preferable over flaring, it is a highly CO_2-intensive source of energy. In the optimistic scenarios, chemicals production using steel mill waste gases is actually more CO_2-intensive than the conventional production processes. The scenarios end up resulting in GHG emissions reductions overall because they also take into account the elimination of electricity production (or flaring) using these waste gases.

If all of the steel mill waste gases in Europe were converted to the products we have explored under an optimistic scenario, instead of being used in energy generation or being flared, we estimate a total of between 36,1 and 79,6 million tonnes of CO_2 emissions could be prevented. As Europe currently emits around 4,45 billion tonnes of CO_2e (EEA, 2017a), this would mean a total impact reduction of between 0,8 and 1,8% of European CO_2 emissions. These are considerable reductions when one considers that the iron and steel industry globally accounts for around 6,7% of the total anthropogenic CO_2 emissions (Worldsteel, 2016; IEA, 2014). Of course, these are maximum benefits if all steel mill waste gases in Europe would be diverted to a single product. However, if just 68,5% of the waste gases in Europe were diverted to methanol and ethanol production, this could supply all European consumption of these two chemicals at a savings of nearly 54 million tonnes of CO_2, which is around 1,2% of European emissions.

The alternative scenarios for utilizing steel mill waste gases have positive effects on water consumption and wastewater production under an optimistic scenario (though increases under a conservative scenario). We estimate that the optimistic waste-gas-based production scenarios, when scaled up to the total amount of waste gases available, would result in an decrease of nearly 500 million m^3 water consumed compared to the fossil-based scenarios for hydrocarbons and methanol. However, compared to the total water abstraction in Europe (247,6 billion m^3, FAO, 2012), this would account for only 0,32% of the current consumption.

When weighing water impacts for ethanol from syngas against biobased production, the water demands decrease even more. Compared to biobased production to produce ethanol, syngas fermentation would lead to a reduction of nearly 10 billion m^3 of water. This is considering a scenario where all waste gases are diverted to ethanol, however, which would be far in excess of meeting European demand. If we only consider meeting European demand with ethanol from waste gases, 4,2 billion m^3 or around 2,9% of Europe's total water footprint could be avoided.

Biobased ethanol also results in a large land footprint, which is just over 0,2 hectares per tonne of ethanol using sugarcane, and 0,4 hectares for wheat-based ethanol (Lovett & de Bie, 2016), which is the main source of biomass for ethanol in Europe. Europe currently produces around 4,9 million tonnes of bio-based ethanol (Flach et al., 2017), which corresponds to an embodied impact of nearly 2 million hectares of land. Producing Europe's nearly 5 million tonnes of ethanol from steel mill waste gases, instead of biomass, would reduce the land footprint of ethanol by around 2 million hectares (which is nearly half of the area of the Netherlands). Considering the increasing demand for ethanol, and the additional pressures this could mean for agricultural systems, the potential for impact reduction by using waste gases instead of biomass is significant.

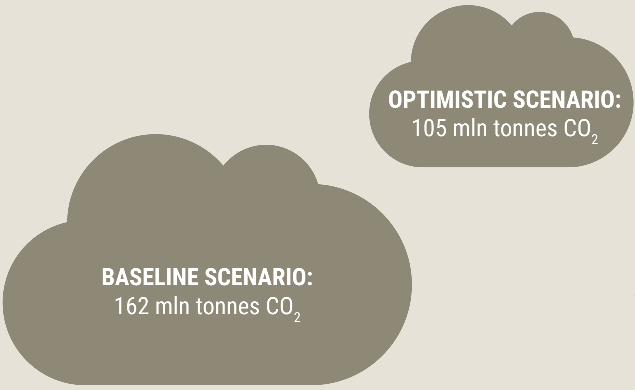
While until this point we have mainly considered the implications of a scenario where all of the steel mill waste gases are converted to a single product, this is unlikely to happen in reality. In particular, the methanol and ethanol markets are not currently large enough to absorb the amount of product that could be generated. To better understand the large-scale implications of process adoption, we have defined a more reasonable scenario, where a large share of waste gases is diverted to chemicals and hydrocarbons production, meeting the full European demand for ethanol and methanol and a small share of the fuel demands (0,1%). This scenario is illustrated in Figure 4.1.

SCALING UP A EUROPEAN CO-RECYCLING SCENARIO:

Here we take a closer look at the implications of CO recycling from steel mills under an optimistic scenario. European demand for methanol and ethanol, as well as a small share of the demand for fuels (0,1%) can be met by recycling 77% of Europe's steel mill waste gases into products.

CO_2 EMISSIONS:

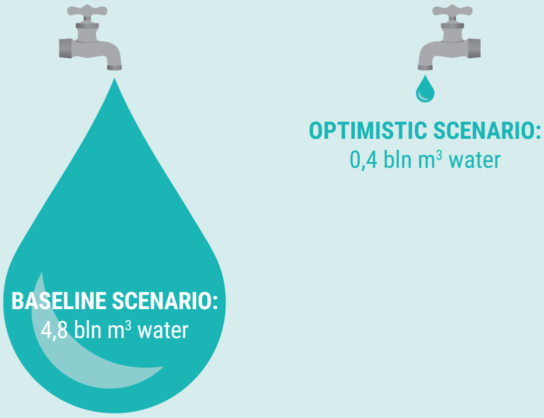
Compared to the baseline, emissions can be reduced by 57 million tonnes, which is 1,28% of Europe's CO_2 emissions.



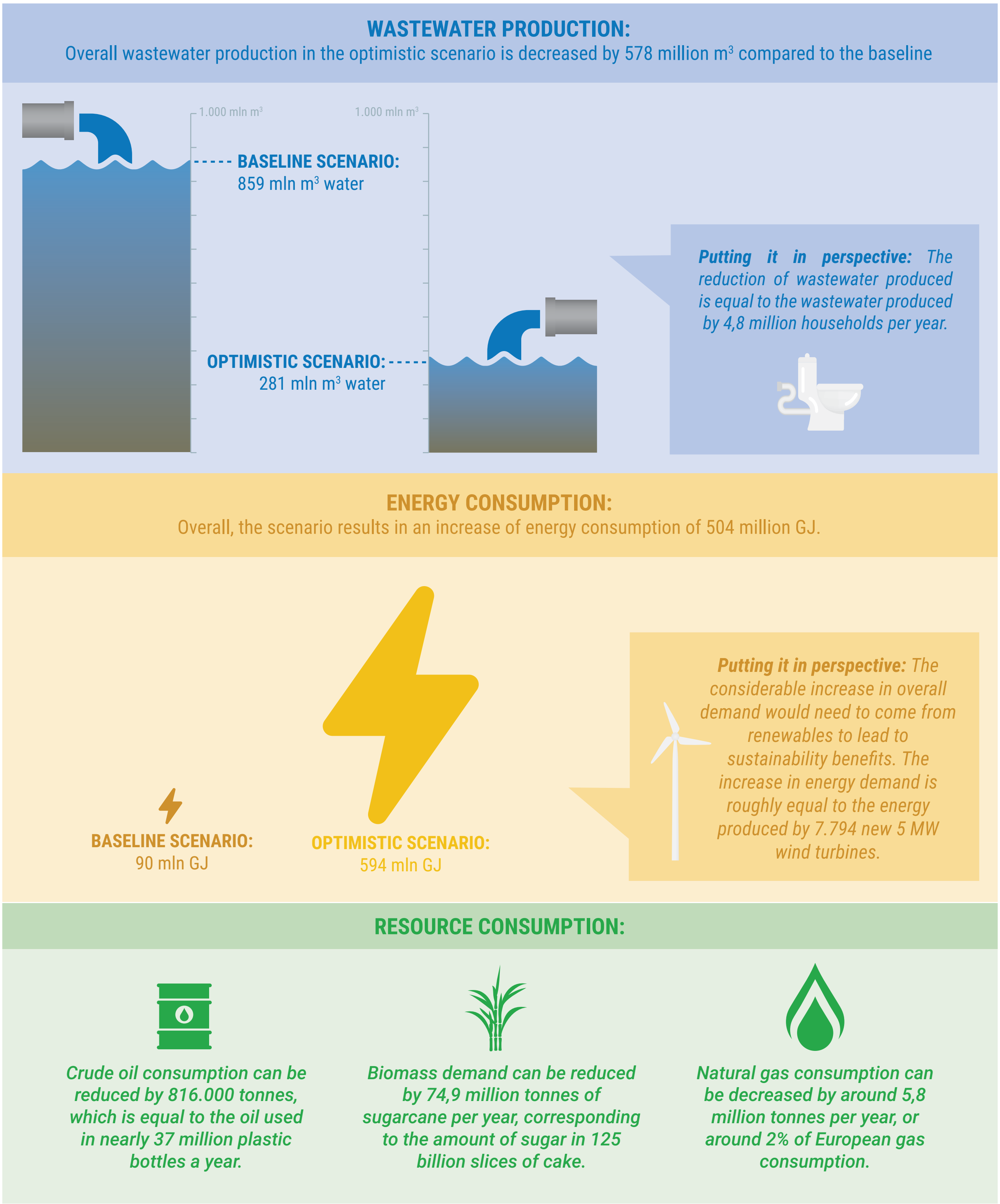
Putting it in perspective: *This CO_2 reduction is equal to the emissions of 12 million passenger cars removed from the road for a year.*

WATER CONSUMPTION:

Water consumption would be reduced by 4 billion m^3, mainly from switching from biobased to waste-based feedstocks for ethanol.



Putting it in perspective: *The reduction in water demand is equal to the water consumed yearly by 28 million households.*



WASTEWATER PRODUCTION:
Overall wastewater production in the optimistic scenario is decreased by 578 million m^3 compared to the baseline

Putting it in perspective: *The reduction of wastewater produced is equal to the wastewater produced by 4,8 million households per year.*

ENERGY CONSUMPTION:
Overall, the scenario results in an increase of energy consumption of 504 million GJ.

Putting it in perspective: *The considerable increase in overall demand would need to come from renewables to lead to sustainability benefits. The increase in energy demand is roughly equal to the energy produced by 7.794 new 5 MW wind turbines.*

RESOURCE CONSUMPTION:

Crude oil consumption can be reduced by 816.000 tonnes, which is equal to the oil used in nearly 37 million plastic bottles a year.

Biomass demand can be reduced by 74,9 million tonnes of sugarcane per year, corresponding to the amount of sugar in 125 billion slices of cake.

Natural gas consumption can be decreased by around 5,8 million tonnes per year, or around 2% of European gas consumption.

Figure 4.1. *Large-scale sustainability implications of European waste gas diversion scenario*

Overall, the benefits of steel mill waste gas recycling are high under an optimistic scenario, particularly for ethanol production, which comes with additional benefits for biodiversity through the mitigated biomass demands, in addition to decreased resource demands and CO$_2$e emissions. From these impact reductions, there is a clear case for implementing steel mill waste gas recycling on a large scale, assuming that some of the conditions for impact reduction (electricity from renewables, hydrogen from electrolysis, etc) are also met.

SYSTEMIC SECTOR AND MARKET IMPACTS

IMPACTS ON MARKETS

In Europe, production of methanol amounted to 1,3 million tonnes in 2015 (Prodcom database, 2016), while the demand is 9 million tonnes, making the region highly dependent on imports and exposed to global supply fluctuations (Yeung, 2015). If all steel mill gases in Europe were to be converted to methanol, there would be an additional supply of 34 million tonnes per year. The global industry can already supply a maximum of 110 million tonnes of methanol (Methanol Institute, 2016), while global demand is only around 70 million tonnes (Methanol Institute, 2016). It a very large shift to methanol produced from steel mill gases would result in large market disruptions, though it is unlikely that all, or even a large share of the waste gases would be converted to methanol alone.

If all European steel mill gases were used in the Fischer-Tropsch process, this would enable the industry to produce just over 9 million tonnes of hydrocarbons per year. The global liquid fuel production (oil, biofuels, and other liquid fuels) amounted to 4,96 billion tonnes in 2016 (EIA, 2017b), while European liquid fuel production is nearly 209 million tonnes, including production in Norway (EIA, 2017b). An additional production of 9 million tonnes would only represent a small increase in supply. Producing a mix of hydrocarbons from Europe’s steel mill gases would not saturate the market demand for fuels, especially considering the rising demand for fuels, and would fit into policy goals of moving away from conventional fossil fuels.

ArcelorMittal’s pilot project with Lanzatech aims to produce around 47.000 tonnes of bioethanol per year (ArcelorMittal, 2017). If all of the European steel mill gases were directed to ethanol production, this would enable the industry to produce 11,8 million tonnes ethanol per year. The worldwide production of ethanol is 72,25 million tonnes (ePure, 2015a), of which the majority, around 71,4 million tonnes, is biobased (ePure, 2015a). This would mean that if all steel mill waste gases were diverted to additional ethanol production, this would increase the global ethanol supply enough to disrupt the market. However, if steel mill waste gases were instead used as a replacement for the use of biomass (largely Brazilian sugarcane on a global level), this would reduce pressures on natural ecosystems and free up land for food production.

Finally, we can consider the impact of process adoption on the energy market, as diverting the waste gases would require replacement of electricity. In total, if we assume that 50-100% of the steel mill waste gases are used in energy generation in Europe, this represents an additional 49.000-97.000 GWh that would need to be replaced. On the short-term, this would likely come from fossil sources (which currently account for around two thirds of electricity production in Europe (WEC, 2016)). If we imagine that this replacement would instead come from 5MW wind turbines running at 41% capacity (EWEA, 2013), around 2.700-5.400 wind turbines would be required, with a total capacity of between 13.500-27.000 MW. Considering that the current installed wind capacity in Europe is only 153.700 MW (Pineda and Tardieu, 2017), this represents a considerable increase in demand, which would be difficult to satisfy with renewables on the short term.

A benefit of these technologies is that fossil fuels used in chemicals production could be avoided in the future under an optimistic scenario, though the short term might lead to additional consumption of natural gas (conservative scenario). If we scale up our conservative scenario, we could expect an increase of natural gas consumption and a decrease in crude oil consumption, while under an optimistic scenario, both decrease drastically. These changes in fossil fuel consumption could have an effect on international trade of fossil fuels such as natural gas and crude oil.

IMPACTS ON FUTURE PRODUCTION SYSTEMS

The large scale implementation of facilities for the use of steel mill gases will result in a restructuring of production systems as a whole in the participating industries and beyond. The obvious changes would be in the new connection between the petrochemical industry and the steel industry, as well as the changed connection between steel and energy producers who utilize waste gases. This restructuring would also have spatial implications for locations of steel and chemical sectors and the infrastructure which would connect them. Additional changes to production systems would result from the production of hydrogen and renewable energy, as depicted in Figure 4.2.

While there is hydrogen already present in the steel mill gases, additional hydrogen is necessary. Electrolysis is seen as the future of hydrogen, and involves the production of hydrogen and oxygen from water. While there are many valuable uses for the hydrogen, finding a use for the oxygen produced at the same time is key. Demand for the oxygen could come from the glass industry, electric power plants, gasification, or medical care (Kato et al., 2005), however, by far the largest consumer of oxygen globally is the steel industry (Gasworld, 2007). Industrial electrolysis for hydrogen production could facilitate the setup of closed-loop collaboration between steel, chemical, and hydrogen-producing industries, as oxygen as a byproduct of the production of hydrogen could be fed back to the steel companies for use in their production processes.

In the future, we expect that renewables will provide the energy both to replace steel mill waste gases and produce hydrogen. Hydrogen production has been explored as a means for "storing" energy when there is an excess of renewable energy. Nuon, among others, is exploring the possibility of using excess renewable power for electrolysis for hydrogen production and joined an innovation project with Statoil and Gasunie to convert natural gas into hydrogen and CO_2 (Statoil, 2017) and start producing electricity from hydrogen by the year 2023 (Institute for Sustainable Process Technology, 2017). One of the biggest challenges of using renewables to produce hydrogen when there is an overcapacity is adapting the chemicals production processes to make them able to cope with the fluctuating production capacity.

Besides the possibility of selling hydrogen as a fuel or for other purposes, hydrogen can also help provide constant power and stabilize the utility grid when the renewable power is not available, as it can be converted back to electricity (Thomas, 2016). Projects have already been launched for the development of energy storage through hydrogen, including facilities in Canada (Hydrogenics, 2014), Japan (Watanabe, 2014), and Singapore (Hanting, 2017). In Europe, the first projects are being announced, such as the Hydrogen Valley/CEMTEC-project in Denmark (Udby, 2016).

In addition to direct changes on production systems, large-scale waste gas valorization can present both a pathway and a barrier for other types of developments in production systems. On one hand, the successful utilization of carbon monoxide would stimulate development and application of carbon capture and utilization technologies (CCU) and could prove to be a stepping stone to other technologies which capture carbon dioxide from other industries for conversion to carbon monoxide for use in chemicals production. On the longer-term, when we expect less concentrated sources of emissions from industry, even technologies which extract CO_2 from the atmosphere (direct-air capture (DAC) technologies) may become feasible (Marucci et al., 2017).

On the other hand, there is also a risk that investments made to utilize waste gases could lead to technological lock-in, delaying a shift away from coal-based production or high emission production practices in general. As shown in figure 4.2, a number of industries would face new interdependencies linked to coal-based steel production. While efforts are being made to move towards coal-free steelmaking (Burns, 2017), there is also a risk that setting up CO valorization systems could lead to the creation of specific pathways that are difficult and costly to escape. Consequently, this technology could persist for extended periods, even in the face of competition from potentially superior substitutes (Perkins, 2003). For this reason, steel mill waste gas recycling must be seen as a stepping stone to other pathways: important to explore on the short term, but not a permanent solution for emissions.

Eventually, carbon valorization could not only change production systems of European companies, but could also develop into a prime example for a sustainable and profitable use of waste gases for countries outside of the EU, including developing countries. Leapfrogging effects could be expected for companies of the latter, who can while building up steel and chemical industries and setting up production processes skip the practice of releasing emissions into the air and move straight to capturing and utilizing the accruing emissions within inter-sectoral partnerships.

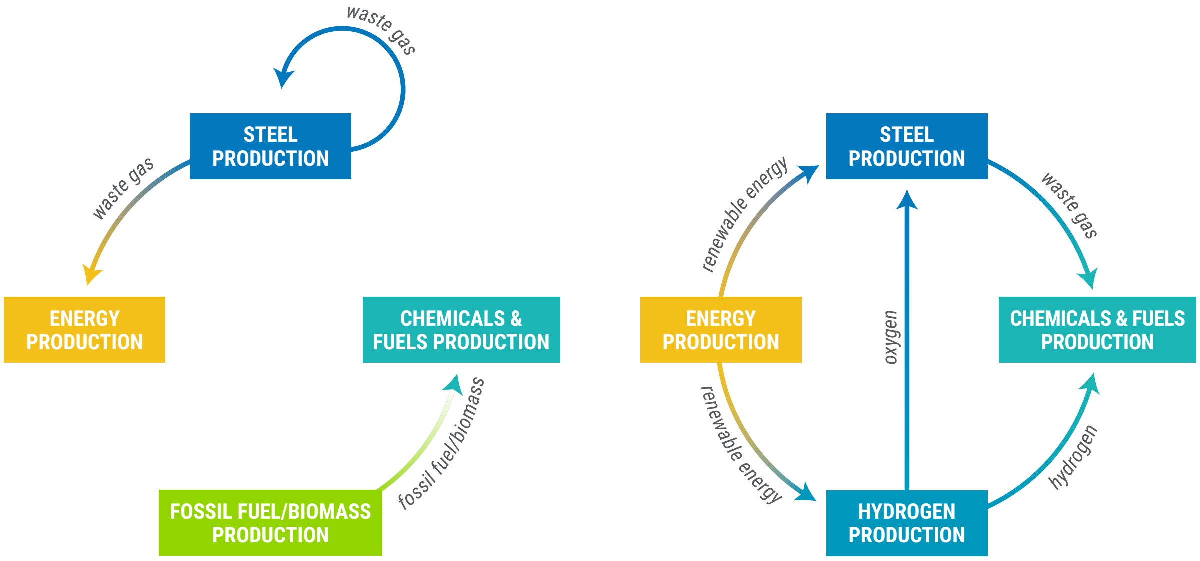


Figure 4.2. *Potential for industrial symbiosis in new production system structure*


89.635
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05

BARRIERS AND OUTLOOK

BARRIERS

There are three main barriers that could prevent the large scale implementation of steel mill waste gas valorization.

TECHNO-ECONOMIC BARRIERS

Four main options are selected in this work for large scale reusing of carbon monoxide from steel mill gases:

- methanol synthesis for fuel and base chemical application either with low-inert-level syngas or with high-inert-level syngas,
- Fischer-Tropsch synthesis aimed at diesel/jet fuel for transportation purposes,
- Fischer-Tropsch synthesis aimed at naphtha for chemical products
- fermentation of the gases for the production of ethanol for fuel and chemical applications.

These options can be considered a short list and they are selected from an extended long list of possible chemical components and processes that are available for using carbon monoxide. The selection criteria are of a technical and economical nature.

On the technical side, the choice was made to include only the options that are technologically mature and well demonstrated to avoid technical risks as much as possible. However, some critical issues remain here. When applying methanol synthesis with low inert level syngas, the challenge is the accomplishment of the separation of H_2 and CO, for use in the make-up syngas, from the unwanted CO_2 and inerts. In the case of methanol synthesis with the high inert level syngas, the design of the synthesis reactor is of specific concern. At the usual operating temperatures applied for this type of reactors, the conversion can be thermodynamically limited, due to the dilution of the active syngas components, to such low values that economic operation is endangered. Operation at lower temperatures, however, require attention to the design in order to achieve suitable catalyst activity and prevent unrealistically large reactor vessels.

The methanol and Fischer-Tropsch processes require a continuous availability of syngas for continuity of the operating conditions especially in the synthesis loops. The processes cannot be put on standby and taken into production on a short notice, for example in a daily tact. This requires a provision to smooth out any peaks and lows in steel mill gas availability.

The supply of external hydrogen, needed for the thermo-catalytic conversions, is preferably obtained from sustainable hydrogen production processes. A suitable option is the hydrogen generation with electrolysis using renewable energy, say from wind energy parks. An additional advantage of this method is that the co-produced oxygen can all be used in the steel mills to replace the in-house produced pure oxygen that is currently obtained from energy intensive cryogenic separation of air. Current electrolysis systems appear to suffer from high costs, especially investment costs, that, at the moment, prevent their successful competition with conventional, fossil fuel based, hydrogen production methods. The development of electrolysis facilities with lower investment costs is a challenge that, expectantly, in the near future will be advanced by an increase of scale and market size.

From the analysis so far it is found that chemicals and hydrocarbons can be obtained from steel mill gases on a technical basis. The concept results in a substantial amount of avoided fossil carbon emission into the atmosphere. An important recommendation for follow-up work is a detailed analysis of the investment and variable costs. To achieve this a detailed design and sizing of the installations is needed. The connection of on-site available utilities is important to consider, such as the availability of waste heat or steam. The availability of ample energy can have an impact on the equipment choices, or the technologies to be applied (for example TSA vs PSA for gas separation). The outcome of such a detailed analysis, when compared to the data of fossil carbon based products, will give valuable insights into questions concerning the economic feasibility of the concept of steel mill gases conversion into chemicals and hydrocarbons, such as product costs, capex, opex, payback period, expected cash flow, etc..

EXISTING INFRASTRUCTURE AND PARTNERSHIPS BETWEEN INDUSTRIES

The existing infrastructure and current partnerships between industries represent a second potential barrier, One issue is in the form of lock-in, in the case that investments have been made into utilization of waste gases for energy production. On the other side, chemical companies have already made investments in production systems which utilize other feedstocks. In this case, simply switching feedstock sources would not be possible, so new production systems would need to be established.

Another concern is whether there is enough motivation for industries to look for new partners for carbon monoxide valorization. Notable efforts have already been made in this direction in countries such as Germany (thyssenkrupp AG, 2016) and China (LanzaTech, 2011). In Germany the steel, chemicals, and energy-gene sectors, are already collaborating through the "Carbon2Chem" program (Emig, 2017), while more than fifty steel production plants worldwide have been identified as suitable for this type of collaboration. Also in France, ArcelorMittal's R&D project "Valorco" aims to determine the best solutions to valorize steel mills CO_2–rich gases and identify the most promising products (Uribe-Soto, 2014). In this context, the ongoing partnership in the Netherlands and Belgium between steel producers (ArcelorMittal, Tata Steel) and chemical industries (DOW Chemicals, AkzoNobel) is a pressing necessity to remain competitive and at the forefront of technological development.

SET OF INCENTIVE STRUCTURES AND OTHER POLICY STRUCTURES

The third major barrier concerns the set of policies and incentive structures currently in place, which can make or break attempts at carbon utilization.

How waste gases are defined or assigned carbon credits in production systems plays a major role. Waste gases fit the description of by-products, which are defined as "a substance or object, resulting from a production process, the primary aim of which is not the production of that item" (European Commission, 2016a) and could thus be considered waste. However, they are not only excluded from the European List of Waste (European Commission, 2000), but - as "gaseous effluents emitted into the atmosphere" - also excluded from the scope of the directive 2008/98/EC on waste management (European Parliament and Council, 2008). There is a clear focus on solid and liquid waste.

Waste gases are considered within the separate directive 2010/75/EU on industrial emissions (European Parliament and Council, 2010). This document is solely focused on prevention and control and does not go deeper into the waste management hierarchy as applied for general solid and liquid waste. Measures of lower priority like preparation for re-use, recycling, or recovery, are left out of consideration. While these directives allow for carbon credits for electricity produced from waste gases (European Parliament and Council, 2009a), directives aimed at the production of chemicals and hydrocarbons do not provide credits, providing a disincentive for uses other than energy generation.

At the same time, the European Commission aims to promote the use of bio-based resources and is supporting the bio-based industry through a variety of measures (European Commission, 2015). One measure is the support of investments in integrated biorefineries, capable of processing biomass and biowaste for different end-uses and other innovative bioeconomy-based projects through research funding (European Commission, 2015d). Various bioeconomy-based projects, such as the production of bio-based elastomers from Europe-grown feedstock, are receiving targeted funding support (European Commission, 2015c). Additionally, in light of the pressures of large-scale biobased production on land, water, and biodiversity, these types of policy measures potentially lead to perverse incentives, in addition to counteracting the potential use of CO as an input for products.

PUBLIC SUPPORT

As a final thought we can reflect briefly on the role of public support of waste gas utilization, which could in turn shape policy supports or barriers. Individuals and organizations may harbor reservations about waste gas utilization, out of a concern about technological lock-in, a desire to reduce the sources of emissions rather than utilize them, or more localized concerns around the expansion of existing facilities or new facilities and infrastructure. Public support is often low for large-scale developments involving new and untested facilities and technologies (Blomeyer & Sanz, 2012). This being the case, in addition to ensuring that potential negative effects of carbon utilization are avoided, project participants may need to prevent potential concerns with intensive communication during the planning and construction phase and clearly communicate the environmental benefits of the technologies.

While the previous section has highlighted some of the issues which carbon monoxide utilization is faced with, we anticipate changes on the horizon which will affect the feasibility as well as the impacts of new projects. Some of these technological, political, and industry trends are discussed briefly in this section.

TRENDS AND OUTLOOK

TECHNOLOGICAL TRENDS

Electrolysis progress

Large bottlenecks remain on the side of hydrogen availability due to high production costs. Currently, producing hydrogen is an energy- and cost-intensive process (Dincer and Acar, 2014). The key to lower emissions and savings in the process of producing hydrogen is affordable and industry-useable electrolysis. On one hand developments in hydrogen production could be accelerated by large-scale use of steel mill gases, while the opposite is also true; cost-competitive hydrogen production through electrolysis would not only lower the production costs of many chemicals, but potentially also open up new possibilities for the usage of CO within the chemical industry. Considering recent breakthroughs in technologies and costs (Thorpe, 2016), and assuming markets for hydrogen develop accordingly, it can be expected that electrolysis will be ready for industrial use as soon as 2020 (Goodall, 2017).

