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Master’s thesis 2020

Pallav Shrestha

CARBON FOOTPRINT COMPARISON BETWEEN TRADITIONAL DIESEL AND SYNTHETIC DIESEL PRODUCTION PATHWAYS

Examiners: Assistant professor, D. Sc. (Tech), Ville Uusitalo
Professor, D.Sc. (Econ) Lassi Linnanen

ABSTRACT

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The objective of this Master's thesis is to compare the carbon footprints of traditional fossil diesel to synthetic diesel produced from Fischer-Tropsch synthesis (FTS) using electricity. Carbon footprint analysis was conducted in accordance to ISO 14067:2018 and ISO 14040:2006 standards using life cycle assessment (LCA) approach. GaBi (Education version 9.2.1) was used to model and calculate the carbon footprints. The carbon footprint comparisons were conducted with a modelled euro-6 diesel vehicle for a journey of 1000km distance with each fuel. Solid oxide electrolysis cell (SOEC) and alkaline electrolysis cell (AEC) were modelled for hydrogen synthesis. Flue gas capture (FGC) and direct air capture (DAC) were modelled for carbon source. Finnish grid (2015) was used as the electricity source. Comparison with German grid (2015), wind based grid (Finland) and solar photo voltaics (PV) based grid (Finland) were also conducted.

It was found that synthetic diesel had 85% less carbon footprint from vehicle emissions than traditional diesel but had 2% to 40% more carbon footprint than traditional diesel when the whole process was considered. SOEC had the highest carbon footprint followed by AEC. Both carbon capture methods had negative footprint while DAC had higher energy consumption than FGC. Synthetic diesel had 75% higher carbon footprint when German grid (2015) electricity was used instead of Finnish grid (2015). When renewable energy sources were used, synthetic diesel had a negative carbon footprint. Usage of wind based grid had a lower footprint than solar PV based grid.

With modifications to SOEC to use waste heat from FTS or other exothermic processes, the process had net neutral carbon footprint. This caused the carbon footprint of synthetic diesel to decrease by 250% and have a negative footprint even with 2015 Finnish grid. From the models it was found SOEC for hydrogen and FGC for carbon would yield the lowest carbon footprint and was seen to have a negative carbon footprint of (-)440 gCO_2e/kg or (-)120 gCO_2e/MJ of fuel produced.

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In Lappeenranta 8th of December 2020

Pallav Shrestha

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LIST OF SYMBOLS

C	Carbon
CH_4	Methane
CO_2	Carbon dioxide
CO	Carbon monoxide
gCo_2e	gram of Carbon dioxide equivalent
H_2	Molecular Hydrogen
kg	kilogram
$kgCo_2e$	kilogram of Carbon dioxide equivalent
kJ	Kilojoules
kWh	Kilowatt-Hour
MJ	Megajoules

Abbreviations

DAC	Direct Air Capture
EPA	Environmental Protection Agency
EU	European Union
FGC	Flue Gas Capture
FTS	Fischer-Tropsch Synthesis
GHG	Green House Gases
IPCC	Intergovernmental Panel on Climate Change
NOx	Nitrogen oxides
PM	Particulate Matter
PV	Photo Voltaic
REPA	Resource and Environmental Profile Analysis

1 INTRODUCTION

With the rate of progress we humans have undergone in the last ten thousand years, we have achieved quite an accomplishment. The achievement although has not come for free. For most of those ten thousand years, the primary source of energy were biological muscles: humans or beast. People didn’t own things that were produced outside of their communities. This only changed around the end of 18th century which is heralded as the industrial revolution and beginning of the modern age. John Green, (2012) defines the industrial revolution as “An increase in production brought about by the use of machines and characterized by use of new energy sources”. Before the ‘Industrial Revolution’, 80% of the people in the world were farmers who worked towards producing food for the rest of the population. Comparing to that of 2012 where less than 1% of the population of the United States were registered farmers. In the whole world, 26.7% (approximately 2 billion) of the world population derive their livelihoods from agriculture as 3.4 billion people (approximately 45% of the world population in 2018) lived in rural areas. There are 570 million farms in the world where 90% of them are run buy individual or a family and rely on family labour. They were also accountable for 80% of the world’s food (Global agriculture, 2019).

Industrial revolution is attributed to everything; from living somewhere other than a farm, blue berries in February, every piece of tool and equipment we use daily, the 12 years of formal education before one starts out in life and chattel slavery (Green, 2012). More recently, industrialization has been attributed to global warming and climate change.

The revolution, on one hand, brought ease in human life and increase in life expectancy and standards, but it has also caused the environment to change. Most of the changes to the environment can be observed as changes in cityscapes, land usage changes, visible changes in air quality and changes in climate. Standardized metrics are required to estimate the actual impacts to help address and alleviate the cause at their point of origin. Since the industrial revolution, we as human beings have increased from 1 billion to 7.8 billion and have moved on to the age of information with global access to the internet. The demand to minimize adverse effects to the environment or even reverse them has increased so has the demand for tools for monitoring the impacts.

In the 1960s, when evidence first emerged that human activities was causing pollution, Resource and Environmental Profile Analysis or REPA was created to monitor the adverse effects from product chain (Soukka et al., 2020). In 1988, United Nations Environment Program (UN Environment) and World Meteorological Organization (WMO) created IPCC to provide scientific assessments and climate change and to study and predict future risks (IPCC). The first international ISO standard for life cycle assessment was created in 1996. There are also tools like carbon footprint which measures the negative impacts of a product and more recently carbon handprint which considers the positive impacts of a product due to replacement of an alternative.(Grönman et al., 2019)

The main cause of these adverse effects and change in the environment is primarily attributed to Greenhouse Gase (GHG) emissions due to anthropogenic activities (IPCC, 2013, 12). IPCC has painted a grim picture of the future if we continue in the current trend of GHG emissions. There could be irreversible changes in the environment, atmospheric conditions, climate, and weather patterns as soon by 2025 if we do not adhere to a low emission strategy (IPCC, 2018). The strategy suggests global warming to be kept under 1.5°C to that of pre-industrial conditions by 2050 by lowering emissions and adopting carbon neutral technologies.

