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DECARBONISATION OPTIONS FOR THE DUTCH SILICON CARBIDE INDUSTRY

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Manufacturing Industry Decarbonisation Data Exchange Network

Decarbonisation options for the Dutch silicon carbide industry

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MIDDEN project coordination and responsibility

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An earlier version of this report was reviewed by ESD-SIC B.V. Delfzijl. PBL and TNO remain responsible for the content. The decarbonisation options and parameters are explicitly not verified by the company.

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FINDINGS

Summary

The Dutch silicon carbide production is formed by the ESD-SIC B.V. industrial site in Farmsum, Delfzijl municipality, which is subsidiary of the German company REF-Processing GmbH. It has a production capacity of 65,000 tonnes of silicon carbide per year, but the actual production fluctuates with the international market, being around 80% of this figure. The Dutch industry is the fifth largest player in the silicon carbide market worldwide, it is also considered a reference for environmentally friendly initiatives such as wastewater management and energy recovery (European Commission, 2007).

The silicon carbide process is intrinsically energy and carbon intensive. ESD-SIC is the eighth biggest individual electricity consumer in the Netherlands, with an energy consumption of around 1.3 PJ per year, mostly used to heat the ovens and to generate energy for the silicon carbide synthesis. However, its emissions are mostly exclusively originated from the chemical reactions that take place in the furnaces, since the remaining process does not utilize fossil fuels and does not present other sources of CO₂. Nevertheless, the industrial site's direct emissions registered in the ETS are approximately 130 kilotonnes (kt) of CO₂ per year.

This study identifies as main decarbonisation alternatives for the silicon carbide sector in the Netherlands the following:

- feedstock substitution, from current petroleum coke to biocoke;
- carbon capture, and use with methanol/ethanol synthesis;
- carbon capture and storage;
- process design changes, mechanical activation, and microwave heating;
- process substitution with magnesium as reducing element; and
- recycling.

Biocoke as an alternative feedstock has relevant characteristics for the silicon carbide industry, as it is similar in chemical composition and molecular structure to petroleum coke. It can eliminate the feedstock related emissions. Biocoke still has a small production volume compared to its full potential and is currently restricted to Asian markets to replace fossil fuels, not for use as a feedstock. Despite this, it presents good growth prospects in response to a future increase in demand, having in potential a competitive value with fossil alternatives for feedstock.

For carbon capture and storage (CCS) applied to the energy recovery plant, the technologies of post-combustion capture, oxyfuel capture, and pre-combustion capture, would also reduce ESD-SIC's direct emissions largely. The market conditions for these technologies are relatively mature and are expected to grow, with ongoing projects in different industries and with various capacities. Also, the ESD-SIC flue gas composition demonstrates high potential for carbon capture and utilisation (CCU) with ethanol/methanol synthesis as it presents high content of hydrogen and carbon monoxide in its mix. The other alternatives discussed in this report are promising, but need further research and demonstration to be considered as a solution at the industrial scale.

FULL RESULTS

Introduction

This report describes the current situation for silicon carbide production in the Netherlands and the options and preconditions for its decarbonisation. The study is part of the MIDDEN project (Manufacturing Industry Decarbonisation Data Exchange Network). The MIDDEN project aims to support industry, policymakers, analysts, and the energy sector in their common efforts to achieve deep decarbonisation. The MIDDEN project will update and elaborate further on options in the future, in close connection with the industry.

Scope

The only silicon carbide producer in the Netherlands is ESD SIC B.V. Production processes include mixer, freiland furnace with core graphite electrode, desulphurization plant, steam boiler and turbine, transformer and water treatment plant. Products include crystalline and metallurgical silicon carbide and sulphur. The main options for decarbonisation identified are feedstock substitution, carbon capture, and utilization, carbon capture and storage, process design changes, process substitution and recycling.

Reading guide

Section 1 introduces the Dutch silicon carbide industry. Section 2 describes the current situation for silicon carbide production processes in the Netherlands, and Section 3 describes the relevant products of these processes, while options for decarbonisation are systematically quantified and evaluated in Section 4. The feasibility of and requirements for those decarbonisation options are discussed in Section 5.

1 Current silicon carbide production

Silicon carbide (SiC) is a remarkably hard synthetically manufactured crystalline composite produced from silica sand or quartz and petroleum coke. Besides being the second hardest synthetic known material, its high thermal conductivity, high-temperature strength, low thermal expansion, and resistance to chemical reactions, make it valuable in many manufacturing industries (Mukherjee, 2011). The next sections will discuss more specifically the current production of this material, followed by further process description and product application.

The Dutch industrial SiC production coincides with the founding of Elektroschmelzwerk Delfzijl (ESD) in 1973, being for many years the main player and having the biggest production capacity in the European market. The silicon carbide production in the Netherlands is centralized in this industrial site, presented in Figure 1, which is since 2009 a subsidiary of the German REF-Processing GmbH and is located in Delfzijl. The production process is carried out on a large scale and supplies crystalline and metallurgic silicon carbide to several countries, with Germany as the principal buyer (European Commission, 2007). Although the silicon carbide production is made in the ESD-SiC B.V. industrial site in Delfzijl, the product is distributed worldwide by ESK-SiC GmbH in Frechen, Germany. The German company is partly responsible for the management of the deliveries and the logistic of supply with granular fractions as requested by the customer. They also offer consulting, analyses, and tests on the use of silicon carbide, playing a key role especially in the development of new products.



Figure 1 – ESD SIC B.V. industrial site in Farmsum, Delfzijl (Lubrafil, 2020)

Today, the Dutch silicon carbide production is recognized for being one of the most advanced and sustainable in the world. The production process of ESD-SIC was used as best reference for the description of best reference techniques in the reference document on Best Available Techniques for the Manufacture of Large Volume Inorganic Chemicals – Solids and Others (European Commission, 2007). The ESD-SIC industrial site was granted with certifications for its quality management (ISO - 9001), environmental management ISO - 14001, and energy management certification ISO - 50001 (ESD-SIC, 2020a). Although the Dutch production is recognized as best practice and the most environmentally friendly in the industry sector, it still emits around 130 kt/yr of greenhouse gases to the atmosphere and is the eighth-largest individual electricity consumer in the country. The large electricity consumption and flexible operation of the ESD-SIC process allows for balancing the electricity grid (described in more detail in ANNEX B).

2 Silicon carbide production process

Silicon carbide (SiC) only occurs in nature as the mineral moissanite, found in the meteorite iron of Canon Diablo in Arizona, in the US. Other than that, it has to be manufactured, and its production dates back to the end of the 19th century when Acheson developed a method of reacting clay and coke in a resistance furnace while trying to produce diamonds. As a result, this process had little crystals of silicon carbide crusted in the electrodes, being the first register of non-natural silicon carbide production. The current manufacturing method for the abrasives, metallurgical, and refractory industries is the same as the one developed by Acheson, but in a bigger scale.

Silicon carbide is produced under high-temperature via an electrochemical reaction between silica sand (quartz) and petroleum coke with a low sulphur composition, specially selected for its purity and particle size. The chemical process today is carried out in batches inside a highly energy-intensive electric resistor furnace (typically 6.2 – 8 MWh or 22-28 GJ per tonne SiC) with a production capacity of around 200 to 500 tonnes of SiC per furnace (European Commission, 2007). The primary overall chemical reaction is:



The industrial process consists of immersing the graphite core in the raw materials and heat it to elevated temperatures (between 2100 and 2700 °C), obtaining different structures of silicon carbide as a product and process gases as a by-product. The simplified industrial production process is shown below in Figure 2:

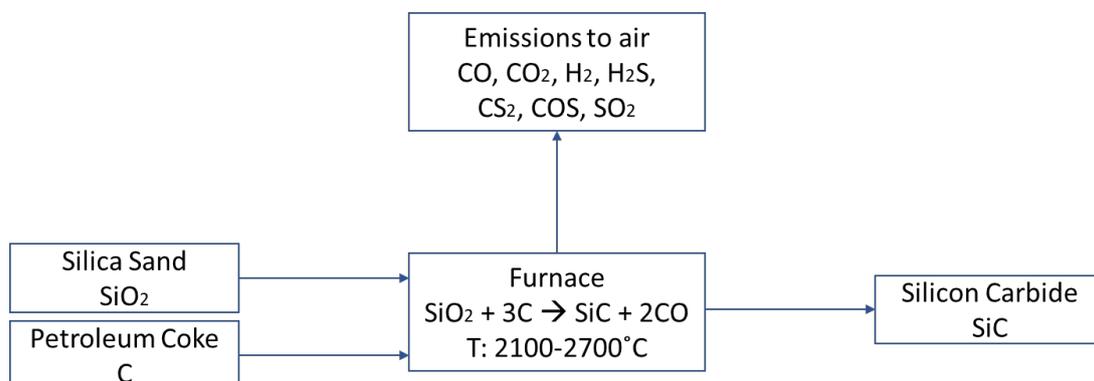


Figure 2 - Simplified diagram of silicon carbide production

According to the reference document Best Available Techniques for the Manufacture of Large Volume Inorganic Chemicals (European Commission, 2007), the main differences in the SiC industrial production are related to the type of furnace used and the accessory subprocesses. Two different types of furnaces are commonly used in this sector. The traditional model, used in most SiC production facilities in the world, is usually made up of two to six furnaces per group inside a furnace hall with a transformer and equipped with removable refractory sides and ranges from 10 to 20 m. Their thermal efficiency varies from 50 to 65%, and the reaction time is about one to three days. A relevant characteristic of this traditional set-up is a higher yield of crystalline SiC compared to the other furnaces, due to a relatively steep temperature gradient. Another type of furnace and the one used at the ESD-SiC industrial site is the freiland design, up to 60 m long with bottom electrodes (straight line or U-shape) and without end of sidewalls. They are placed outdoors, and the reaction time is about eight days. Although thermodynamic efficiency of the freiland furnace without gas collection is reported to be at a similar range as for the traditional furnace set, this process has better energy efficiency due to larger furnace capacity and better insulation and have the possibility to collect the process gas for desulphurizing and further purposes such as energy recovery.

The following sub-sections provide a description of each of the processes involved in the silicon carbide production, with associated material, energy and CO₂ flows utilizing data reported by both ESD-SiC B.V. and also relevant literature to provide good approximations. This forms a basis for the decarbonisation options to compare energy and CO₂ intensities as well as material requirements.

2.1 ESD-SiC Process Description

As previously mentioned, the production of silicon carbide in the Netherlands is carried out exclusively by the ESD-SiC industrial site in Delfzijl, in the north of the country. The site has a production capacity of 65,000 tonnes per year. The company operates utilizing the freiland type of furnace equipped with several environmental measures processes such as the energy recovery plant and the wastewater treatment plant, which will be discussed further in the next subtopics.

In general, the ESD-SiC silicon carbide production generates almost no process-related waste. The unreacted material from the furnaces is re-used in the next new batch, and it can be used as an insulation or reaction material according to its distance of the graphite core. Process-related waste fractions from the operation of conventional traditional furnaces include mainly scrapped fragments of furnace walls and spent electrodes. Although, some waste streams can be identified in connection with the use of the environmental measures in the Dutch process of collecting the process gas in the polyethylene (PE) foil and the sludge from the wastewater treatment plant. Recovered sulphur of the desulphurization plant can be used as raw material such as the fertilizer industry.

2.1.1 Overview of the Production Process

Figure 3 shows a simplified view of the industrial production of silicon carbide in the ESD-SiC industrial plant located in Delfzijl. Mass and energy flows are presented as well as the main processes related to production with its mass and energy flows. Each step of the process will be described in the following section, and for better visualization of this flow, there is a more detailed representation in ANNEX A. The scheme represents the production per batch/oven, and there are 24 furnaces on-site, with a maximum of seven operating and 17 either in cooling, building or maintenance stage.