Predictions on the costs of producing hydrogen from electrolysis are however divided. While some sources suggest a 50% decrease of costs to 450 - 550 USD/kW by 2050 (Hydrogen Council, 2017), others argue that large-scale alkaline electrolysers (e.g. 400 MW) are now already able to run at €383/kW (Philibert, 2017). The future cost development ultimately is highly dependent on the cost of electricity, as this represents around 58% of the cost of hydrogen production (Ivy, 2004).

On the other hand, increased hydrogen availability and lower costs could also lead to a move away from coal-based steelmaking. An up-and-coming technology is hydrogen-based steelmaking, whereby hydrogen is used as a reducing agent instead of coke (Cavaliere, 2016). This technology will presumably not be ready for industry-use before 2037 (Pooler, 2017), but an implementation within the steel industry would result in a notable decrease in steel production emissions and thus a shrinking importance of CO valorization within this range of use.

Future advances in CCU

Carbon capture and conversion advances will certainly influence the meaning of CO_2 valorization for the industry as well. Just recently, a new catalyst, which can convert CO_2 to CO at ambient temperatures and pressures was announced (UvA Persvoorlichting, 2017). New conversion technologies such as this catalyst can give rise to an increasing supply of CO generated which can be utilized in products. Industry actors with experience in capturing CO from steel mill gases will profit from their know-how in the usage of carbon monoxide for industrial processes and will most likely be able to expand their activities within new business models. Thus, future advances in carbon capture and conversion to CO will increase the importance of CO valorization significantly.

Genetic engineering of bacteria

Technological advances in genetic engineering can be expected to have a mixed impact on the outlook of steel mill gas valorization, as advances have been made in both the fermentation of biomass and syngas. These technologies provide great promise of improvement of the efficiency of several industrial processes, though the current focus has mainly been on biobased production.

As one example, with the help of genetic engineering, researchers have found a way to use all carbon of the feedstock sugar when producing ethanol from biomass, resulting in the avoidance of carbon dioxide emissions and the production of 50% more output of ethanol (Bullis, 2013). Moreover, genetic engineering of bacteria could lead to progress in the production of cellulosic bioethanol. Compared to regular bioethanol, which is derived from sugar or starch produced by food crops, cellulosic ethanol can be produced from the cellulose of the plant, making it possible to use agricultural residues, other lignocellulosic raw materials or energy crops, which is a more cost effective and sustainable production method that has a less direct impact on the food supply (ETIP Bioenergy-SABS, 2015). The genetic engineering of materials used in producing bioethanol from cellulose can significantly accelerate and reduce costs of this production process (Illinois Institute of Technology, 2016).

Another technological trend are the quite novel syngas fermentation processes. Regarding this trend, synthetic biology will certainly play a major role for the production of biofuels in terms of genetic engineered bacteria serving as biocatalysts in syngas fermentation (Bengelsdorf, 2013). An example for new products developed this way is the conversion of syngas to 2-HIBA, which is a precursor used in the manufacture of Plexiglas (Evonik, n.d). Hence, genetic engineering is also expected to expand the product spectrum beyond products like ethanol, acetate, and butanediol to a range of higher-value hydrocarbons and commodity chemicals (National Research Council, 2015).

POLICY TRENDS

The European Commission will increasingly take measures to accelerate the pace of emissions cuts. From 2021 onwards this means a decline of the overall number of emission allowances at a higher annual rate (of 2.2%) (European Commission, 2015a), leading to greater CO_2 emission costs. Due to this, Morfeldt, Nijs, and Silveira (2015) estimate that the price of steel will rise to 500USD per tonne. Subsequently this would represent an incentive towards the development and implementation of new technologies. For the steel industry this could imply an intensified usage of low-emission EAF steel production.

However, while the overall objective on EU and country levels is to reduce carbon emissions, the capture and utilization of gases that have already been emitted is also attracting the attention of policymakers. In 2015, the European Commission advocated for a forward-looking approach to CCS and CCU for power as well as industrial sectors, considering these critical technologies to reach climate objectives for 2050 in a cost-effective way. Requirements according to the European Commision include an enabling policy framework, entailing a reform of the Emissions Trading System and the Innovation Fund to increase business and investor clarity (European Commission, 2015b). Considering the expected rise of carbon allowance prices, we should expect a stronger policy framework supporting the utilization of emissions, including the use of steel mill waste gases.

INDUSTRY TRENDS

Steel sector trends

According to the European Union and to representatives of the steel industry, European steel producers face significant challenges in remaining competitive and in operation in the coming decades. The industry reports consistent losses in competitivity and employment. This is related to the international landscape of the steel market, as Asian producers, especially China, have increased their output and recently have exported production surpluses to European markets (Hornby, 2017). In the light of these recent developments, political action regarding anti-dumping duties for Chinese steel products will determine the future of the European steel industry to a large extent.

Nevertheless, currently European production remains relatively stable in terms of output (World Steel Association, 2016a). The demand for steel is high as it is one of the most important materials in our economy. Despite high recycling rates and other materials coming on the market, most experts expect the demand for steel to continuously increase (Morfeldt, Nijs, and Silveira (2015) say until 2050), partly owed to its crucial role in renewable energy technologies (World Steel Association, 2015a).

The quality of iron ore has fallen 5 percentage points in the last 10 years which induces high costs on the steel makers and leads to more emissions (Bhattacharjee, 2014). Thus, the steel industry is increasingly developing and adopting new technologies to increase its carbon efficiency (European Commission, 2013). Research projects with the aim of developing innovations for the steel industry include the HIsarna project, which aims to reduce coal use and CO_2 emissions (TATA Steel, n.d.). Furthermore, various other optimizations are being worked towards, such as top gas recycling (European Commission, 2014), H_2-based steelmaking (Patisson, Da Costa and Wagner, 2013), and the usage of O_2 instead of preheated air in processes with the goal of avoiding unwanted nitrogen. The current technology for iron reduction (BF) has not changed fundamentally in the last 50 years (or maybe more) and since the 1970s, the amount of carbon needed in the process has plateaued (Bhattacharjee, 2014), emphasizing the great need for new technologies that can reduce carbon emissions either through efficiency gains or carbon capture (like carbon monoxide utilization).

Currently, iron and its transportation account for 23% of the operational costs in BOF-steel production, while steel scrap and its transportation represent 62% of the operational costs in EAF-steel production. Energy costs (from coal and its transportation for BOT and electricity for EAF), account for 45% and 10%, respectively (MCI, 2017a; MCI, 2017b). As costs for electricity decrease and electric arc furnace production becomes more competitive in the market, current scenarios (Pardo and Moya, 2013) expect European demand for imports of scrap steel to increase in the coming decades. However, the prospective ratio of the two production methods in the industry will be highly dependent on the development of relative prices of iron (for BOF) and steel scrap (for EAF), thus influencing the opportunity for and profitability of steel mill waste gas valorization. If the price of iron decreases in the coming decades, it would provide further incentives for traditional coal-based production, thus increasing the opportunities for collaboration of steel producing industry with the chemical industry. This brings uncertainties on the prospects of decarbonization for the sector, as it would provide additional incentives to delay a shift to EFA-based production.

Chemical sector trends

In Europe, growth of chemical sales is expected to be moderate at just 1%. This slow growth coupled with labor productivity gains have led to estimations that 30 percent of jobs will be lost in the European chemical industry by 2030 (AT Kearney, 2012). Even now, despite a decent performance in 2016, a challenging operating environment persists (Zacks Equity Research, 2017). Increasing agility is necessary in the light of constantly arising new competitors for current chemical companies, which are coming from non-traditional sectors like energy, utilities, and mining, but also especially from healthcare, pharma, and life sciences companies (Guertzgen, 2015). Furthermore, changes in the competitive landscape of the chemical industry through recent mergers and acquisitions urge the involved actors to take action. One opportunity to increase competitiveness is to consider innovative inter-sectoral collaborations.

One trend influencing the outlook of steel mill gas valorization is the one towards the use of renewable feedstocks for chemicals, with many chemical companies being focused on a shift to biobased production. Whereas in 2001 globally only 30 billion USD were generated through the use of biotechnology processes in the chemical industry, this number already increased to 310 billion in 2010 (Philp, Ritchie, and Allan, 2013). While these biobased production processes usually rely on the input of biomass, using steel mill gases instead spares chemical companies hurdles in the cost and logistics of acquiring satisfactory amounts of plant-based feedstock (Bomgardner, 2012), making the alternative of steel mill waste gases an attractive option. These waste gases do however originate from a non-renewable resource, putting it in a different arena than biobased production.

OUTLOOK FOR THE PRODUCTION AND DEMAND OF METHANOL, ETHANOL, LIQUID FUELS, AND ELECTRICITY

Developments in the production and demand for products such as methanol, ethanol, hydrocarbons, and electricity will also have an effect on the feasibility of steel mill waste gas recycling.

Demands for methanol and ethanol are expected to increase in the near term. For example, the demand for methanol is expected to grow at an annual rate of 10.70% up to 2021 (Mordor Intelligence/Research and Markets, 2017), partly owed to explosive growth primarily in China through new MTO plants (S&P Global Platts, 2016), though this development is dependent on the oil price (Alvarado, 2016a). Future production systems for methanol and ethanol will increasingly involve biobased or waste-based feedstocks, which could either compete with, or pave the road for waste-gas production systems. Some examples include AkzoNobel's municipal waste to methanol pilot project in Rotterdam called Waste2Chemicals, but also biomethanol production from glycerine (waste product from biodiesel production) (Kable, 2010), and biobased production of ethanol from lignocellulosic material, which could be advanced by developments in bacterial genetic engineering (Karimi and Chisti, 2015).

With more efficient vehicles and the shift towards electrification of vehicles, we can expect that the demand for fuels will decrease in the long-term. EU28 demand for all fuels has fallen since 2007 with the exception of renewables, which have seen a strong growth (Barker et al., 2016). Global demand is even expected to increase to 5,62 billion tonnes per year by 2035 (BP, 2017). Even though the consumption of liquid fuels in the automotive industry is expected to reduce, 93% of the vehicle fleet is projected to still use, at least partly, liquid fuels in 2030 (Betarenewables, 2017). Some types of fuels, such as jet fuel, will persist for longer as alternatives will take many years to develop, which means that demand on the short-term is guaranteed. On the longer term, investments in technologies to convert waste gas to products such as naphtha, which can be used as a feedstock instead of as a fuel, will have benefits both in terms of sustainability (by avoiding loss of carbon), and in terms of security (given the shift away from liquid fuels).

Finally, we can consider the shifts taking place within the energy sector. Due to the diffusion of more efficiency technologies (Barker et al., 2016), energy consumption in the EU is experiencing a prolonged downturn in consumer energy revenue and slow growth (0,8%). At the same time, the share of renewable energy is increasing. While a shift towards renewable electricity has been slow, the share of renewable energy currently already accounts for 26,7% of total European energy production (Eurostat, 2017b), though Europe also imports non-renewable energy. As part of the EU's energy and climate goals for 2030, EU countries have agreed on a renewable energy target of at least 27% of final energy consumption, including imported energy (European Commission, 2017d).

Bringing it all together: Implications of trends for sustainability performance

Under the optimistic scenario we assessed for CO-recycling, we found there are large impact reductions possible, but only in the case that this goes hand in hand with low-impact electrolysis and renewable electricity production. While these are expected to be available and cost-competitive in the coming years, Hydrogen-based steelmaking or other innovative technological developments in the steel industry will reduce the amount of waste gases considerably on the long term and we do not want to create a situation where technological lock-in delays a shift to low-impact steelmaking or where a loss of feedstock results in stranded assets.

To understand these issues, we have plotted some of the expected developments on a timeline in Figure 5.1. If we expect that industrial-scale electrolysis will become available around 2020, this would be an ideal time to begin bringing large-scale CO recycling online from a

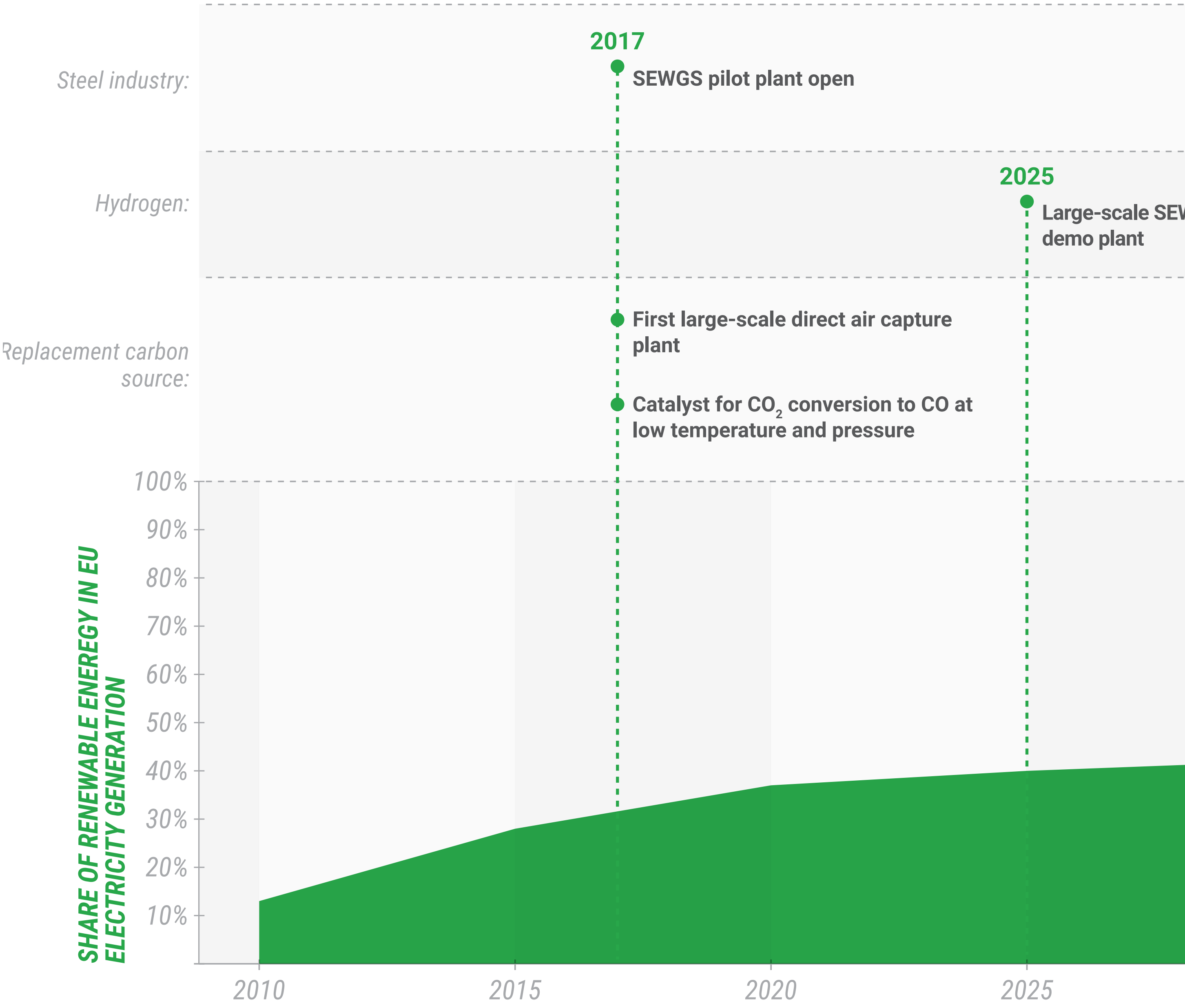
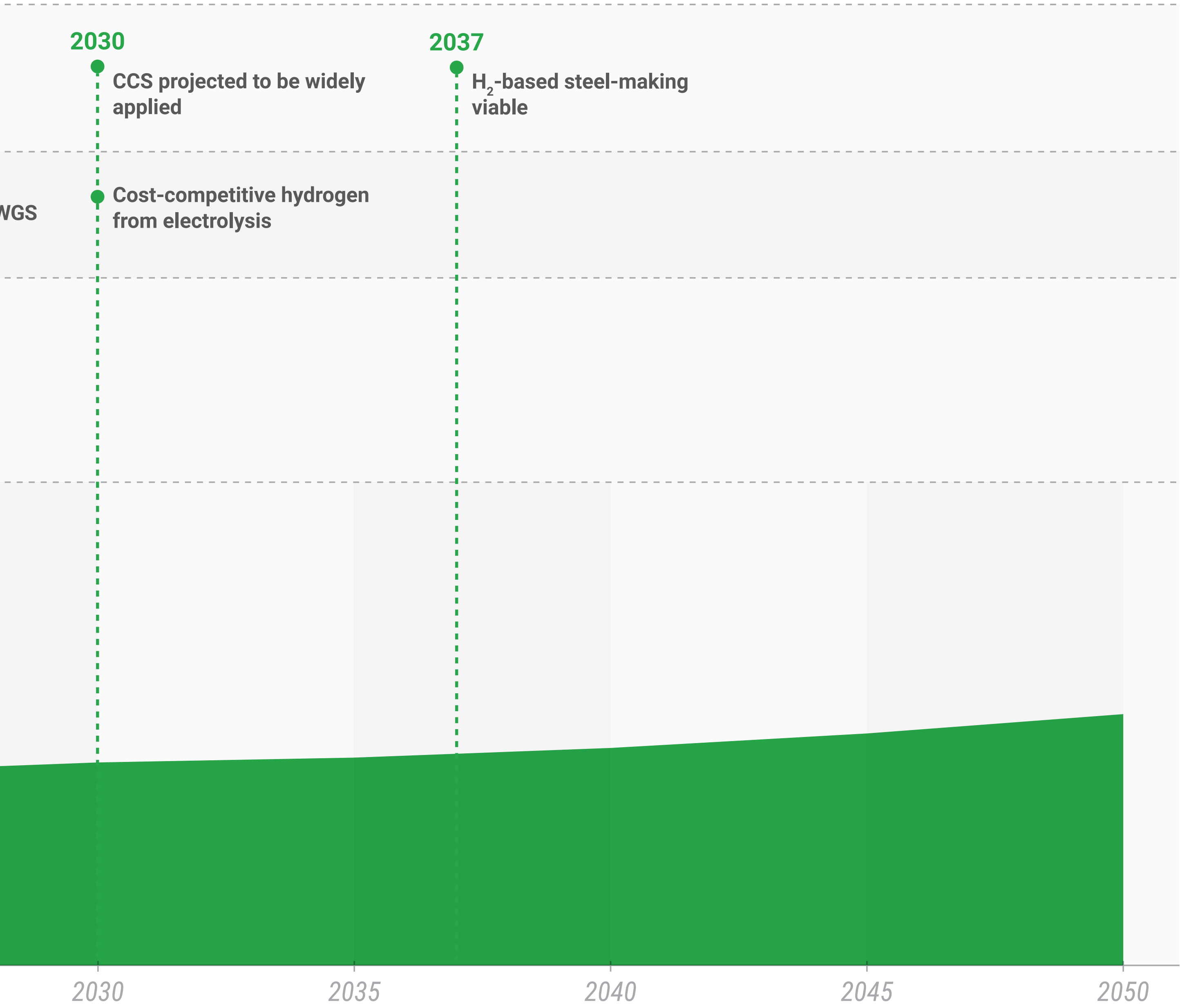
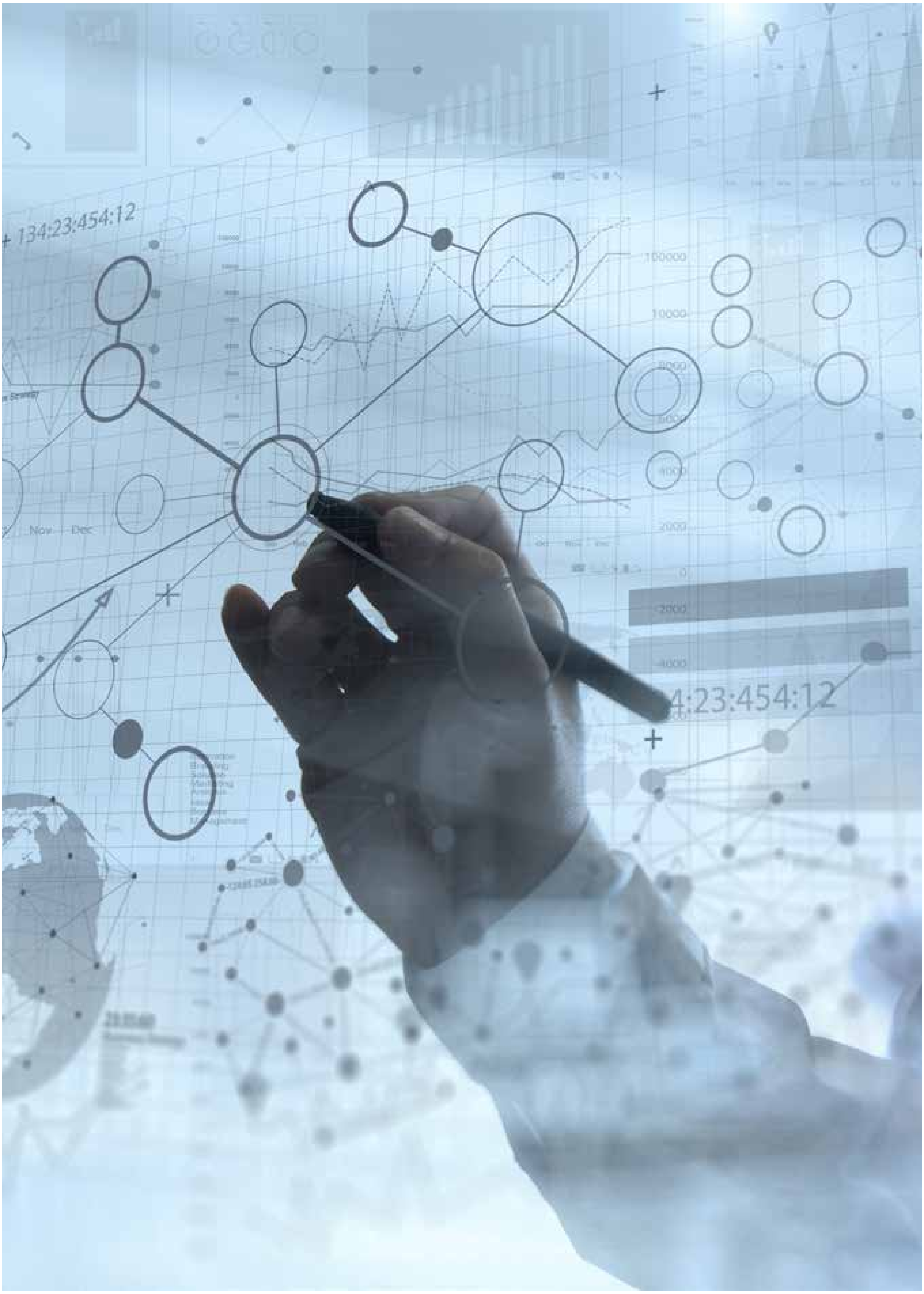


Figure 5.1. *Timeline of projected trends around CO-recycling*

sustainability standpoint, but the technologies will not likely yet be cost-competitive. In this period until 2030, CO-recycling as a whole could be considered in a pilot phase. Incentive structures for investments in cleaner technologies would need to be available to enable a shift to electrolysis. Later, when electrolysis is cost-competitive, H_2-based steelmaking will also become a more viable option. From around 2030-2040, very low impact carbon monoxide recycling from steel mill waste gases is likely to be a commercially viable solution. After this point, the reduction in waste gases from the steel industry makes this source of feedstock less attractive, and if investments with a long payback period have been made, the industry will need alternative sources of CO. If CO_2 capture and conversion technologies are advancing in this period, this could be the alternative that enables CO from steel mills to serve as a stepping stone to new carbon utilization processes.

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CONCLUSIONS AND NEXT STEPS

CONCLUSIONS

Carbon in steel mill waste gases currently represents a missed opportunity for circularity.

In Europe, large amounts of potentially valuable waste gas are produced by the steel industry, but this value is currently lost by low-value energy production, or even flaring of gases. Instead, we could produce 340 kg of methanol, 118 kg of ethanol, 90 kilograms of hydrocarbons (eventually producing ethylene for a route to plastics) alongside each tonne of steel. On the longer term, this shift is important for enabling a circular carbon value chain around the steel industry (see Figure 6.1).

CO-rich waste gases can be converted into products with a reduction of CO_2 emissions and other negative impacts.

Roughly a third of the direct emissions from waste gases can be mitigated through use as a feedstock, an additional third is made capture ready in the process. If CCS is implemented alongside waste gas recycling at a European scale, this could result in a reduction of up to 3% of European CO_2 emissions. In addition to reducing CO_2 emissions, when substituting waste gases for biobased feedstocks, water demands, wastewater production, and land use can be reduced, with positive implications for biodiversity.

CO-recycling has systemic implications for steel, chemicals, and energy sectors and can be a stepping stone to carbon recycling on the long term.

The scale of potential chemicals production from steel waste gases is significant, far exceeding the current market volumes used in Europe in some cases. If a promising option (such as the SEWGS to methanol route) is fully exploited, this could mean significant changes for the chemicals sector, such as an increasing dominance of methanol as a platform chemical for other products (for example with the methanol to olefins (MTO) route).

Within a CO-recycling value chain, there will be unique opportunities and challenges for industrial symbiosis. H_2 production through electrolysis, for example, also results in a large stream of oxygen as a byproduct, which the steel industry (as the largest oxygen consumer) can make use of. H_2 can also be produced as a means for using excess renewable energy production in peak periods. CO recycling will result in logistical and operational implications for the steel, energy, and chemicals sectors and require a redesign of major parts of operations.

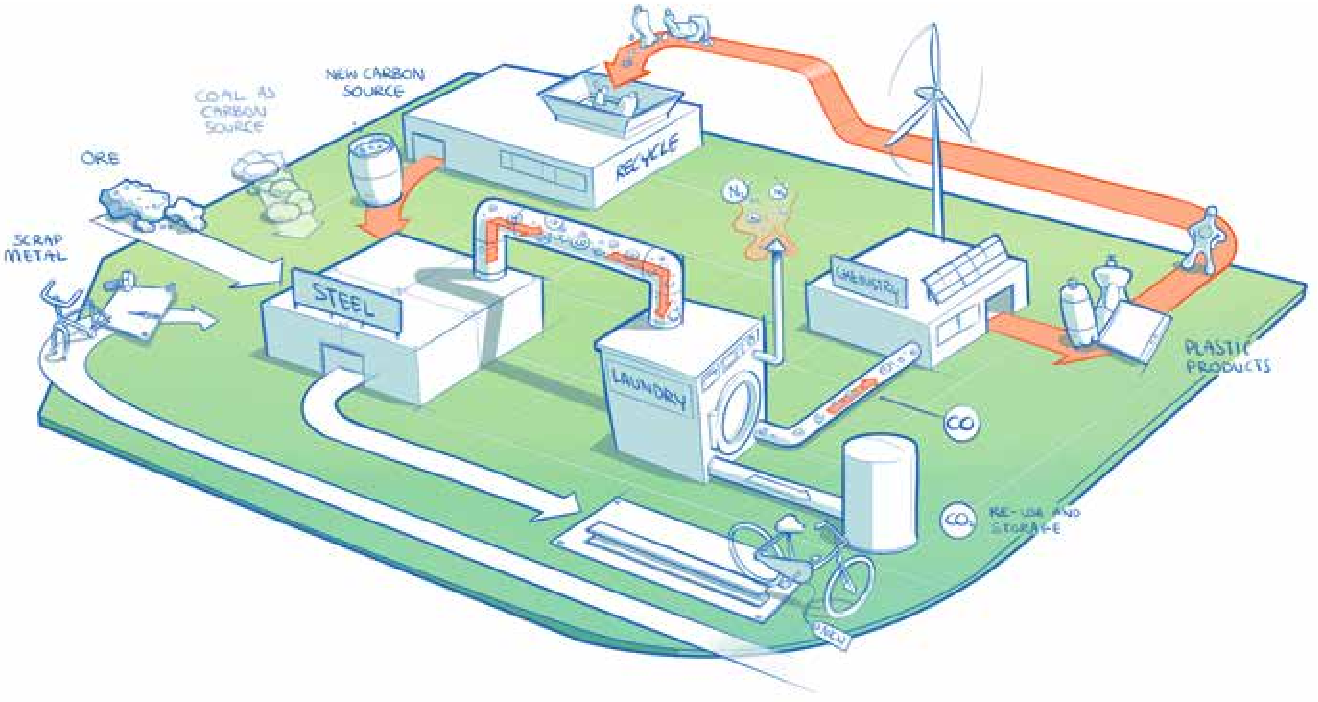

Figure 6.1. Outlook for a circular carbon chain around steel mill waste gases

Finally, an important systemic issue around waste gas recycling is the creation of new dependencies between the steel, energy, and chemical sectors, which poses a risk of technological lock-in (for example delaying a shift to H_2-based steelmaking). However, the expectation is the waste-gas pathway will be feasible at the required scale sooner than direct air capture (DAC) plants. This route offers a transition route that enables a circular carbon value chain on the shorter term. With new technologies for CO_2 conversion to CO and atmospheric CO_2 capture becoming available in the future, a long-term transition towards this route could fill the gap as the steel industry shifts towards lower emission steelmaking processes.