IPCC has estimated the average global temperature has risen by 1°C since industrialization and may further rise by 1.5°C between 2030 and 2052. The Paris Agreement of 2015 commits participating nations to mitigate climate change and maintain global temperature below 2°C by cutting GHG emissions. A new study by Randers and Goluke (2020), which uses the Earth System Climate Interpretable Model (ESCIMO), projects the global temperatures to increase to +3°C and sea level rise of +3 m by 2500. The model tests two scenarios where in scenario 1, humanity reduces anthropological GHG emissions to zero by 2100 and in scenario 2 it happens by 2020 (which they mention is impossible). Both cases showed the same result. The model predicts a temporary decrease of temperatures from +2.3°C in 2075 to +2°C in 2150 and the temperatures rises again rises 2500. A chain reaction starts which is caused by numerous reasons such as: self-sustained melting of permafrost due to methane escaping from under the permafrost, lower surface albedo or decrease in reflected radiation from the sun resulting from loss of ice and snow, and increased atmospheric humidity resulting from higher temperature (Randers and Goluke, 2020). The report suggests this reaction cycle is triggered by global warming of just +0.5°C than that of pre-industrial level. Taking the report into account, it is not enough to only stop GHG emissions but also imperative to remove atmospheric GHG (carbon dioxide) to prevent climate change. Apart from carbon sequestration by afforestation, re-purposing atmospheric and flue gas carbon dioxide could be some solutions.

According to EPA, 65% of GHG is attributed to carbon dioxide from fossil fuel and industrial processes. Out of which, 34% comes from transportation alone. As the population increases and more people move out of poverty line, the demand of transportation will most likely increase in the future. Increase in GDP will lead to increase in energy consumed for transportation. A renewable and carbon neutral source of transportation energy is urgently required to satisfy the future need while keeping the global warming goals in check. Electricity produced from renewable sources could supply the transportation system with electrical vehicles (EVs), however, certain sectors like marine transportation, aviation and long-haul trucks are yet to be successfully electrified. Certain factors such as gravimeter energy density of energy storage where the vehicle requires to be lightweight and retain a high level of autonomy, and shorter refuelling time leads to carbon based liquid fuel preference to electric vehicles (Guzzella et al., 2013). Fossil fuel is limited and dwindling, and substitutions are only slowly being realized. Adoption of next best technology will possibly require time and investment. Continuing with fossil fuels in the meantime will only add on to GHG emissions. Biofuels are another alternative but there is limited availability. Providing food for the future will be a priority over fuel crops. Agricultural and forestry waste are the optimal sources for sustainable biofuel production but the supply will hardly be sufficient to meet the demand as the replacement option, taking sustainability into account.

Electric vehicles are the other replacement option. It is estimated that there are roughly about a billion cars (personal vehicles) in the world. Assuming a cost of €50 000 per electric vehicle, the world needs 50 trillion euros of new electric vehicles (Vice News, 2018). Then there is also consideration of energy supply for all the cars and also raw materials for batteries and components such as lithium or zinc. Synthetic fuels or e-fuels can be produced with carbon dioxide, hydrogen and a clean energy source. The synthetic fuels are identical to fossil fuels and can be used in current gasoline or diesel vehicles without any changes or with minor changes. Usage of such fuel will make any vehicle running on fossil fuel carbon neutral. Synthetic Fuels could be the solution either as an intermediate or primary replacement for future transportation needs.

1.1 Problem definition

To accurately portray the advantages and disadvantages of the different fuel systems, their environmental impacts need to be compared. The consensus is that e-fuels are ‘cleaner’ than fossil fuels because they don’t add more carbon content from the lithosphere to the atmosphere. This paper attempts to estimate exactly how much better are e-fuels to their fossil fuel counterparts. The whole lifecycle of the fuel production is considered for the comparison. The analysis is made by estimating carbon footprint of synthetic fuels and comparing it to that of fossil fuels. Following are the research questions this paper aims to answer:

i. Which pathway of synthetic fuel manufacture has the least carbon footprint?
ii. What is the difference in carbon footprint between fossil fuel and synthetic fuel?

1.2 Scope and Boundary

Different varieties of synthetic fuels are available today. Many companies like Sunfire and Carbon Engineering already have a working model to produce synthetic fuels which are claimed to be market competitive with fossil fuels and also have comparable or higher performance (Sunfire; Vice News, 2018). This paper focuses on synthetic diesel as a competitor to fossil diesel. Hence, impacts due to synthesis of e-diesel and fossil diesel are compared.

The aim is to calculate the impacts of synthetic diesel when energy used is taken from the Finnish grid. The system boundary can be visualized from Figure 1. Synthetic diesel require hydrogen and carbon. Two different process for each hydrogen and carbon sourcing are compared to conclude the synthetic diesel with the least amount of carbon footprint production pathways.