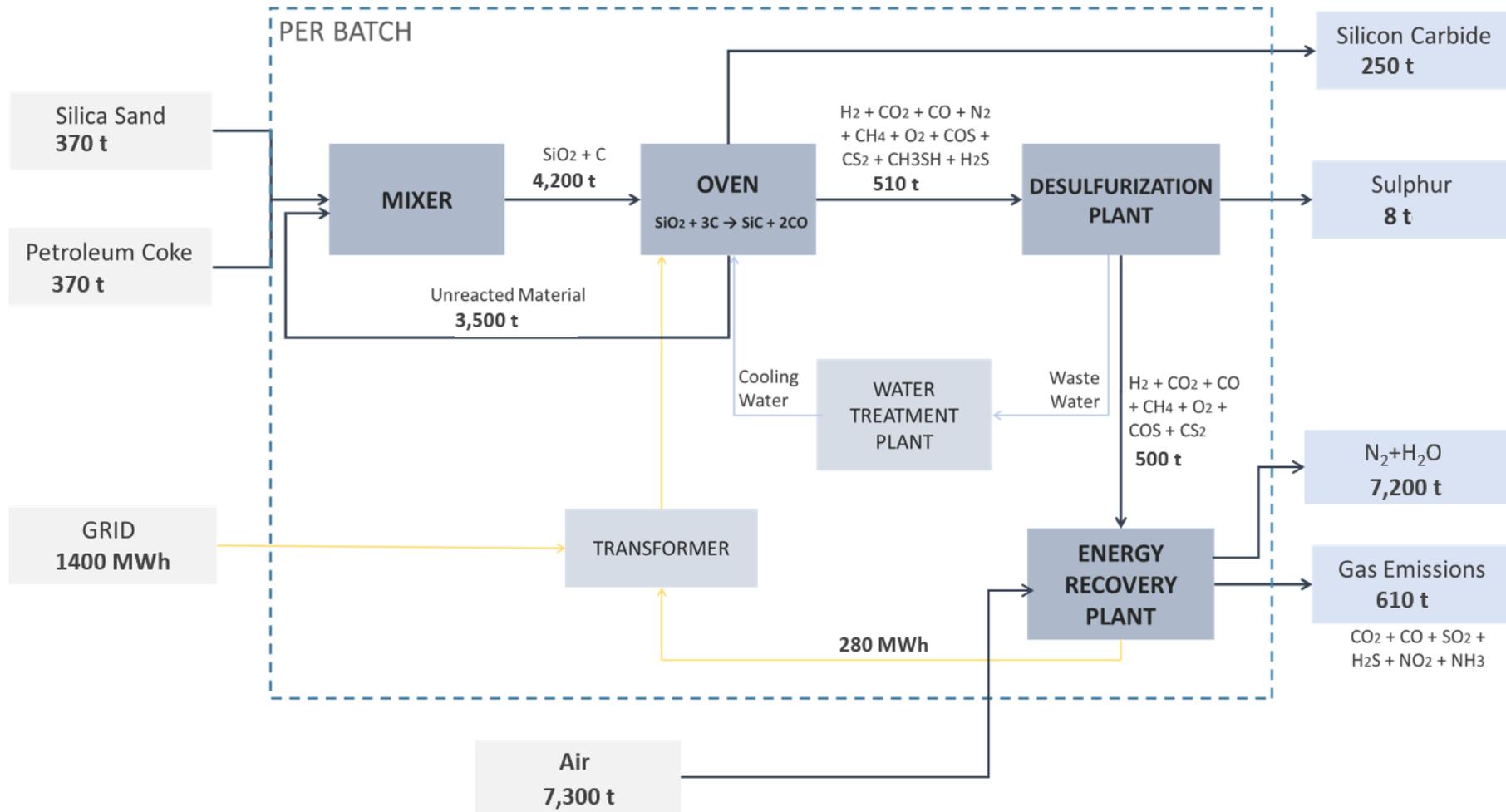


Figure 3 - Estimated material and energy flow overview of the silicon carbide process per batch, based on the stoichiometrically required amount of silica sand. Note that in the actual process, the amounts of supplied feedstock are larger, due to side reactions and impurities. All numbers are rounded to two significant digits.

2.1.2 Feedstock Input and Mixing

The first stage of the industrial process is receiving and mixing the raw materials. ESD-SIC B.V. uses pure silica white sand, either supplied by ship or return freight by truck. Petrochemical (pet) coke is delivered by ship. After both raw materials are unloaded in the port of Delfzijl or directly on the site (sand by truck), they are stored, broken (petroleum cokes) and mixed, resulting in thousand tonnes of mixture (500 tonnes each), partly mixed up with unreacted circulation material, placed around a graphite core and covered with the remaining part of over 3,000 tonnes of unreacted circulation material (mainly sand/coke). Figure 3 present the estimated mass flows for silica sand and petroleum coke, based on the amount of silica sand required according to the primary reaction. This shows that feeding the oven with 500 tonnes of each material guarantees that the mixture is always in abundance of both feedstocks. Unused material is re-used for the next batch. In the ESD-SIC process, the ratio mix of silica sand and pet coke is circa 1:1, with petroleum coke in excess due to volatiles and low sulphur content. The pile of mixed raw material with 500 tonnes of silica sand (SiO_2) and 500 tonnes petroleum coke is deposited around the graphite core, and the unreacted recirculated material is used again (Utilities, 2020). The 1:1 ratio is different from the stoichiometric ratio based on the primary reaction, due to side processes taking place.

2.1.3 Process Reaction in the Oven

After the furnace is build, a polyethylene (PE) foil is placed above it. The PE foil is used to capture all the process gas that will be collected for energy recovery. Thus, the oven/furnace is composed of the mountain of raw material and insulation material, the emerged U-shape format graphite core, and the PE Foil, as shown in Figure 4. The graphite core works as a power conductor, where the electricity is transformed into thermal heat, reaching peak temperatures of 2700°C . Each oven uses as much electricity per twenty minutes as an average household consumes per year. That high temperature is fundamental for the chemical reaction between the SiO_2 (silica sand) and C (pet coke).

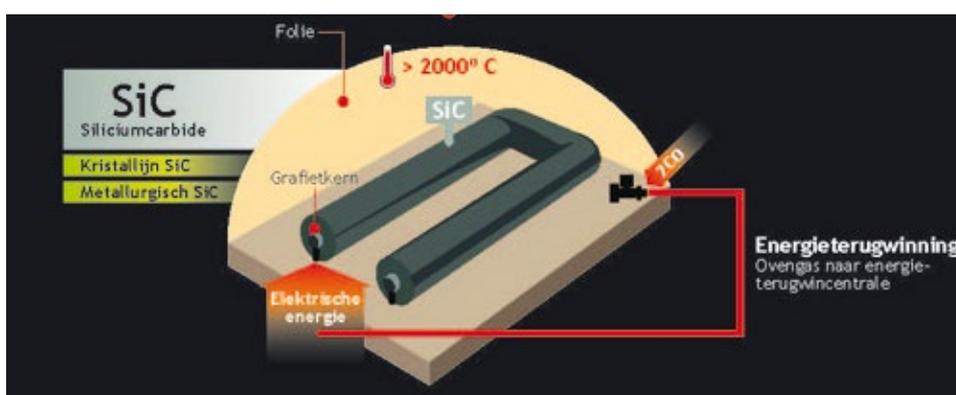


Figure 4 – Representation of the ESD-SIC oven with the graphite core and the PE foil in detail (ESD-SIC, 2020b)

The amount of raw material mix disposed around the graphite core is purposefully beyond its heating capacity. This guarantees that the material close to the graphite core process into silicon carbide while the rest is used as isolation, keeping the heat inside the furnace and

improving its energy efficiency. As a result, most heat usable for the reaction will be used. In that way, the type of silicon carbide formed depends on what temperature it was exposed to. The closer to the centre, the more heat, and the more crystalline the SiC is formed. In the same way, the further from the centre, the more amorphous/metallurgical the SiC is. This difference between the SiC formation is shown in Figure 5.



Figure 5 – Different forms of Silicon Carbide produced according to its distance to the graphite core. ESD SIC B.V., Delfzijl (ESD-SIC, 2020)

After this process, the silicon carbide as a final product is already available. It has only to be separated according to its characteristics as crystalline and metallurgical SiC. Every oven produces around 250 tonnes of silicon carbide and 600 tonnes of gases every batch. On the other hand, the gas under the PE foil goes through a common collection system that takes it to the next stages of the process. This gas is rich in hydrogen and carbon monoxide and carbon dioxide and in the ESD-SIC industrial site it is captured under the foil to be used further in the energy recovery plant. More about its composition will be discussed in Section 2.3. At this stage, sometimes also the phenomenon of blow-outs occur, representing a kind of uncontrolled emissions of combusted gas and eventual dust.

2.1.4 Process Gas Desulphurization – PRF Plant

The process gas collected under the PE foil comes from a common system to the desulphurization plant (PRF). This gas consists of circa 1% hydrogen sulphide (H_2S), and its removal is necessary to reduce finally SO_2 emission. The combustion of H_2S (that will be the next stage of the process) could cause problems for the boiler and produce more SO_2 than ESD-SIC has permission to emit, so the captured process gas is purified in the PRF. The so called LoCat process is used to desulphurize the gases, catalytically transforming H_2S into elemental sulphur. As a result, the hydrogen sulphide is more than 99% converted, producing around 1600 tonnes per year of sulphur. Only a small part (10%) of COS and CS_2 remains and will be combusted into SO_2 . Additionally, 75% of organic nitrogen is washed out in the PRF, decreasing the final NO_x emissions at the final stages (Gedeputeerde Staten der Provincie Groningen, 2012). From the desulphurization plant, there are two main output streams, one with degenerated catalytic fluid and the other with the remaining gases of the process. This stream is used as a nutrient in an external saltwater treatment installation.

2.1.5 Water Treatment Plant

There are different water streams treated in this process, such as furnace drain water, containing traces of gas condensate, rainwater and not evaporated spraying water used for cooling down the furnaces, and pure gas condensate. In the Dutch SiC plant, the treated water is used to spray the furnaces and cool them down after the production cycle is completed and before the SiC cylinder is removed. Most of the spray water evaporates on the surface of the furnace, also preventing emissions of dust and odour from the furnace. Both wastewater streams contain polycyclic aromatic hydrocarbons (PAH) and H₂S and are treated in the water treatment plant. If the wastewater unit is not working (due to a breakdown or a maintenance stop), untreated water is collected in individual basins. Water is temporarily stored here before it can be treated in the wastewater unit (European Commission, 2007).

2.1.6 Energy Recovery Plant and Transformer

The gas stream that left the desulphurization plant is burned into a steam boiler in the energy recovery plant to produce electricity. That practice that saves around 17% of ESD SiC electricity consumption, and it is the main reason for this industrial site to be one of the references in environmentally friendly silicon carbide use. The energy recovery plant is equipped with a boiler, a turbine, and a transformer. The boiler is used to burn the process gas and generates thermal energy to produce steam and has a nominal capacity of 45 MW_{th} (Gedeputeerde Staten der Provincie Groningen, 2012). The steam is then used to power the turbine-generator that produces energy that is sent to the 10 MWe transformer. Then, the electrical current both from the energy recovery plant and from the grid are transformed to the specifications needed to power the oven.

2.2 Energy Consumption

Silicon carbide production is an energy-intensive process intrinsically due to the endothermic characteristic of the chemical reaction between the sand and the coke. The specific energy consumption in traditional furnace installations varies between 25.2 to 28.8 GJ per tonne 100 % SiC produced (European Commission, 2007). On the other hand, installations using the freiland furnace, such as those owned by ESD-SiC, need less energy. Those furnaces are larger, have better insulation, and enable the recovery of energy from the process gas. For example, the Dutch plant, being one of the most environmentally friendly and using the energy recovery plant, reported an energy consumption of 24.3 GJ/ton 100% SiC produced but already reached values of 22.32 GJ/ton SiC in the past (European Commission, 2007). ESD-SiC consumptions can peak in around 1512 TJ/yr (Utilities, 2020). The company is today the eighth largest electricity customer in the Netherlands. As stated before, the company has been using the process gas generated in the ovens to produce energy in the Energy Recovery plant, which provides around 17% of the energy consumption and gives them more autonomy (Utilities, 2020).