Current developments provide an optimistic outlook for gas recycling profitability. However, most low-impact technologies for CO-recycling are not yet profitable on their own.

To make waste gas recycling possible, large investments are required. For a steel mill of roughly the size of Tata Steel's plant in IJmuiden (producing around 7 Mt of steel per year), an investment of around 1-2 billion euros would be required. Including Carbon Capture and Storage (CCS), this scale could enable around 5 Mt of CO_2 mitigation (around 2,6% of Dutch emissions). By comparison, we can consider that the Netherlands currently supports the burning of biomass in coal power plants with around 3,6 billion euros, which accounts for around 40% of the sustainable energy subsidies (Fluxenergie, 2017).

According to our assessment, investments in waste gas recycling will only be possible on the short term with financial incentives in place, though LanzaTech claims a positive business case for fermentation with a short payback period of 3-5 years. On the longer term, the very promising SEWGS route will become available on a commercial scale.

Development is required to scale existing technologies and find new options for remaining technical challenges.

Scaling up the SEWGS process (currently at pilot scale), is one important advancement which can enable profitable waste gas recycling, however the technical challenges around gas separation present another opportunity for further development. Steel mill waste gases contain a very large share of nitrogen. When left in the gas stream, nearly twice the volume of gas must be processed, compressed, heated, etc. Separation of nitrogen from CO is technically challenging because the molecules are very similar (e.g. same boiling point, molecular weight and size). This is where the SEWGS process has an advantage; CO is converted to CO_2, which makes N_2 separation simple. If other alternative options for nitrogen separation become attractive, the efficiency of other process routes can be improved.

Affordable low impact hydrogen and renewable energy are key to short term costs.

Carbon monoxide recycling typically requires additional hydrogen (around 0,1 - 0,4 kg/kg product) and additional energy. In the CORESYM study, we have shown that under a conservative scenario (producing energy and hydrogen from natural gas), waste gas recycling can potentially result in CO_2 increases, so we must ensure this route does not occur. While it may be possible to produce ethanol using only the small amount of hydrogen present in the waste gases or to make use of stranded hydrogen that is currently produced as a byproduct, the profitability of low-impact waste gas recycling will largely depend on the price of renewable energy and hydrogen.

The current price of hydrogen from electrolysis is more than 2,9 - 3,8 euros/kg, though will like reach the 2 euros/kg price relatively quickly. At this price, CO_2 abatement costs during the production of ethanol, methanol, or hydrocarbons range between 46 and 157 euros/tonne for the current options of methanol, ethanol, or Fischer-Tropsch. If we assume a hydrogen price approaching zero (either due to the use of stranded hydrogen or extremely low-cost hydrogen from renewable water electrolysis) then the CO_2 reductions could occur alongside a profit for methanol and ethanol and at a cost of 31 euros per tonne CO_2 for Fischer-Tropsch hydrocarbons. To put this into perspective, we can consider that CO_2 abatement from renewable energy production has also been estimated in the range of 32 euros/tonne in Germany (McKinsey & Company, 2007).

KEY TAKEAWAYS FOR POLICY MAKERS

Incentive structures must be established which work for, not against waste gas recycling.

Achieving the potential impact of CO recycling will not come easily and materializing these routes with a high public value requires clear support of policy measures. For one, the use of waste gases in energy production is currently incentivized by policy, while support for the production of value-added products is not. Support for other alternative industrial feedstocks, such as primary biomass, also creates an uneven playing field for the use of waste gases - even though the environmental footprint of biomass production puts more pressure on the environment than that of waste gas recycling.

Smart carbon pricing can push waste gas recycling into profitable areas, but must also ensure a level playing field.

Carbon taxation can accelerate the development and implementation of waste gas re-use, but only if an international level playing field is warranted - within Europe and with border-tax adjustments between the EU and the rest of the world. At a carbon price of around 60 euros per tonne of CO_2, some of the routes for carbon monoxide recycling already become profitable, even with high costs for energy and hydrogen.

Support must continue for renewable energy, low-impact hydrogen production, and CCS technologies which affect the prospects for waste gas recycling indirectly.

If large-scale hydrogen production from electrolysis with renewable energy becomes affordable in the coming ten years, then the business case outlook for CO recycling becomes much more positive. Policy support for speeding up this development is highly recommended (both in ramping up renewable energy production and in scaling-up H_2 production) to support waste gas recycling. Support for implementation of CCS should extend to CCS alongside steel mill gas valorization.

Additional support is required to research or scale up novel new technologies for waste gas recycling.

There are still technological barriers to overcome to mature the necessary technologies to the correct scale. Supporting policies that speed up the innovation pathways and support scale-up and demonstration experiments are needed to de-risk the required development trajectories. In particular, support should be put into place for innovation (from research to large-scale demonstration plants) of gas upgrading technologies, such as technologies to separate N_2 from CO-rich waste gases, and for exploring alternative processes and finding economic and environmental optimizations at different scales and with different process setups.

KEY TAKEAWAYS FOR INDUSTRY

The steel and chemicals sector should lead the way in maturing technologies required in CO recycling

There needs to be a push from industry to mature technologies around CO recycling such as the SEWGS process, CO-N_2 gas separation technologies, and syngas fermentation. Looking toward the future, in addition to continuing work on these technologies, research and innovation should be pursued for new routes of waste carbon recycling. Industry should be actively seeking new routes for exploration.

The energy sector should move quickly to scale up low-impact hydrogen production and increase total renewable energy capacity.

Affordable hydrogen from electrolysis and renewable energy are key to the costs of waste gas recycling. Scaling up these parallel developments is necessary to enable waste gas recycling. We have seen that these developments are not happening at a fast enough pace. Additional efforts should be made on the part of the energy sector to ensure a timely shift to renewables.

The steel, chemicals, and energy sectors will need to work together to enable circular carbon value chains and should already be exploring the possibilities now.

Waste gas recycling requires a joint effort of industries, with many implications for infrastructure, operations, and partnerships. There are also many new opportunities for synergies between industries which are associated with waste gas recycling. These opportunities for industrial symbiosis should already be researched and explored in full now, while technological and policy developments are taking place.

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APPENDIX III: DEFINITIONS

Abbreviations:

BF	blast furnace
BFG	blast furnace gas
BOF	basic oxygen furnace
BOFG	basic oxygen furnace gas
COG	coke oven gas

Frequently used chemical formulae

Ar	argon
CH_3OH	methanol
CH_4	methane
CO	carbon monoxide
CO_2	carbon dioxide
H_2	hydrogen
N_2	nitrogen
O_2	oxygen

Additional definitions

Syngas The term syngas, or synthesis gas, is used to refer to a gas mixture of carbon monoxide, carbon dioxide, and hydrogen, which has been prepared for use as a feedstock. The term syngas does not indicate that this gas mixture is derived from the conventional routes of syngas production (e.g. hydrocarbon reforming or through gasification of materials).

APPENDIX IV: LONG LIST OF CHEMICALS FROM CO

The steelwork off-gases contain significant amounts of carbon monoxide with a reaction potential for the manufacture of chemical products. The utilization via the synthesis of high-added value products by thermochemical processes requires separation and reactive processes to reach the appropriate composition and to perform the synthesis. In commercial petrochemistry pure carbon monoxide is used in the manufacture of a number of components that are based on four principal classes of chemical reaction: Reppe chemistry, Koch carbonylation, phosgenation, and ethylene–CO co-polymers.

- With Reppe chemistry, CO is added to an organic substrate using a metal catalyst. Chemicals including acetic acid, acetic anhydride, formic acid, propionic acid, dimethyl carbonate, and methyl methacrylate are examples of final products obtained this way.
- With Koch carbonylations an olefin reacts with CO in a two stage reaction. Important compounds obtained this way are adipic acid and trialkyl acetic acid.
- Phosgene is obtained from CO and chlorine and mainly used in the production of diisocyanates and polycarbonate.
- Copolymerization of CO with ethylene results in polyketones, a series of high performance engineering plastic.

A second route is to utilize the steelwork off-gases to produce synthesis gas, a mixture of CO, CO_2 and H_2. The synthesis gas is a feedstock for the manufacturing of methanol using conventional low-pressure synthesis. The methanol obtained can serve as the starting point for the production of a wide range of products such as dimethyl ether, formaldehyde, methyl tert-butyl ether, olefins, aromatics and gasoline. Alternatively, the synthesis gas is also input for the Fischer-Tropsch technology for the production of a range of hydrocarbons or higher alcohols.

A third route that can be distinguished is the conversion of the carbon monoxide and hydrogen parts in the steel mill output gases using biological processes. In a first instance, ethanol is the major product that is obtained from the bioconversion technology.

ACETIC ACID

Acetic acid is synthesized by carbonylation of methanol by the following reaction:

$$CH_3OH + CO \xrightarrow{catalyst} CH_3COOH$$

The catalyst can be cobalt iodide, rhodium iodide, or iridium iodide. Other syntheses can be used to manufacture acetic acid, such as oxidation of n-butane or naphtha, oxidation of acetaldehyde, and terephthalic acid coproduct. However, methanol carbonylation is the preferred process now because of its favorable raw material (methanol) and energy costs. The CO purity required for methanol carbonylation is in the range of 98 to 99% pure, with low concentrations of methane, hydrogen, nitrogen and argon. The feed pressure of CO in the reactor is approximately 35 MPa The primary use for acetic acid is feedstock for the production of vinyl acetate monomer (VAM). It is also a solvent for the air-based oxidation of p-xylene to terephthalic acid.

Table IV.1: Acetic acid key data

GLOBAL DEMAND & PRICE	STARTING MATERIALS FOR MANUFACTURE	MATERIALS AND ENERGY DEMAND	DOWNSTREAM	MAIN USES
15 Mtpa(1) 700 $/ton	methanol and CO catalyst: indium with iodine-promotor	0.93 kg CO/kg acetic acid conditions T = 150 – 200°C P = 30-40 bar CO	selectivity >99% for methanol, main by-product propionic acid (≈0.05%) selectivity for CO 95-98%	VAM, Acetic anhydride, acetate esters, PTA (80%) AkzoNobel: MCA

(1) *Mtpa = million tonnes/year*

ACETIC ANHYDRIDE

Acetic anhydride is the largest commercially produced carboxylic acid anhydride. Its main industrial application is for acetylation reactions. Over 85% of acetic anhydride production goes into cellulose acetate flake, which is in turn used to make filament yarn, cigarette paper and cellulose ester plastics. Eastman Chemical also uses it as an intermediate to make photographic film base, Tenite cellulose plastics, textile chemicals, and coating chemicals. Acetic anhydride (qv) can be made by carbonylation of methyl acetate, by methanol carbonylation, as follows:

$$CH_3COOH + CH_3OH \longrightarrow CH_3COOCH_3 + H_2O$$

$$CO + CH_3COOH \longrightarrow (CH_3CO)_2O$$

The catalyst system is rhodium and iodide complexes and chromium metal powder on an alumina support. The CO feed for second freaction must be anhydrous, of high purity, and pressured at 15–18 MPa.

Table IV.2: Acetic anhydride key data

GLOBAL DEMAND & PRICE	STARTING MATERIALS FOR MANUFACTURE	MATERIALS AND ENERGY DEMAND	MAIN USES
2.5 Mtpa 1250 $/ton	methyl acetate CO (purified) catalyst: Rh/I-complex and metallic Cr on Al_2O_3	1.1 kg CO/kg acetic anhydride P = 150-180 bar	cellulose acetate (60%), pharmaceuticals (10%), TAED (5%)

VINYL ACETATE MONOMER (VAM)

Vinyl acetate monomer, VAM, is currently the most important vinyl ester. It is used mainly for the production of polymers and copolymers for paints, adhesives, textiles, and for the production of poly(vinyl alcohol), and poly(vinylbutyral). VAM can be produced by reacting methyl acetate with CO and hydrogen:

$$CH_3COOH + CH_3OH \longrightarrow CH_3COOCH_3 + H_2O$$

$$2CH_3COOCH_3 + 2CO + H_2 \longrightarrow CH_3CH(OOC - CH_3)_2 + CH_3COOH$$

$$CH_3CH(OOC - CH_3)_2 \longrightarrow CH_3COOCH = CH_2 + CH_3COOH$$

Although viable, this synthetic method has not yet been used in industrial applications. It could become more attractive depending on future raw material prices.

Table IV.3: Vinyl acetate monomer key data

GLOBAL DEMAND & PRICE	STARTING MATERIALS FOR MANUFACTURE	MATERIALS AND ENERGY DEMAND	MAIN USES
6.5 Mtpa 1200 $/ton	acetic acid, methanol and CO	1.3 kg CO/kg VAM	PVA and copolymers, adhesives, textiles, ...

FORMIC ACID

Formic acid like acetic acid, is produced by methanol carbonylation followed by methyl formate hydrolysis:

$$CO + CH_3OH \longrightarrow HCOOCH_3$$

$$HCOOCH_3 + H_2O \longrightarrow HCOOH + CH_3OH$$

Carbon monoxide specifications for this reaction is typically 98% pure, with low levels of methane, hydrogen, chlorine, nitrogen, and a very low sulfur content of less than 1 ppm. The CO feed pressure in the reactor is around 1.5 MPa. Formic acid is a medium volume commodity chemical that has a variety of applications, including processing of natural rubber, textile finishing, production of dyes, flavors and fragrances, and as a chemical intermediate.

Table IV.4: Formic acid key data

GLOBAL DEMAND & PRICE	STARTING MATERIALS FOR MANUFACTURE	MATERIALS AND ENERGY DEMAND	MAIN USES
	water and CO (carbonylation of methanol followed by hydrolysis of methyl formate)	0.6 kg eq. CO/kg formic acid P = 15 bar	

PROPIONIC ACID

Propionic acid is used in the production of cellulose esters, plastic dispersions, herbicides, and to a limited extent in pharmaceuticals, and in flavors and fragrances. It is gaining importance for the preservation of forage cereals, and animal feeds because many putrefying and mold-forming micro-organisms cannot survive in its presence. Propionic acid can be commercially produced by carbonylation of ethylene, a one-step Reppe process catalyzed with nickel carbonyl ($Ni(CO)_4$), at 300 °C and 22 MPa.

$$CO + H_2C = CH_2 \xrightarrow{Ni(CO)_4} CH_3CH_2COOH$$

Table IV.5: Propionic acid key data

GLOBAL DEMAND & PRICE	STARTING MATERIALS FOR MANUFACTURE	MATERIALS AND ENERGY DEMAND	MAIN USES
500 ktpa 2600$/ton	ethylene and CO catalyst: $Ni(CO)_4$	0.38 kg CO/kg propionic acid T = 300°C P = 220 bar	preservation of feed, grain, food (80%), cellulose esters, chemicals

DIMETHYL CARBONATE (DMC)

Dimethyl carbonate, DMC, is an extremely versatile chemical. It is used as an organic solvent, additive for fuels, reagent, as a substitute for phosgene, and in the synthesis of other alkyl or aryl carbonates used as synthetic lubricants, solvents, and in methylation and carbonylation reactions for the preparation of isocyanates, urethanes, and polycarbonates. DMC can be commercially produced by oxycarbonylation of methanol catalyzed by copper salts at 150 8C and 1–5 MPa.

$$\mathrm{CO + 2CH_3OH + {}^{1}\!/_{2}\, O_2 \longrightarrow (CH_3O)_2CO + H_2O}$$

Table IV.6: Dimethyl carbonate key data

GLOBAL DEMAND & PRICE	STARTING MATERIALS FOR MANUFACTURE	MATERIALS AND ENERGY DEMAND	MAIN USES
500 ktpa 880 $/ton	a) phosgene and methanol or b) CO, methanol and O_2 catalyst: Cu-salts	0.93 kg CO/kg DMC T = 150°C P = 10-50 bar	solvent, Li-ion electrolyte, polymer synthesis, high performance resins, ...

METHYL METHACRYLATE (MMA)

Methyl methacrylate, MMA, polymerizes to form a clear plastic that has excellent transparency, strength, and outdoor durability. The automotive and construction markets create the largest demand for acrylic sheet. It is also used in the manufacturing of acrylic paints, including latex paints, and lacquers. MMA can be commercially produced from acetone, methanol and high purity CO (99.8%) at approximately 4 MPa.

Table IV.7: Methyl methacrylate key data

GLOBAL DEMAND & PRICE	STARTING MATERIALS FOR MANUFACTURE	MATERIALS AND ENERGY DEMAND	MAIN USES
4.5 Mtpa 1500$/ton	ethylene or propylene CO (>99.8%) methanol and/or formaldehyde	0.84 – 1.4 kg CO/kg MMA P = 40 bar	poly(methyl methacrylate) (PMMA, 75%), MBS, PVC-additive

ADIPIC ACID

Adipic acid, also known as hexanedioic acid, is the most significant commercially of all the aliphatic dicarboxylic acids. Appearing in nature in only minor amounts, it is synthesized on a very large scale worldwide. The principal use of adipic acid is to produce nylon 6/6, a linear polyamide made by condensing adipic acid with hexamethylene diamine, HMDA. The market for nylon 6/6 is predominantly in fibers. The other uses of adipic acid are in plasticizers, unsaturated polyesters, and polyester polyols (for polyurethane resins). Adipic acid can be synthesized by carbonylation of 1,3-butadiene. This process is attractive from a raw material cost, but requires high operating CO pressure.

Table IV.8: Adipic acid key data

GLOBAL DEMAND & PRICE	STARTING MATERIALS FOR MANUFACTURE	MATERIALS AND ENERGY DEMAND	MAIN USES
3 Mtpa 2000 $/ton	butadiene and CO catalys: 1. $Co_2(CO)8$/pyridine 2. Rh	0.38 kg CO/kg adipic acid yield 72% based on butadiene 1. T = 100-150°C P > 310 bar 2. T = 170°C P = 150 bar	nylon-6,6 (fibers and chips), polyurethane resins, engineering plastics, ...

PHOSGENE COCL$_2$

Phosgene is an inorganic, intermediate produced by the catalytic reaction of chlorine and carbon monoxide. It is a gaseous product, that cannot be stored or conveniently shipped owing to its extreme toxicity. As a result, it is usually produced on demand for intermediate use. Phosgene is an important starting compound in the production of intermediates and end-product in many branches of large-scale industrial chemistry. Most phosgene (80%) is used for the production of diisocyanates. The next largest phosgene application is the production of polycarbonates. The commercial production of phosgene is by the following reaction:

$$CO + Cl_2 \longrightarrow COCl_2$$

An activated carbon catalyst is used. This reaction is strongly exothermic. Because of the toxicity and corrosiveness of the phosgene product, strict and extensive safety procedures are incorporated in plant and operation design. CO purity requirements for this reaction vary considerably depending on the end-products. However, a low content in methane and hydrogen is always required for safety reasons to prevent spontaneous exothermic HCl formation when mixing CO and chlorine. Typically, low sulfur impurities (COS, $CSCl_2$) are also required, as those compounds affect the quality of the end-products.

Table IV.9: Phosgene key data

GLOBAL DEMAND & PRICE	STARTING MATERIALS FOR MANUFACTURE	MATERIALS AND ENERGY DEMAND	MAIN USES
approximately 3 Mtpa	CO and chlorine ($COCl_2$ is produced on-site as an intermediate, is not transported/shipped) catalyst: activated carbon	0.28 kg CO/kg phosgene high toxicity and corrosiveness → extreme material and safety requirements	diisocyanates (80%), polycarbonates

DIISO-CYANATES

Diisocyanates, including toluene diisocyanate (TDI) and 4,40-methylene diphenyl diisocyanate (MDI), have become large-volume raw materials for addition polymers, such as polyurethanes, polyureas, and polyisocyanurates. By varying the reactants (isocyanates, polyols, polyamines, and others) for polymer formation, a myriad of products have been developed ranging from flexible and rigid insulation foams to the high modulus automotive exterior parts to high quality coatings and abrasion-resistant elastomers unmatched by any other polymeric material. The most common method of preparing isocyanates on a commercial scale is the reaction of phosgene and aromatic or aliphatic amine precursors. The overall reaction is shown below:

$$R - NH_2 + COCl_2 \longrightarrow R - NHCOCl + HCl$$

$$R - NHCOCl \longrightarrow R - N = C = O + HCl$$

Nonphosgene routes to isocyanate production have been developed, but none has been commercialized. The term nonphosgene route is primarily used in conjunction with the conversion of amines to isocyanates via the use of carboxylation agents. These approaches are becoming more attractive to the chemical industry as environmental or toxicological restrictions involving chlorine or phosgene are increasingly enforced.

Table IV.10: Diiso-cyanates key data

GLOBAL DEMAND & PRICE	STARTING MATERIALS FOR MANUFACTURE	MATERIALS AND ENERGY DEMAND	MAIN USES
global market estimated at $30-35 billion	Mature technology: aromatic or aliphatic amines and phosgene. Non-phosgene routes are being developed.	0.32 kg CO/kg TDI (2) 0.22 kg CO/kg MDI (2) 0.33 kg CO/kg HDI (3) 0.21 kg CO/kg HMDI (3)	mainly polyurethanes (many types, properties)

(2) *Important aromatic diisocynates are: TDI = toluene diisocyanate; MDI = methylene diphenyl diisocyanate.*
(3) *Important aliphatic diisocynates are: HDI = hexamethylene diisocyanate; HMDI = methylene dicyclohexyl diisocyanate.*

POLY-CARBONATE

Polycarbonates are an unusual and extremely useful class of polymers. The vast majority of polycarbonates are based on bisphenol A (BPA). The economically most important polycarbonate is the Bisphenol A polycarbonate (BPA–PC). Its great commercial success is owing to its unique combination of properties: extreme toughness, outstanding transparency, excellent compatibility with several polymers, and high heat distortion resistance. Some of its main uses include coatings, films, fibers, resin for shatterproof windows, computer housings, tape reel housings, gas meter covers, lenses for automobiles and appliances, and pipe. Polycarbonates can be commercially produced by the Schotten-Bauman reaction, the interfacial polycondensation of phosgene and BPA, or by base-catalyzed transesterification of a bisphenol with a monomeric carbonate such as dimethyl carbonate (which in turn is obtained from methanol and carbon monoxide, vide supra).

Table IV.11: Diiso-cyanates key data

GLOBAL DEMAND & PRICE	STARTING MATERIALS FOR MANUFACTURE	MATERIALS AND ENERGY DEMAND	MAIN USES
4 Mtpa	bisphenol A and phosgene	0.12 kg CO/kg BPA polycarbonate (4)	

(4) *BPA = bisphenol-A or 2,2-bis(4-hydroxyphenyl)propane.*

POLYKETONES

Polyketones are defined as polymers with 1:1 molar ratio of carbon monoxide to ethylene. Carilon was the first polyketone commercially produced by Shell Chemicals in 1995: it is a new family of polymers called aliphatic polyketone, and results from the polymerization of perfectly alternating structures of CO and olefins (such as ethylene). The product's great strength lies in its broad range of high performance characteristics, allied with its ease of processing. It has a number of properties which make it ideally suited for use in the automotive sector, including: superior energy absorption capacity, dimensional stability at elevated temperature, good impact resistance over a broad temperature range, insensitivity to moisture, and excellent resistance to automotive fuels and their vapors. The polymerization is catalyzed by a single-site late transition-metal (ie, palladium) as follows:

$$nCH_2 = CH_2 + nCO \xrightarrow{Pd} \text{-}(CH_2CH_2 \text{ - } C(O))_n\text{-}$$

Table IV.12: Polyketones key data

GLOBAL DEMAND & PRICE	STARTING MATERIALS FOR MANUFACTURE	MATERIALS AND ENERGY DEMAND	MAIN USES
approximately 60 ktpa	CO and ethylene (propylene)	0.5 kg CO/kg polyketon(1)	high-performance thermoplastic polymers

(1) *Based on polyketon without propylene addition.*

TRIALKYL ACETIC ACIDS

The lowest member of the series of trialkyl acetic acids is the C5 acid, trimethylacetic acid, also called neopentanoic acid or pivalic acid. The principal commercial products are the C5 acid and the C10 acid (also known as Exxon's neodecanoic acid, or Shell's Versatic 10). The trialkylacetic acids have a number of uses in areas such as polymers, pharmaceuticals, agricultural chemicals, cosmetics, and metal-working fluids. Commercially important derivatives of these acids include acid chlorides, peroxyesters, metal salts, vinyl esters and glycidyl esters.

Pivalic acid (C5), for example, is prepared by hydroxycarbonylation of isobutene via Koch's reaction:

$$(CH_3)_2C = CH_2 + CO + H_2O \longrightarrow (CH_3)_3CCOOH$$

where the strong acid catalyst is either a Bronsted acid (H_2SO4, H_3PO_4, HF), or a Lewis acid such as BF3.
The C10 tryalkylacetic acid is manufactured using the same process and catalysts. For the C10 acids, a branched C9 olefin is typically used. The resulting C10 acid is typically a mixture of isomers due to chemical rearrangement, olefin dimerization, and oligomerization.

Table IV.13: Trialkyl acetic acids key data

GLOBAL DEMAND & PRICE	STARTING MATERIALS FOR MANUFACTURE	MATERIALS AND ENERGY DEMAND	MAIN USES
	pivalic acid (Me3C-COOH) from methyl propene, CO and H_2O	0.3 kg CO/kg pivalic acid	polymers, pharmaceuticals, agricultural chemicals, cosmetics, ...

DIMETHYL ETHER

Dimethyl ether (DME), also known as methoxymethane, it is a colorless gas that is a useful precursor to other organic compounds and an aerosol propellant that is currently being demonstrated for use in a variety of fuel applications. Industrially, dimethyl ether can be produced by a dehydration reaction of methanol

$$2CH_3OH \longrightarrow (CH_3)_2O + H_2O$$

The largest use of dimethyl ether is as the feedstock for the production of the methylating agent, dimethyl sulfate, which entails its reaction with sulfur trioxide. Dimethyl ether can also be converted into acetic acid using carbonylation technology related to the Monsanto acetic acid process. In recent years, the application of dimethyl ether as a potential diesel substitute used in compression ignition engines has attracted considerable attention.

Table IV.14: Acetic acid key data

GLOBAL DEMAND & PRICE	STARTING MATERIALS FOR MANUFACTURE	MATERIALS AND ENERGY DEMAND	DOWNSTREAM	MAIN USES
9 Mtpa 420 \$/ton(1)	methanol catalyst: γ-Al_2O_3	1.2 kg CO/kg DME conditions T = 200-400ºC P = 1 bar and higher	methanol conversion 80% per pass selectivity > 99% recovery of unreacted methanol by flashing	methylation, fuel (in LPG), refrigerant, aerosol propellant

FORMALDEHYDE

Because of its relatively low cost, high purity, and variety of chemical reactions, formaldehyde has become one of the world's most important industrial and research chemicals. Formaldehyde's principal use is in the production of resins, mainly urea-formaldehyde, phenol-formaldehdye, polyacetals, and melamine-formaldehdye.