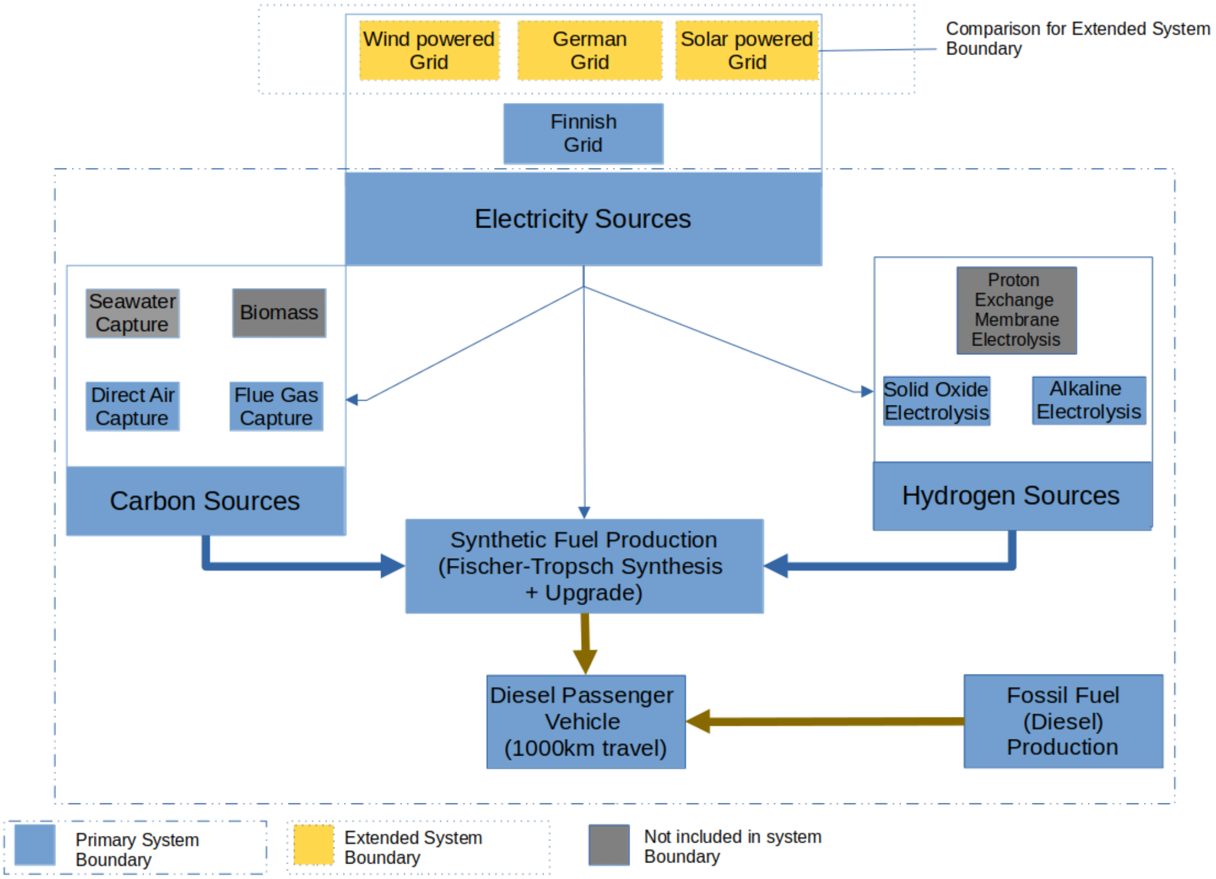

Figure 1: System Boundary of the study

The study is only a carbon footprint analysis that includes the production of fuels. Impacts of establishment of process facilities due to construction and material acquisition are not considered in this study.

There are also options such as methanol and its subsequent synthate: dimethyl ethers (DME) which is claimed to further remove nitrous oxides emissions but require minor valves and piston modification to diesel engines (International DME Organization, 2010). These alternatives are not considered in this paper.

2 A BRIEF OVERVIEW OF RELEVANT TECHNOLOGIES

Synthetic fuels (also e-fuels) production require a source of carbon, typically as carbon monoxide (CO) which is obtained from CO_2 after Reverse water gas shift (RWGS) reaction, and a source of hydrogen (H_2) from which different chain of hydrocarbon fuels can be produced as required. Energy as heat or electricity is required in all the processes.

According to Hänggi et al. (2019, 556) Life Cycle of Synthetic Fuels can be divided into five steps:

i. Electrolysis of water to produce hydrogen
ii. Separation of Carbon dioxide from atmosphere or other sources
iii. Chemical synthesis and purification of the desired fuel
iv. Transportation and storage
v. Oxidation of the fuel in a fuel cell or combustion engine with release of gaseous water and carbon dioxide to the atmosphere

The main chemical synthesis processes include Fischer-Tropsch method to produce desired fuels or usage of CO and H_2 in methanol production which further can be refined into dimethyl ether (DME) or olefins and gasoline. An overview of available synthetic hydrocarbon production can be seen in Figure 2 with relevant synthetic fuels usable in transportation circled in green.