Table 1 – Main energy sources to ESD-SiC processes (Utilities, 2020).

Energy source	Value	Unit
Grid	1255	TJ/yr
Energy Recovery Plant	257	TJ/yr
TOTAL	1512	TJ/yr

2.3 Greenhouse Gases Emissions

During the silicon carbide process in general, there are several small possible sources of greenhouse gas (GHG) emissions, such as emissions from the storage of pet coke and the mixing, grinding, and transporting of SiC and raw materials. In some plants such as ESD-SIC, the existence of an extra environmental process of desulphurization, energy recovery, and wastewater treatment can also represent a small GHG emission source, depending on the equipment utilized. However, the process gas is by far the main source of GHG emissions to air. At the moment it leaves the oven, about 92-95% of the process gas is formed by CO, H₂, and CO₂. The remainder contains H₂S, CS₂, COS, N₂, O₂, CH₄, and traces of CH₃SH (European Commission, 2007). The volatile sulphur composites (SO₂, H₂S, CS₂, COS, and CH₃SH) originate from the sulphur present in the pet coke and from side-reactions in the SiC production. The H₂S emission and other volatile components can cause several odour problems even in the lowest concentrations and have to be controlled according to the environmental rules. The coke also contains additional polycyclic aromatic hydrocarbons (PAHs) and heavy metals in small amounts which also needs to be addressed (European Commission, 2007).

In ESD-SIC, the composition of the process gas emitted by the oven follows the general rules, having around 90-95% of CO, H₂ and CO₂ and the remaining part contains H₂S, CS₂, COS, N₂, O₂, CH₄ and traces of CH₃SH (European Commission, 2007). However, this is not the gas that is emitted into the atmosphere since the composition of the gas changes along this process. The composition changes after the desulphurization plant, that decreases the amount of sulphuric components (especially H₂S) in the flue gas mix. Also, after the combustion in the energy generation plant, the composition of the macro components changes considerably with the combustion process of the H₂ and CO and the synthesis of CO₂. The emission that actually goes to the atmosphere is essentially limited to CO₂, oxygen, nitrogen, and water vapour (Rijksoverheid, 2017).

One interesting fact about silicon carbide industry emissions relates to its composition, which is closely similar to a syngas composition after its synthesis. Syngas is a mix of gases rich in carbon monoxide and hydrogen obtained from fossil fuel reservoirs and natural gas, and is primarily used for fuel synthesis and other industrial processes. Table 2 compares the composition of the ESD-SIC emissions after desulphurization and syngas used for chemical synthesis of methanol.

Table 2 - Molar compositions of ESD-SIC emissions before Energy Recovery Plant and Syngas (Rostrup-Nielsen & Christiansen, 2011; European Commission, 2007)

	Silicon carbide plant emissions	Syngas composition
H ₂	40%	57%
CO	28%	29%
CO ₂	27%	3%

Regarding the quantity of emissions, ESD-SIC is under the ETS system, with considerable emissions of 130 kt/yr of CO₂ on average in the last seven years. In Figure 11, the behaviour of the emission of the Dutch factory in these years is illustrated.

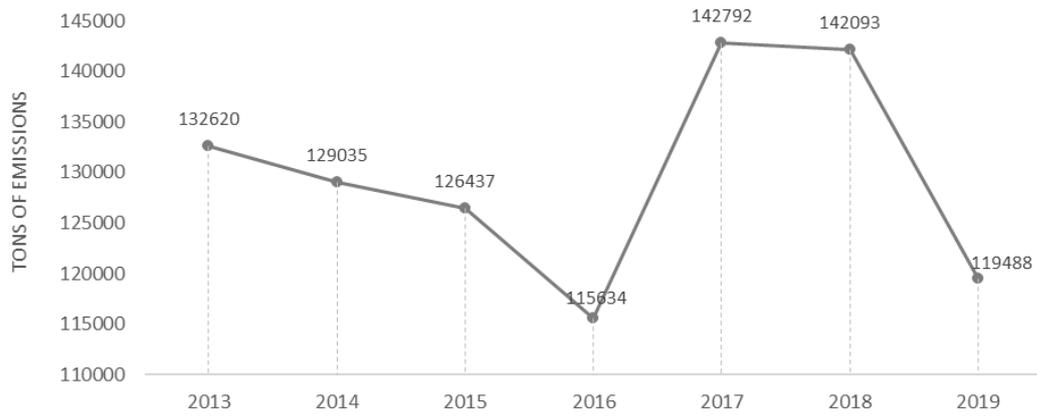


Figure 6 - ESD SIC emissions from 2013 to 2019 (EEA, 2020)

3 Silicon carbide products and application

Silicon carbide is a very distinguished material with valuable characteristics used in several applications, both in industry and in daily life products. Due to its physical hardness, it can be used from coarse to very fine in several applications being an essential material in the abrasive processes like grinding, honing, sandblasting, and water jet cutting. Moreover, this high surface hardness allows it to be used in many engineering applications where a high degree of sliding, erosive and corrosive wear resistance is required. Typically, it can also be applied as a component in pumps or in valves in oilfield applications, where conventional metal components would display excessive wear rates that would drive to rapid failures (ESD-SIC, 2020). Those properties and applications are important for different industrial processes and equipment, making the SiC an essential material for the industry, although not usually mentioned.

3.1 Products and Applications

There are different types of silicon carbide produced in the industries worldwide, the two main ones produced by ESD-SIC B.V. are crystalline and amorphous silicon carbide, as shown in Figure 7. The crystalline silicon carbide is the purest form of the product with hardness compared to a diamond and presents a hexagonal structure. It is used in the electronic industry to replace silicon chips in semiconductors as it provides better efficiency and form factor (GVR, 2019). It is also more suitable for the production of diesel particulate filters, refractories, abrasives, technical ceramics, steel, and construction industry. The amorphous SiC is formed further to the graphite core in lower temperatures in comparison to crystalline SiC and is used for the alloying, reduction, and pre-inoculation of cast iron and/or steel. Besides crystalline, ESD-SIC produces as by-product amorphous 'metallurgical' SiC in granules for use in induction furnaces for cast iron and of SiC briquettes for cupola furnaces (ESD-SIC, 2020).

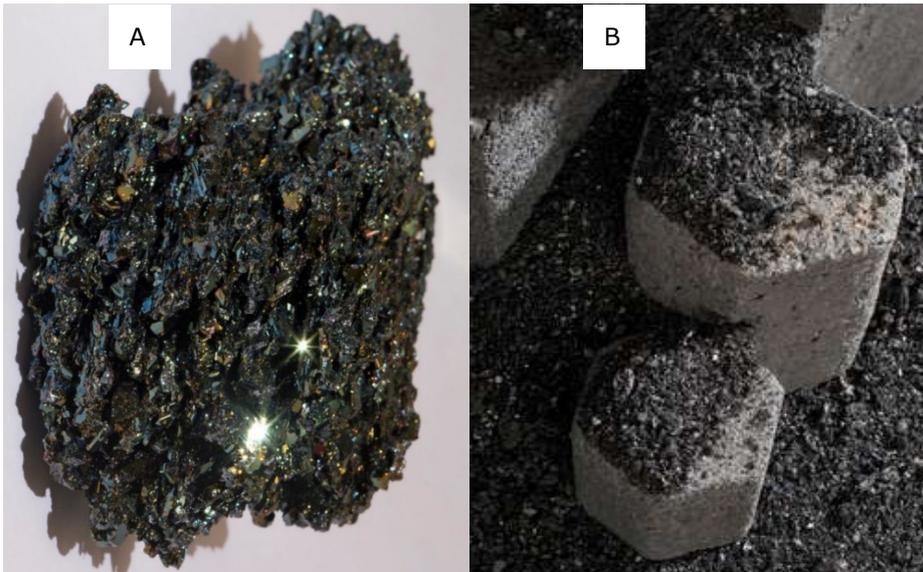


Figure 7 - Crystalline (A) and Amorphous (B) silicon carbide.

In 2019, amorphous (metallurgical) silicon carbide accounted for a 55.3% revenue share of the silicon carbide market, owing to the increasing consumption of steel and growing automobile and construction industries (GVR, 2019). The silicon carbide has essential applications in the automotive segment, such as in the manufacturing of power electronic devices for electric vehicles that operate at elevated temperatures. The share of this segment in the SiC market is expected to grow even more; according to the International Energy Agency, the global sales of electric vehicles are anticipated to reach 44 million per year by 2030 (IEA, 2019). Figure 8 shows the market applications for silicon carbide in 2019, revealing the important position held by the steel, aerospace and automotive sectors.

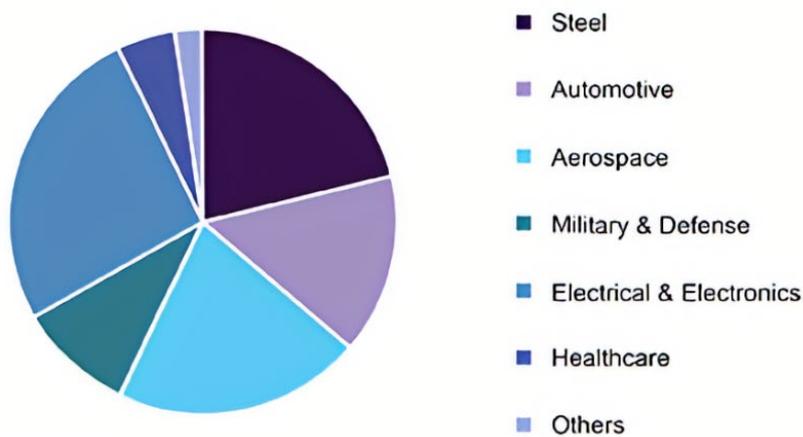


Figure 8 - Global Silicon Carbide market share by application (GVR, 2019)

The ability of Silicon Carbide to resist very high temperatures without breaking or distorting broaden its use in technical ceramics. One of the significant advantages it represents to these applications is the high thermal conductivity of the material, which allows to dissipate the frictional heat generated at a rubbing interface. The material is therefore suitable to be used in parts that are usually more exposed to high temperatures, large temperature ranges or extreme wear. Its use in the manufacture of ceramic brake discs for sports cars and also in rotating parts of industrial machines, ball bearings, and heat shields for the aerospace industry are examples of such application.

There are also new applications of SiC that are worthy to mention, such as diesel particulate filters for diesel engines, use in bulletproof vests as an armour material and as a seal ring material for pump shaft sealing - where it frequently runs at high speed in contact with a similar silicon carbide seal (INSACO, 2019).

In addition to the physical properties, the electrical properties of silicon carbide have influenced the material to become increasingly important in the electrical and electronic sectors. SiC semiconductors use is becoming an innovative alternative for silicon semiconductors for power electronic designers due to its low switching losses, high power density, high thermal conductivity, reduced sink requirements, and high-temperature operation. Besides this use, the combination of electrical and heat resistance makes it also valuable in other industrial sectors, such as in the aerospace industry as an ideal mirror material for astronomical telescopes, and in nuclear power structures, gas collectors, and high temperature sensors.

Silicon carbide is considered vital for future technologies with a trend for higher demands for purity and unique properties. Among the future technologies, those that stand out as the most promising are SiC membranes and additive manufacturing, modern composites, particulate filters and other technologies for water treatment. Some of these applications already present a particular established market that started using silicon carbide in finer qualities, such as functional fillers, high experimental and laboratory electronics and photovoltaic solar systems (ESD-SIC, 2020).