Formaldehyde is produced industrially by the catalytic oxidation of methanol. The most common catalysts are silver metal or a mixture of an iron and molybdenum or vanadium oxides. In the commonly used formox process, methanol and oxygen react at ca. 250–400 °C in presence of iron oxide in combination with molybdenum and/or vanadium to produce formaldehyde according to the chemical equation:

$$CH_3OH + \tfrac{1}{2}O_2 \longrightarrow CH_2O + H_2$$

The silver-based catalyst usually operates at a higher temperature, about 650 °C. Two chemical reactions on it simultaneously produce formaldehyde: the partial oxidation shown above and the dehydrogenation reaction:

$$CH_3OH \longrightarrow CH_2O + H_2O$$

In principle, formaldehyde could be generated by oxidation of methane, but this route is not industrially viable because low selectivities are achieved in practice.

Table IV.15: Formaldehyde key data

GLOBAL DEMAND & PRICE	STARTING MATERIALS FOR MANUFACTURE	MATERIALS AND ENERGY DEMAND	DOWNSTREAM	MAIN USES
27 Mtpa 350 $/ton	methanol and air catalyst: Ag or Fe_2O_3/MoO_3	0.93 kg CO/kg FA conditions Ag: T = 600-650ºC atmospheric pressure Fe/Mo: T = 300-400ºC atmospheric pressure	overall yield 90-92% on methanol main byproducts DME and CO absorption (distillation)	urea, melamine, phenol resins (65%), ...

METHYL TERT-BUTYL ETHER

Methyl tert-butyl ether, MTBE, is used as a fuel component in fuel for gasoline engines. It is used as an oxygenate to raise the octane number, replacing tetraethyl lead. MTBE is also extensively used in industry as a solvent as a safer alternative to diethyl ether as the tert-butyl group prevents MTBE from forming potentially explosive peroxides. MTBE is manufactured by reaction isobutylene with methanol.

$$(CH_3)_2C = CH_2 + CH_3OH \longrightarrow (CH_3)_3C - O - CH_3$$

Table IV.16: methyl tert-butyl key data

GLOBAL DEMAND & PRICE	STARTING MATERIALS FOR MANUFACTURE	MATERIALS AND ENERGY DEMAND	DOWNSTREAM	MAIN USES
10 Mtpa	methanol and isobutylene catalyst: acidic ion exchange resin	32 kg CO/kg MTBE conditions: T = 60-80ºC P = 6-10 bar	reactive distillation: conversion = 99% based on isobutylene recovery of excess methanol for recycling	anti-knock gasoline additive (raises the octane number)

MTO METHANOL TO OLEFINS

Many institutions and companies have put great effort to the research of the methanol-to-olefins, MTO, reaction since it was first proposed by Mobil Corporation in 1977, mainly aimed at the reaction principle, catalyst synthesis and process research and development (R&D).

The production of olefins from methanol is catalysed by zeolites. However, the exact mechanism is still being investigated. The process produces approximately equal amounts of ethylene and propylene, and additionally a mixture of butenes, C5+ hydrocarbons and fuel gas. During the process the zeolite catalyst suffers from heavy carbon depositing (coke formation) and has to be continuously refreshed and regenerated.

Table IV.17: methyl tert-butyl key data

GLOBAL DEMAND & PRICE	STARTING MATERIALS FOR MANUFACTURE	MATERIALS AND ENERGY DEMAND	DOWNSTREAM	MAIN USES
>10 Mtpa	methanol catalyst: acidic zeolites	2 kg CO/kg olefines$^{(3)}$ T = 300 – 400°C	separation of products continuous regeneration of catslyst	ethylene and propylene for polymers coproduction of mixed butenes

MTA METHANOL TO AROMATICS

The conversion of methanol to a mixture of aromatic products is currently intensively studied. The reaction proceeds over a metal on zeolite catalysts and produces a mixture of benzene, alkylated benzenes (xylenes, trimethyl benzene), toluene and a range of C1-C5 hydrocarbons and light olefines. Also, as with the MTO process, heavy coke formation at the catalyst occurs.

Table IV.18: Methanol to aromatics key data

GLOBAL DEMAND & PRICE	STARTING MATERIALS FOR MANUFACTURE	MATERIALS AND ENERGY DEMAND	DOWNSTREAM	MAIN USES
>1 Mtpa, 1000 $/ton	methanol catalyst: Zn/ZSM-5	2.15 kg CO/kg benzene T = 250-450°C P = 40-80 bar	separation of products continuous regeneration of catalyst	BTX product chain

MTG METHANOL TO GASOLINE

The methanol to gasoline technology is being developed and marketed by ExxonMobil and Uhde. In the process, methanol is converted using a zeolite catalyst. The product is claimed to be almost 90% naphta, suitable for gasoline production, with 10% by products consisting of LPG and fuel gas. In the past, the process was commercial in New Zealand. Currently, facilities are under construction in the USA.

Table IV.18: methyl tert-butyl key data

GLOBAL DEMAND & PRICE	STARTING MATERIALS FOR MANUFACTURE	MATERIALS AND ENERGY DEMAND	DOWNSTREAM	MAIN USES
>1Mtpa 800 $/ton	methanol catalyst: $Al_2O_3 \rightarrow$ DME ZSM-5 $\rightarrow$ gasoline	approximately 2 kg CO/kg gasoline$^{(4)}$ T = 350°C P = 30 bar	yield: 80% of C5+ separation of products distillation stripping blending	fuel

APPENDIX V: TECHNO-ECONOMIC ASSESMENT DOCUMENTATION

ADDITIONAL DETAILS ON SHORT-LISTED PROCESSES

HYDROGEN PRODUCTION

Hydrogen production by CO shifting

The water-gas-shift reaction (WGSR) is a reversible chemical reaction that consists in the production of CO_2 and H_2 from a mixture of CO and H_2O:

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \qquad \Delta H^0 = -41\ \text{kJ/mol}$$

Via the WGSR, an increase in the amount of available H_2 can be carried out at the cost of the CO content. Because the reaction is exothermic lower temperatures favour high equilibrium conversion. However, historically this process took place at a relatively high temperature, in order to have high reaction rates, using an iron catalyst. Nowadays, new more active copper catalysts are available and the CO shifting can be performed in two steps. So, at industrial scale, the WGSR is mainly performed using a cascade of adiabatic reactors with a high temperature step (HTS: High Temperature Shift) followed by a low temperature step (LTS: Low Temperature Shift) with inter-stage cooling. The HTS takes advantage of high reaction rates, but is thermodynamically limited, which results in an incomplete conversion of CO with a corresponding content in the output between 2% and 4% (molar fraction) *(Schumacher, 2005)*. With the decreased temperature in the LTS, the equilibrium is moved towards the production of H_2, which enables to obtain a CO content of less than 1% *(Byron, 2010)*.

The first stage HTS is operated with iron and chromium based catalyst, with inlet and outlet temperatures of around 350 °C and 450 °C, respectively. The second stage LTS uses copper and zinc oxide on alumina catalyst, and inlet and outlet temperatures of around 200 °C and <280 °C, respectively. The LTS catalyst, although very active at low temperature, is sensitive to sulfur poisoning. *(Byron, 2010; Callaghan, 2006)*

The applications of the WGSR at thermodynamic equilibrium specifically to steel mill off gases COG and BFG were studied by Turpeinen (2008) and Chen (2011), see Figure V.1.

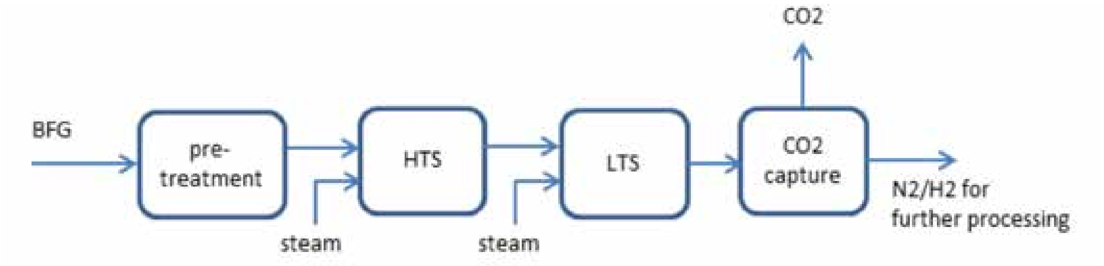


Figure V.1. Scheme for H_2 production from blast furnace gas by CO shifting.

Hydrogen production by methane reforming

Natural gas reforming also known as reforming of methane can be accomplished by means of an exothermic or endothermic reaction depending on the chemical process selected to perform the catalytic reforming of methane. There are seven reforming processes available for the production of syngas from natural gas, whose major component is methane. These are:

1. Steam Methane Reforming (SMR),
2. Partial Oxidation (POX),
3. Auto Thermal Reforming, (ATR),
4. Dry Reforming of methane (DMR),
5. Combined Reforming of methane (CMR),
6. Reforming with Membrane
7. Tri-reforming of Methane (TMR).

While the top three methods are well established and are widely employed by industry the last four methods are innovations to minimize greenhouse gases emissions, minimize energy consumption and improve the reforming process yields. The methods differ in the composition of syngas produced i.e. their H_2/CO ratio as shown in Figure V.2.

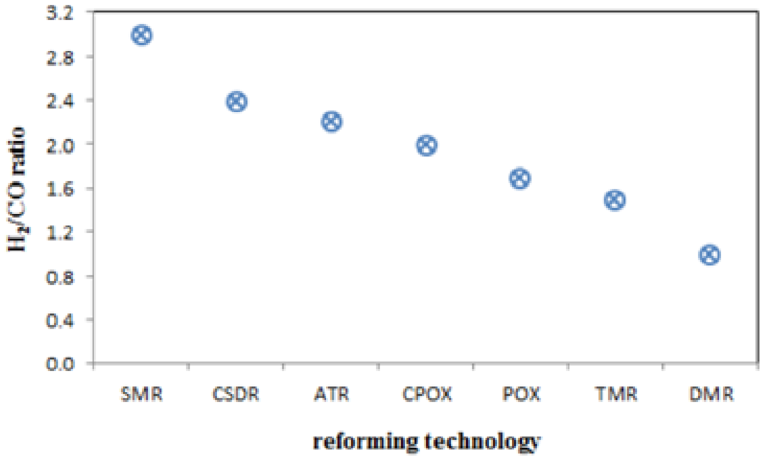


Figure V.2. H_2/CO ratio of syngas from various methane reforming technologies.

Steam reforming or steam methane reforming (SMR) is the reaction where steam and hydrocarbons, such as natural gas or refinery feed stock, react in a reformer at temperature of 800 oC – 900 oC and moderate pressure (around 30 bar) in the presence of metal based catalyst for the production of syngas. The carbon monoxide in the syngas reacts further with additional steam to give more hydrogen and carbon dioxide via the water gas shift (WGS) reaction, which is a side reaction in steam reforming.

$$CH_4 + H_2O \longleftrightarrow CO + 3H_2 \qquad \Delta H^0 = 206 \text{ kJ/mol}$$

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \qquad \Delta H^0 = -41 \text{ kJ/mol}$$

Steam reforming of natural gas produces syngas with a H_2:CO molar ratio close to 3. Because the reaction is endothermic, an external source of energy is needed to provide for the heat taken up by the reaction. Because it leads to syngas with the highest H_2/CO ratio, steam reforming of methane is not only used to produce syngas, but also to obtain high purity hydrogen gas by subsequent shifting of CO and further treatment for CO_2 separation (using PSA).

Partial oxidation (POX) and catalytic partial oxidation (CPOX) occur when sub-stoichiometric fuel-air mixtures are partially combusted in a high temperature reformer. (C)POX produces hydrogen rich syngas.

$$CH_4 + {}^1/_2O_2 \longleftrightarrow CO + 2H_2 \qquad \Delta H^0 = -36 \text{ kJ/mol}$$

Partial oxidation is an exothermic reaction and therefore has the advantage that no extra energy supply is needed. On the other hand, the hydrogen yield is lower and the oxidation requires a supply of pure oxygen. Also, careful process control is needed for operating the process with mixtures of methane and oxygen at high temperature. The use of catalyst in the production of syngas lowers the required reaction temperature to around 800 oC – 900 oC instead of 1200-1500 oC without catalysts. In the CPOX reaction, methane is converted with oxygen over noble (Pt, Rh, Ir, Pd) and non-noble (Ni, Co) metal catalysts to syngas in a single step process. CPOX has been studied extensively during the past decade.

Although auto-thermal reforming (ATR) of methane is an old idea, its application just appears to start now with to date several commercial sites. The H_2/CO ratio of the syngas obtained in the auto-thermal reforming is a function of the input gaseous reactant fractions. Thus, the H_2/CO ratio can vary from 1 to 2. Natural gas is mixed at high temperature with a mixture of oxygen and steam and ignited in a combustion chamber where partial oxidation occurs at ≈2200 oK, in a subsequent zone at 1200 - 1400 oK reforming reactions take place. By proper adjustment of oxygen to carbon and steam to carbon ratios, the partial combustion in the thermal zone supplies the heat for completing the subsequent endothermic steam and CO_2 reforming reactions. ATR is also utilized as a “secondary reformer” (for lowering the CH_4 residue) and it is placed after a primary SMR in syngas plants integrated with Ammonia synthesis reactors. In this case the “secondary” ATR is fed with the syngas produced from SMR and Air.

Dry reforming of methane (DMR) is a process that uses waste carbon dioxide to produce syngas from natural gas. The synthesis gas produced by steam reforming has high H_2/CO ratio which is not suitable for Fischer-Tropsch synthesis in the production of long chain higher hydrocarbons due to the excess hydrogen which suppresses chain growth and decreases the selectivity of higher hydrocarbons (Hou, 2006). Conversely, methane reforming with CO_2 plays an important role in the industries due to the production of syngas with a low H_2/CO ratio (≈1.0) which can be preferentially used for production of liquid hydrocarbons in Fischer-Tropsch synthesis network specifically those based on iron catalyst (Luna, 2008).

$$CH_4 + CO_2 \longleftrightarrow 2CO + 2H_2 \qquad \Delta H^0 = 247 \text{ kJ/mol}$$

Dry methane reforming is slightly more endothermic than steam methane reforming. It is favored by low pressure and high temperature. The presence of CO_2 gives rise to an increased danger of carbon formation on catalyst surface due to production of CO and consumption of H_2 via RWGS reaction. The dry reforming of methane with CO_2 has received special attention in recent years because 1) it produces syngas with a H_2:CO molar ratio that is suitable for products including F-T fuels and DME, and 2) the reaction consumes two types of greenhouse gases, CO_2 and CH_4. A combination of technologies results in Combined Steam and Dry Reforming (CSDR).

From a comparison between the different methods for reforming of methane, steam reforming is the main reforming process of methane that is predominantly utilized because it has the largest value for H_2/CO ratio. However, since steam reforming requires additional external energy input, depending on the scale of the operation and the energy prices, other types of methane reforming can become more profitable alternatives. The choice of process type for reforming of methane must also take the destination of the syngas, i.e. the H_2/CO ratio into consideration. A comparison of syngas generation technologies using natural gas as feed is shown in Table V.1.

Table V.1. Comparison of syngas generation technologies with natural gas feed [5].

TECHNOLOGY	ADVANTAGES	DISADVANTAGES
POX	Feedstock desulfurization not required	Very high process operating temperature Usually requires oxygen plant
SMR	Most extensive industrial experience. Oxygen not required, lowest process operating temperature. Highest H_2/CO ratio.	Highest air emissions. More costly than POX and auto-thermal reformers. Recycling of CO and removal of the excess hydrogen by means of membranes
ATR	Lower process temperature requirement than POX. Syngas methane content can be tailored by adjusting reformer outlet temperature	Limited commercial experience. Usually requires oxygen plant.
DMR	Greenhouse gas CO_2 can be consumed instead of releasing into atmosphere Almost 100% of CO_2 conversion.	Formation of coke on catalyst. Additional heat is required as the reaction takes place at 873 K
CSDR	Best H_2/CO ratio for production of liquid fuels Coke deposition drastically reduced.	Separation of unreacted methane from SMR syngas. Project installation cost.

Hydrogen production by electrolysis

High-quality hydrogen (100% hydrogen) can be produced by the electrochemical conversion of water to hydrogen and oxygen through a process known as water electrolysis. The reaction with the thermodynamic energy values is described in the equation

$$H_2O_{(l)} + 237\ kJ_{elec.}/mol + 49\ kJ_{therm.}/mol \longrightarrow H_2 + {}^{1}\!/_{2}O_2$$

The energy theoretically needed for the production of hydrogen amounts to 286 kJ/mol or 40 kWh/kg H_2.

Commercially available electrolysers are currently of the proton exchange membrane (PEM) type or alkaline type. These operate at low temperatures (40-90 °C). High temperature electrolysers operate at a lower electrical energy input; 25% less at 800 °C when compared to 100 °C. High temperature electrolysers are not yet commercially available, but R&D is put into their development. An example is the solid oxide electrolysis cell (SOEC) that operates as a reversed solid oxide fuel cell, at temperatures around 900 °C.

Recently, Rabobank has drafted a financial model to assess the financial feasibility for the construction and operation of two electrolysis (and two biomass gasification plants) each of 500 MW (Van Wijk, 2017). Based on an electricity price of €25/MWh and a 70% electrolysis efficiency a hydrogen price of €2.60/kg H_2 was obtained. This amount consisted of electricity costs at €1.4/kg H_2 and capex, opex, transport, financing and other costs at €1.2/kg H_2 in total. The total price mentioned here does not include any credits that can be obtained from useful application of the oxygen co-produced with the hydrogen electrolysis, where the oxygen production rate is 8 kg O_2/kg H_2.

METHANOL SYNTHESIS FROM STEEL MILL WASTE GASES

Description of process

The industrial production of methanol can be broken up into three steps:

- production and/or conditioning of syngas;
- the actual methanol synthesis loop;
- purification of the product methanol, usually via distillation.

The manufacturing and purification of syngas is the starting point of methanol production. The reformer section usually takes more than half of the total investment in existing plants when natural gas is the feedstock. When coal is used as the raw material then syngas production and conditioning can take up to 70-80% of the total investment.

The synthesis of methanol can start from both CO and CO_2:
The water-gas-shift reaction will also occur at the catalyst. Other side reactions such as methanation and dimethyl ether formation are effectively suppressed by modern catalysts. The make-up gas can be characterized by the parameter S, that is obtained from the molar fractions in the feed as

$$CO + 2H_2 \longleftrightarrow CH_3OH \qquad \Delta H^0 = -91 \text{ kJ/mol}$$

$$CO_2 + 3H_2 \longleftrightarrow CH_3OH + H_2O \qquad \Delta H^0 = -50 \text{ kJ/mol}$$

For an exactly stoichiometric mixture, the parameter S has a value of 2, as can easily be appreciated from the methanol forming reactions from CO and CO_2 above. A value larger than 2 indicates a mixture rich in H_2, and vice versa. Therefore, a syngas composition with a stoichiometric number S slightly above 2 is the optimum for methanol synthesis. The syngas fed to the methanol synthesis reactor contains compounds considered as inert gases. The usual inert compounds for methanol synthesis are N_2 and CH_4.

$$S = \frac{y_{H_2} - y_{CO_2}}{y_{CO} + y_{CO_2}}$$

The methanol synthesis is an equilibrium reaction, thus recycling of unconverted reactants is necessary, see Figure V.2. To avoid accumulation of inerts, a purge stream is required involving a loss of reactants. So there is a trade-off between the concentration of inert gases and the production cost that has to be optimized. If the inert gases level increases, the purge and recycled ratios increase, which implies a loss of reagents and an increase in capital cost (larger compressors and reactors) and operational cost (compression power). In some cases the H_2 contained in the purge is recovered by a membrane separation unit, a cryogenic separation unit or a PSA unit.

To utilize the steel mill gases in methanol synthesis two options are considered here. In the first option, the inerts and surplus of CO_2 are removed from the steel mill gas and external H_2 is used to get S=2. In the second option, the steel mill gas is used almost as-is, including the inerts, but with supplemented H_2 to obtain the proper stoichiometric ratio.

In the first option, after sulfur removal from the steel mill gas, the hydrogen is recovered using pressure swing adsorption. The adsorbents used for the separation of H_2 are primarily activated carbon, alumina oxides or zeolites *(Bermúdez, 2013)*. This way it is possible, when desired, to obtain high purity hydrogen with a recovery of around 90%. The technology is well known in the hydrogen production from methane reforming.

Next, the CO_2 is separated. The standard technique here is the use of aqueous amine scrubbers that can remove CO_2 quantitatively. Similarly, PSA over zeolite 13X can be used, with about the same recovery. Although the purity of the absorption process is higher (99.99%) compared to the PSA process (92%), in the literature the PSA system is preferred because of about 50% lower costs *(Kim, 2015)*.

The separation of CO from the remaining gases, mostly nitrogen, can be achieved by absorption using an organic $CuAlCl_4$ scrubbing liquid that selectively absorbs CO. The CO recovered stream has a purity of 99% with a recovery around 98% *(Keller, 1988)*. The use of a PSA system for CO recovery is also reported in the literature. In this case, physical adsorbents, such as activated carbon and zeolite, adsorb CO_2 more strongly than CO, which makes it impossible to recover high purity CO by single stage PSA. Therefore, CO_2 is removed first before CO is recovered in a next stage. Because the CO_2 removal is not complete, the CO-rich stream contains some CO_2; the flow of CO_2-rich gas is adjusted for this.

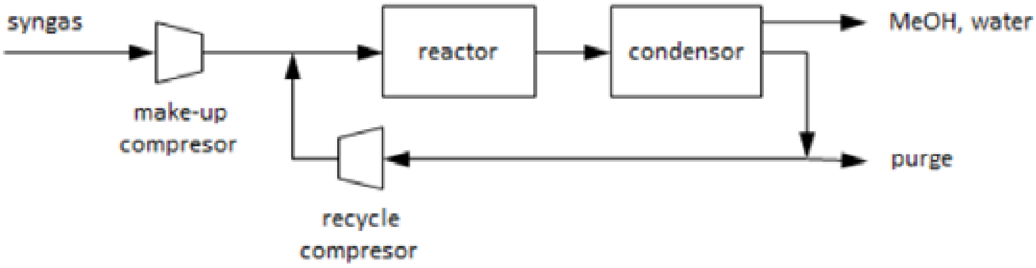


Figure V.2. The methanol synthesis loop.

This way, a make-up gas with 22% CO, 8% CO_2 and 69% H_2 and a minor amount of inert can be obtained.

A scheme of the process is shown in Figure V.3. A table with calculated data on the various flows of Figure V.3 is shown in Table V.2. Details of the methanol reactor and syngas recirculation can be found in Appendix VII: methanol synthesis loop.

In the second option considered here, the steel mill gas is cleaned of catalyst poisons, mainly sulphurous components. The resulting gas is replenished with hydrogen to obtain a correct stoichiometric ratio: S=2. The make-up gas obtained this way contains 12.1% CO, 10.0% CO_2, 54.7% H_2 and 23.1% inerts.

A scheme of the process is shown below, in Figure V.3. A table with calculated data on the various flows of Figure V.4 is shown below as Table V.3. Details of the methanol reactor and syngas recirculation can be found in Appendix VII: methanol synthesis loop.

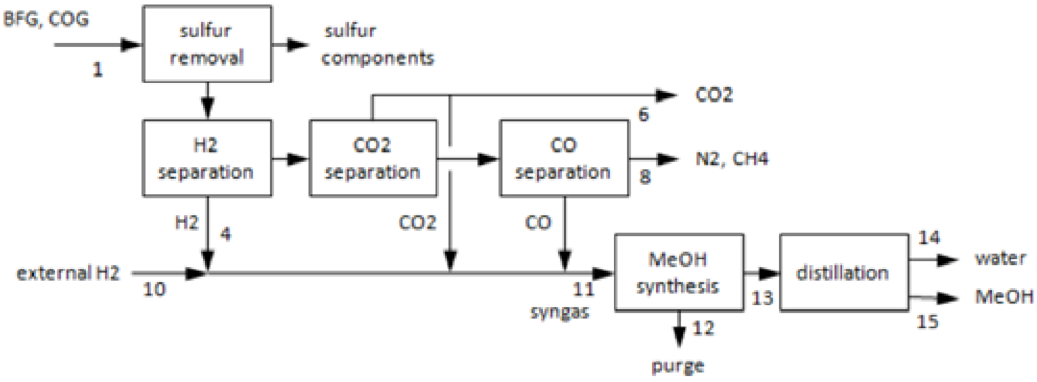


Figure V.3. Process layout for methanol from steel mill gas where inerts are removed.

Table V.2. Calculated properties of various flows (for 400 kton/a methanol) in figure V.3.

	FLOW NR.	**1**	**4**	**6**	**8**	**10**	**11**	**12**	**13**	**14**	**15**
	P[bar]	3	5	1	1	20	85	78	1	1	1
	T[K]	298	298	298	298	298	493	298	298	298	298
	total flow [mol/s]	1.50E+03	1.74E+02	1.65E+02	6.77E+02	9.35E+02	1.61E+03	1.90E+02	5.50E+02	1.16E+02	4.34E+02
	y-CO	0.236					0.22	0.186			
	y-CO_2	0.196		1			0.08	0.068			
	y-H_2	0.116	1			1	0.69	0.661			
	y-inert	0.452			1		0.01	0.085			
	y-MeOH								0.789		1
	y-H_2O								0.211	1	
	flow CO [mol/s]	3.54E+02					3.54E+02	3.53E+01			
	flow CO_2 [mol/s]	2.94E+02		1.65E+02			1.29E+02	1.29E+01			
	flow H_2 [mol/s]	1.74E+02	1.74E+02			9.35E+02	1.11E+03	1.26E+02			
	flow inert [mol/s]	6.77E+02			6.77E+02		1.61E+01	1.62E+01			
	flow MeOH [mol/s]								4.34E+02		4.34E+02
	flow H_2O [mol/s]								1.16E+02	1.16E+02	
av. enthalpy [kJ/mol]		-1.03E+02	-3.94E+02	0	0		-4.74E+01		-2.42E+02	-2.01E+02	
enthalpy flow [MJ/s]		-1.55E+05	-6.50E+04	0	0		-9.00E+03		-2.81E+04	-8.74E+04	
exergy [kJ/s]:	physical	4.08E+03		0	0	6.94E+03		2.05E+03		0	0
	chemical	1.45E+05		3.28E+03	4.93E+02	2.21E+05		3.96E+04		1.04E+02	3.12E+05
	total	1.49E+05		3.28E+03	4.93E+02	2.28E+05		4.17E+04		1.04E+02	3.12E+05
carbon [kg/s]	in CO	4.24E+00					4.24E+00	4.24E-01			
	in CO_2	3.52E+00		1.98E+00			1.54E+00	1.55E-01			
	in CH_3OH								5.21E+00		

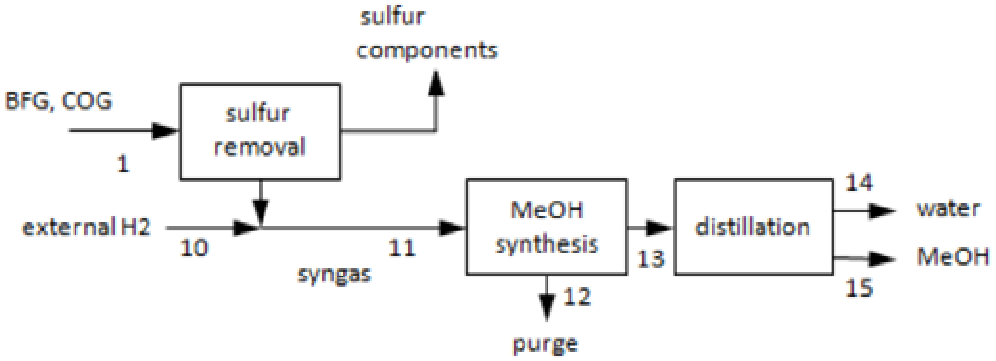


Figure V.4. Process layout for methanol from steel mill gas where only sulphurous components are removed.