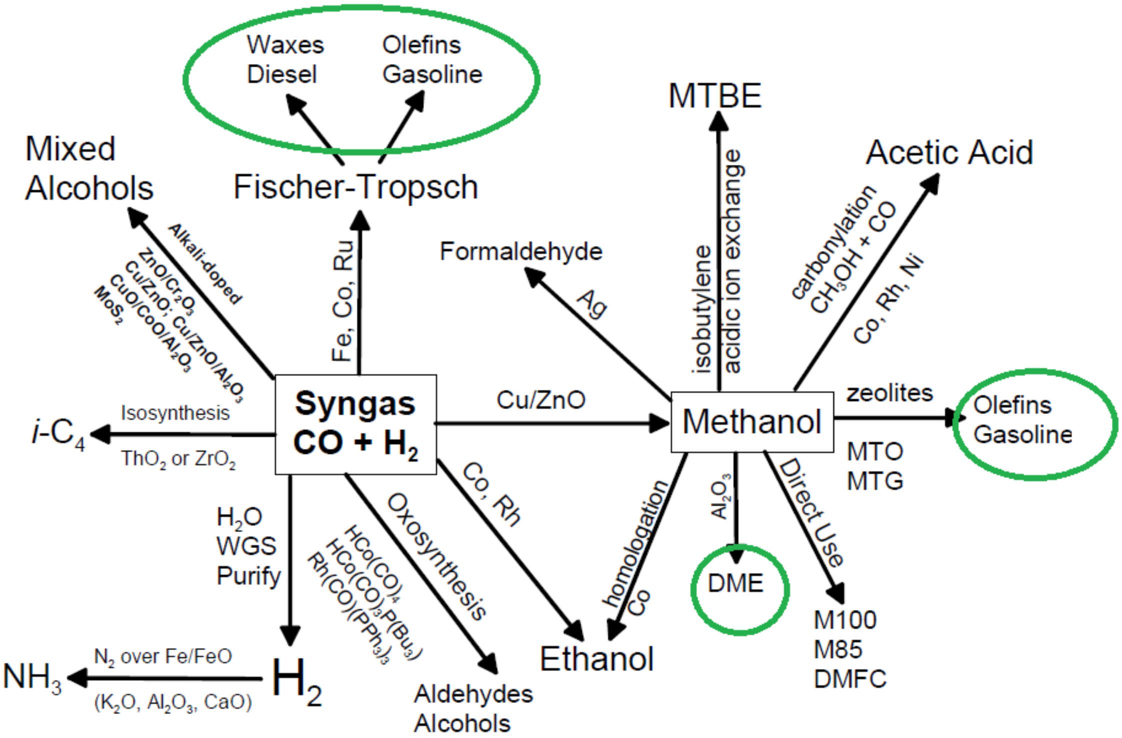

Figure 2 Available syngas technologies, fossil fuel replacement circled in green. (adapted from Spath and Dayton, (2003))

2.1 Hydrogen

Hydrogen is one of the three main component required in synthetic fuels production. Hydrogen can be produced by using different electricity sources which include nuclear, natural gas, coal, biomass and renewable sources like solar, wind, hydroelectric or geothermal (Kalamaras and Efstathiou, 2013, 2-5). In 2013, about 50% of the commercial hydrogen was produced from fossil fuels by steam reforming of natural gas, partial oxidation of methane and coal gasification, 30% from oil/naphtha reforming or chemical industrial gases, 18% from coal gasification, 3.9% from water electrolysis and 0.1% from other sources (Muradov and Veziroğlu, 2005, 225-227). Steam reforming of natural gases cause high level of green house gases emissions (Konieczny et al., 2008; Balat and Balat, 2009). For this study, the hydrogen production method used is electrolysis. Depending on the pathway and energy sources used, it has the potential to be a nearly zero GHG emission method. The emissions from synthetic diesel mostly originate during equipment manufacturing and acquisition.

Electrolysis is the process of breaking water into its constituents: hydrogen and oxygen. The process was known and already used commercially in 1890. Electrolysis requires passing a current through two electrodes: a negatively charged cathode and a positively charged anode in a water solution. The passage of current breaks the chemical bond present in water molecules. Hydrogen is collected at cathode and oxygen is collected at anode. (Kalamaras and Efstathiou, 2013, 6)

Electrochemical production of hydrogen has the potential to reduce environmental impacts by replacing current dominant industrial production method which utilizes fossil fuels. Although the interest in ‘clean’ hydrogen production has increased recently and researches are being conducted to assist in cleaner and cheaper hydrogen production, the market share of electrolysis in hydrogen production was only 5% in 2019 (Keçebaş et al., 2019, 299).

Following are the main technologies available for electrolysis of water:

i. Alkaline Electrolysis Cell (AEC)
ii. Proton Exchange Membrane Electrolysis Cell (PEMEC)
iii. Solid Oxide electrolysis cell (SOEC)

2.1.1 Alkaline Electrolysis Cell

Alkaline Electrolysis Cell (AEC) is a mature technology which can be used for water electrolysis. Alkaline Electrolysis Cell (AEC) or Alkaline Electrolysis (AEL) uses most commonly Nickel (Ni), Cobalt (Co), Iron (Fe) or Platinum/Carbon (Pt/C). 25-30% Potassium hydroxide (KOH) is used as electrolyte and a solution of sodium hydroxide (NaOH) and sodium chloride (NaCl) is used as the catalyst. It is possible to obtain 99% pure hydrogen. It can further be purified to obtain hydrogen purity that can be used in Hydrogen Fuel Cells. The efficiency of hydrogen production is estimated to be 80% (Hänggi et al., 2019, 559).