3.2 Product Market Worldwide

In 2019, the market size for silicon carbide production was estimated to be 2.52 billion dollars worldwide (GVR, 2019). The growth in the manufacturing steel production to satisfy the increasing demand from end-use industries is expanding the demand for refractories, which is likely to promote the SiC market increase over the following years since it is utilized as the primary raw material in refractories production. Also, there is an increasing interest in silicon carbide semiconductors as they are faster and have outstanding resistance when compared to the silicon ones. In that case, the market is driven by the two sectors: the electronics industry and the growing utilization of renewable energy. In this scenario, it is expected to have a compound annual growth rate (CAGR) of nearly 16.1% from 2020 to 2027 in the silicon carbide market (GVR, 2019). Figure 9 shows the expected growth in the silicon carbide market for the next years, according to the actual patterns of distribution of the global market per product.

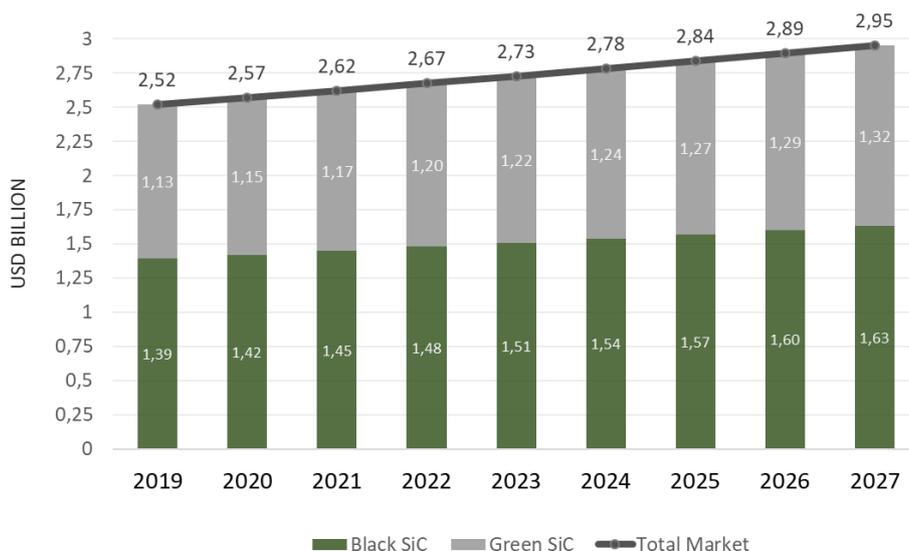


Figure 9 - Silicon carbide market size by product from 2019 to 2027. Adapted from GVR (2019). Green silicon carbide is more pure compared to black silicon carbide.

When evaluating the whole global production, Asia Pacific is the primary producer of silicon carbide, responsible for 59.4% of the market share in 2019, mainly because of the growing manufacturing sector in countries like India and China. In India, this growth is related to the increasing expenses in infrastructure, the necessity to provide housing, which triggers the demand for crude steel. As a result, approximately a cost of 650 billion dollars in city infrastructure is expected for the following 20 years. Another critical player in the market is North America. The growing interest of lightweight vehicles is boosting silicon carbide abrasive producers to engage in long term contracts offering various products that match the necessities of automakers. Europe is also anticipating a growth in the market in the next years, mainly due to new investments in aerospace technology, the expansion of defence industries and the automotive production, pushing to a Compound Annual Growth Rate (CAGR) of 7.5% in volume from 2020 to 2027 (GVR, 2019).

3.3 Dutch Silicon Carbide Market

The field of silicon carbide companies is highly active, with industries adopting different tactics such as mergers, acquisitions and joint ventures to develop their commodity portfolio and to achieve leading positions in the market. The major market players are: AGSCO Corporation, Carborundum Universal Limited, Dow Chemical Co., Entegris, Inc., ESD-SIC B.V., ESK-SIC GmbH, Grindwell Norton Ltd, and Saint Gobain Ceramic Materials GmbH. The silicon carbide industry consumes a significant amount of energy, which has driven many producers to locate their plants close to low-cost energy sources (GVR, 2019). The Dutch production of silicon carbide is primarily exported, and the main trading partners are the countries from the European Union, holding around 94% of the exports in 2019 (Figure 10). Germany is the leading trading partner and is where most of the Dutch production is sent to internationally. A small amount of this material is still imported by the industry, in which the leading trading partners are currently countries outside the European Union and are responsible for 90% of the total imports to the Netherlands. The volume of imports is lower in the Dutch market, representing about 27% of the volume of exports in 2019 (CBS, 2020).

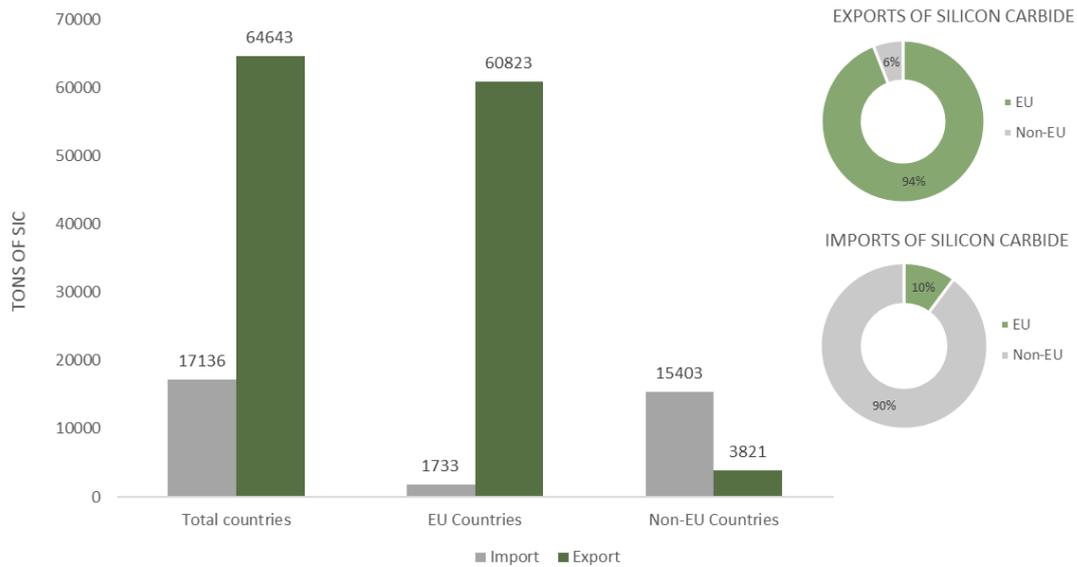


Figure 10 - Import and export volumes in the Dutch silicon carbide market between January and November 2019. Adapted from CBS (2020).

Regarding the Dutch annual export rate, the analyses of the last data reported in the CBS (2020) database for mineral and chemical goods shows that there is a fluctuation around 60 to 80 kt of silicon carbide per year. Figure 11 shows that data, where the only outlier is the year of 2009, where the imports were low principally due to the economic crises of 2008, recovering in the following year. It is possible to distinguish a slight increase in average exports in the last years, a trend that was supported by the GNV (2019) study, but that will have to be re-evaluated with the 2020 post-pandemic economics outcomes.

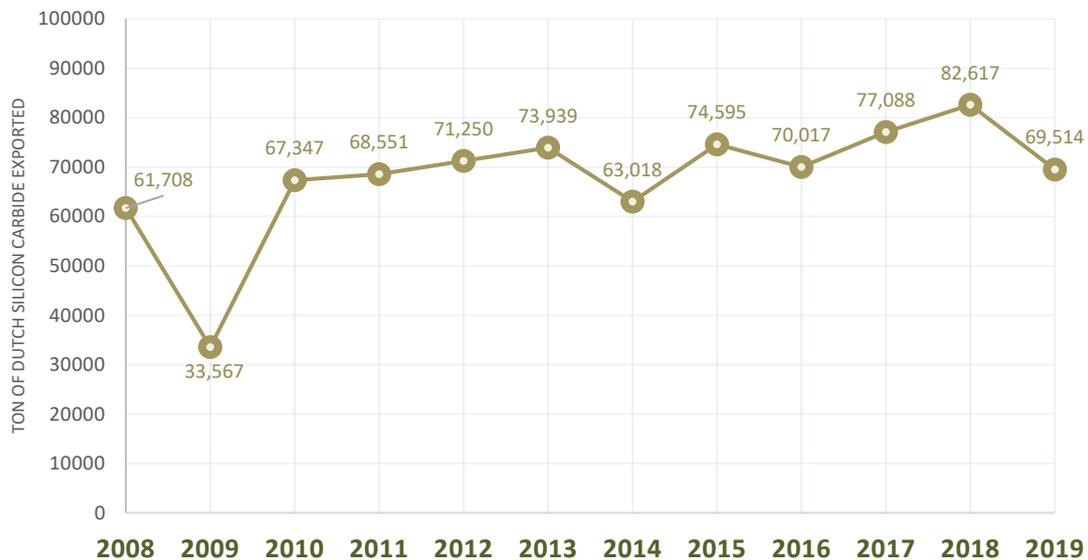
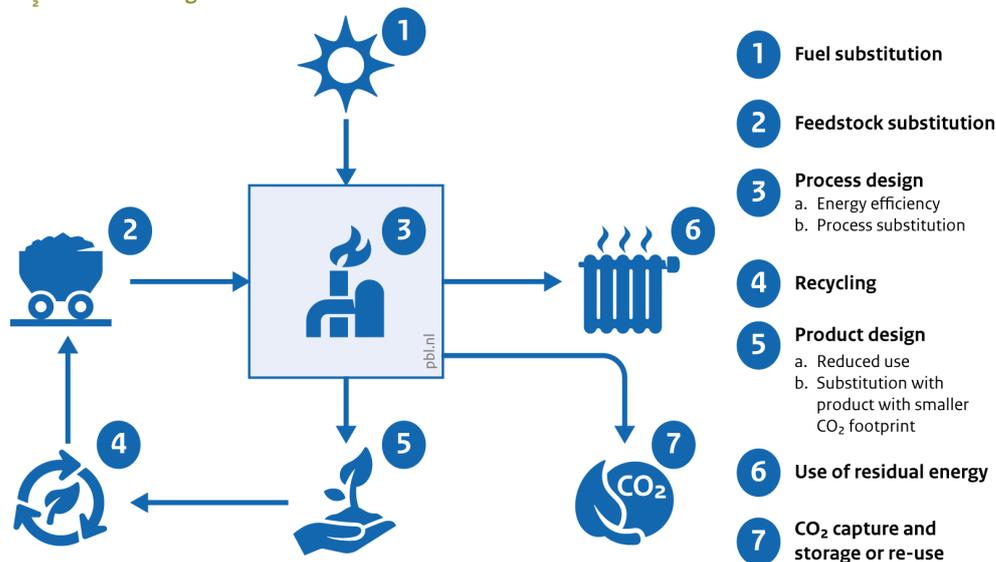


Figure 11 - Dutch silicon carbide exports from 2008 to 2019 (CBS, 2020).

4 Options for decarbonisation

This section describes possible decarbonisation options for the silicon carbide manufacturing process. Conceptually, there are several different actions that can reduce carbon emissions in an industrial process. The methodology adopted in MIDDEN to explore and evaluate each option is illustrated by Figure 12. Literature review and analysis of each specific technology were key aspects of the investigation.

CO₂ reduction categories



Bron: PBL

Figure 12 - CO₂ reduction categories

The main decarbonisation options for the ESD-SIC that have been identified are:

- Alternative feedstock using biocoke as a substitute for the petroleum coke as a carbon source.
- Carbon Capture and Storage (CCS) to reduce the greenhouse gas emission after the energy recovery plant.
- Carbon Capture and Utilization (CCU) with methanol and ethanol/ethylene synthesis to reduce the greenhouse gas emission after the silicon carbide production in the oven.

Other decarbonisation options that are discussed in this report are:

- Process design changes with mechanical activation of feedstock and microwave heating.
- Process substitution with use of magnesium as a reducing component and changing the chemical reaction.

- Recycling.