Table V.3. Calculated properties of various flows in Figure V.4.

	FLOW NR.	1	10	11	12	13	14	15
	P[bar]	3	20	85	78	1	1	1
	T[K]	298	298	493	298	298	298	298
	total flow [mol/s]	1.11E+03	1.06E+03	2.1751E+03	6.76E+02	6.307E+02	1.97E+02	4.34E+02
	y-CO	0.236		0.121	0.039			
	y-CO_2	0.196		0.100	0.032			
	y-H_2	0.116	1	0.547	0.184			
	y-inert	0.452		0.232	0.745			
	y-MeOH					0.68810		1
	y-H_2O					0.31190	1	
	flow CO [mol/s]	2.63E+02		2.64E+02	2.64E+01			
	flow CO_2 [mol/s]	2.18E+02		2.19E+02	2.19E+01			
	flow H_2 [mol/s]	1.29E+02	1.06E+03	1.19E+03	1.24E+02			
	flow inert [mol/s]	5.04E+02		5.04E+02	5.04E+02			
	flow MeOH [mol/s]					4.34E+02		4.34E+02
	flow H_2O [mol/s]					1.97E+02	1.97E+02	
av. enthalpy [kJ/mol]		-1.03E+02	0	-1.70E+01		-2.42E+02	-2.01E+02	
enthalpy flow [MJ/s]		-1.15E+05	0	-1.15E+04		-4.76E+04	-8.74E+04	
exergy [kJ/s]:	physical	3.03E+03	7.86E+03		7.31E+03		0	0
	chemical	1.08E+05	2.50E+05		3.75E+04		1.77E+02	3.12E+05
	total	**1.11E+05**	**2.58E+05**		**4.48E+04**		**1.77E+02**	**3.12E+05**
carbon [kg/s]	in CO	3.16E+00		3.16E+00	3.16E-01			
	in CO_2	2.62E+00		2.62E+00	2.62E-01			
	in CH_3OH					5.21E+00		

If we look at the methods for producing the additional hydrogen needed for the conversion of steel mill gas into methanol then we can consider three scenarios.

With hydrogen from electrolysis, the CO can be converted to methanol, and no additional fossil carbon source is used, and no CO_2 is formed. From a carbon footprint point of view this would be a profitable situation, see Figure V.5.

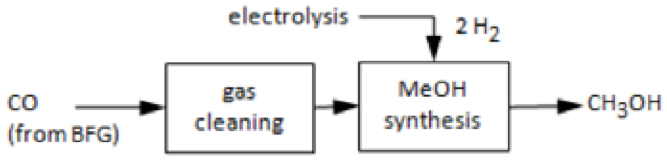


Figure V.5. Conversion of steel mill gas to methanol with hydrogen from electrolysis

Overall synthesis reaction: $CO + 2H_2 \longrightarrow CH_3OH$

In case methane reforming is used to obtain the additional hydrogen then for every two molecules of CO converted to methanol a molecule of methane is converted to CO_2. From an environmental point of view, a (semi-) definitive storage facility for the CO_2 is needed here, see Figures V.6.

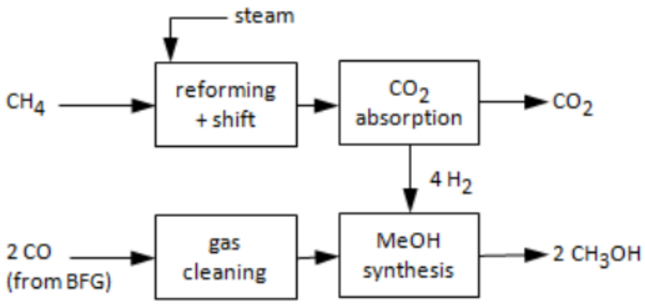


Figure V.6. Conversion of steel mill gas to methanol with hydrogen from methane reforming.

Overall synthesis reaction: $2CO + CH_4 + 2H_2O \longrightarrow 2CH_3OH + CO_2$

If the additional hydrogen is obtained from shifting part of the CO contained in the steel mill gas, see Figure V.7, then for every molecule of methanol two molecules of CO_2 re formed. Although, contrary to the previous case, no additional fossil carbon is used, the need for CO_2 storage is higher here.

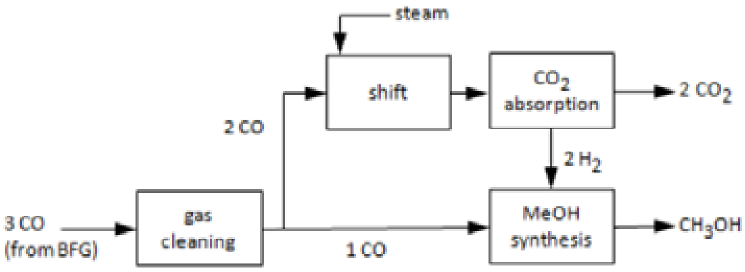


Figure V.7. Conversion of steel mill gas to methanol with hydrogen from partial CO shifting.

Overall synthesis reaction: $3CO + 2H_2O \longrightarrow CH_3OH + 2CO_2$

Methanol option 1: major flows for 400 ktpa

	MATTER FLOW	ENERGY FLOW (GJ/H)	C IN CO (TON/H)	C IN CO_2 (TON/H)	C IN PRODUCT (TON/H)
		INPUT			
COG+BFG	123,000 Nm³/hr	674	15.3	12.7	
external H_2	6.73 ton/hr	815			
		OUTPUT			
methanol	50 ton/h	1060			18.7
water	7.52 ton/h				
purge gas	15,500 Nm³/h	146	1.53	0.56	
reaction heat: available at 250oC		142			
CO_2 separation	26 ton/h			7.13	

Methanol option 2: major flows for 400 ktpa

	MATTER FLOW	ENERGY FLOW (GJ/H)	C IN CO (TON/H)	C IN CO_2 (TON/H)	C IN PRODUCT (TON/H)
		INPUT			
COG+BFG	91,100 Nm³/hr	501	11.4	9.43	
external H_2	7.62 ton/hr	922			
		OUTPUT			
methanol	50 ton/h	1060			18.7
water	12.7 ton/h				
purge gas	55,300 Nm³/h	136	1.14	0.94	
reaction heat: available at 250oC		142			

FISCHER-TROPSCH PROCESSES

Liquid transportation hydrocarbon fuels and various other chemical products can be produced from syngas via the well-known and established Fischer-Tropsch (FT) synthesis process, named after the original German inventors, Franz Fischer and Hans Tropsch in the 1920s. During World War II, FT synthesis provided the hydrocarbon fuels for the German war effort. Later, facing isolation during the apartheid era, South Africa turned to FT synthesis from coal gasification to supply significant quantities of its hydrocarbon fuel and chemical needs. Since then, many refinements and adjustments to the technology have been made, including catalyst development and reactor design.

The scheme in Figure V.8 shows the main parts of the FT process. The syngas preparation block consists of all the supporting process technologies of feed preparation, heat recovery, syngas cleanup and conditioning, water-gas-shift, sulfur recovery, etc. In traditional FT installations, the syngas preparation and conditioning section takes between one half and two thirds of the total capital costs (De Klerk, 2011; Steynberg, 2004). The clean syngas is sent onto the FT synthesis reactor, where it is converted into the products of hydrocarbons, tail gas, reaction water, and wax. The wax, if present, is usually sent to a hydrocracking unit, where it is split into smaller molecular weight hydrocarbon liquids. The reaction products, along with that from the upgrading section, are fractionated into the final products of jet fuel/ diesel, naphtha, and other light ends, depending on the desired product mix. The production facility is often supported by several utility plants, including the power train.

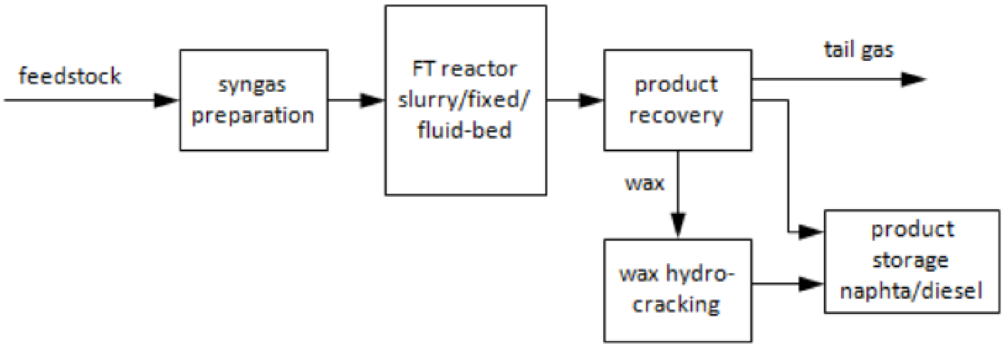


Figure V.8. Block scheme of FT hydrocarbon synthesis.

The chemistry of the FT process consists of a catalytic reaction where CO and H_2 react to hydrocarbons according to

$$2H_2 + CO \longrightarrow -(CH_2)- + H_2O$$

where -(CH_2)- denotes a methylene functionality in a hydrocarbon chain. Depending on the catalyst, temperature, and type of process employed, hydrocarbons ranging from methane to higher molecular paraffins can be obtained. Small amounts of olefines and low molecular weight oxygenates (e.g., alcohol and organic acids) are also formed. The Fischer-Tropsch synthesis reaction, in theory, is a condensation polymerization reaction of CO. Its products obey more or less the Anderson-Shultz-Flory distribution, where the weight fraction of hydrocarbons carrying n carbon atoms is given by α

$$W_n = n(1 - \alpha)^2 \ \alpha^{n-1}$$

where denotes the chain growth probability. Generally is determined to a large extent by the catalyst and the specific process conditions (temperature, partial pressures, residence time).

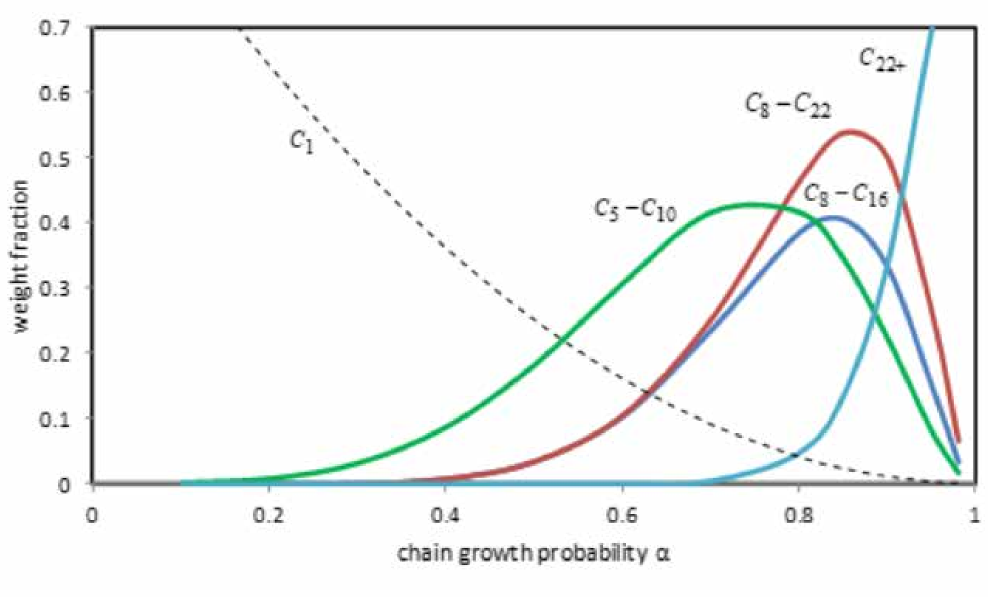


Figure V.9. Product distributions vs the chain growth probability ,
for naphtha (C_5 - C_{10}), jet fuel (C_8 - C_{16}), diesel (C_8 - C_{22}) and wax (C_{22+}) fractions.

The Anderson-Shultz-Flory distribution is illustrated in Figure V.9 for naphtha, jet fuel and diesel as a function of α. The figure illustrates that the optimum yield of both jet fuel and diesel are obtained at α ≈ 0.85, with product weight percentages of 40% and 55%, respectively. The maximum yield of naphtha is obtained at a significant lower value of α ≈ 0.75 with a product weight percentage of 45%.

A large amount of research is performed on the FT process, especially on modifying the catalysts to achieve higher yields of specified products. For example, recently it was shown that with a modified Co-Re/Al_2O_3 catalyst a selectivity of 63% for the C10-C20 diesel fraction was obtained, far higher than 39% of the Anderson-Shultz-Flory distribution (Dong, 2017).

The FT process operates at temperatures of approximately 200-350 °C. The temperature has a major influence on the product distribution; higher temperatures lead to higher reaction rates and thus to higher conversions. At the same time, higher temperatures tend to lead to chain termination, i.e. reduced α-values and on average lower molecular weight products. Increasing the pressure of the FT reactors leads to higher conversion rates and also increases the chain growth probability and thus results in the formation of long chain hydrocarbons. Typical operating pressures are in the range of 10-35 bar.

Iron based catalyst can operate at both higher and lower temperatures. These catalyst also can operate with low H_2/CO ratios (<1). Cobalt-based catalysts are more active and operate at the lower temperatures. At higher temperatures these catalysts lead to more methane formation. For these Co-type of catalysts the optimum H_2/CO ratio is around 1.8-2.1.

For the product distribution, the temperature is the most important factor. At high temperature, with α = 0.75, then amount of naphtha is double the amount of diesel; low temperatures, with α = 0.85, the situation is reversed and the amount of diesel is double the amount of naphtha.

It turns out that in order to maximize the naphtha output it is best to use an iron catalyst at high temperature in a fixed bed reactor. If a high diesel/jet fuel fraction is desired, a slurry reactor with cobalt catalyst is the best choice. Slurry reactors offer better temperature control: a crucial advantage because the FT reactions are highly exothermic.

The process scheme for FT synthesis is shown in Figure V.10. Carbon monoxide from the steel mill gases has to be cleaned and separated from the other gases. Also inerts (N_2) have to be removed, otherwise these end up in all the product streams obtained, especially the light weight, gaseous products. The FT-reactor is designed for optimizing the yield of the desired product range: fixed bed rector with iron catalyst operated at high temperature to maximize naphta output, or a slurry reactor with cobalt catalyst at low temperature for a large diesel/jet fuel. From separation of the reactor exit flow, the unconverted syngas together with the methane fraction are recycled. A considerable amount of water is obtained co-produced in the reactor; approximately 0.9 kg water/kg hydrocarbons when optimized for diesel and 1.1 kg water/kg hydrocarbons when optimized for naphtha. Other fractions are directly forwarded to product work-up sections, while the heavy hydrocarbons of the wax fraction are first broken into smaller components. This step, the hydrocracking of waxes, produces some methane by-product that is also recycled.

The combined recycle flows of unconverted syngas and methane are sent to the reformer where the methane is turned back into syngas. Next the H_2/CO ratio is adjusted in the shift reactor, and CO_2 is removed from the recycle gases before they return to the FT-reactor.

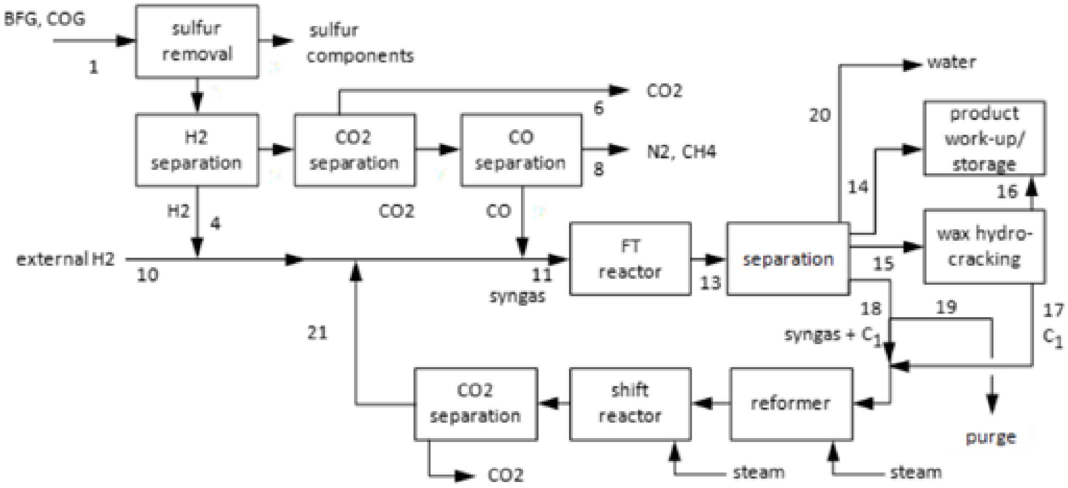


Figure V.10: Process scheme for Fischer-Tropsch synthesis of diesel/jet fuel or naphtha.

Fischer-Tropsch optimized for diesel

If the product distribution is optimized for the yield of the diesel fraction, the process conditions and catalyst are adjusted to achieve a chain growth probability, α, of 0.86. This can be achieved by operating a slurry reactor with cobalt catalyst at low temperatures (200-250°C) and high pressures (30-35 bar). The optimum H_2/CO ratio is in the range of 2.05 to 2.15 (Steynberg, 2004). The per pass CO conversions are in the order of 50-70%. The cobalt catalysts typically have a cycle time of 9-12 months and a lifetime of 5 years (Schrauwen, 2004).

The resulting hydrocarbon reactor product distribution is given in Table V.4. The hydrocarbon weight fractions are shown in Figure V.11.

Table V.4. Fischer-Tropsch hydrocarbon reactor product distribution when optimized for diesel yield.

	WEIGHT FRACTION
c1	0.020
c2-c4	0.127
c5-c7	0.164
c8-c22	0.541
wax c23+	0.148

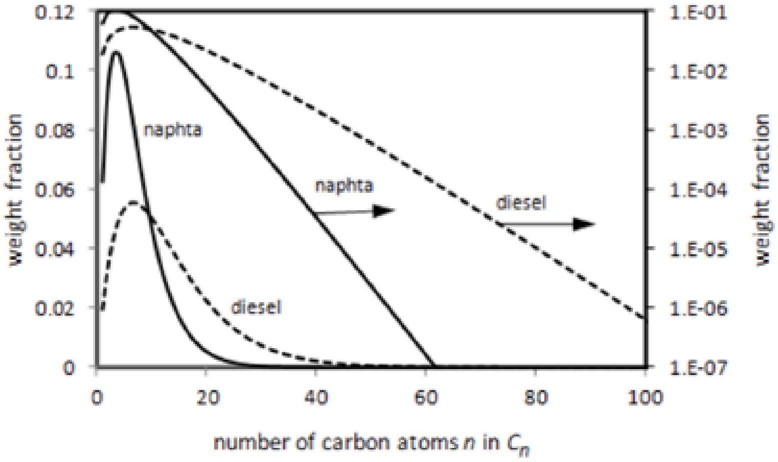


Figure V.11. Weight fractions of the hydrocarbons in the FT reactor product optimized for diesel yield on a linear and logarithmic scale.

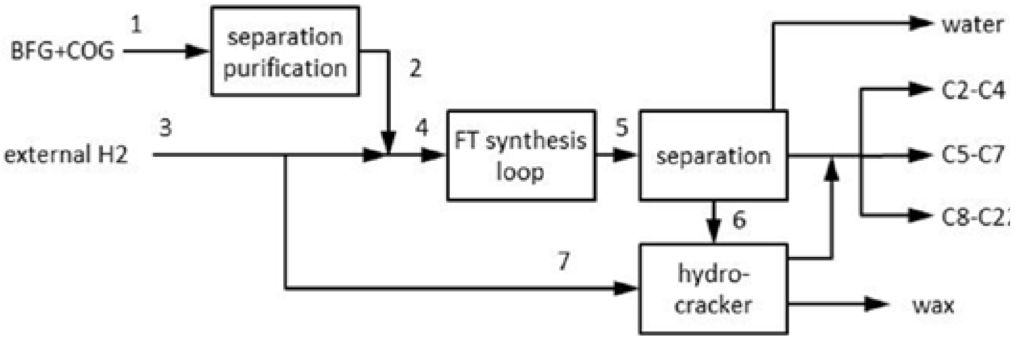
The mass flows are calculated for the simplified process scheme given in Fig. V.10. The calculations are based on a diesel production of 400 kton/a and an on-stream time of 8000 h/a. Further assumptions are an overall conversion based on carbon monoxide of 95%, a hydrogen excess of 2%. The waxes produced in the reactor are converted in the hydrocracker using 400 Nm^3 of hydrogen per ton of wax intake. The product distribution of the hydrocracker was estimated as 10% C2-C4, 15% C5-C7, 65% C8-C22 and 10% C23+ fractions, respectively. The resulting mass flows are given in Table V.5.

Table V.5. Mass flows of the scheme in Fig. V.12 for FT synthesis optimized for diesel.

	FLOW NR.								
	2(*)	**3**	**4**	**5**	**6**	**7**	**PRODUCT STREAMS**		
CO [kg/s]	44.13		44.13				flow rate	carbon	LHV
H_2 [kg/s]	1.87	5.09	6.85			3.27	kg/s	kg/s	[kJ/kg]
C2-C4 [kg/s]				2.77			3.09	2.60	
C5-C7 [kg/s]				3.58			4.07	3.42	
C8-C22 [kg/s]				11.80			13.89	11.68	
wax C23+ [kg/s]				3.22	3.22		0.32	0.27	
water [kg/s]				27.49			26.95		

(*): the components of stream 2 are obtained from 182 Nm^3/s of BFG+COG.

Figure V.12 Fischer-Tropsch scheme



Fischer-Tropsch optimized for naphtha

If the product distribution is optimized for the yield of the naphtha fraction, the process conditions and catalyst are adjusted to achieve a chain growth probability, α, of 0.75. This can be achieved by operating a fixed bed reactor with iron catalyst at high temperatures (250-300°C) and low pressures (10-20 bar). Because the iron catalysts are also active for the water-gas-shift reaction the actual H_2/CO ratio is not determining, but rather the stoichioetric S-ratio $(H_2-CO_2)/(CO+CO_2)=2$. Per pass conversion of CO is in the range of 80-90%. The iron catalysts typically have a life time of 1-3 months (Mako, 1984).

The resulting hydrocarbon product distribution is given in Table V.6. The hydrocarbon weight fractions are shown in Figure V.11. For comparison, Figure V.11 also shows the hydrocarbon fractions obtained when optimizing for the diesel yield. The comparison nicely shows the more narrow distribution concentrated at low molecular weight hydrocarbons when optimizing for naphta, with a distinctive maximum of the C6 weight fraction.

Table V.6. Fischer-Tropsch hydrocarbon reactor product distribution when optimized for naphtha yield.

	WEIGHT FRACTION
c1	0.063
c2-c4	0.305
c5-c10	0.436
c11-c22	0.186
wax c23+	0.012

The mass flows are calculated for the simplified process scheme given in Fig. V.10. The calculations are based on a naphta production of 400 kton/a and an on-stream time of 8000 h/a. Further assumptions are an overall conversion based on carbon monoxide of 95%, a hydrogen excess of 2%. The waxes produced in the reactor are converted in the hydrocracker using 400 Nm^3 of hydrogen per ton of wax intake. The product distribution of the hydrocracker fractions was estimated as 10% C2-C4, 25% C5-C10, 55% C11-C22 and 10% C23+, respectively. The resulting mass flows are given in Table V.7.

Table V.7. Mass flows of the scheme in Fig. V.12 for FT synthesis optimized for naphta.

	FLOW NR.								
	2(*)	3	4	5	6	7	PRODUCT STREAMS		
CO [kg/s]	60.40		60.40				flow rate	carbon	LHV
H_2 [kg/s]	2.55	7.30	9.84			0.013	kg/s	kg/s	[kJ/kg]
C2-C4 [kg/s]				9.65			9.68	7.90	
C5-C10 [kg/s]				13.80			13.85	11.63	
C11-C22 [kg/s]				5.87			6.11	5.19	
wax C23+ [kg/s]				0.37	0.37		0.04	0.03	
water [kg/s]				39.35			36.89		

TECHNO-ECONOMIC ASSUMPTIONS

ASSUMPTIONS OFF-GAS WORK-UP INTO SYNGAS WITH A H_2 OVER CO RATIO OF 2

- Basis for the techno-economic analysis: TATA production @ 7 mln ton steel per year
- Amount of off-gas production: 2 ton per ton of steel, results in 14 mln ton per year
- Technical availability of all units 96% (high), results in 350 stream days per year, results in 40.000 ton off-gas per stream day
- Off-gas composition in wt %: 1% H_2; 43% N_2; 22% CO; 32% CO_2 and 2% CH_4 . This off-gas has a density of 1.25 kg/Nm^3 and LHV of 4.4 GJ/ton
- Two off-gas upgrading steps: (1) removal of CO_2 by Acid Gas Removal technology (e.g. by Selective MDEA); (2) removal of N_2 by a PSA type of technology (e.g. COSORB type with Cu immobilized as adsorbent)
- Capital for removal of 12.500 ton CO_2 per day is based on literature data[1] with Capex of 80 mln$ for 3 vol% of CO_2 separation[2] from 1140 MMSCFD[3] of wet gas (with density of 0.94 kg/Nm^3 this would amount to some 1850 ton CO_2 per day) and Opex of 7 mln$/a. For target CO_2 removal upscaling assumed to be feasible @ 0.67 scaling factor: Capex for target CO_2 removal = $(12500/1850)^{0.67}$ * 80 mln$ = 290 mln$, with Opex requirements to be scaled linearly: 12500/1850 * 7 = 47.5 mln$/a
- Capital for N_2 removal could not be retrieved from literature. A PSA reference by JFE[4] has been used to estimate Capex and Opex for the Nitrogen / CO separation. The reference discusses a double PSA for the separation of BFG components (in vol%: 23% CO, 22% CO_2, 52% N_2 and 3% H_2) in a CO_2 rich stream, an N_2 rich stream and a CO/H_2 stream. For 1.25 mln t/a CO_2 to be removed from 4 mln t/a BFG the corresponding Capex has been listed at 70 mln$ and Opex at 11 $/ton CO_2 or 14 mln$/a. In our case with 14 mln t/a off-gas to be treated for N_2 separation, some 14/4*70 = 245 mln$ Capex would be needed (linear scaled) and some 50 mln$/a Opex.
- Hence, the off-gas work-up (syngas preparation) step calls for 535 mln$ Capex and 97.5 mln$/a Opex
- Table V.8 indicates some 13,5 kt/d of CO_2 that is capture ready. The work-up will emit 2,2 kt/d of CO_2.

Table V.8. Mass balance considered including extra hydrogen to make up for the H2/CO ratio of 2 for syngas as a basis for CO-upgrading

	OFF-GAS 40000 TON/D	FEED MDEA (T/D)	SPLIT FACTORS MDEA	MDEA OFF GAS (T/D)	FEED N_2 REMOVAL (T/D)	SPLIT FACTORS N_2 REMOVAL	N_2 OFFGAS (T/D)	SYNGAS (T/D)	HYDROGEN FEED (T/D)	ADJUSTED SYNGAS (TMOL/D)
H_2	1%	400	0,85	60	340	0,85	51	289	740	515
N_2	43%	17200	0,7	5160	12040	0,03	11679	361		13
CO	22%	8800	0,95	440	8360	0,85	1254	7106		254
CO_2	32%	12800	0,03	12416	384	0,85	58	326		7
CH_4	2%	800	0,8	160	640	0,9	64	576		36
Total	**100%**	**40000**		**18236**	**21764**		**13105**	**8659**		
CO_2eq		28829 t/d		13547 t/d			2205 t/d	13077 t/d		

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[1] Acid Gas Removal: Open Art or Licensed Process, by Arif Habibullah, ReseachGate, October 2017

[2] Density CO_2: 2 kg/Nm^3

[3] Conversion factor: 37.3 scf/Nm^3

[4] Development of PSA System for the Recovery of CO from Blast Furnace Gas, by H.Saima, Y.Mogi, T.Haraoka, JFE Steel Corp

ASSUMPTIONS SYNGAS CONVERSION INTO METHANOL

- Methanol synthesis with a carbon efficiency of 83% has been assumed. This corresponds with a methanol production of some 6750 t/d, or some 2.36 mln ton per year.
- According to the Air Liquide - Lurgi Technical Handbook a capital intensity of some 500 $ per metric ton per year on a Total Installed Cost basis is feasible. This is for the methanol synthesis and purification block only. This would call for an investment of 1200 mln$
- Caloric value methanol is 21.1 GJ/ton
- Methanol pricing @ 50 $/bbl around 350 $/ton (see Methanex pricing overview)
- Amount of CO_2eq emitted is 3,8 kt/d, being: (1-0,83) * 7106/28*44 t/d + 326 t/d + 576/16*44 t/d → 1333 kt/a
- Check on “flooding the market”: assuming that in case all steel producers in Europe (jointly producing some 80 mln ton of steel per year) decide to upgrade all their off-gases into methanol, some additional 27 mln ton of methanol will be brought to the European market. Current European methanol consumption amounts to some 7 mln ton per year (5 mln t/a import and 2 mln t/a own production). Against this backdrop the 27 mln ton per year extra can be considered disruptive[5].