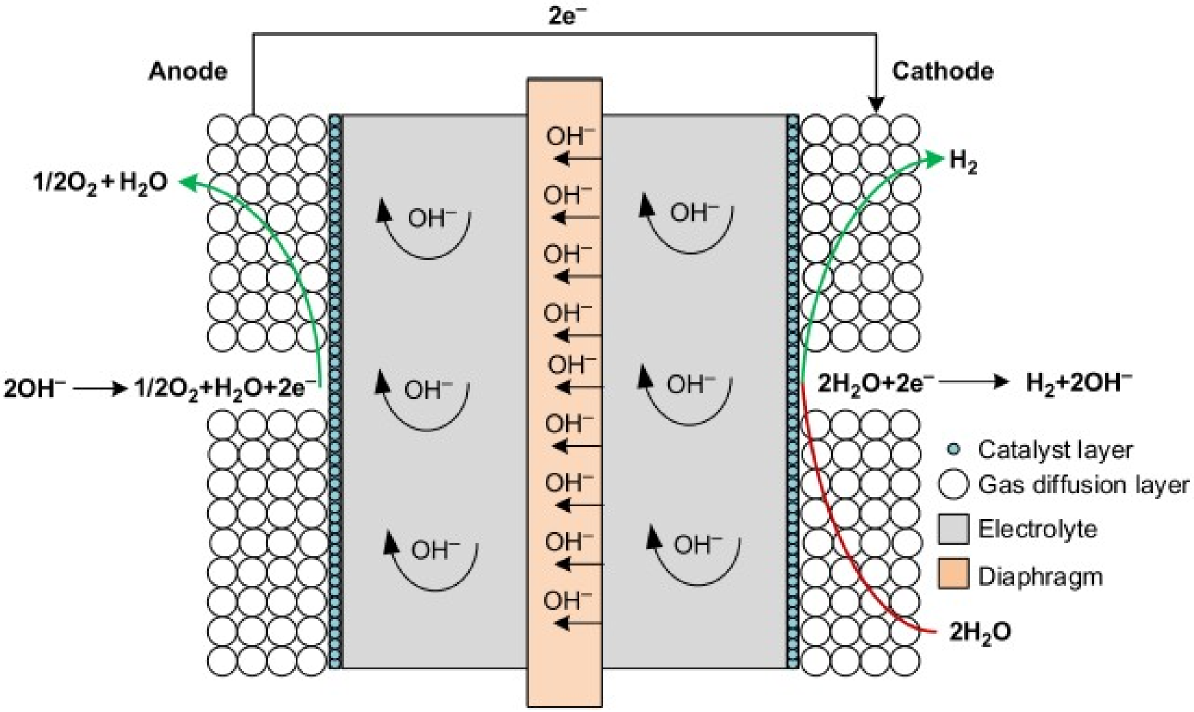

Figure 3: The alkaline electrolyzer. (Keçebaş et al., 2019)

In electrolysis, water molecule is split into hydrogen and oxygen molecules (equation 3). In simple AEC, the following partial reactions occur at cathode (equation 1) and anode (equation 2).

Cathode (reduction):

$$2H_2O+2e^- \rightarrow H_2+2OH^- \tag{1}$$

Anode (oxidation):

$$2OH^- \rightarrow H_2O+\frac{1}{2}O_2+2e^- \tag{2}$$

Overall reaction:

$$2H_2O \rightarrow 2H_2+O_2 \tag{3}$$

The process requires a diaphragm, as seen in Figure 3, and porous white asbestos is commonly used ($Mg_3Si_2O_5(OH)_4$). Asbestos is known to be toxic and has been linked with lung cancer. Also, due to asbestos corroding in the electrolyte, increasing the efficiency by elevating the temperature is not possible (Rosa et al., 1995, 697). Rosa et al., (1995), in their paper, ‘New materials for water electrolysis diaphragms suggest; a composite of potassium (K_2TiO_3) fibres and polytertrafluoroethylene (PTFE), polyphenylene sulphide, PTFE (as felt and as woven), polysulfone, and asbestos coated with polysulfone as alternative diaphragms. Pletcher & Li, (2011) research on zero gap water electrolyzers which used a hydrocarbon based polymeric membrane as diaphragm has shown better yields and efficiency.

2.1.2 Proton Exchange Membrane Electrolysis (PEMEC)

In a proton exchange membrane electrolyzer, electrolyte is not required and polymer is rather used as a proton exchange membrane. The polymer membrane is selectively permeable to proton (H^+). Apart from the permeable membrane, the system consists of an anode/catalyst layer where water is decomposed and oxygen is formed and a cathode/catalyst layer where hydrogen is formed. In Figure 4, it can be observed that water is introduced to the system from the anode outlet where it breaks into hydrogen (H^+) and oxygen (O_2) where oxygen is collected. The proton (H^+) passes through the permeable membrane and receives electrons in the cathode layer and is converted into hydrogen gas and then collected.(Keçebaş et al., 2019)

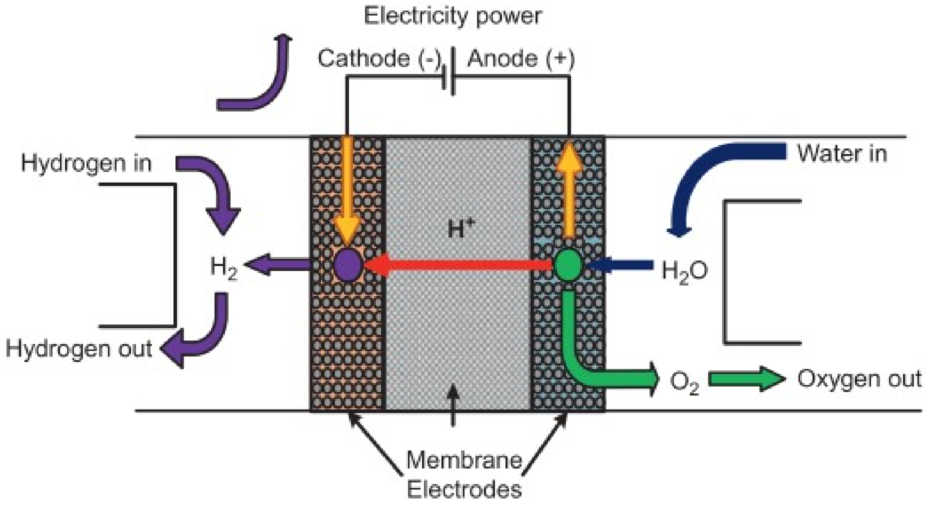

Figure 4: PEM electrolyzer (Keçebaş et al., 2019)

Partial reactions at cathode and anode and the complete reaction are presented in equations 4, 5 and 6

Anode Reaction:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{4}$$

Cathode Reaction:

$$4H^+ + 4e^- \rightarrow 2H_2 \tag{5}$$

Overall Reaction:

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \tag{6}$$

Electricity for electrolysis is partially converted into heat energy but the water circulation can dissipate excess heat and maintain temperature. Depending on the flow and heat transfer conditions, the temperature of the system can sometimes increase which can cause corrosion. Therefore, the cell temperature of 40-60ºC is suggested for increased performance and life of the cell.

2.1.3 Solid Oxide Electrolysis Cell (SOEC)

Solid Oxide Electrolysis Cell is a high temperature electrolysis method using solid oxides. The structure of a SOEC, as seen in Figure 5 is similar to a high-temperature fuel cell. The mechanism can be considered as working in reverse to that of a high-temperature fuel cell (Godula-Jopek, 2015, 193). Temperature range of the operation is 650-800 ºC (Godula-Jopek, 2015, 390). Due to the high operational temperature, SOEC has better reaction kinetics. It can also be used in heat recovery system and used to fuel other endothermic reaction if worked in tandem. Equation 7 and 8 represent the reaction at the electrodes.