4.1 Alternative Feedstock: Biocoke

Petroleum coke is widely used as feedstock in the silicon carbide manufacturing industry due to its properties (high carbon purity), high rate of fixed carbon (less volatiles) and relatively low prices in the market. This material is a by-product from oil refineries and contains traces of sulphur and nitrogen in its composition, being responsible for NO_x and SO₂ emissions in the combustion process of the waste gas (Wanga, Anthonya, & Abanades, 2004). For a product from a fossil fuel source, the continuous use of this material is unlikely in a decarbonised future scenario, which drives researchers to find alternatives. This section presents a novel possible option for the future of this sector.

Biocokes are secondary products from the high-temperature pyrolysis upgrading processes to produce renewable fuels from biomass. This material can be efficient in greenhouse gas emission mitigation by allowing carbon-neutral processes, as it is not produced from fossil sources. This because using biomass instead of petroleum sources means not increasing the amount of carbon present in the natural cycle, allowing for more sustainable production if sustainably managed. Research on the current production of biocoke from pyrolysis shows that its moisture levels are below 2 wt.%, having also zero sulphur, almost no ash, and low oxygen content when compared to petroleum coke. This represents less side reactions and volatile products in the oven. However, more nitrogen retained can increase the NO_x emissions (Sanna, Ogbunike, & Andrésen, 2009). This product has been viably produced from different kinds of sources such as fruit peels, waste shells, woody and vegetal biomasses, rice wastes, biomass sawdust, oil palm biomass, and green wastes (Mansor, et al., 2018). It can have slightly different compositions regarding its carbon, oxygen, nitrogen, and ash content according to which biomass and pyrolysis process is used.

Biocoke with high fixed carbon (C_{FIX}) content and low volatiles are produced in high-temperature processes, with at least 700°C pyrolysis. Volatiles are a mixture of hydrocarbons, aromatic hydrocarbons, and sulphur that are released in high temperatures and promote side-reaction and lower reaction efficiency (Stockman, Turnbull, & Kretzmann, 2013). Fixed carbon is a measure of the amount of pure carbon in a carbon-rich material sample. For petroleum coke, this parameter represents its dry mass minus the volatiles and ash weight. The term calcined biocokes used here addresses the biocokes produced in even higher temperatures and with carbon content similar to the petroleum coke. In Table 3 different temperatures of pyrolysis and its biocoke composition show that the increase in temperature also increases the biocoke purity, reaching similar levels to calcined petroleum coke. Also, a comparison with the petroleum coke used by ESD-SIC was added for further consideration.

Table 3 - Biocoke, calcined biocoke and calcined petroleum coke compositions with different carbonation temperatures (Stockman, Turnbull, & Kretzmann, 2013).

	Temperature (°C)	C _{fix} (%)	Volatiles (%)	Others(%)
Biocoke	715	85.0	11.0	4.0
Calcined Biocoke	978	93.0	2.0	5.0
Petroleum Coke	-	91.0	9.0	0.0

A study by Huang et al. (2018) gives another comparison between calcined biocoke and calcined petroleum coke regarding its composition and microstructure when carbonized at

the same temperature (1200°C). Again, the ESD-SIC petroleum coke was added for comparison. The composition analyses also showed that both materials at same temperature have a similar C_{FIX} , but they have considerable differences on its sulphur and oxygen content. As shown in Table 4, calcined petroleum coke has more sulphur and less oxygen than calcined biocoke. On the other hand, when compared to the petroleum coke, we see that for this calcination temperature, the calcined biocoke reaches better levels of C_{FIX} and sulphur content. Besides that, the microstructure analyses done by Huang et al. (2018) showed small differences on its particles, with biocoke being more reactive and usually have bigger and more porous grains. Despite these differences, the article concluded that, in general, the calcined biocoke was suited for being used as a substitute to calcined petroleum coke.

Table 4 - Petroleum coke and Calcined biocoke compositions (C, O, S) calcined at the same temperature (Huang, Kocaefe, & Kocaefe, 2018).

AT 1200°C	CARBON (C) WT %	OXYGEN (O) WT %	SULPHUR (S) WT %
Calcined petroleum coke	96.62	1.94	1.45
Calcined biocoke	92.97	6.4	0.63
Petroleum coke	91.18	-	2.56

Different forms of biocoke production with different biomass raw materials can produce distinct biocoke that can achieve certain characteristics. Figure 13 presents a production process for high CFIX carbon biocoke produced after bio-oil pyrolysis according to Elkasabi et al. (2018). That production process could result in a biocoke with the suitable specifications of the ones required by silicon carbide production.

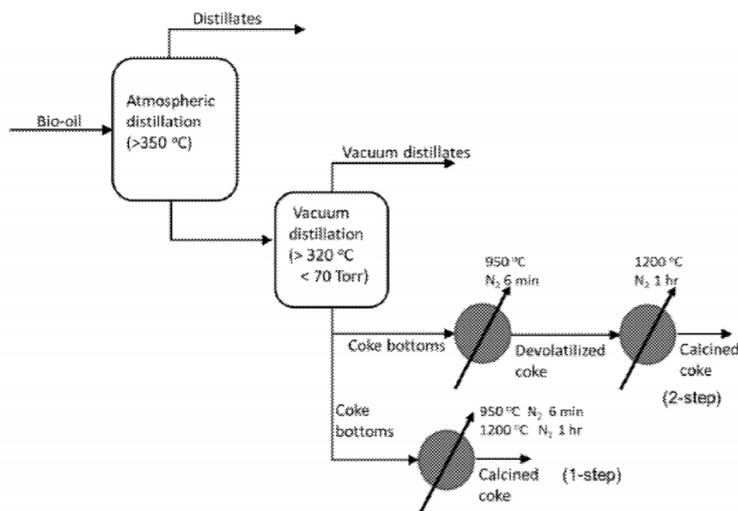


Figure 13 - Method for producing calcined biocoke from biomass (Elkasabi et al. 2018).

Testing with different types and amounts of biocokes needs to be done to find out if a same or even better high quality of SiC can be produced with the same or less energy consumption, and without furnace disturbances and undesirable side reactions. ESD-SIC is currently researching biocoke utilisation and is considering doing trials starting with 1% biocoke feedstock with gradual increases. The company claimed that this option demands more research on the possible outcomes from the differences in composition when applied to the silicon carbide industry, such as an increase in the flue gas production (internal

communication with ESD-SIC, 2020). Another limitation regarding biocoke is the lack of large-scale production for this material with the specifications needed. ESD-SIC requires about 70,000 tonnes per year of petroleum coke (internal communication with the company, 2020). According to Fuchigami, Hara, Kita, Uwasu, & Kurimoto (2016), biocoke production related emissions are around 1.01 tonne CO₂/tonne, while this number is 3.36 tonne CO₂/tonne for petroleum coke (Stockman, Turnbull, & Kretzmann, 2013). For the biocoke, this value corresponds to its manufacturing and transportation processes. It can be lowered by 75% with renewable energy use, corresponding to an emission of 0.25 tonne/CO₂ per tonne. Thus, the alternative feedstock can represent a GHG emission reduction from around 164.5 up to 208 kt of CO₂ per year in scope 3 emissions, as shown in Table 5. Besides that, the use of biocoke has the advantage of no need for process gas desulphurisation, due to the low content of sulphur in its composition. Also, it allows further processes of separating H₂ by catalysis, which is not done due to S-content that contaminates the catalytic reactor.

Table 5 – Estimated scope 3 CO₂ emissions (related to feedstock production and transport) for petroleum coke and biocoke

	ESD-SIC feedstock Demand (kt/year)	Feedstock production and transport emissions (t CO ₂ /tonne)	Estimated scope 3 emissions for ESD-SIC related to feedstock (kt CO ₂ /year)
Petroleum Coke	70	3.36	235
Biocoke	70	1.01	71
Difference			-165

Biocoke has a recent market scaling up from experimental to industrial in some countries, especially in Japan. This country already produces biocoke in industrial sites, such as NANIWA ROKI, which exports biocoke to other countries. Currently, the annual production in Asia is 3,000 tonnes, Japan is responsible for 2,100 tonnes and Thailand for 900 tonnes (Japan International Cooperation Agency, 2013). The production is geared exclusively to biocoke as fuel (as an alternative to coal in industrial processes). Thus, the C_{FIX} and composition are not the same ones needed for the silicon carbide industry. Besides that, the production facilities would support the production of calcined biocokes if there was a demand for it. Two different market analyses developed studies in two types of biocoke production, Japan International Cooperation Agency, (2013) and Fuchigami et al. (2016). The main results regarding the targeted selling price are presented in Table 6.

Table 6 - Biocoke market price

	TARGETED SELLING PRICE JAPAN ¹	TARGETED SELLING PRICE JAPAN ²	TARGETED SELLING PRICE THAILAND ¹
BIOCOKE	327 €/tonne	416 €/tonne	365 €/tonne

¹ (Japan International Cooperation Agency, 2013)

² (Fuchigami, Hara, Kita, Uwasu, & Kurimoto, 2016)

By selecting the lowest price discovered in this benchmarking it is possible to estimate future cost for the feedstock substitution. Once the product is not imported yet, both target selling prices are used for comparison, as presented in Table 7.

Table 7 - Costs of the alternative feedstock.

	BIOCOKE	PETROLEUM COKE	COST DIFFERENCE
Selling Prices	327 € ₂₀₁₉ /tonne	100 € ₂₀₁₉ /tonne (excluding EU ETS price of combustion emissions ¹)	+ 227 € ₂₀₁₉ /tonne
Costs For ESD-SIC (67.000 tonne)	21.9 MEUR ₂₀₂₀ /year	6.7 MEUR ₂₀₂₀ /year	+ 15.2 MEUR₂₀₂₀/year

4.2 Carbon Capture and Storage

Carbon Capture and Storage (CCS) involves capturing the carbon dioxide emitted from fuel combustion or industrial processes, transporting it, and storing it permanently in a safe space. Capture includes either pre-combustion separation of CO₂ from other gases or separation of CO₂ after combustion. The transport usually consists of the compression of CO₂ and shipping from the producing area to the storage place, done through pipelines, ships, or by road or rail. Storage requires inserting this CO₂ into underground rock formations at depths of kilometres and can be done either onshore or offshore (IOGP, 2019).

CCS is a common theme for decarbonising industry due to its wide application among different sectors and relatively limited adjustments to existing processes. Growing investments and research on CCS technologies focus on improving the actual technologies towards higher capture efficiency and lower costs (IEA, 2019a). ESD-SIC releases its emissions after the energy recovery plant, when the hydrogen and carbon monoxide content are burned. Its composition is shown below in Table 8, disregarding water vapor and nitrogen emissions.

Table 8 - ESD-SIC emissions to the environment in Vol% (excluding water vapour and nitrogen) (Rijksoverheid, 2017)

CO ₂	SO ₂	CO	NO ₂	CH ₄	NH ₃	H ₂ S
99.4%	0.31%	0.23%	0.02%	0.01%	0.005%	0.003%

4.2.1 Post-combustion capture

The most straight-forward capture of CO₂ emissions generated by the combustion of fuels in the atmosphere is post-combustion capture. Alternately of being released straight to the air, flue gas goes through separation steps in which most of the CO₂ is recovered from the main flow. The CO₂ goes to a storage tank, where it is compressed, and the remaining gas is released to the environment. The most relevant technology for this process currently is a chemical sorbent process (Wang, Lawal, Stephenson, Sidders, & Ramshaw, 2010). It brings the related emission flow in contact with a liquid or solid absorbent able to capture the CO₂. Other methods can also be analysed, but they do not have such an advanced stage of development. These other methods include adsorption, cryogenics separation, and membranes (Wang, Lawal, Stephenson, Sidders, & Ramshaw, 2010). In theory, post-combustion capture methods can be used to flue gases generated from the burning of every sort of fuel (IPCC, 2005). However, the CO₂ concentration in the flue gas can be a limiting

¹ CO₂ emissions due to combusting one tonne of petroleum cokes are 3.4 tonne CO₂, using emission factors reported by RVO (RVO, 2020). A EU ETS price of 66 EUR/tonne would represent a value of 227 EUR/tonne cokes in EU ETS allowances.

factor because the lower it is, the more costly the implementation of the technology. According to Ferguson & Stockle (2012), the higher the concentration of CO₂ (particularly above 10%) of the flue gas, the most suitable it will be for post-combustion capture.