ASSUMPTIONS SYNGAS CONVERSION INTO FT NAPHTHA

- For the conversion of synthesis gas into FT naphtha a carbon efficiency of 75% has been assumed by Metabolic. This would lead to an amount of FT naphtha of some 2700 t/d or some 930 kt naphtha per year.
- A typical large-scale GTL plant[6] has a capital intensity of some 2300 $ per metric ton per year on a Total Installed Cost basis. This includes 5 key process sections: syngas production & purification, syngas conversion into heavy FT wax; hydro-processing (cracking) into final FT products; utilities (steam and power production) and water treatment (on weight basis a GTL plant produces some 30% more water than FT products). Compared to a full GTL process flow scheme and in view of the “naphtha – only” only scheme, capital needed for syngas conversion and purification can be left out. Apart from capex needed for syngas conversion and water treatment (estimated @ 30% of capex), only part of the capital needed for product upgrading and a simplified utilities scheme will be needed (estimated @ 20% of capex). Hence a capital intensity of 1150 $/ton naphtha has been assumed. The corresponding call for capex is 1070 mln$.
- FT naphtha is valued at 50 $/bbl Brent plus a premium of 3,5 $/bbl for its parafinicity (almost 100%) and hence superior cracker feed potential (yielding more ethylene and propylene than typical cracker naphtha’s with some 70% paraffins). Assuming a barrel factor of 8.4 bbl/ton (@ naphtha density of 750 kg/m^3), this 53 $/bbl corresponds with a 445 $/ton naphtha.
- The amount of CO_2eq per year: 4,7 kt/d: being (1-0,75) * 7106/28*44 t/d + 326 t/d + 576/16*44 t/d 1646 kt/a
- Check on “flooding the market”: the 1 mln ton of FT naphtha produced per 7 mln steel can easily be absorbed by the European ethylene producers. A typical naphtha cracker turns 3 to 4 mln tons of naphtha into 1 mln ton of ethylene. Assuming that Europe produces some 30 – 40 mln ton of ethylene from naphtha, the corresponding call on naphtha is at least 100 mln ton. Hence, the 11 mln ton of FT naphtha from steel-off gas (assuming all steel producers would invest in FT naphtha), can be absorbed.

ASSUMPTIONS SYNGAS CONVERSION INTO ETHANOL

- For the conversion of synthesis gas into ethanol a carbon efficiency of 40% has been assumed. This would lead to an amount of ethanol of some 2350 t/d or some 820 kt ethanol per year
- Liquid density of ethanol @ 20 Deg C: 0,79 ton/m^3
- The capital requirements for a syngas to ethanol fermentation plant have been estimated at 1055 $ per ton per year on TIC basis[7], or 865 mln$. Arcelor-Mittal is quoting an investment of 2000 € per mtpa (120 mln € for a 60-65 ktpa syngas to ethanol plant)

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[5] Based on an investment (ISBL) of 35 mln$ for a 25ktpa (32000 m^3/a) ethanol facility (ref: European Commission: SubGroup on Advanced Biofuels; Cost of Biofuels, 12 February 2017, by Ingmar Landalv). Scaling factor of 0.8 applied due to the significant step up in capacity: from 25 ktpa to 820 ktpa. OSBL has been set @ 50% of ISBL

[6] Communication Eric de Coninck (Arcelor Mittal)

[7] Defined as Total Capex / Net revenues. In case of negative net revenues, the outcome is denoted as N/A (not applicable)

- The amount of CO_2eq per year: 8.6 kt/d being (1-0,4) * 7106/28*44 t/d + 326 t/d + 576/16*44 t/d → 3013 kt/a
- Caloric value of ethanol: 27.8 GJ/ton
- Pricing: 1,5 $/gallon with 3,785 liter/gallon and liquid density @ 790 kg/m^3 (0,79 kg/liter)   500 $/ton.
- Check on “flooding the market”: the current European “ethanol for fuel” market is some 5-6 mln t/a, with little growth projected. Hence, every 0.8 mln ton of ethanol per 7 mln ton of steel off-gas would significantly disrupt this market.

ASSUMPTIONS SYNGAS CONVERSION INTO METHANOL VIA SEWGS OPTION

- Syngas to Methanol conversion via the SEWGS (Sorption Enhanced Water-Gas Shift) technology consists of 3 key units: (1) the SEWGS step for the conversion of CO into CO_2 and H_2; (2) separation of H_2 from the N_2 stream; (3) the reaction of H_2 and CO_2 into Methanol. Apart from the second key unit, the other units are only demonstrated at pilot plant / development scale. Data from references for SEWGS (e.g. Swedish Energy Agency – STEPWISE project) and from CRI (Carbon Recycling International) on their H_2+CO_2 → CH_3OH plant have been used to develop Capex and Opex estimate for these unit.
- The ECN SEWGS demo unit @ Lulea for the upgrading of 800 Nm^3/h Blast Furnace Gas is quoted[8] at 15 mln$. Given the unit size required for the upgrading of the CORESYM off-gases (40000 t/d equivalent to some 1425 tmol/d) normal upscaling practices cannot be applied. Alternatively, given projected H_2 production level (some 1000 t/d) and CO_2 removal level (some 25000 t/d) it would be fair to assume that capex requirements for such a large SEWGS unit would compare to capex needed for H_2 production plant and an Acid Gas Removal plant of similar sizes
- According to the Air Liquide Technical Handbook a 200 kNm^3/h Hydrogen plant (430 t/d) would call for 200 mln$. Hence, a capital intensity of some 1350 $/mtpa. A 1000 t/d H_2 production level (350 ktpa) would there call for an investment of some 500 mln$
- With the AGR data used earlier, the production of 25000 t/d CO_2 would require an investment of some 600 mln$.
- Lacking any reliable public SEWGS data, floor / ceiling investment levels related to H_2 production and CO_2 removal have been used for the techno-economic analysis: Capex of 600 mln$ for the upgrading of 40 ktpd of off-gas has been assumed. Corresponding Opex (e.g. steam for the water-gas shift reaction) has been set at 30 mln$/a (shifting 9000 t/d of CO with 2.35 MMBTU/ton CO @ 4 $/MMBTU and 350 d/a)
- The separation of H_2 and N_2 stream leaving the SEWGS is straightforward and is assumed to be accomplished by a conventional PSA system. With reference to the Air Liquide Technical Handbook, p. 33 a typical large-scale PSA unit for a H_2/N_2 separation of 200.000 Nm^3/h calls for an investment of 20 mln$. An investment of 100 mln$ would then be needed to meet the CORESYM duty requirement of some 1.1 mln Nm^3/h.
- For the H_2+CO_2 το CH_3OH unit, only one credible reference has been found: the George Olah plant in Iceland. This facility reclaims about 4500 t/a of CO_2 from air and produces some 5 mln liter per year of methanol (corresponding with 4000 ton methanol per year @ liquid density of 0.792 kg/liter). CRI mentions an investment of 8 mln$ for this unit.
- With reference to the H_2+CO_2 το CH_3OH flowsheet as prepared by RUG, the amount of methanol produced for the CORESYM case would be some 1.5 mln ton per year. Given the significant scale-up from 4 ktpa to 1500 ktpa (factor is 375), the scale-up exponential has been set at 0.8 (rather than the typical 0.67). This in view of scale-up barriers to be addressed when moving up in TRL levels. Hence, the corresponding capex would be some 920 mln$. In terms of capital intensity (610 $ per mtpa of methanol produced) this is close to the 500 $/mtpa claimed for conventional methanol synthesis units (see above). Furthermore, current insights in catalysis for methanol synthesis confirm the view that scaling up the H_2+CO_2 το CH_3OH process would not be that different from scaling up the conventional methanol synthesis process.

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[8] Communication Eric de Coninck (Arcelor Mittal)

ASSUMPTIONS FOR THE “SEWGS TO HYDROGEN” OPTION

- The SEWGS concept can obviously also be deployed to produce H_2 for internal use of sold to nearby H_2 off-takers (refineries or petrochemical complexes)
- For H_2 purity reasons the Capex of the N_2 rejection unit (now Hydrogen purification unit has been adjusted with some 50 mln$ (arbitrary)
- A value of 2000 $/ton has been assigned to H_2 sales

GENERAL ASSUMPTIONS FOR THE TECHNO-ECONOMIC ANALYSIS

- Brent @ 50 $/bbl as reference for product values (methanol, FT Naphtha and ethanol)
- The off-gas heat content is valued @ 4 $/MMBTU
- Renewable Hydrogen is purchased @ 4000 $/ton H_2
- Costs per ton of CO_2 avoided have been calculated. Basis for this analysis is the amount of CO_2 avoided as calculated by Metabolic (for methanol: 0.7 ton CO_2/mln ton of steel; for ethanol: 0.8 ton CO_2/mln ton of steel; for FT Naphtha: 0.5 ton CO_2/mln ton of steel). For the “SEWGS + Methanol” option the amount of CO_2 avoided has been estimated in the same way at 0.3 ton CO_2/mln ton of steel and for the “SEWGS + H_2” option the amount of CO_2 avoided has been estimated at 0.45 ton CO_2/mln ton of steel.
- For the conversion of US Dollar (USD) to Euro the following graph has been taken and an average of 0.85 Euro per USD has been assumed.

APPENDIX VI : SUSTAINABILITY ASSESSMENT DOCUMENTATION

In the sustainability assessment, we started with a standard unit of waste gases resulting from producing a single tonne of steel. Once we have determined how much energy and product this unit of gas can produce for each case (our reference units), we calculate the scenarios with this unit to keep the cases consistent with each other.

The scope of the life cycle data included in the assessment was limited to direct inputs of the process (e.g. catalysts, solvents, energy, water, biomass, fossil fuels) and did not include machinery. Outputs from the processes (e.g. wastes, wastewater, and emissions) include only direct outputs, those of feedstocks, and those from energy consumption.

When a process produces multiple product streams (e.g. petroleum refining) and we must allocate a share of the impact of this process as an input to another process, then we apply a mass-based allocation, based on the share of that product in the product mix.

Scenarios

First, we provide a simplified process diagram which depicts the scenarios and briefly describe each case (methanol, liquid fuel mix, and ethanol). Each case has one baseline scenario (where steel mill gases are used in electricity and other resources go to producing products) and two alternative scenarios (steel mill gases are used to produce products and an energy replacement scenario is included). One alternative scenario is the conservative scenario (worst case) based on the cheapest options currently available, including steam reforming of methane for hydrogen production and electricity from natural gas. The other alternative scenario is an optimistic scenario (best case), where all electricity comes from wind power and hydrogen is produced using electrolysis. The process diagrams are meant only as a guide to understanding the scenarios and as a link to the data and assumptions.

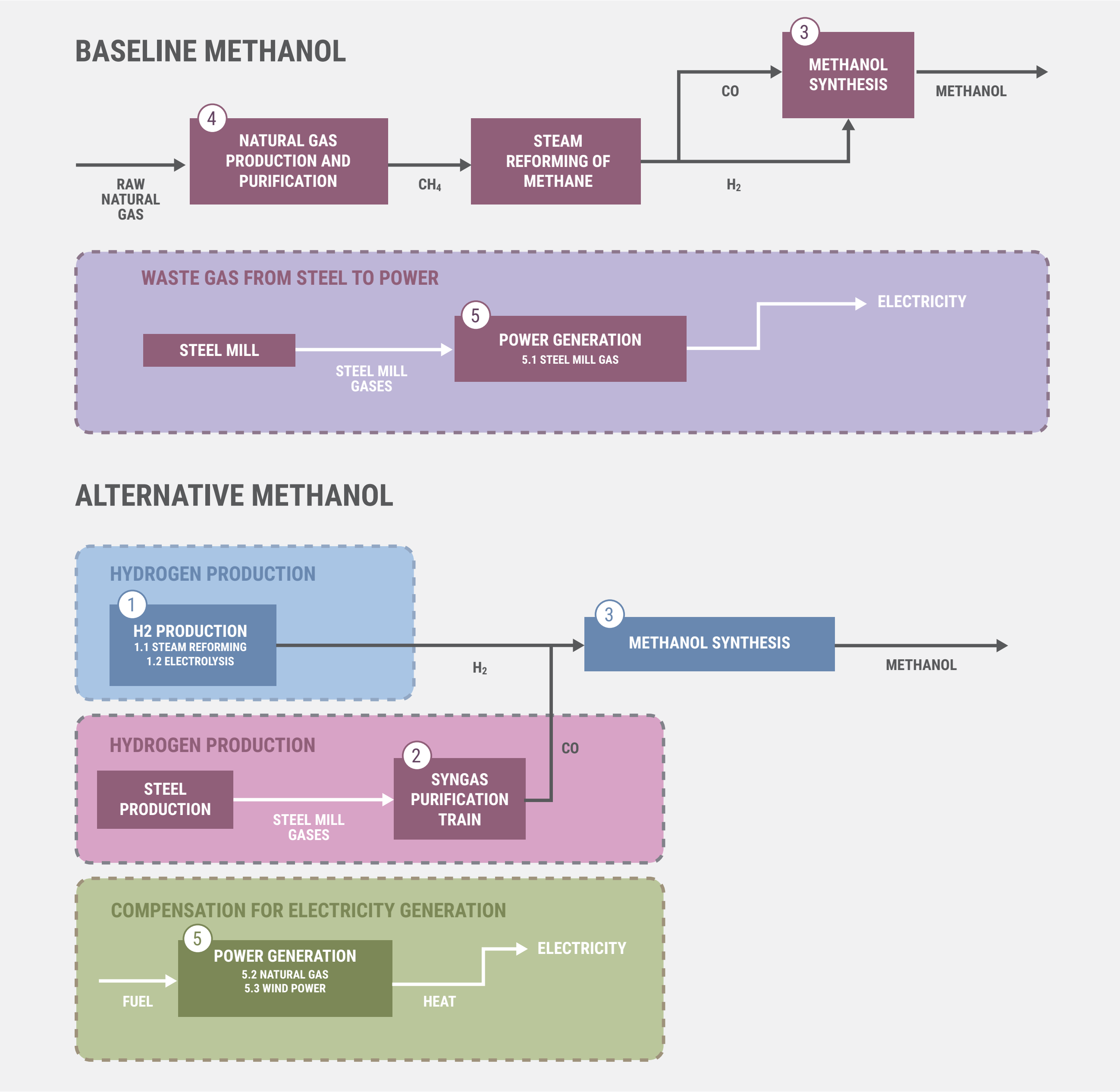
Data and assumptions

Secondly, for each of the main steps in these process diagrams, we provide information on the assumptions, parameters used, and the main references used.

SCENARIOS

Methanol production case

Figure VI.1: Scenarios for methanol case



Baseline methanol scenario

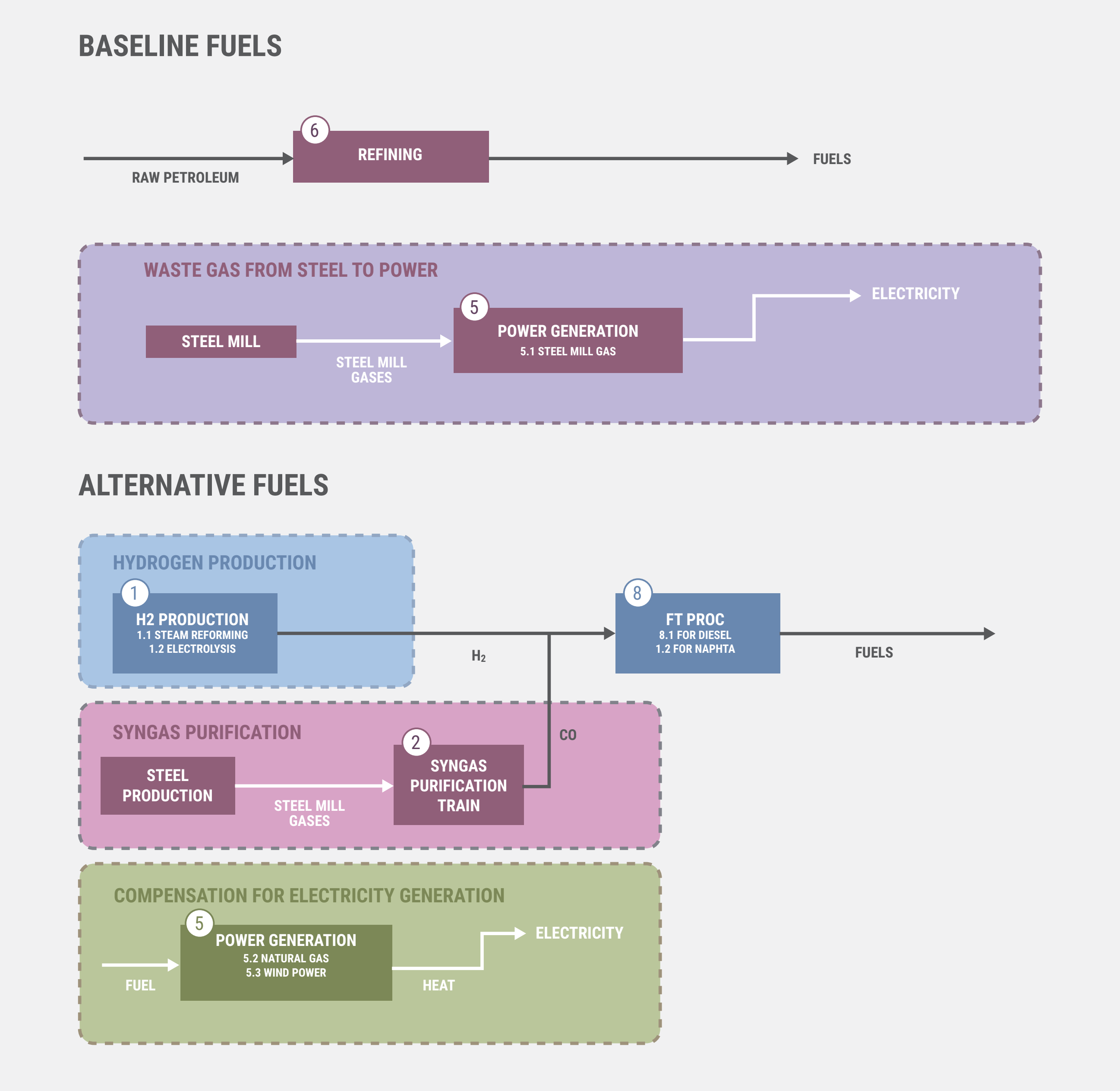
In the methanol baseline scenario, we assume methanol is being produced using the conventional route, through process steps 4 (natural gas production and purification) and 3 (methanol synthesis, which includes steam reforming of methane to CO and H2). To complete the scenario, we add the impact associated with using the steel mill gases in energy production.

Alternative methanol scenarios

In the alternative scenarios, we look at the impacts associated with the steel mill syngas treatment processes, additional hydrogen production through steam reforming (conservative scenario) or electrolysis (optimistic scenario), and the methanol synthesis process. For energy replacement, we consider natural gas in the conservative scenario and wind power in the optimistic scenario.

Fuels production with Fischer-Tropsch

Figure VI.2: Scenarios for fuels mix with Fischer-Tropsch case



Baseline fuel mix scenario

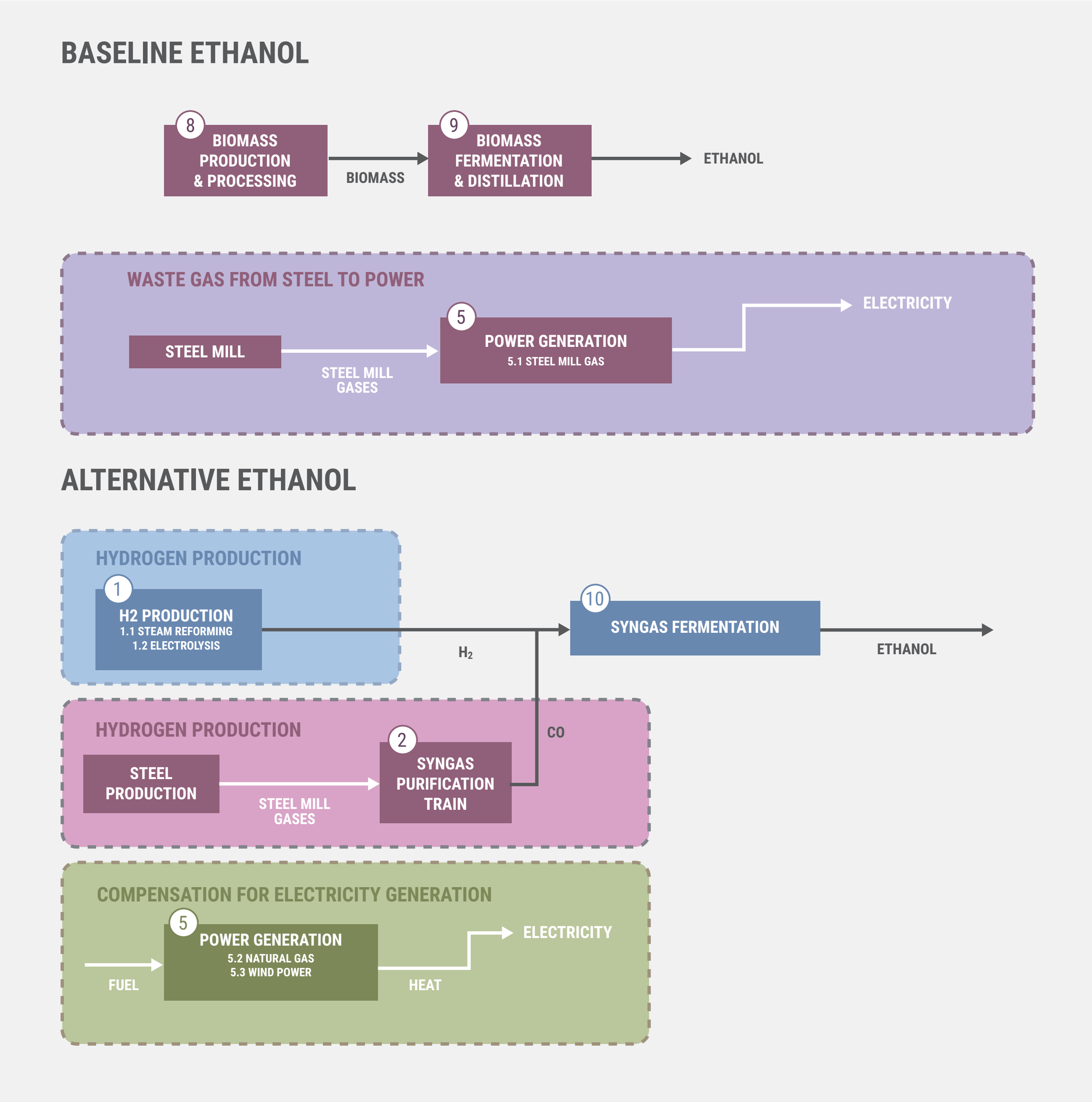
For the baseline scenario, we include electricity production from steel mill waste gases and fuel production from petroleum refining.

Alternative fuel mix scenarios

In the alternative scenarios, we look at the impacts associated with the steel mill syngas treatment processes, additional hydrogen production through steam reforming (conservative scenario) or electrolysis (optimistic scenario), and the Fischer-Tropsch process. For energy replacement, we consider natural gas in the conservative scenario and wind power in the optimistic scenario.

Ethanol from fermentation

Figure VI.3: Scenarios for ethanol case



Baseline ethanol scenarios

For ethanol production, we include a biobased ethanol production process, as this is the most common route for ethanol production. We also include energy production from steel mill waste gases.

Alternative ethanol scenarios

In the alternative scenarios, we look at the impacts associated with the steel mill syngas treatment processes, additional hydrogen production through steam reforming (conservative scenario) or electrolysis (optimistic scenario), and the syngas fermentation to ethanol process. For energy replacement, we consider natural gas in the conservative scenario and wind power in the optimistic scenario.

DATA AND ASSUMPTIONS

1. Hydrogen production

We considered a few possibilities for hydrogen production scenarios. The dominant method for hydrogen production is currently steam reforming of methane in natural gas. However, this option is not desirable from a sustainability viewpoint as it results in high emissions of CO_2. The production of hydrogen using electrolysis is considered the way forward by CORESYM partners. One of the large barriers for electrolysis currently is the high energy use. Nuon is exploring options for producing hydrogen (which will be converted to ammonia) from renewable energy when there is an excess available, as a means for energy storage.

In our scenario, we decided to use the steam reforming of methane for the hydrogen production scenario in the conservative scenario, as it is the most likely scenario on the short term. We also evaluated the anticipated environmental impact improvements from using electrolysis in the optimistic scenario. The factors used for the hydrogen production scenarios and the sources are given in Tables V1.1 and V1.2.

Table VI.1: Hydrogen production parameters steam reforming

1. H_2 PRODUCTION: STEAM REFORMING		
INPUTS		
Raw Natural gas	Value	3.6423
	Unit	kg/kg H_2
	Reference	Spath and Mann. 2001. Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming
Coal	Value	0.1592
	Unit	kg/kg H_2
	Reference	Ozturk & Ozek, 2012
Crude Oil	Value	0.0164
	Unit	kg oil/ kg H_2
	Reference	Ozturk & Ozek, 2012
Water	Value	19.8
	Unit	L/kg H_2
	Reference	Spath and Mann. 2001. Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming
Electricity	Value	19
	Unit	MJ/kg H_2
	Reference	GREET database
Catalyst, solvent, or other key input	Value	
	Unit	Zinc oxide
	Reference	Spath and Mann. 2001. Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming
OUTPUTS		
CO	Value	0.0057
	Unit	kg/kg H_2
	Reference	Spath and Mann. 2001. Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming

1. H_2 PRODUCTION: STEAM REFORMING

Water	Value	14.098
	Unit	L/kg H_2
	Reference	Ozturk & Ozek, 2012
Hydrogen	Value	1
	Unit	kg H_2
	Reference	-
Catalyst, solvent, or other key input	Value	21.4
	Unit	g iron / kg H_2
	Reference	Ozturk & Ozek, 2012
Catalyst, solvent, or other key input	Value	16
	Unit	g limestone/ kg H_2
	Reference	Ozturk & Ozek, 2012
Catalyst, solvent, or other key input	Value	16.4
	Unit	g oil/ kg H_2
	Reference	Ozturk & Ozek, 2012
CO_2	Value	10.6206
	Unit	kg/kg H_2
	Reference	Spath and Mann. 2001. Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming
Nox	Value	0.01234
	Unit	kg/kg H_2
	Reference	Spath and Mann. 2001. Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming
SOx	Value	0.0095
	Unit	kg/kg H_2
	Reference	Spath and Mann. 2001. Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming
$PM_{2.5}$	Value	0.002
	Unit	kg/kg H_2
	Reference	Spath and Mann. 2001. Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming
VOCs	Value	0.0182
	Unit	kg/kg H_2
	Reference	Spath and Mann. 2001. Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming
Solid Waste	Value	0.2016
	Unit	kg/kg H_2
	Reference	Spath and Mann. 2001. Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming

Table VI.2: Hydrogen production parameters electrolysis

1. H_2 PRODUCTION: ELECTROLYSIS		
INPUTS		
Water	Value	90.1
	Unit	kg/kg H_2
	Reference	GREET, 2016, original author is Lampert et al., 2015
Electricity	Value	176.23498
	Unit	mj/kg H_2
	Reference	Personal contact Nuon
Catalyst, solvent, or other key input	Value	
	Unit	ion exchanger
	Reference	delft
Catalyst, solvent, or other key input	Value	-
	Unit	sulfuric acid
	Reference	-
Catalyst, solvent, or other key input	Value	-
	Unit	25% KOH
	Reference	-
OUTPUTS		
Hydrogen	Value	1
	Unit	kg H_2
	Reference	
CO_2	Value	0.31
	Unit	kg/kg H_2
	Reference	GREET database, 2016, original author Lampert et al., 2015
Nox	Value	0.63
	Unit	g/kg H_2
	Reference	GREET database, 2016, original author Lampert et al., 2015
SOx	Value	0.47
	Unit	g/kg H_2
	Reference	GREET database, 2016, original author Lampert et al., 2015
$PM_{2.5}$	Value	26.26
	Unit	mg/kg H_2
	Reference	GREET database, 2016, original author Lampert et al., 2015
VOCs	Value	0.11
	Unit	g/kg H_2
	Reference	GREET database, 2016, original author Lampert et al., 2015

2. Syngas production and treatment from steel mill gases

Steel mill waste gas composition varies per site (Table VI.3). Based on steel mill inputs (Table VI.4) and estimated gas composition, we estimated the gas composition per tonne of steel (Table VI.5). Most interest in converting steel mill waste gases into products focuses on the high volume of hydrogen in coke oven gases and the high carbon monoxide volume in blast furnace gases. For this reason, we decided to include these two gases as potential syngas feedstocks in the environmental assessment and ignore the gas from the basic oxygen furnace.