Anode Reaction:

$$O^{2-} \rightarrow \tfrac{1}{2}O_2+2e^- \tag{7}$$

Cathode Reaction:

$$H_2O+2e^- \rightarrow H_2+O^{2-} \tag{8}$$

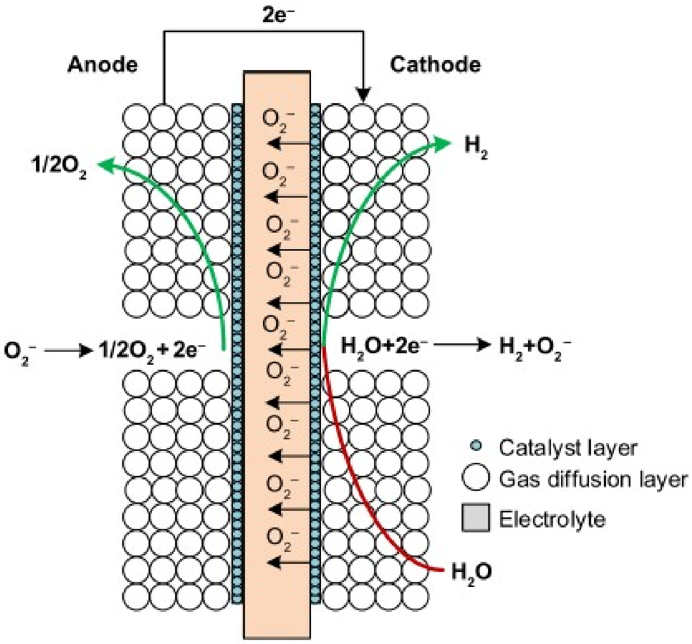

Figure 5: Solid oxide electrolysis cell. (Keçebaş et al., 2019)

Briefly comparing the different available technologies for electrolysis, PEMEC has a better start-up time and efficiency than AEC, and SOEC operates in higher temperature (Millet and Grigoriev, 2013; Millet, 2015). The short startup time is useful when considering renewable energy as a power source which could fluctuate. SOEC, as it operates at a higher temperature, can replace electricity required in Fischer-Tropsch plants with heat. It can also be possible to design a plant capable of co-electrolysis of water and carbon dioxide, which eliminates the necessity of reverse water-gas shift plants for carbon monoxide production (Fasihi et al., 2016).

2.2 Carbon Dioxide

Carbon is the other constituent of synthetic fuel. The carbon required is either supplied as carbon monoxide (CO) or carbon dioxide (CO_2). Carbon monoxide can be obtained by reduction of CO_2 through reverse water-gas shift reaction. (Hänggi et al., 2019, 561)

$$H_2O(l) \rightarrow H_2 + \frac{1}{2}O_2 + 286\,kJ/mol \tag{9}$$

Reverse water shift reaction:

$$H_2 + CO_2 \rightleftharpoons CO + H_2O(g) + 41\,kJ/mol \tag{10}$$

From equation 9 and 10, the total reaction enthalpy is 327 kJ/mol.

High-temperature electrolysis process (like SOEC) can produce hydrogen-carbon monoxide mixture ready for synthetic fuel production (Fu et al., 2010, 1384). Co-electrolysis of hydrogen together with carbon dioxide eliminates the necessity of reverse water-gas shift reaction.

$$CO_2 \rightleftharpoons CO + \frac{1}{2}O_2 + 283\,kJ/mol \tag{11}$$

The reaction removes water evaporation and hence the enthalpy is 13.5% lower compared with reverse water-gas shift reaction (Hänggi et al., 2019, 561).

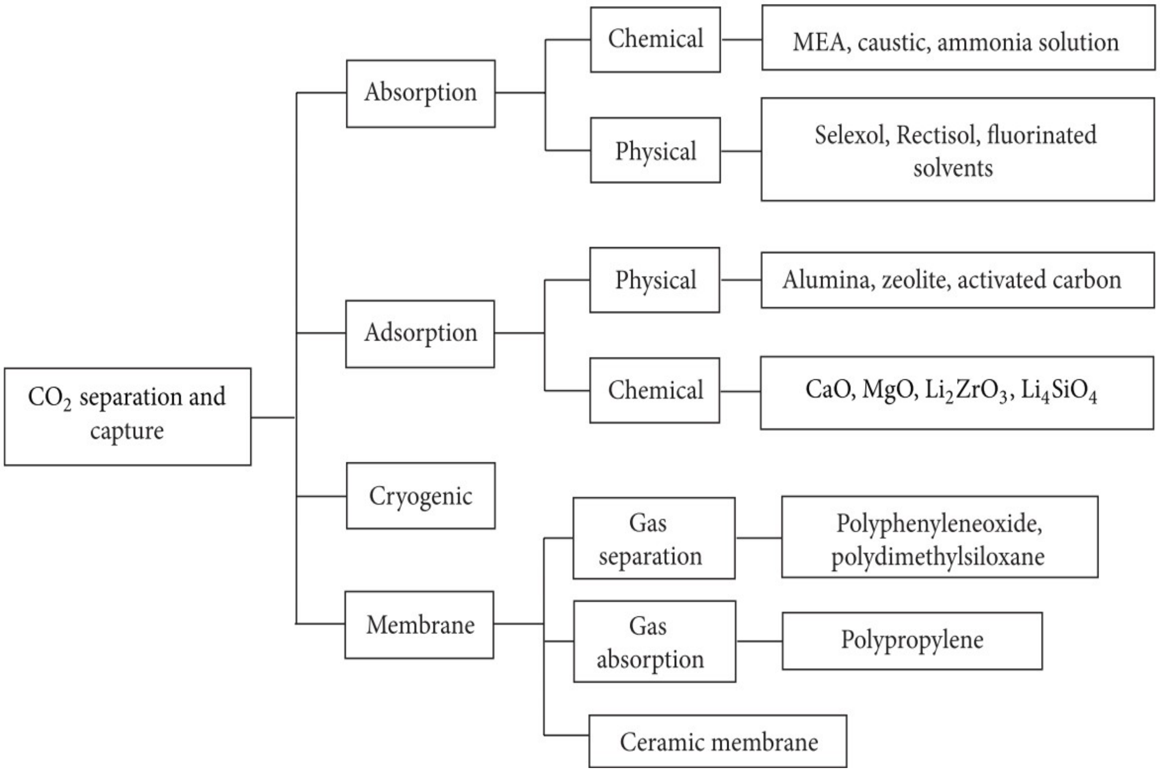

Figure 6 Summary of technologies for CO_2 separation. (Songolzadeh et al., 2014, 4)