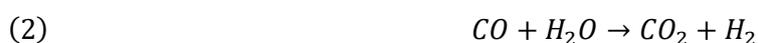
4.2.2 Oxyfuel combustion and capture

In oxy-fuel combustion, almost pure oxygen is utilized in the combustion process instead of air, increasing the concentration of CO₂ in the flue gases and reducing the efforts for CO₂ separation and facilitating its capture after the combustion. With this method, the combustion emissions consist essentially of CO₂ and water vapor with excess oxygen, that also helps to guarantee a total combustion (IPCC, 2005). This procedure can include different installations such as an air separation unit (ASU), a CO₂ capture and compression unit and utilities. The oxygen is separated at a low temperature (cryogenic) air separation. New methods and technologies can provide different routes to produce oxygen to the fuel, such as membranes and chemical looping cycles (Falkenstein-Smith, Zeng, Pingying, Ahn, & Jeongmin, 2017). In ESD-SIC the main fuels are hydrogen and CO, and the oxidation of the combustion process is atmospheric air. Thus, this method is relevant for simplifying the post-combustion separation, in theory producing mainly CO₂ and water as final emissions – components that can be relatively easily separated.

4.2.3 Pre-combustion capture

The traditional route for a pre-combustion capture requires, first, reacting the hydrocarbon fuel with oxygen/air and steam, producing syngas. The second reaction would be in a catalytic reactor between the carbon monoxide and steam, consuming all CO and producing more CO₂ and more hydrogen. Finally, with a gas containing only carbon dioxide and hydrogen, the CO₂ can usually be separated by an absorption process. It results in a hydrogen-rich fuel that can be utilized in several applications, such as boilers, furnaces, gas turbines, engines, and fuel cells (IEA, 2019a).

For ESD-SIC, however, this process should be done differently. As discussed in Section 2.3 and shown in Table 2, the ESD-SIC pre-combustion gas is already similar to the syngas used in this process. For that reason, it would be possible to jump the first step of this method, since it already has H₂ and CO in the pre-combustion stream. The route for ESD-SIC would only follow the chemical reaction in Equation 2 (DECHEMA, 2017), transforming all CO in CO₂ to then be followed by the absorption and separation step.



4.2.4 Cost Analyses

There are three different technologies to be considered regarding the capture of CO₂ with different prices that will be analysed individually. The costs of transport and storage of CO₂, however, are assumed to be the same for these technologies. The cost analyses for the Pre combustion and post-combustion technologies are based on the "*Eindadvies Basisbedragen SDE++ 2021*" report from Lensink & Schoots (2021). It considers a scenario with new CO₂ capture at existing installations using capture, liquified transport and storage. The document presents the current status of the technology according to parameters and on a similar industrial scale. The investment costs include capture, purification, compression and liquefaction. The fixed O&M costs include salary costs, administrative and overhead costs, operation and maintenance, insurance and local taxes, and are assumed to be 3% of the

investment costs. The oxyfuel combustion technology was not present in the analysis of the SDE++ document, so the basis used on the estimation was the study on "The cost of CO₂ capture and storage" by Rubin, Davison, & Herzog (2015). This study presents an analysis for large plant capacity, applied to a power plant. To scale down these parameters, the rule of six-tenths was applied, as is explained in ANNEX C. The O&M costs do not include utilities. The storage costs assume the use of the Porthos CO₂ storage infrastructure in Rotterdam. Table 9 presents an overview of the results.

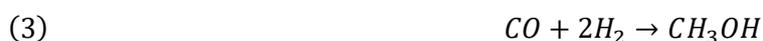
Table 9 - Cost overview for CCS alternatives for ESD-SIC (costs rounded to nearest integer)

	INVESTMENT COST [EUR ₂₀₂₀ /annual tonnes of CO ₂ avoided]	ANNUAL FIXED O&M COSTS [EUR ₂₀₂₀ /annual tonnes of CO ₂ avoided]	SOURCE
PRE-COMBUSTION CAPTURE	€ 325	€ 10	(Lensink & Schoots, 2021)
OXYFUEL COMBUSTION CAPTURE	€ 151	€ 5	(Rubin, Davison, & Herzog, 2015)
POST COMBUSTION CAPTURE	€ 573	€ 15	(Lensink & Schoots, 2021)
TRANSPORT COSTS (BY SHIP)		€ 20-60	(Lensink & Schoots, 2021)
STORAGE COSTS		€ 17	(Lensink & Schoots, 2021)

4.3 Carbon Capture and Utilization

4.3.1 Carbon Capture and Utilization with Methanol Synthesis

Methanol is a liquid material with the chemical formula CH₃OH. It is a type of alcohol that is usually produced using syngas as its primary reagent. It is one of the largest commodities produced in volume in the chemical industry. It has several different applications, of which the main ones are as feedstock for other chemicals synthesis (e.g. MTBE) and as fuel² (Cheng & Kung, 1994). Since the first fossil fuel exploitations, its reservoirs are the primary source utilized for methanol generation in the industry, principally because of its suitable mixture of gases. For this case, the primary chemical reaction is presented below:



More recent research in decarbonisation techniques shows that this synthesis can also be done using CO₂ in a slightly different chemical route, which is a good option for the CCU process. In this alternative route, the CO₂ reacts with H₂ to create the carbon monoxide needed for the main reaction. The following reaction then is between the produced carbon monoxide with hydrogen to produce methanol. The most significant difference between this route and the traditional one is that syngas has already reasonable amounts of hydrogen and carbon monoxide within its components, even though sometimes the composition mix needs to be modified by addition of extra H₂. In contrast, for the process that uses exclusively fossil fuels, the H₂ and the CO have to be produced deliberately (DECHEMA, 2017). Figure 14

² Note that when the methanol is used as fuel, the CO₂ is eventually released when it is combusted.

shows the scheme for an industrial synthesis route. Equation 4 and Equation 5 are the two main reactions for the production of methanol via CCU.

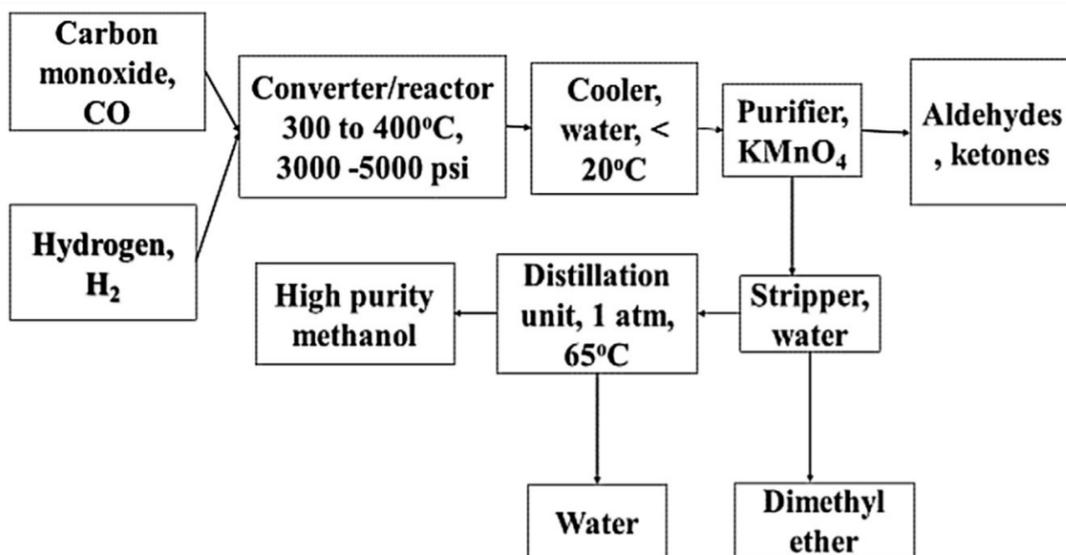


Figure 14 - Process scheme for CCU methanol synthesis

Application to ESD-SIC site

ESD-SIC emission's composition is already similar to the syngas mostly found in literature. Thus, the process of synthesising methanol from the company emissions would require lower amount of hydrogen than if the flue gas presented had only carbon dioxide. For this reason, the potential of methanol production via CCU from ESD-SIC emissions was investigated. The synthesis is stimulated by more H₂ and less CO₂, fact that is explained by Hankin & Shah, (2017), which presents Equation 6 to demonstrate the ideal mix of gases:

(6)
$$S_R = \frac{(H_2 - CO_2)}{(CO + CO_2)}$$

The stoichiometric value for S_R for a complete reaction should be 2, but the real optimal ratio changes according to the reactor used, ranging between 2.1 and 5. The bigger the S_R number, the more H₂ concentrations relative to CO₂ are needed. For this reason, obtaining a high S_R number for the synthesis is a challenge for the CCU technologies, since usually the industries emit mainly CO₂, which leads to a high demand of H₂ to balance it. Even for syngas, normally, the composition is not ideal and it has to go for a process of pre-treatment, that removes carbon dioxide or increases hydrogen quantity. Given the estimated SiC production emissions in Table 10, its S_R number was obtained (Equation 7).

Table 10 - ESD-SIC emission composition in moles and mass

	SIC Emissions (%mol)	Total (10 ⁹ Mols)	Molar Mass (g/mol)	Mass (kt)
H₂	40%	2.03	2	4
CO	28%	1.42	28	40
CO₂	27%	1.50	44	66

$$(7) \quad S_R = \frac{(40 - 27)}{(28 + 27)} = \mathbf{0.24}$$

Increasing the S_R number by removing CO₂ is not an option for the CCU alternative, once the objective is to utilise those emissions. For this reason, the solution is to increase the quantity of H₂ in the gas mix. For achieving an S_R ratio of 2.1, the lowest according to literature (Hankin & Shah, 2017), the theoretical minimum amount of H₂ that would be needed is approximately 15.3 kt/yr, which would allow to produce around 93.5 kt/yr of methanol. Table 11 shows the calculation process for those values.

Table 11 - Hydrogen demand and methanol production by CCU in ESD-SIC

Components	Mol x 10 ⁹ /yr	kt/yr
H ₂ needed for full capacity	7.63	15.3
H ₂ to be extra produced	5.60	11.2
Total methanol producing capacity	2.92	93.5

The utilization of CO₂ itself is the direct emission reduction. Stoichiometrically, 1.43 tonnes of the ESD-SIC emissions are used per tonne of methanol for the synthesis. Compared to the current final emissions of the industrial site with the ongoing industrial process, it would represent an emission reduction of 130 kt of CO₂ per year. However, emission related to eventual combustion of the methanol or the products for which it is used, should be included in the full analysis of the emission effects.

Cost Analysis

The cost analyses of this method are based on the research "*Comparison between two methods of methanol production from carbon dioxide*" by Anicic, Trop, & Goricanec (2014). This study presents all sub-installations needed for applying the methanol synthesis and the correct parameter for scaling them up or down in a cost analysis giving the capacity. That structure allowed this study to adjust the costs for H₂ production according to the ESD-SIC necessity, in a potentially more precise way. More about this can be found in ANNEX C. Table 12 presents the results of the cost analyses. The operational cost considers labour and maintenance but excludes costs for utilities. In the CCU installation:

- water electrolysis is the process to produce hydrogen;
- Reverse Water Gas Shift reactor (RWGS) correspond to the first reactor that reduces CO₂ transforming it to CO;
- the methanol reactor transforms the syngas (CO and H₂) into the product;
- the distillation increases the concentration of methanol in the stream;
- the PSA unit removes its impurities;

- then the methanol goes to the compressors to be prepared for the transport and storage.