Table VI.3: Steel mill waste gas composition

PROCESS EMISSIONS (SHARE VOLUME IN STEEL MILL WASTE GASES)		
	COKE OVEN	BLAST FURNACE
EMISSIONS	*OUTPUT: COKE*	*OUTPUT: PIG IRON/HOT METAL*
Hydrogen	58 - 65%	1 - 4%
Methane (CH_4)	24 - 33%	-
Carbon monoxide (CO)	4.6 - 6.8%	20 - 35%
Carbon dioxide (CO_2)	1.5 - 2.5%	20 - 30%
TOTAL (Nm^3 per tonne output product)	**445**	**1380**

Table VI.4: Steel mill inputs per process step

INPUTS PER TONNE STEEL	
INPUT	INPUT MASS (KG)
Coke	330
Iron ore	1600
Hot metal/pig iron	1000
Coal	800
Limestone	300

Table VI.5: Steel mill waste gas composition, prior to treatment

PROCESS	COKE OVEN	BLAST FURNACE	TOTALS PER TONNE OF STEEL			CO_2 EQ
EMISSIONS	**IN NM^3/T STEEL**		**VOLUME BF+COG (NM^3)**	**MASS BF+COG (KG)**	**MOLES BF+COG (MOLES)**	**MASS BF+COG (KG)**
Hydrogen	94	55.2	149.2	13.41	6652.18	
Nitrogen (N_2)	12.16	720.24	754.15	853.24	30,457.71	
Methane (CH_4)	45.04	0.00	45.04	30.08	1,875.22	82.53
Carbon monoxide (CO)	8.51	363.09	422.06	432.92	15,455.86	680.20
Carbon dioxide (CO_2)	2.46	334.41	350.79	620.52	14,099.79	620.52
Oxygen (O_2)	0.00	0.00	0.03	0.00	0.00	
Argon (Ar)	0.44	9.21	9.66	16.04	401.46	
Ethene (C_2H_4)	3.10	0.00	3.10	3.66	130.33	11.47
Ethane (C_2H_6)	1.46	0.00	1.46	1.85	61.45	5.41
Propene (C_3H_6)	0.26	0.00	0.26	0.46	10.81	0.91
Propane (C_3H_8)	0.10	0.00	0.10	0.19	4.27	0.56
TOTAL	**199.67**	**1,483.44**	**1,770.10**	**1,975.36**	**70,638.99**	**1,401.59**

The composition shown in this section of the appendix does not include the impurities, such as sulfur compounds, which are problematic components of the steel mill waste gases that will need to be removed prior to syngas utilization. These impurities are not shared publicly by the steel industry partners, though from the literature we can gather what these generally include. The composition of gas impurities is largely similar to that of coal gasification.

When syngas is utilized in fermentation processes, as in the ethanol production scenario, the demands in terms of gas purity are lower. The fermentation process can, for example, tolerate a higher amount of sulfur compounds in the gas. However, there is no data publicly available on syngas treatment process chains for fermentation. For this reason, we assume the purification train is the same in each case, with the understanding that there would also be decreases in energy inputs and sulfur outputs. On the other hand, an additional requirement for fermentation is a low amount of oxygen, to maintain an aerobic environment for the fermentation process. If we were looking at the basic oxygen furnace gases as a feedstock, this might require an additional treatment step.

As we have no information available from the industry partners on the inputs and outputs of the waste gas treatment steps prior to the gas stream being a usable syngas quality, it is difficult to properly perform an environmental assessment of the syngas treatment and compare this to the conventional cases. At the same time, this is a key issue to assessing the environmental performance, especially for methanol production, as the main difference in performance will be determined by the difference in treating syngas from natural gas compared to syngas from the steel mill processes.

The few environmental studies which have been performed looking at this issue have used coal gasification values as a proxy for steel mill gas cleanup. One such study often referred to is that of Bibber et al., 2007, which documents extensively the inputs and outputs for each step of a process chain which converts coal to syngas, which is subsequently used in the Fischer-Tropsch process. From this, the process steps of syngas treatment can be isolated and serves as a reasonable proxy for the treatment steps for use in the environmental assessment (though this presents only a rough indication of this part of the routes and should be further detailed in follow up work).

The syngas treatment steps included in this report include:

- Quenching and cooling the syngas in a water scrubber to remove particulates and other trace components
- Heating the syngas and passing it through a COS hydrolysis reactor to convert COS and HCN to H_2S, then cooling to remove water and ammonia
- Using beds of sulfur-impregnated activated carbon to remove mercury and other heavy metals including arsenic
- H_2S removal using the Selexol process, followed by processing in a Claus plant to convert this to elemental sulfur
- Final sulfur reduction using a zinc oxide sulfur polishing bed

The composition of the gas before and after this process is given in the report, as well as the energy consumption for each installation. The mass flows of the syngas before and after treatment are given in Table VI.6, while the total input and output parameters are provided in Table VI.7. From the mass flows, we can derive the outputs in terms of energy-related emissions and removed byproducts and wastes. In total, around 0.51 kg of each kilogram that enters the purification process is removed as a solid or gaseous waste stream. For energy-related emissions, we assume the electricity consumed is provided by natural gas.

Table VI.6: Syngas mass flows before and after treatment processes, adapted from Bibber et al., 2007

	SYNGAS (FLOW 6 IN PROCESS)	CLEAN SYNGAS (FLOW 10 IN PROCESS)	DIFFERENCE	WEIGHT/ MOL	WEIGHT/H				
	MOLAR RATIO	MOLES/HR	KG/HR	MOLAR RATIO	MOLES/HR	KG/HR	MOLES/HR	G/MOL	KG/HR
Ar	.0100	1,073,898	42,900	.0136	859,013	34,316	214,885	39.95	8,584
CH_4	.0279	2,996,176	48,068	.0380	2,400,184	38,506	595,992	16.04	9,561
CO	.4040	43,385,482	1,215,227	.5495	34,707,925	972,169	8,677,558	28.01	243,058
CO_2	.1387	14,894,966	655,513	.0073	461,088	20,292	14,433,878	44.01	635,221
COS	.0005	53,695	3,225	.00			53,695	60.07	3,225
H_2	.2773	29,779,194	60,031	.3771	23,818,668	48,016	5,960,525	2.02	12,016
H_2O	.1193	12,811,604	230,805	.0001	6,316	114	12,805,288	18.02	230,691
H_2S	.0080	859,118	29,280	.00			859,118	34.08	29,280
N_2	.0120	1,288,678	36,101	.0144	909,543	25,480	379,134	28.01	10,621
NH_3	.0023	246,997	4,207	.00			246,997	17.03	4,207
O_2	.00			.00					
SO_2	.00			.00					
TOTAL FLOW RATE IN LBMOL/ HR	236,754			139,250					
TOTAL FLOW RATE IN MOL/ HR	**107,389,808**	**107,389,808**	**2,325,356**	**63,162,738**	**63,162,738**	**1,138,892**	**44,227,070**		**1,186,464**

Table VI.7: Parameters for syngas treatment, adapted from Bibber et al., 2007

2. SYNGAS PURIFICATION TRAIN: SYNGAS TREATMENT FROM COAL GASIFICATION (ONLY PURIFICATION PARTS OF PROCESS)		
	INTPUTS	
Gas input	Value	2.042
	Unit	kg raw syngas per kg treated syngas
	Reference	Bibber et al., 2007
Raw Natural gas	Value	0.0202256
	Unit	m^3/kg output
	Reference	Bibber et al., 2007
Water	Value	0.475
	Unit	kg/kg syngas output
	Reference	Bibber et al., 2007
Electricity	Value	0.08
	Unit	kWh/kg syngas output
	Reference	Bibber et al., 2007
Catalyst, solvent, or other key input	Value	0.0042
	Unit	kg methanol for sulfur removal/kg
	Reference	Bibber et al., 2007
Catalyst, solvent, or other key input	Value	0.0047
	Unit	kg sulfur impregnated activated carbon/kg
	Reference	Bibber et al., 2007
Catalyst, solvent, or other key input	Value	0.0013
	Unit	kg zinc oxide/kg
	Reference	Bibber et al., 2007
Catalyst, solvent, or other key input	Value	0.0037
	Unit	carbonyl sulfate
	Reference	Bibber et al., 2007
	OUTPUTS	
Water	Value	0.2076958824
	Unit	kg/kg syngas output
	Reference	Bibber et al., 2007
CO_2	Value	0.740
	Unit	kg/kg output
	Reference	Bibber et al., 2007
NOx	Value	0.00004024
	Unit	kg/kg output
	Reference	Bibber et al., 2007

2. SYNGAS PURIFICATION TRAIN: SYNGAS TREATMENT FROM COAL GASIFICATION (ONLY PURIFICATION PARTS OF PROCESS)

SOx	Value	0.0000003944
	Unit	kg/kg output
	Reference	Bibber et al., 2007
$PM_{2.5}$	Value	0.0000003944
	Unit	kg/kg output
	Reference	Bibber et al., 2007
VOCs	Value	0.00000404
	Unit	kg/kg output
	Reference	Bibber et al., 2007
Sulfur	Value	0.02032085774
	Unit	kg/kg output
	Reference	Bibber et al., 2007
Metals	Value	0.0000000000237
	Unit	kg/kg output
	Reference	Bibber et al., 2007
Dioxins	Value	0.0000000000000000
	Unit	kg/kg output
	Reference	Bibber et al., 2007
Solid Waste	Value	0.0000007888000000
	Unit	kg/kg output
	Reference	Bibber et al., 2007

For the production of the products we consider, the ratio of H_2:CO in the syngas is important. For Fischer-Tropsch processes, ratios of between 1:1 to 3:1 were found. Similarly, for methanol production, ratios of around 2:1 were common in the literature. For fermentation processes, ratios of 1:1 were common, though with additional hydrogen, more CO_2 in the gas can be converted to product, making a higher ratio of H_2:CO ideal for maximum carbon capture, even though no specific ratio is required (a biological water gas shift reaction occurs during fermentation). In general, this means that we would like to increase the amount of H_2 to a ratio of around 2:1, and have used this as an assumption in all three processes. In total, around 40 kg of additional H_2 will be needed to adjust the ratios of BF and COG gas produced per tonne of steel. We add this to the expected syngas mass, following the syngas treatment steps.

The final syngas composition, following syngas treatment and addition of hydrogen, which we used in the calculation of maximum product produced is given in table VI.8:

Table VI.8: Parameters for for syngas treatment, adapted from Bibber et al., 2007 (gray shows inputs and white is outputs)

SYNGAS COMPOSITION, POST CLEANUP TREATMENT, BASED ON BIBBER ET AL., 2007			
GAS	KG	MOLES (PRIOR TO ADDITIONAL H_2)	MOLES (INCLUDING ADDITIONAL H_2, 2:1 RATIO)
Hydrogen	13	6,512	24,730
Nitrogen (N_2)	602	21,497	21,497
Methane (CH_4)	24	1,502	1,502
Carbon monoxide (CO)	346	12,365	12,365
Carbon dioxide (CO_2)	19	436	436
Argon (Ar)	13	321	321
TOTAL	**1,018**	**42,634**	**60,852**

3. Methanol production

For methanol production, we considered the following set of reactions:

$$(1)\ CO + 2\,H_2 \longrightarrow CH_3OH$$
$$(2)\ CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O$$
$$(3)\ CO_2 + H_2 \longrightarrow CO + H_2O$$

as reported in Ott (2012), Ullmann's Encyclopedia of Industrial Chemistry and assumed that 100% of CO and CO_2 participate in the reactions, while CH_4 did not participate in any reaction. Ott (2012) reports an 83% carbon efficiency for the reaction.

Based on this, we accounted for 12365 mol CO and 436 mol CO_2 entering the reaction to yield 10,625 12,801 mol CH_3OH (out of a theoretical maximum of 12,801 mol), or 339.9 kg of methanol. The remainder of the CO and CO_2 (as well as the CH_4) was assumed to be flared under complete combustion, yielding 2200 mol CO_2 or 97 kg of CO_2-eq.

For the methanol baseline scenario, we use data from the Ecoinvent database for conventional methanol production (steam reforming and synthesis) (Table VI.9).

Table VI.9: Conventional methanol production parameters

3. METHANOL PRODUCTION: METHANOL PRODUCTION FROM NATURAL GAS		
	INPUTS	
Clean syngas	Value	1.155
	Unit	kg syngas/kg methanol
	Reference	Machado et al., 2014
Purified natural gas (CH_4)	Value	0.65179
	Unit	m^3/kg methanol
	Reference	Ecoinvent database 3, Original source is Althaus et al., 2007
Water	Value	0.00901
	Unit	m^3/kg methanol
	Reference	Ecoinvent database 3, Original source is Althaus et al., 2007

3. METHANOL PRODUCTION: METHANOL PRODUCTION FROM NATURAL GAS		
Electricity	Value	0.555556
	Unit	kwh/kg methanol
	Reference	GREET NG to Methanol for feedstock
Heat	Value	6.96
	Unit	MJ/kg methanol
	Reference	Ecoinvent database 3, Original source is Althaus et al., 2007
Catalyst, solvent, or other key input	Value	0.00024
	Unit	kg aluminium oxide/kg methanol
	Reference	Ecoinvent database 3, Original source is Althaus et al., 2007
Catalyst, solvent, or other key input	Value	9.00E-05
	Unit	kg copper oxide/kg methanol
	Reference	Ecoinvent database 3, Original source is Althaus et al., 2007
Catalyst, solvent, or other key input	Value	2.00E-05
	Unit	kg nickel/kg methanol
	Reference	Ecoinvent database 3, Original source is Althaus et al., 2007
Catalyst, solvent, or other key input	Value	3.00E-05
	Unit	kg zinc/kg methanol
	Reference	Ecoinvent database 3, Original source is Althaus et al., 2007
Catalyst, solvent, or other key input	Value	1.00E-05
	Unit	kg molybdenum/kg methanol
	Reference	Ecoinvent database 3, Original source is Althaus et al., 2007
	OUTPUTS	
Methanol	Value	1
	Unit	kg
	Reference	-
Water	Value	0.0056738
	Unit	m^3/kg
	Reference	Ecoinvent database 3, Original source is Althaus et al., 2007
CO_2	Value	0.39
	Unit	kg/kg
	Reference	Ecoinvent database 3, Original source is Althaus et al., 2007
NOx	Value	0.000455
	Unit	kg/kg methanol
	Reference	Ecoinvent database 3, Original source is Althaus et al., 2007
SOx	Value	0.0002569
	Unit	kg sulfur dioxide
	Reference	Ecoinvent database 3, Original source is Althaus et al., 2007

3. METHANOL PRODUCTION: METHANOL PRODUCTION FROM NATURAL GAS		
$PM_{2.5}$	Value	0.00025
	Unit	kg/kg
	Reference	Ecoinvent database 3, Original source is Althaus et al., 2007
VOCs	Value	0.00046
	Unit	kg/kg
	Reference	Ecoinvent database 3, Original source is Althaus et al., 2007
Solid Waste	Value	2.00E-05
	Unit	kg suspended solids, unspecified
	Reference	Ecoinvent database 3, Original source is Althaus et al., 2007

For methanol production from syngas, instead of from natural gas, the steam reforming step must be excluded, though most of the parameters remain the same. For this process, we again use Ecoinvent data, complemented with additional sources to account for the altered scope of the methanol production step (Table VI.10).

Table VI.10: Methanol production parameters, excluding steam reforming

3. METHANOL PRODUCTION: METHANOL SYNTHESIS STEP ONLY		
	INPUTS	
Water	Value	0.00901
	Unit	m^3/kg methanol
	Reference	Ecoinvent database 3, Original source is Althaus et al., 2007
Electricity	Value	0.3842609312
	Unit	kwh/kg methanol
	Reference	Vaswani, 2000
Heat	Value	6.96
	Unit	MJ/kg methanol
	Reference	Ecoinvent database 3, Original source is Althaus et al., 2007
Catalyst, solvent, or other key input	Value	0.00024
	Unit	kg aluminium oxide/kg methanol
	Reference	Ecoinvent database v3, original source Jungbluth et al., 2008
Catalyst, solvent, or other key input	Value	9.00E-05
	Unit	kg copper oxide/kg methanol
	Reference	Ecoinvent database v3, original source Jungbluth et al., 2008
Catalyst, solvent, or other key input	Value	2.00E-05
	Unit	kg nickel/kg methanol
	Reference	Ecoinvent database v3, original source Jungbluth et al., 2008
Catalyst, solvent, or other key input	Value	3.00E-05
	Unit	kg zinc/kg methanol
	Reference	Ecoinvent database v3, original source Jungbluth et al., 2008
Catalyst, solvent, or other key input	Value	1.00E-05
	Unit	kg molybdenum/kg methanol
	Reference	Ecoinvent database v3, original source Jungbluth et al., 2008

3. METHANOL PRODUCTION: METHANOL SYNTHESIS STEP ONLY		
	OUTPUTS	
Methanol	Value	1
	Unit	kg
	Reference	-
Water	Value	0.0056738
	Unit	m^3/kg
	Reference	Ecoinvent database 3, Original source is Althaus et al., 2007
CO_2	Value	0.39
	Unit	kg/kg
	Reference	Ecoinvent database 3, Original source is Althaus et al., 2007
NOx	Value	0.000455
	Unit	kg/kg methanol
	Reference	Ecoinvent database 3, Original source is Althaus et al., 2007
$PM_{2.5}$	Value	0.00025
	Unit	kg/kg
	Reference	Ecoinvent database 3, Original source is Althaus et al., 2007
VOCs	Value	0.00046
	Unit	kg/kg
	Reference	Ecoinvent database 3, Original source is Althaus et al., 2007

4. Natural gas production and purification

For the methanol baseline scenario, we use life cycle assessment data on natural gas production and purification from the National Energy Technology Laboratory (NETL, 2011).

Table VI.11: Natural gas production and purification parameters

4. NATURAL GAS PURIFICATION: NATURAL GAS PURIFICATION		
	INPUTS	
Raw Natural gas	Value	1.19
	Unit	kg/kg purified NG
	Reference	NETL (2011). NETL Life Cycle Inventory Data www.netl.doe.gov/energy-analyses (http://www.netl.doe.gov/energy-analyses)
Water	Value	0.00275
	Unit	kg/kg NG
	Reference	NETL (2011). NETL Life Cycle Inventory Data www.netl.doe.gov/energy-analyses (http://www.netl.doe.gov/energy-analyses)
Electricity	Value	1.38E-05
	Unit	kwh/kg
	Reference	NETL (2011). NETL Life Cycle Inventory Data www.netl.doe.gov/energy-analyses (http://www.netl.doe.gov/energy-analyses)
Heat	Value	68.99554815
	Unit	J/kg
	Reference	NETL (2011). NETL Life Cycle Inventory Data www.netl.doe.gov/energy-analyses (http://www.netl.doe.gov/energy-analyses)

4. NATURAL GAS PURIFICATION: NATURAL GAS PURIFICATION

Catalyst, solvent, or other key input	Value	2.38E-06
	Unit	kg Diethanolamine (DEA) [Organic intermediate products]/ kg NG
	Reference	NETL (2011). NETL Life Cycle Inventory Data www.netl.doe.gov/energy-analyses (http://www.netl.doe.gov/energy-analyses)
	OUTPUTS	
CO	Value	0.0000000452
	Unit	kg
	Reference	NETL (2011). NETL Life Cycle Inventory Data www.netl.doe.gov/energy-analyses (http://www.netl.doe.gov/energy-analyses)
Purified natural gas (CH_4)	Value	1
	Unit	kg
	Reference	NETL (2011). NETL Life Cycle Inventory Data www.netl.doe.gov/energy-analyses (http://www.netl.doe.gov/energy-analyses)
Water	Value	0.00275
	Unit	kg
	Reference	NETL (2011). NETL Life Cycle Inventory Data www.netl.doe.gov/energy-analyses (http://www.netl.doe.gov/energy-analyses)
CO_2	Value	0.087223
	Unit	kg/kg purified NG
	Reference	NETL (2011). NETL Life Cycle Inventory Data www.netl.doe.gov/energy-analyses (http://www.netl.doe.gov/energy-analyses)
NOx	Value	0.00000040905
	Unit	kg/kg purified NG
	Reference	NETL (2011). NETL Life Cycle Inventory Data www.netl.doe.gov/energy-analyses (http://www.netl.doe.gov/energy-analyses)
SOx	Value	0.0000000003
	Unit	kg sulfur dioxide/kg purified NG
	Reference	NETL (2011). NETL Life Cycle Inventory Data www.netl.doe.gov/energy-analyses (http://www.netl.doe.gov/energy-analyses)
$PM_{2.5}$	Value	18.08
	Unit	mg/kg purified gas
	Reference	GREET database, 2016, original source Xie, Wang & Han, 2011 “Assessment of fuel cycle energy use and greenhouse gas emissions for Fischer Tropsch diesel from coal and cellulosic biomass”
VOCs	Value	0.0000000030
	Unit	kg/kg purified NG
	Reference	NETL (2011). NETL Life Cycle Inventory Data www.netl.doe.gov/energy-analyses (http://www.netl.doe.gov/energy-analyses)
Metals	Value	2.69E-13
	Unit	kg Lead (+II) [Heavy metals to air]/kg purified NG
	Reference	NETL (2011). NETL Life Cycle Inventory Data www.netl.doe.gov/energy-analyses (http://www.netl.doe.gov/energy-analyses)

5. Power generation

Looking at the power generation for replacing steel mill gases, we assume that blast furnace gas and coke oven gases will both be diverted to chemicals production, creating a need for additional energy production from another source. In Table VI.12, we show the calculated energy content of these gases (per tonne of steel output). Nuon indicated that their power plants running on steel mill waste gases currently operate at around 39% and 43% energy conversion efficiency, though they also mentioned that they are familiar with higher efficiencies of up to 50%. We decided to assume a conservative 40% conversion efficiency for determining the amount of energy replacement required for diversion.

Table VI.12: Energy production from blast furnace and coke oven gases

STEEL MILL GAS STREAM	COKE OVEN GAS	BLAST FURNACE GAS	TOTAL
Total volume gas per tonne steel (Nm³)	200	1,483	**1,683**
Energy value (MJ/m³)	17.5	3.5	
Total energy value (MJ/tonne of steel)	3,494	5,192	**8,686**
Total energy value (kWh/tonne of steel)	971	1,442	**2,413**
Recoverable energy (MJ/tonne of steel) at 40% efficiency	1,398	2,077	**3,474**
Recoverable energy (kWh/tonne of steel) at 40% efficiency	388	577	**965**

In looking at the energy replacement, we evaluated a number of power generation scenarios in order to examine the sensitivity of the final outcomes to the source of energy. We collected energy production life cycle assessment data for steam turbine energy production from coal and natural gas feedstocks, as well as photovoltaic energy production and wind energy.

The values used in these energy production scenarios is given in Table VI.13. For blast furnace energy production, Nuon has shared information on CO_2, NOx, and SO_2 emissions per kWh. However, the data from Nuon is not as complete as the life cycle assessment data. Most notably, we are missing information on other key pollutants (e.g. metals, dioxins, sulfur, VOCs, PM) and water inputs and outputs (for cleaning, etc). Additionally, we only have data on the emissions associated with producing energy from blast furnace gas, as the coke oven gas is consumed internally by Tata Steel.

Table VI.13: Input parameters for energy production scenarios

5. POWER GENERATION				
		5.1 STEEL MILL WASTE GAS	5.2 NATURAL GAS	5.3 WIND TURBINE
		INPUTS		
BF gas	Value	3.29	-	-
	Unit	kg gas/kWh recoverable energy	-	-
	Reference	Own calculations	-	-
Coke oven gas	Value	0.2	-	-
	Unit	kg gas/kWh recoverable energy	-	-
	Reference	Own calculations	-	-

5. POWER GENERATION

		5.1 STEEL MILL WASTE GAS	5.2 NATURAL GAS	5.3 WIND TURBINE
Raw Natural gas	Value	-	0.25282	-
	Unit	-	m^3/kwh	-
	Reference	-	Ecoinvent database v3, Faist Emmenegger, Heck & Jungbluth, 2007	-
Purified natural gas (CH_4)	Value	-	-	4.08E+01
	Unit	-	-	mg/kwh
	Reference	-	-	Garrett & Rønde, 2012
Coal	Value	-	-	132.1
	Unit	-	-	mg/kwh
	Reference	-	-	Garrett & Rønde, 2012
Crude Oil	Value	-	-	2.26E+02
	Unit	-	-	mg/kwh
	Reference	-	-	Garrett & Rønde, 2012
Water	Value	8.69846	8.69846	4.44E+03
	Unit	m^3/kwh	kg/kwh	mg/kwh
	Reference	Assumed same as with natural gas	Ecoinvent database v3, Faist Emmenegger, Heck & Jungbluth, 2007	Garrett & Rønde, 2012
			OUTPUTS	
CO	Value	-	-	3.24E+00
	Unit	-	-	mg/kwh
	Reference	-	-	Garrett & Rønde, 2012
Water	Value	0.00869853	0.00869853	2700.25
	Unit	m^3/kwh	m^3/kWh	mg/kwh
	Reference	Assumed same as with natural gas	Ecoinvent database v3, Faist Emmenegger, Heck & Jungbluth, 2007	Garrett & Rønde, 2012
Electricity	Value	1	1	1
	Unit	MWh	kWh	kWh
	Reference	Data provided by Nuon	Ecoinvent database v3, Faist Emmenegger, Heck & Jungbluth, 2007	Garrett & Rønde, 2012
CO_2	Value	1401.59	0.55216	453.731
	Unit	kg/MWh	kg/kWh	mg/kwh
	Reference	Own calculations	Nuon suggested a value around 380 kg CO_2e/MWh, based on a combined heat and power system (increasingly common in Europe) and an efficiency of 60%. This corresponds well with ecoinvent data in Treyer & Bauer (2013) for such systems, with values in the range of around 360 kg CO_2e/MWh.	Turconi, Boldrin & Astrup, 2017
NOx	Value	0.4409	0.000503	1.82
	Unit	kg/MWh	kg/kWh	mg/kwh
	Reference	Data provided by Nuon	Ecoinvent database v3, Faist Emmenegger, Heck & Jungbluth, 2007	Garrett & Rønde, 2012

5. POWER GENERATION				
		5.1 STEEL MILL WASTE GAS	5.2 NATURAL GAS	5.3 WIND TURBINE
SOx	Value	0.1795	0.00000493	1.43
	Unit	kg SO2/MWh	kg SO2/kWh	mg/kwh
	Reference	Data provided by Nuon	Ecoinvent database v3, Faist Emmenegger, Heck & Jungbluth, 2007	Garrett & Rønde, 2012
$PM_{2.5}$	Value	0.00000493	0.00000493	-
	Unit	kg/kWh	kg/kWh	-
	Reference	Missing data, assumed same as natural gas	Ecoinvent database v3, Faist Emmenegger, Heck & Jungbluth, 2007	-
VOCs	Value	0.00014	0.0000505	0.244000000
	Unit	kg NMVOCs	kg all VOCs/kWh	mg/kwh
	Reference	Data from Nuon	Ecoinvent database v3, Faist Emmenegger, Heck & Jungbluth, 2007	Garrett & Rønde, 2012
Metals	Value		0.000000000296	-
	Unit		kg all metals (except radioactive ones)/ kWh	-
	Reference		Ecoinvent database v3, Faist Emmenegger, Heck & Jungbluth, 2007	-
Radioactive materials	Value		-	-
	Unit		-	-
	Reference		-	-
Dioxins	Value		0.00000000000000029	-
	Unit		kg/kWh	-
	Reference		Ecoinvent database v3, Faist Emmenegger, Heck & Jungbluth, 2007	-
Solid Waste	Value		0.00000986	1181.22249
	Unit		kg residue from coolingwater/kWh	mg/kwh
	Reference		Ecoinvent database v3, Faist Emmenegger, Heck & Jungbluth, 2007	Garrett & Rønde, 2012

In calculating the outcomes of each scenario, we consistently use natural gas as the source for electricity replacement, as it accounts for a large share of the electricity production in the Netherlands and Belgium and is average in terms of impacts (compared to coal, on the one hand, and renewables on the other).