Carbon dioxide can be extracted from water, air or biomass. There are numerous carbon dioxide separation and capture technologies available which includes physical or chemical absorption, adsorption, cryogenic separation and capture, and membrane separation and capture. Figure 6 provides a summary of available technologies for carbon dioxide separation. Amine adsorption designed as a cyclic process mainly using thermal energy is the option chosen based on the paper by (Hänggi et al., 2019).

2.2.1 Carbon dioxide from Biomass

CO_2 can be produced during bio-gas production where a mixture of methane and carbon dioxide is produced. If methane is used as natural gas then CO_2 is separated and is a by-product. According to Müller et al. (2011) from Hänggi et al., (2019), CO_2 concentration in biogas is between 25%- 55%. The separation process requires approximately 90kJ/mol of energy.

2.2.2 Carbon dioxide from atmosphere

Carbon dioxide share in the atmosphere is approximately 0.04% so a large volume of air is required to obtain significant amount of carbon dioxide from direct air capture. Swiss company Climeworks employ a special cellulose fibre that is supported by solid amines which binds with CO_2 and air moisture. This mechanism allows the plant enough water for its own use. A test plant built by Climeworks was reported to consume 500 kJ/mol CO_2 of thermal (approximately 3160 kWh_{th}/tCO_2) and 80 kJ/mol CO_2 (approximately 500 kWh_{el}/tCO_2) of electrical energy in 2017 (Evans, 2017).

A new and more efficient system required 200-300 kWh_{el}/t CO_2 (roughly 32-48 kJ//molCO_2) for fans and components plus 1500-2000 kWh_{th}/t CO_2 (240-320 kJ/molCO_2) for regeneration as reported by Fasihi et al. (2019, 962).

2.2.3 Carbon dioxide from flue gas

(Hänggi et al., (2019, 561) estimates that there is approximately 250 times higher concentration of CO_2 in flue gas compared to air and thus it takes less energy for CO_2 separation. The report estimates that flue gas CO_2 separation requires 160-250 kJ/mol CO_2 thermal and 2-20kJ/mol CO_2 electrical energy. Assuming the maximum estimated values, the energy required is about 40% less than that of direct air capture. Thermal energy required can be provided by waste heat from other processes like methane synthesis (Reiter and Lindorfer, 2015, 477-489). (Leeson et al., 2017, 71-84) also proposes flue gas capture in iron and steel making industry, petroleum refineries and pulp and paper industry where waste thermal energy can be utilized for CO_2 capture. The waste heat could also be used in RWGS reaction. A complete incorporation of SOEC for H_2, RWGS, flue gas CO_2 capture along with Fischer-Tropsch could utilize waste heat from one process to another which could drastically reduce external thermal energy supply needed.

2.2.4 Carbon capture from seawater

CO_2 can also be separated from seawater. A paper by Willauer et al. (2012) commissioned by the US Navy estimated the cost to about $144 per tonne of CO_2 which was used to produce mostly jet fuels with a cost of $1.78 per litre. The CO_2 concentration of seawater was approximately 140 times higher than in air. The energy required for seawater CO_2 separation was calculated as 242 kJ/mol CO_2 by Eisaman et al. (2012).

2.3 Electricity

Electricity or energy is the third requirement in the production of synthetic gas. Conceptually, usage of 100% renewable source of electricity can result in a completely carbon neutral synthetic fuel when only emissions in production are considered. This could be possible in the near future but as of 2020, national grid mix and emissions and impacts caused by the grid mix have to be considered in synthetic fuel carbon footprint. The impact of electricity will vary with different grid mixes available per region and country. In the future, it is possible to have 100% renewable energy grids that are capable of overproducing electricity which can then be used in various power-to-x processes. Depending on the processes, this abundance in electricity can be used to store energy in different forms which can also be used as carbon sequestration.

2.4 Synthetic fuels

Synthetic fuels are commonly referred to as gas to liquid or GTL (Jaramillo et al., 2008, 7559). Synthetic gas (CO, CO_2 and H_2) can be used to produce variety of synthetic fuels. Hydrogen (H_2) (Fuel Cells and Hydrogen Energy Organisation), Methane (CH_4) (Boshell et al., 2016), Methanol (CH_3OH) (Miller et al., 2007) dimethyl ether or DME (CH_3OCH_3) (International DME Organisation, 2010) and synthetic diesel can all be produced using synthetic H_2 and CO_2 and be used as fuels for transportation.

Hydrogen fuel cells passenger vehicles from Honda were already in production since 2009 (The Washington Times, 2009). Methanol as a fuel was tested in the US since 1976 and methanol is used as high performance fuel in drag racing and also as fuel additives. (Bromberg and Cheng, 2010). DME can be used in diesel engines, gasoline engines and in gas turbines with minor changes to the engines and it is also heralded to by the most promising low carbon alternative fuel solutions. Vehicle and Engine manufacturers: Isuzu, Nissan, Shanghai Diesel and Volvo all have developed vehicles with diesel engines which operate with DME. (International DME Organisation, 2010).