Table 12 - Cost overview for CCU with methanol synthesis for ESD-SIC

CCU-INSTALATION	INVESTMENT COST [EUR ₂₀₂₀ /tCO ₂ /year]	ANNUAL FIXED O&M COSTS [EUR ₂₀₂₀ /tCO ₂ /year]	SOURCE
Water electrolysis	€ 58.33	€ 1.17	(Anicic, Trop, & Goricanec, 2014)
RWGS	€ 83.93	€ 1.68	(Anicic, Trop, & Goricanec, 2014)
Methanol Reactor	€ 90.43	€ 1.81	(Anicic, Trop, & Goricanec, 2014)
Methanol Distillation	€ 20.39	€ 0.41	(Anicic, Trop, & Goricanec, 2014)
PSA	€ 0.04	€ 0.00	(Anicic, Trop, & Goricanec, 2014)
Compressors	€ 6.78	€ 0.14	(Anicic, Trop, & Goricanec, 2014)
Labour		€ 1.53	(Motamedi, 2017)
TOTAL	€ 259.91	€ 6.73	(Anicic, Trop, & Goricanec, 2014)

4.3.2 Carbon Capture and Utilization with Ethanol and Ethylene Synthesis

Another way to use the carbon content present in the ESD-SIC process gas as feedstock for other purposes and avoid direct emissions is the synthesis of ethanol and ethylene. Ethanol, also called alcohol or ethyl alcohol, is a component of a wide variety of products, from personal care and beauty products to varnishes and fuel³. Usually, it is produced as a by-product of biomass fermentation or through the hydration of ethylene, and it's an important feedstock for a vast number of industries. Also, ethylene is another high-value gaseous aggregate normally produced by steam cracking in the petrochemical industry. It has a wide range of use in the industry with many different applications, e.g., anaesthetic or fruit ripening agent and feedstock for polyethylene, ethylbenzene, and other chemical compounds.

Recent studies have found various synthesis routes for ethanol and ethylene production, one of them (highlighted in this Section) is using carbon monoxide as one of the main feedstocks. This route is usually known as the LanzaTech method, named after LanzaTech, a New Zealand based company founded in 2005, which was the first to develop a bacteria capable of fermenting the carbon-monoxide from chemical waste gas and produce ethanol (Karlson, Bellavitis, & France, 2018). This chemical route is patented by LanzaTech, which is working to upscale and adapt the technology to different process gases with a high concentration of carbon monoxide or even using syngas as a feedstock for fermentation.

The process can be defined as an anaerobic fermentation of a CO-rich gas to produce ethanol using bacteria. The LanzaTech method mentions ten different genera of microorganisms that can be applied to this process: Moorella, Clostridia, Rumino coccus, Acetobacterium, Eubacterium, Butyribacterium, Oxobacter, Methanosarcina, and Desulfotomaculum. The ethanol synthesis happens in a bioreactor containing the bacteria culture (with one or more species) and nutrients, such as vitamins and minerals, to allow the microorganism growth,

³ Note that when the ethanol is used as fuel, the CO₂ is eventually released when it is combusted.

where the CO-rich process gas should be injected. The fermentation should happen under suitable circumstances of temperature, CO flow rate, pH, media redox potential, agitation rate, inoculum level, nutrients concentration according to the bacteria species chosen. The process gas stream that enters the bioreactor can contain components other than CO, such as CO₂ and H₂, but the higher the CO concentration, the more efficient is the reaction. The maximum pressure allowed in the system is 10 bar. The resulted bioreactor product is called fermentation broth. It comprises the ethanol and by-products (such as acetate and butyrate) as well as the bacterial content and nutrients (Patent No. US 2013/0157322 A1, 2011).

In some configurations, the ethanol produced during the fermentation is already converted to ethylene while it is still in the fermentation broth. In other cases, it is desired to recover it first, and then use it as ethanol or convert it to ethylene in a second stage. For that reason, it is vital to remove the product from the broth at the right moment according to the desired product. The ethanol/ethylene recovery can be done in different ways. The LanzaTech method describes a continuous removal of a portion of broth that passes through a separation unit to recover bacterial cells from the broth. The results are a cell-free ethanol-containing permeate and a recycle stream to the bioreactor rich in bacterial cells. The ethanol permeate may then be used then for subsequent conversion to ethylene or for other applications. The by-products may also be recovered from the fermentation broth using, for example, an adsorption system involving an activated charcoal filter or electro dialysis (Patent No. US 2013/0157322 A1, 2011).

To convert the ethanol to ethylene, and later the ethylene to other components, several different methods can be used and are already described in the literature. In this technology route, the main method to obtain ethylene is through dehydration of ethanol. The most common way to do this by is using activated clay, phosphoric acid, sulphuric acid, activated alumina, transition metal oxide, transition metal composite oxide, heteropolyacid, or Zeolites as a catalyst. Ethylene can be used subsequently in a variety of processes for producing commercially useful chemical products (Karlson, Bellavitis, & France, 2018). Figure 15 presents the process scheme for the LanzaTech method, with the components of gas reception, compressor, bioreactor, recovery/separation unit and storage tank.

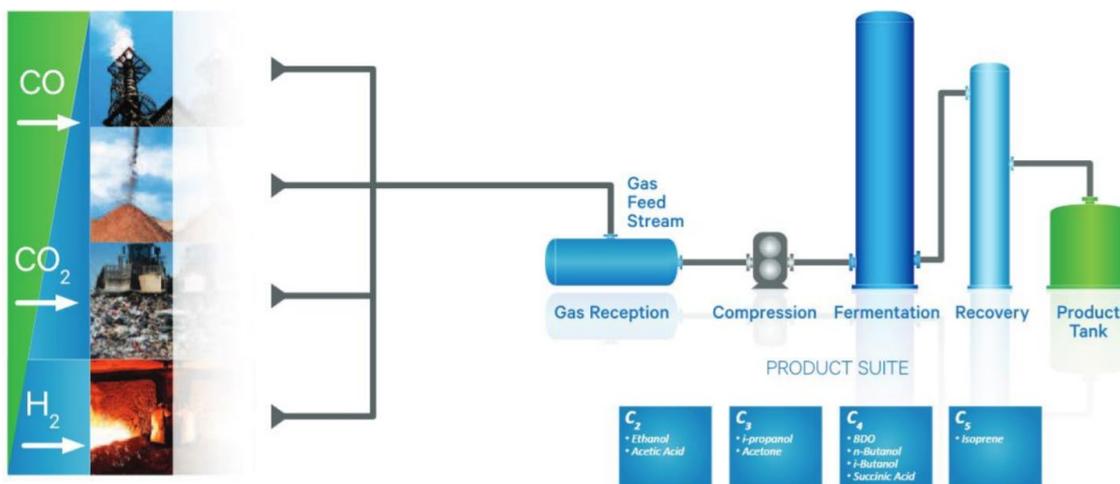


Figure 15 - LanzaTech process scheme for ethanol production with syngas as feedstock (LanzaTech, 2016).

The utility inputs for all process situations are mainly electricity and medium-pressure steam, with different specific requirements depending on the gas mix composition. However, those inputs of electricity and steam are confidential and protected by the patent held by LanzaTech. Even though those inputs are essential information to evaluate the extent of the

environmental impacts generated by this process, the LanzaTech company is audited to ensure that the internally produced steam and electricity is taken into account on its environmental assessment. The decrease in the CO content of the gas streams after this process is registered to be from 67% to 98%, varying according to the composition of the process gas utilized (Handler, Shonnard, Griffing, Lai, & Palou-Rivera, 2016).

For the ESD-SIC site, the process gas composition after the oven has an ideal CO quantity for the development of such a process. With 28% (40 tonnes of carbon monoxide per batch), this method could considerably reduce the gas carbon content. It could also be used to reach zero scope 1 emissions for ESD-SIC if the CO₂ content (27% of the volume, corresponding to 66 tonnes per batch) could also be converted to CO and used to produce ethanol in the bioreactor.

4.4 Process Design Changes

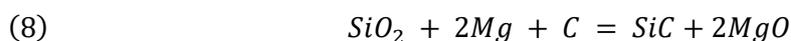
Process design changes are modifications in the current industrial process that could lead to improvements in energy efficiency or a less-carbon intensive alternative for the current production. It is important to recall that improvements in energy efficiency help decrease emissions in scope 2, but they might not lead to complete decarbonisation. In this report, different types of changes found in the literature were studied and discussed.

4.4.1 Microwave Heating

Microwave energy can be an alternative to deliver better results in the silicon carbide industry. By direct coupling, this equipment can volumetrically warm substances with the needed dielectric qualities. The process goes in quite a distinct form from traditional heating methods, not depending on external radiant energy. In the ceramic industry, it also improves the diffusion of certain chemical species and some experimental studies show that microwaving can reduce the reaction time in three times the original one (Dai, et al., 1997). However, there are differences in the microstructure of the silicon carbide produced from ovens and from microwaves, on which the size of SiC powders has smaller size. The lower formation temperature required for the reaction and higher formation rate leads to energy saving and shorter reaction duration, which inhibits the growth of crystal structures and crystallization (Dai, et al., 1997).

4.5 Process Substitution with Magnesium as Reducing Element

Another important route for the production of silicon carbide is described by Mukasyan (2011), utilizing magnesium (Mg) as a reducing element for the reduction synthesis of SiC. For this alternative, the chemical reaction is between silica sand, petroleum coke and magnesium, forming silicon carbide and magnesium oxide as products; following the reaction below:



The thermodynamic estimations report that through conducting tests under optimum gas pressure and adequate feedstock composition, the products obtained can be expected to be synthesised in two solid phases of both SiC and MgO. Also, a simple chemical processing of such mixture deducts completely the MgO phase, obtaining pure silicon carbide powder

(Mukasyan, 2011). However, the author did not suggest how to manage the microstructure of the product synthesized in the SHS.

The most remarkable advantage of this synthesis is its potential of reducing the CO₂ emissions to almost zero, since the process does not have the gas as direct product. Also, it decreases the energy demand of the industrial process, mainly due to this reducing process requiring less temperature for producing SiC. Dasog, Smith, & Veinot, (2013) shows that silica structures were transformed into SiC by reacting stoichiometric amounts of silica sand, magnesium, and carbon at 600 °C, while the conventional process' temperature is around 2500 °C. It is possible to roughly estimate the electricity consumption savings with a direct correlation with the temperature needed for each process, without considering furnace modifications or isolation, representing up to 260 GWh, or a 75% reduction. Following the stoichiometric reaction, to obtain the same production annual rate of 65 kt of silicon carbide by ESD-SiC, the site would need around 79 kt of magnesium as extra feedstock, as shown in Table 13.

Table 13- Stoichiometric mass flow for the SiC synthesis with magnesium as reducing element.

	SiO ₂	2Mg	C	→	SiC	2MgO
Molar Ratio per SiC (mol:mol)	1	2	1		1	2
Molar Mass (g/mol)	60	24.3	12		40	40.3
MM Molar Ratio (g/mol SiC)	60	48.6	12		40	80.6
Total Mass for ESD-SiC (kt/year)	98	79	20		65	131

4.6 Recycling

Recycling of silicon carbide is usually associated with the studies on the separating silicon carbide from other materials it combines with, such as ceramics and steel. Sergiienko, Pogorelov, & Daniliuk (2014) shows technical and reasonably cheap approaches applicable for recycling of silicon carbide and silicon powders from cutting slurry waste. The recovered powder was composed by 95% of silicon carbide, 4% of silicon, and 1% of iron. Tsai, Shih, & Wu (2013) presented another silicon carbide separation process, which applies an electrical field using a ramp settling tank. The experiment showed that this method effectively separated the Si and SiC components on the applied material relatively fast compared to SiC synthesis. Also, this study claims that applying an electrical field for the separation of those materials and further recycling would be the more suitable option for industrial applications. Nevertheless, silicon carbide recycling and reprocessing is not done so far by the sector worldwide. Most of SiC use is in abrasives and ceramics or metallurgical purposes, with difficult separation process and logistics aspects for transportation and reprocessing. The logistic issues are also relevant to the SiC used in the electrical and electronic products as they are usually utilized in small components. Its collection and transporting for recycling and reprocessing could be more expensive and carbon-intensive than the actual production process. Also, limited research and specification for reprocessing is a possible barrier.