6. Petroleum refining

We considered the basic reaction:

$$(2_n+1)\ H_2 + n\ CO \longrightarrow C_nH(2_n+2) + n\ H_2O$$

for the Fischer Tropsch process. We considered experimental data from Bibber (2007), Baseline Technical and Economic Assessment of a Commercial Scale Fischer-Tropsch Liquids Facility. DOE-NETL, to obtain the composition of all input (syngas) and output streams (different streams of hydrocarbons) in the reaction.

Experimental data suggests a carbon efficiency of 51% considering 37.1 million mol of carbon atoms in reactants (CO and CH_4) and 19 million mol of carbon atoms in different hydrocarbons.

Assuming decane as a representative product of the reaction in the scenario, we estimated a yield of 1238 mol of decane from 12365 mol of CO and 12 mol of CH_4 in the reactants. A carbon balance, again, assuming all waste gases to be flared under complete combustion, suggests a production of 6,065 mol CO_2, or 266.86 kg of CO_2-eq.

From these results, we come to a maximum yield of 176 kg and an actual yield of 90 kg, which are used in the calculations for the baseline of petroleum refining and the Fischer-Tropsch process. For the petroleum refining parts of the baseline processes, we used standard life cycle assessment data from the Ecoinvent database version 3. The factors used in the calculations are given in Table VI.14. As this process results in a number of products and therefore has multiple functional units for outputs, when a single output is examined, we must use an impact allocation. In this case, we use an allocation based on the mass of a product in the total product mix.

Data from Bibber (2007) corresponds to a 51% efficiency, but confidential industry data shows a higher conversion efficiency using a different catalyst tailored for naphtha production. Under these conditions, naphtha output would amount to approximately 33 kg of product with additional hydrocarbons as byproducts. We used this data to calculate further impacts from naphtha cracking for ethylene production.

Table VI.14: Input parameters for petroleum refining

6. PETROLEUM REFINING: PETROLEUM REFINING		
	INPUTS	
Crude Oil	Value	1.086956522
	Unit	kg/kg product mix, crude oil or petroleum
	Reference	Ecoinvent v3, original author Jungbluth, 2007
Heavy Fuel Oil	Value	0.9326086957
	Unit	MJ/kg product mix (fuel is burned in the furnace for heat)
	Reference	Ecoinvent v3, original author Jungbluth, 2007
Water	Value	0.005125217391
	Unit	m^3/kg product mix
	Reference	Ecoinvent v3, original author Jungbluth, 2007
Electricity	Value	0.04032608696
	Unit	kWh/kg product mix
	Reference	Ecoinvent v3, original author Jungbluth, 2007
Heat	Value	2.717391304
	Unit	MJ/kg product mix
	Reference	Ecoinvent v3, original author Jungbluth, 2007

6. PETROLEUM REFINING: PETROLEUM REFINING

Catalyst, solvent, or other key input	Value	0.002663043478
	Unit	kg sodium hydroxide/kg product mix
	Reference	Ecoinvent v3, original author Jungbluth, 2007
	OUTPUTS	
Diesel	Value	0.1083353195
	Unit	kg/kg fuel mix total
	Reference	Ecoinvent v3, original author Jungbluth, 2007
Heavy Fuel Oil	Value	0.1906701623
	Unit	kg/kg fuel mix total
	Reference	Ecoinvent v3, original author Jungbluth, 2007
Kerosene	Value	0.07236799341
	Unit	kg/kg fuel mix total
	Reference	Ecoinvent v3, original author Jungbluth, 2007
Light Fuel Oil	Value	0.2903386562
	Unit	kg/kg fuel mix total
	Reference	Ecoinvent v3, original author Jungbluth, 2007
Liquefied Petroleum Gas	Value	0.03065889541
	Unit	kg/kg fuel mix total
	Reference	Ecoinvent v3, original author Jungbluth, 2007
Naphtha	Value	0.07355968193
	Unit	kg/kg fuel mix total
	Reference	Ecoinvent v3, original author Jungbluth, 2007
Unleaded petrol (gasoline)	Value	0.2329209369
	Unit	kg/kg fuel mix total
	Reference	Ecoinvent v3, original author Jungbluth, 2007
Pitch	Value	0.001148354386
	Unit	kg/kg fuel mix total
	Reference	Ecoinvent v3, original author Jungbluth, 2007
Water	Value	0.004760869565
	Unit	m^3, incl. .004 of water for cooling and .0007 of water from river/ kg fuel mix
	Reference	Ecoinvent v3, original author Jungbluth, 2007
Electricity	Value	0.0225
	Unit	kWh/kg fuel mix
	Reference	Ecoinvent v3, original author Jungbluth, 2007
CO_2	Value	0.2189484277
	Unit	kg/kg product mix
	Reference	ICCT, 2010

6. PETROLEUM REFINING: PETROLEUM REFINING

Nox	Value	0.00003163043478
	Unit	kg/kg product mix
	Reference	Ecoinvent v3, original author Jungbluth, 2007
SOx	Value	0.0004010869565
	Unit	kg/kg product mix
	Reference	Ecoinvent v3, original author Jungbluth, 2007
$PM_{2.5}$	Value	0.00001086956522
	Unit	kg of PM10+/kg product mix
	Reference	Ecoinvent v3, original author Jungbluth, 2007
VOCs	Value	0.0003206522
	Unit	kg VOCs/kg product mix
	Reference	Ecoinvent v3, original author Jungbluth, 2007
Ammonia	Value	0.00000007989130435
	Unit	kg/kg product mix
	Reference	Ecoinvent v3, original author Jungbluth, 2007
H_2S	Value	0.00000003804347826
	Unit	kg of sulfides/kg product mix, average of two values in reference
	Reference	Ecoinvent v3, original author Jungbluth, 2007
Sulfur	Value	0.006010869565
	Unit	kg/kg product mix
	Reference	Ecoinvent v3, original author Jungbluth, 2007
Metals	Value	6.65E-06
	Unit	kg/kg product mix
	Reference	Ecoinvent v3, original author Jungbluth, 2007
Solid Waste	Value	6.73E-03
	Unit	0.00027kg petroleum coke, 0.000388kg refinery sludge, 0.00553kg refinery sulfur, 1.00E-06kg spent catalytic converters, all per 0.92 kg product mix, converted to per kg
	Reference	Ecoinvent v3, original author Jungbluth, 2007

7. Fischer-Tropsch

The data for the standard Fischer-Tropsch process comes from two sources. The first is the GREET life cycle assessment database and model and the second is from a paper and supplementary information from van der Giesen, Kleijn & Kramer (2014). In this paper, the authors examine a case of production of synthetic fuels by conversion of CO_2 to syngas, but they provide data on the separate steps involved in this process. The parameters used are provided in Table VI.15. To ensure internal consistency, CO_2 emissions are calculated on the basis of the direct emissions from carbon which does not end up in the product and indirect emissions from electricity demand.

Table VI.15: Input parameters for Fischer-Tropsch

7. FISCHER-TROPSCH: 7.1 FT FOR LIQUID FUEL MIX		
	INPUTS	
Water	Value	5067.16
	Unit	cm^3/kg fuel
	Reference	GREET database, original source Xie, Wang & Han, 2011
Electricity	Value	0.38142
	Unit	MJ/kg
	Reference	GREET database, original source Xie, Wang & Han, 2011
Heat	Value	10.79467283
	Unit	MJ/kg
	Reference	van der Giesen, Kleijn, Kramer, 2014
Catalyst, solvent, or other key input	Value	
	Unit	cobalt or iron
	Reference	
	OUTPUTS	
Diesel	Value	0.364
	Unit	kg/kg fuel mix
	Reference	van der Giesen, Kleijn & Kramer, 2014
Kerosene	Value	0.175
	Unit	kg/kg fuel mix
	Reference	van der Giesen, Kleijn & Kramer, 2014
Naphtha	Value	0.2352
	Unit	van der Giesen, Kleijn & Kramer, 2014
	Reference	
Base oil	Value	0.2258
	Unit	kg/kg fuel produced
	Reference	van der Giesen, Kleijn & Kramer, 2014
CO	Value	1.3
	Unit	g/kg
	Reference	GREET database, original source Xie, Wang & Han, 2011
Water	Value	5067.16
	Unit	cm^3/kg fuel
	Reference	GREET database, original source Xie, Wang & Han, 2011

7. FISCHER-TROPSCH: 7.1 FT FOR LIQUID FUEL MIX		
Heat	Value	10.795
	Unit	GJ/ton
	Reference	van der Giesen, Kleijn & Kramer, 2014
CO_2	Value	1
	Unit	kg/kg
	Reference	GREET database, original source Xie, Wang & Han, 2011
NOx	Value	1.87
	Unit	g/kg
	Reference	GREET database, original source Xie, Wang & Han, 2011
SOx	Value	0.72
	Unit	g/kg
	Reference	GREET database, original source Xie, Wang & Han, 2011
$PM_{2.5}$	Value	0.56
	Unit	g/kg
	Reference	GREET database, original source Xie, Wang & Han, 2011
VOCs	Value	0.52
	Unit	g/kg
	Reference	GREET database, original source Xie, Wang & Han, 2011

7.5 Ethylene production from naphtha

Naphtha cracking is the main mode of ethylene production, although mixtures of hydrocarbons can also be used in the process. Seifzadeh (2013) reports a 34.1% ethylene mass output for the process, with longer hydrocarbons accounting for about 38% of the weight and methane about 20%. This results in a conversion rate of 66%, by mass. Ren (2006) reports a 14-17 MJ/kg high value chemicals as energy intensity for the process, as opposed to a conventional attribution of around 28 MJ/kg ethylene when all the energy costs are allocated to the main product. We use the lower value in our calculations.

8. Sugarcane production

For sugarcane production, we use standard life cycle assessment factors from the GREET life cycle assessment database (2016 version) for emissions. Water inputs come from Chapagain & Hoekstra (2010) and only include “blue water”, or irrigation water. Other inputs, such as energy, fertilizers, and pesticides are derived from Flury & Jungbluth, 2012, while the land footprint is calculated on the basis of data from the Food and Agriculture Organization of the United Nations (FAO, 2017, for the year 2014). These factors are provided in Table VI.16.

Table VI.16: Sugarcane production input parameters

8. SUGARCANE PRODUCTION: SUGARCANE PRODUCTION		
	INPUTS	
Water	Value	52
	Unit	m^3/ton
	Reference	Chapagain & Hoekstra, 2010
Diesel	Value	78.875
	Unit	MJ/ton
	Reference	Flury & Jungbluth, 2012
Fertilizers	Value	0.537
	Unit	ton/ton
	Reference	Flury & Jungbluth, 2012
Pesticides	Value	0.0694
	Unit	kg/ton
	Reference	Flury & Jungbluth, 2012
Land	Value	0.01439470275
	Unit	ha/ton
	Reference	FAOSTAT, 2017 for year 2014
	OUTPUTS	
Sugarcane	Value	1
	Unit	ton
	Reference	
CO_2	Value	0.03072
	Unit	ton CO_2e/ton
	Reference	GREET model, 2016, original author Wang et al., 2008 “Life Cycle Energy Use and Greenhouse Gas Emission Implications of Brazilian Sugarcane Ethanol Simulated with the GREET Model”
NOx	Value	0.00014
	Unit	ton/ton
	Reference	GREET model, 2016, original author Wang et al., 2008 “Life Cycle Energy Use and Greenhouse Gas Emission Implications of Brazilian Sugarcane Ethanol Simulated with the GREET Model”
SOx	Value	0.00003674
	Unit	ton/ton
	Reference	GREET model, 2016, original author Wang et al., 2008 “Life Cycle Energy Use and Greenhouse Gas Emission Implications of Brazilian Sugarcane Ethanol Simulated with the GREET Model”

8. SUGARCANE PRODUCTION: SUGARCANE PRODUCTION		
$PM_{2.5}$	Value	0.00015
	Unit	ton/ton
	Reference	GREET model, 2016, original author Wang et al., 2008 “LifeCycle Energy Use and Greenhouse Gas Emission Implications of Brazilian Sugarcane Ethanol Simulated with the GREET Model”
VOCs	Value	0.00015
	Unit	ton/ton
	Reference	GREET model, 2016, original author Wang et al., 2008 “LifeCycle Energy Use and Greenhouse Gas Emission Implications of Brazilian Sugarcane Ethanol Simulated with the GREET Model”

9. Biomass fermentation to ethanol

For fermentation to ethanol, we use standard life cycle assessment factors from the Ecoinvent database, version 3 for ethanol produced from sugarcane fermentation. These factors are provided in Table VI.17.

Table VI.17: Biomass fermentation to ethanol input parameters

9. BIOMASS FERMENTATION: 11. SUGARCANE FERMENTATION		
	INPUTS	
CO_2	Value	0.4305295483
	Unit	kg/kg
	Reference	Ecoinvent v3, original source Jungbluth et al., 2007
Sugarcane (biomass)	Value	14.9801513
	Unit	kg/kg ethanol
	Reference	Ecoinvent v3, original source Jungbluth et al., 2007
Water	Value	0.03107332784
	Unit	m^3/kg (from environment and decarbonized water)
	Reference	Ecoinvent v3, original source Jungbluth et al., 2007
Electricity	Value	0.40189
	Unit	kwh/kg
	Reference	Ecoinvent v3, original source Jungbluth et al., 2007
Catalyst, solvent, or other key input	Value	0.03585649015
	Unit	kg lime/kg ethanol
	Reference	Ecoinvent v3, original source Jungbluth et al., 2007
Catalyst, solvent, or other key input	Value	0.01084562954
	Unit	kg of sulphuric acid/kg ethanol
	Reference	Ecoinvent v3, original source Jungbluth et al., 2007
	OUTPUTS	
Ethanol	Value	1
	Unit	kg
	Reference	

9. BIOMASS FERMENTATION: 11. SUGARCANE FERMENTATION

Vinasse	Value	16.45064432
	Unit	kg/kg ethanol
	Reference	Ecoinvent v3, original source Jungbluth et al., 2007
Water	Value	0.0311587147
	Unit	m^3/kg ethanol, incl. to water and to air
	Reference	Ecoinvent v3, original source Jungbluth et al., 2007
Electricity	Value	0.08778368662
	Unit	kwh/kg ethanol
	Reference	Ecoinvent v3, original source Jungbluth et al., 2007
CO_2	Value	4.722490076
	Unit	kg/kg ethanol
	Reference	Ecoinvent v3, original source Jungbluth et al., 2007
NOx	Value	0.002471724964
	Unit	kg/kg ethanol
	Reference	Ecoinvent v3, original source Jungbluth et al., 2007
SOx	Value	0.00006815968841
	Unit	kg/kg ethanol
	Reference	Ecoinvent v3, original source Jungbluth et al., 2007
$PM_{2.5}$	Value	0.001229870422
	Unit	kg/kg ethanol
	Reference	Ecoinvent v3, original source Jungbluth et al., 2007
VOCs	Value	0.00005392854468
	Unit	kg/kg ethanol
	Reference	Ecoinvent v3, original source Jungbluth et al., 2007
Ammonia	Value	0.00004763688113
	Unit	kg/kg ethanol
	Reference	Ecoinvent v3, original source Jungbluth et al., 2007
Metals	Value	0.00002441764662
	Unit	kg/kg ethanol
	Reference	Ecoinvent v3, original source Jungbluth et al., 2007
Dioxins	Value	0
	Unit	kg/kg ethanol
	Reference	Ecoinvent v3, original source Jungbluth et al., 2007
Solid Waste	Value	0.1045614561
	Unit	kg/kg ethanol (includes ash, municipal solid waste, waste mineral oil, wood ash)
	Reference	Ecoinvent v3, original source Jungbluth et al., 2007

10. Syngas fermentation

For the reference unit for ethanol production, experimental data from BOF waste mill gas fermentation in a bioreactor, reported in Handler (2016), Life Cycle Assessments of Ethanol Production via Gas Fermentation: Anticipated Greenhouse Gas Emissions for Cellulosic and Waste Gas Feedstocks, indicate that 2120 kg of CO_2-eq (CO and CO_2, accounted for as if flared) yield 1000 kg of ethanol, producing 49.9 kg of biosolids. The paper reports a carbon efficiency of 20-40%. After consultation with industry experts, we utilized a value of 40% for our calculations. However, some literature sources show higher carbon conversion efficiencies and LazaTech also claims higher efficiencies. These should be considered in follow-up work.

We then took these values to the syngas stream, assuming no reaction from the methane due to the anaerobic conditions, and estimated that 12,801 mol of CO and CO_2 would yield 2560 mol of ethanol or 118 kg. A carbon balance of 6,890 mol of carbon atoms or 303 kg of CO_2 eq is accounted as emissions, after discounting 6% as biosolids. Together with 66 kg from methane flaring, this amounts to 369 kg of CO_2-eq.

Data on syngas fermentation in terms of inputs and outputs is the hardest to come by, as much of the information is still protected by the companies who own the intellectual property for syngas fermentation technologies, which are relatively new. For this reason, the data comes from a wider variety of literature sources, given in Table VI.18. Besides CO_2 emissions, the other emissions are never specified. To complete the data, we assume additional emissions associated with the energy consumption (assumed natural gas), but this data is missing any other additional direct emissions from the fermentation process.

Table VI.18: Input parameters syngas fermentation to ethanol

10. SYNGAS FERMENTATION: SYNGAS FERMENTATION		
INPUTS		
Water	Value	9.007
	Unit	kg water/kg EtOH
	Reference	Handler et al., 2016
Electricity	Value	2.239952719
	Unit	kWh/kg ethanol, for both the fermentation process and the distillation (fermentation value is 0.8510648298 kWh/kg, while distillation is 5 MJ energy per kg ethanol distilled, when ethanol broth is at 6%)
	Reference	van Kasteren et al., 2005 for fermentation process and Molitor et al., 2016 for distillation
Catalyst, solvent, or other key input	Value	Not included in calculations
	Unit	acetogenic bacteria
	Reference	-
Catalyst, solvent, or other key input	Value	0.00186
	Unit	magnetite, kg per kg EtOH
	Reference	Handler et al., 2016
Catalyst, solvent, or other key input	Value	Not included in calculations
	Unit	calcium chloride, iron chloride
	Reference	
Catalyst, solvent, or other key input	Value	Not included in calculations
	Unit	ammonia
	Reference	

10. SYNGAS FERMENTATION: SYNGAS FERMENTATION

Catalyst, solvent, or other key input	Value	
	Unit	superphosphate
	Reference	
OUTPUTS		
Water	Value	1.293
	Unit	kg water/kg ethanol
	Reference	Handler et al., 2016
CO_2	Value	0.9575
	Unit	kg CO_2e/kg ethanol
	Reference	Handler et al., 2016
Nox	Value	0.001126696217
	Unit	kg/kg
	Reference	Only emissions from electricity consumption (assumed natural gas)
SOx	Value	0.0000110429669
	Unit	kg/kg
	Reference	Only emissions from electricity consumption (assumed natural gas)
$PM_{2.5}$	Value	0.0000110429669
	Unit	kg/kg ethanol
	Reference	Only emissions from electricity consumption (assumed natural gas)
VOCs	Value	0.0001131176123
	Unit	kg/kg ethanol
	Reference	Only emissions from electricity consumption (assumed natural gas)

APPENDIX VII: METHANOL SYNTHESIS LOOP

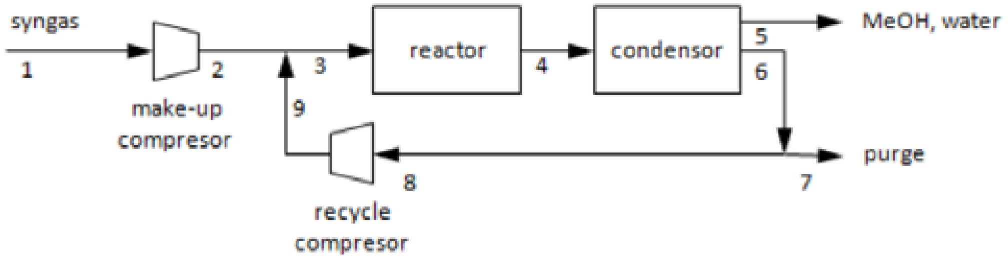


Figure VII.1: Results for a methanol synthesis loop, based on a production of 400 kton/a, carbon conversion of 90% and recycle ratio of 5.5.

Table VII.1: Make-up obtained from separation of CO and H_2 from COG+BFG, supplemented with pure H_2 to obtain $(H_2\text{-}CO_2)/(CO+CO_2)=2$ and with pure CO_2 to obtain 8% CO_2 in the feed stream.

FLOWNR	1	2	3	4	5	6	7	8	9
P[bar]	25	85	85	78	1	78	78	78	85
T[K]	298	493	493	513	298	298	298	298	493
total flow [mol/s]	**1.61E+03**	**1.61E+03**	**9.64E+03**	**8.78E+03**	**5.50E+02**	**8.23E+03**	**1.90E+02**	**8.04E+03**	**8.04E+03**
y-CO	0.22	0.22	0.192	0.175		0.186	0.186	0.186	0.186
y-CO_2	0.08	0.08	0.070	0.064		0.068	0.068	0.068	0.068
y-H_2	0.69	0.69	0.666	0.620		0.661	0.661	0.661	0.661
y-inert	0.01	0.01	0.072	0.079		0.085	0.085	0.085	0.085
y-MeOH				0.049	0.789				
y-H_2O				0.013	0.211				

	FLOWNR	1	2	3	4	5	6	7	8	9
	flow CO [mol/s]	3.54E+02	3.54E+02	1.85E+03	1.53E+03		1.53E+03	3.54E+01	1.50E+03	1.50E+03
	flow CO_2 [mol/s]	1.29E+02	1.29E+02	6.73E+02	5.58E+02		5.58E+02	1.29E+01	5.45E+02	5.45E+02
	flow H_2 [mol/s]	1.11E+03	1.11E+03	6.42E+03	5.44E+03		5.44E+03	1.25E+02	5.31E+03	5.31E+03
	flow inert [mol/s]	1.61E+01	1.61E+01	6.97E+02	6.97E+02		6.97E+02	1.61E+01	6.81E+02	6.81E+02
	flow MeOH [mol/s]				4.34E+02	4.34E+02				
	flow H_2O [mol/s]				1.16E+02	1.16E+02				
av. enthalpy [kJ/mol]	-5.58E+01		-4.28E+01	-5.07E+01	-2.10E+02		-4.73E+01			
enthalpy flow [MJ/s]	-8.98E+04		-4.13E+05	-4.45E+05	-1.15E+05		-8.98E+03			
exergy [kJ/s]:										
	physical	1.28E+04				0.00E+00		2.05E+03		
	chemical	3.62E+05				3.12E+05		3.96E+04		
	TOTAL	**3.75E+05**				**3.12E+05**		**4.16E+04**		

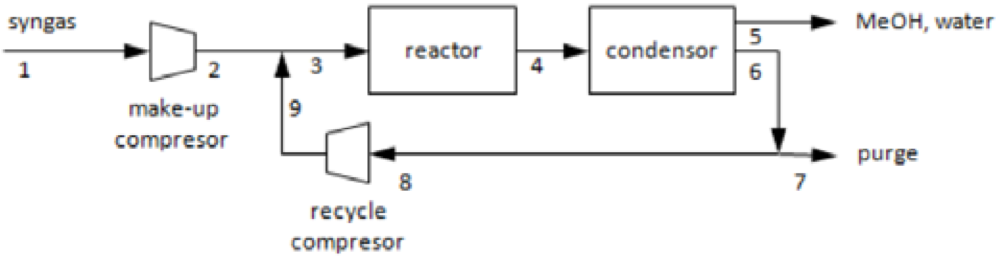


Figure VII.2: Results for a methanol synthesis loop, based on a production of 400 kton/a., carbon conversion of 90% and recycle ratio of 5.

Table VII.2: Make-up obtained from COG+BFG (as is), supplemented with pure H_2 to obtain (H_2-CO_2)/(CO+CO_2)=2.

	FLOWNR	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
	P[bar]	25	85	85	78	1	78	78	78	85
	T[K]	298	493	493	513	298	298	298	298	493
	total flow [mol/s]	**2.18E+03**	**2.18E+03**	**1.31E+04**	**1.22E+04**	**6.31E+02**	**1.16E+04**	**6.76E+02**	**1.09E+04**	**1.09E+04**
	y-CO	0.1212	0.1212	0.053	0.037		0.039	0.039	0.039	0.039
	y-CO2	0.1005	0.1005	0.044	0.031		0.032	0.032	0.032	0.032
	y-H_2	0.54675	0.54675	0.245	0.175		0.184	0.184	0.184	0.184
	y-inert	0.23155	0.23155	0.659	0.706		0.745	0.745	0.745	0.745
	y-MeOH				0.036	0.688				
	y-H_2O				0.016	0.312				
	flow CO [mol/s]	2.64E+02	2.64E+02	6.88E+02	4.50E+02		4.50E+02	2.64E+01	4.24E+02	4.24E+02
	flow CO_2 [mol/s]	2.19E+02	2.19E+02	5.70E+02	3.73E+02		3.73E+02	2.19E+01	3.51E+02	3.51E+02
	flow H_2 [mol/s]	1.19E+03	1.19E+03	3.19E+03	2.13E+03		2.13E+03	1.25E+02	2.00E+03	2.00E+03
	flow inert [mol/s]	5.04E+02	5.04E+02	8.60E+03	8.60E+03		8.60E+03	5.04E+02	8.10E+03	8.10E+03
	flow MeOH [mol/s]				4.34E+02	4.34E+02				
	flow H_2O [mol/s]				1.97E+02	1.97E+02				
av. enthalpy [kJ/mol]	-5.30E+01		-1.71E+01	-2.05E+01	-2.14E+02		-1.70E+01			
enthalpy flow [MJ/s]	-1.15E+05		-2.24E+05	-2.50E+05	-1.35E+05		-1.15E+04			
exergy [kJ/s]:										
	physical	1.74E+04				0.00E+00		7.31E+03		
	chemical	3.58E+05				3.12E+05		3.71E+04		
	TOTAL	**3.75E+05**				**3.12E+05**		**4.44E+04**		

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