5 Discussion

This section discusses the decarbonisation alternatives in terms of feasibility, requirements, and preferences. Despite being an environmental leader in the sector, ESD-SiC's feedstock depends on the oil refinery industry to produce petroleum coke. Moreover, its significant energy consumption, and its process-related carbon emission indicates the process would need to modify in order to mitigate CO₂ emissions. The given options discussed in this report address these relevant points concerning the carbon footprint of the ESD-SiC industrial process.

Firstly, the feedstock substitution can represent a notable change in the production process, considering that the current raw material is produced from fossil fuels. In that sense, the use of biocoke can be relevant. For ESD-SiC, the purity and high fixed carbon percentage needed for industrial production make it challenging to substitute it by other materials (e.g. regular charcoal or vegetal coal), indicating that the calcined biocoke has high application potential. Also, literature presented similar characteristics between the high-temperature calcined biocoke and the industry's one. However, the market's targeted prices are still distant from the current prices for petroleum coke, mainly because the one currently used in the ESD-SiC industrial site is market competitive and has a high sulphur composition (non-calcined petroleum coke). However, the current biocoke market is still undefined for calcined production, targeting only the biocoke for coal substitution with low carbon fixed content. Nevertheless, the need for high purity carbon in other industries, such as aluminium, can be an extra impulse for its production to grow (Huang, Kocaefe, & Kocaefe, 2018). Even with a small market, calcinated biocoke is currently considered by ESD-SiC as a possible biocoke substitution and trials starting with 1% biocoke feedstock with gradual increase are in the company's future plans.

Regarding the process emissions, the CCUS alternatives are the most promising for the ESD-SiC site. Once those emissions are intrinsic to the chemical reaction and not from fossil fuels, capturing and storing/using the carbon content is the most plausible solution. From that view, the analysis of the ESD-SiC emissions gave a new perspective on its options. Its process waste gas is rich in hydrogen and carbon monoxide, which makes it particularly suitable for CCU with methanol synthesis, CCU with ethanol synthesis, or pre-combustion CCS. Those methods are dependent on either hydrogen availability or CO conversion. CCS today is a more mature technology and is already considered as one of the options for emission reduction in different industrial sectors. However, it strongly depends on infrastructural costs inside the industrial site in technical installations, and outside the site related to transport and storage. For CCU with methanol synthesis, the technology is not as mature yet, and the investment and operational costs are also high, but more related to hydrogen production. In the case of CCU with ethanol/ethylene synthesis, all the information and the technology are protected within the patent with projects running still in the pilot phase, making it difficult to estimate its real potential for the SiC industrial site. For CCU, it is also relevant to consider the production of methanol and ethanol (or ethylene) as a second product and revenue source.

Regarding the remaining mentioned alternatives, not much detailed information can be found in literature, limiting the comprehension on how they could in fact support the silicon carbide industry. The process substitution with magnesium as a reducing element could represent a big improvement on the production process, for allowing it to happen without direct carbon emissions and in lower temperatures. But there is still a lack of information on this method

applied to industrial-scale and on the microstructure and characteristics of the SiC formed. Other considerations are the increased costs and amount of feedstock and the magnesium oxide (MgO) destination as a second product. Despite this, that would be an interesting option for developing further research and for improving SiC manufacturing.

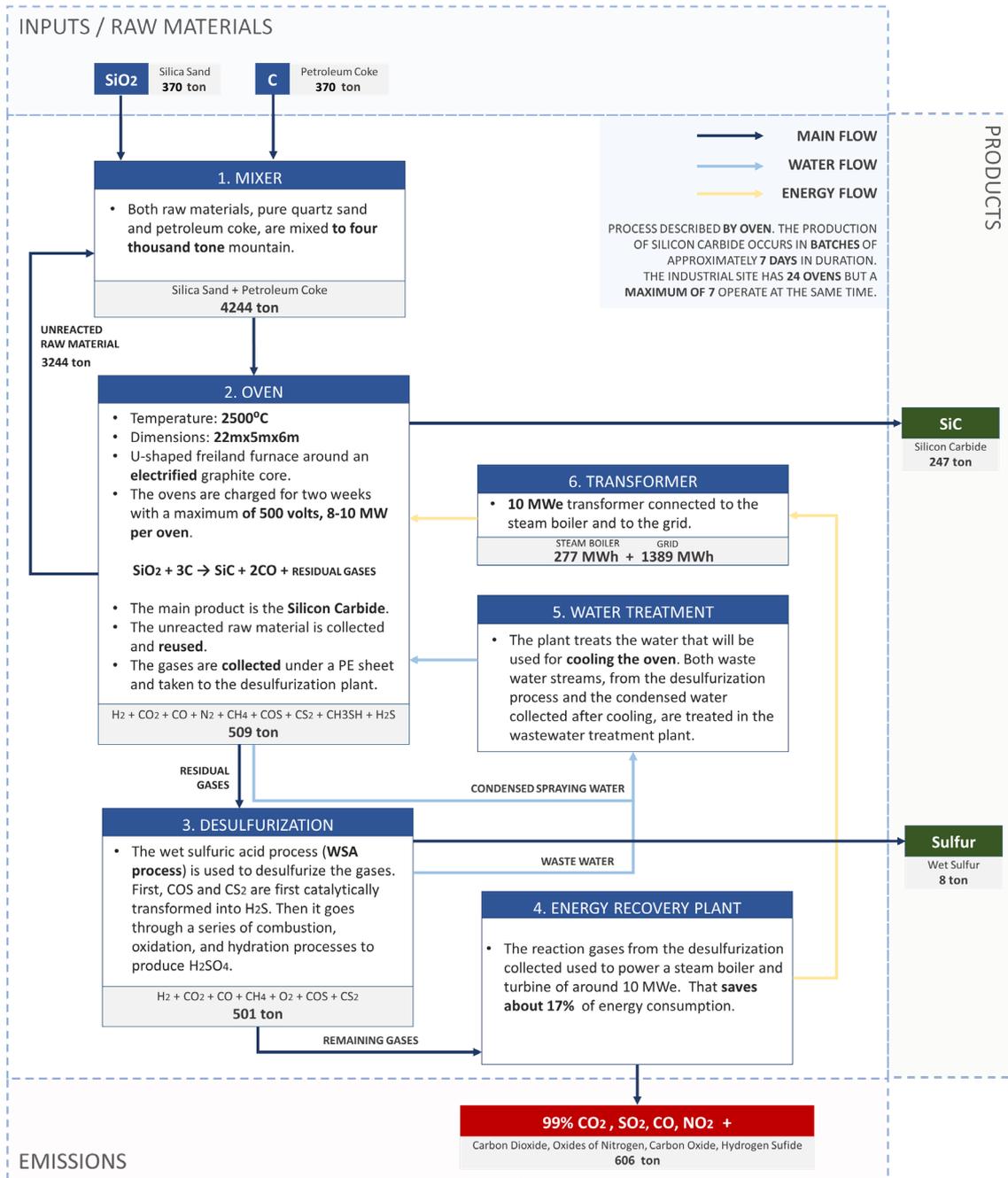
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ANNEX A – ESD-SIC Complete Industrial Process Scheme



ANNEX B – Flexibility of Electricity Consumption in ESD-SIC

The silicon carbide production in furnaces using a graphite core as the heating element is the most common practice for its industrial process worldwide. For the synthesis to begin, this electrically heated furnace has to achieve high-temperatures for a large amount of raw material, thus consuming a massive amount of electricity. That considerable energy demand is also apparent and an increasingly relevant topic for the Dutch production in ESD-SIC. The industrial site uses 1330 to 1510 TJ per year (370,000 to 420,000 MWh per year), being the eighth biggest electricity consumer in the Netherlands (Utilities, 2020). Thus, reducing energy costs and energy demand, next to increasing energy efficiency is a big concern in the industrial process, leading to the energy recovery plant installation described in Section 2.1.6 of this report.

An essential characteristic of ESD-SIC is that it can start and stop the production of silicon carbide whenever it wants. As described in Section 2.1.1, the production process happens in batches, and the company has control of when to start it. That condition offers opportunities when purchasing surpluses demand of sustainable energy. Until recently, ESD-SIC bought and sold power in a normal process, not considering the supply and demand of the energy market. Thus, it did not evaluate the impact in the grid that its consumption could have when added up, especially during peak hours. That situation changed when the company started to consider those factors and gave more control to the energy producer, about its energy consumption (Utilities, 2020).

The high temperatures in the well-isolated furnace and the use of the energy recovery plant help the ESD-SIC to be able to shut down its energy demand during peak hours. Giving that peculiar quality, Engie has found an energy company that can intervene in ESD's energy management, determining when the company produces or not, depending on the off-peak hours. Now, the entire ESD-SIC production process can be shut down within two minutes. In this way, the energy company has a great instrument to regulate the supply and demand of, in particular, sustainably generated energy in the electricity grid. The energy requirement of ESD-SIC is so high that this measure has a neutralizing effect on the Dutch electricity grid, saving money for the industry and avoiding problems in the electricity grid. Therefore, this partnership is based on a win-win situation, which looks at the customer and supplier and the stability promoted. Due to the growth of sustainably generated energy, more and more solutions like this will be needed in the coming years, having an essential role in the energy transition (Utilities, 2020).

ANNEX C – Method for estimating the capital costs for CCU and oxyfuel combustion CCS

To estimate the capital expenditure for the oxyfuel combustion CCS and the methanol synthesis CCU technology, this report will use the rule of six-tenths, common for estimations regarding technical investments in the chemical industry, correlating production capacity and prices of two similar installations. This is needed since the values present in literature have a capacity way larger than what is needed by the ESD-SIC installations. This method follows the equation below, where “C_i” is the unknown cost, “C₀” is the reference cost, “S” is the parameter for the industrial site evaluated, “S₀” is the reference parameter, and “f”, “n” and “e” are scale parameters.

$$C_i = n^e C_0 \left(\frac{S}{n S_0} \right)^f$$

For oxyfuel combustion CCS, Table 14 presents the results of this estimation for the three different capture technologies, using Rubin, Davison & Herzog (2015) references and parameters.

Table 14 - Capital expenditure estimation for carbon capture in ESD-SIC

REFERENCE	S CO ₂ Captured (kt)	S ₀ ESD-SIC Emissions (kt)	C ₀ [MEUR ₂₀₁₉]	n; f; e	C [MEUR ₂₀₁₉]
Oxy-Fuel Combustion Capture	3,900	130	191.3	1; 0.67; 1	19.59

For ESD-SIC, methanol synthesis will be useful application for its emissions. For this cost analysis, the assumption is that the CCU methanol synthesis would happen at the industrial site, as a complementary process to the current industrial process. In order to convert all the CO and CO₂ emissions into methanol, the industrial site would need extra supply amount of H₂ corresponding to 15.3 kt/yr besides the content that already exists in the flue gas. For CCS with methanol synthesis, the references and parameters were described in the work of Anicic, Trop, & Goricanec (2014) related to green methanol synthesis. See Table 15:

Table 15 - Calculation of costs of methanol synthesis in ESD-SIC (Anicic, Trop, & Goricanec, 2014)

Equipment	Scaling Parameter	S	S ₀	C ₀ MUSD ₂₀₁₄	n	f	e	C _i MEUR ₂₀₂₀
Water electrolysis	MW	18.29	220	33	2	0.67	0.90	7.45
RWGS	CO (kg/s)	2.52	2	7	3	0.67	0.90	10.71
Methanol Reactor	CH ₃ OH (tonne/day)	261	5000	81.96	1	0.67	0.90	11.54
Methanol Distillation	CH ₃ OH (tonne/day)	261	5292	19.20	1	0.67	0.90	2.60
PSA	H ₂ (kg/h)	1.91	23	0.02	3	0.67	0.90	0.005
Compressors								0.87
Total Capital Cost (MEUR₂₀₂₀)								33.2