Synthetic diesel like all synthetic fuels are considered “sufficiently non-toxic” and “environmentally benign” so they are categorized as bio degradable (DeHaan et al.). This is because of negligible amount of sulphur and extremely low level of aromatics hydrocarbon present in the fuel. Due to the nature of synthesis of fuel, reduced emissions have been reported on same vehicles without any modification compared to fossil fuel diesel. About 60% reduction in hydrocarbons, 45% in CO, 4% in CO_2 and 55% reduction in particulate matter have been recorded (Alleman et al., 2005). The changes could mostly be due to slightly different composition and molecular structure of fuel. Synthetic fuels are created from building blocks and thus have lower impurities and simpler chain structure. Fossil fuels, which are broken down from crude oil, are sub-surface sedimentary deposits from thousands if not millions of years ago and can have many impurities and complex chain structures which results in higher emission levels.

2.5 Fischer-Tropsch Synthesis

Sabatier and Sanderens in 1902 first discovered the process of hydrocarbon synthesis CO hydrogenation. In 1923, Fischer and Tropsch reported the first liquid hydrocarbon production rich in oxygenated compounds and named it Synthol process. Many iterations later the process of converting CO and H_2 mixtures to liquid hydrocarbons over a transition metal catalyst finally became known as Fischer-Tropsch (FT) synthesis (Spath and Dayton, 2003, 92).

The main process of FT synthesis is denoted by equation 12 (Fasihi et al. 2016, 251).

Fischer-Tropsch Synthesis :

$$nCO_2 + 2nH_2 \rightarrow (\text{-}CH_2\text{-}) + nH_2O - 209\,kJ/mol \tag{12}$$

FT synthesis can also include reverse water-gas shift reaction (RWGS) as the first step as seen in equation 10. Specific FTS products are synthesized with specific reactions presented below. (Spath and Dayton, 2003, 94)

Methanation:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{13}$$

Paraffins:

$$nCO + (2n+1)H_2 \rightarrow C_n H_{2n+2} + nH_2O \tag{14}$$

Olefins:

$$nCO + 2nH_2 \rightarrow C_n H_{2n} + nH_2O \tag{15}$$

Alcohols:

$$nCO + 2nH_2 \rightarrow C_n H_{2n+1}OH + (n-1)H_2O \tag{16}$$

FT synthesis is followed by enriching or upgrading the products (from CO to paraffins and olefin chains). The obtained product also known as synthetic crude or e-crude is broken down into usable products like diesel, naphtha kerosene and wax. Fasihi et al. (2016, 251) have presented a compendium of different modes of hydro-cracking which produces various mixtures of naphtha, jet fuel/kerosene and diesel. Jet fuel/ kerosene and diesel can be used as is as fuels and naphtha can be used in the chemical industry. A study by FVV (Forschungsvereinigung Verbrennungskraftmaschinen E.V.), the Germany based research organization of combustion engine, shows the most desired mixture with two modes; one with kerosene focus and one with focus in diesel (Albrecht et al., 2013). The model was developed from a presentation by Lurgi AG at the International Conference on IGCC & XtL, Freiberg (Liebner and Schlicting, 2005). The different composition of products by % mass can be observed from Table 1.

Table 1: Final composition of hydro cracking (%mass)

	Naphtha	Jet Fuel/Kerosene	Diesel
Diesel Mode	15	25	60
Kerosene Mode	25	50	25

Apart from methane and synthetic fuels/crude (e-crude), alcohols and subsequently DME can also be synthesized as seen in equation 17 and 18. Alcohols and DME are synthesized in separate processes. They can also be combined to a single process in order to directly obtain DME (Azizi et al., 2014, 150-172).

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O - 50\,kJ/mol \tag{17}$$

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O - 23\,kJ/mol \tag{18}$$

3 METHODOLOGY

Environmental impacts are estimated by monitoring and measuring possible negative effects at the point of origin of every step of a process. The 1960s gave rise to REPA system, when environmental impact accounting had begun. In the present times, standards are developed and documents such as life cycle assessment framework (ISO 14040, 2006; ISO 14044,2006) and carbon footprint calculation standards (ISO 14067, 2018) are available. ISO 14067:2018 is guidelines for reporting carbon footprint which itself is based on Life Cycle framework, ISO 14040 and ISO 14044.

British standards also has PAS 2050 (Publicly Available Standard) for greenhouse gases quantification. World Resources Institute and World Business Council for Sustainable Development also have published a standard simply called Greenhouse Gases Protocol (GHGP) which is adopted by many companies.

Apart from these there is also carbon handprint framework which reports on the positive impact of a product. Unlike carbon footprint, which measures the negative impacts of a process or product, carbon handprint comments on the reduction of GHG emissions due to usage of alternative product or due to modified practices. The framework is based on carbon footprint calculation (ISO 14067:2013, WBCSD and WRI,2004) and LCA (ISO 14040:2006; ISO 14044,2006) (Grönman et al., 2019).

This study is a comparison of carbon footprint of synthetic diesel compared to traditional fossil fuel diesel. The study and findings demonstrate the difference in carbon footprint and hence it can be categorized under carbon handprint framework which is based on attributional Life Cycle Assessment (ISO 14040:2006).

LCA is a tool by which impacts on the environment of products is estimated by accounting the material, energy and emissions at each stage of product’s life cycle. Process modelling and material flow are analysed to visualize different phases of product life cycle so that the process with the highest impacts can be isolated and addressed. The tool allows for comparison of different products available and observe deviations in the system due to small variation in a process to demonstrate the differences in overall environmental impacts. The LCA framework states four main phases (ISO 14040:2006):

- goal and scope definition
- life cycle inventory analysis (LCI)
- life cycle impact assessment (LCIA)
- life cycle interpretation

The goal and scope definition phase details the aim of the project and the scope and boundaries are set accordingly. Goals depend on the study being conducted. Inventory analysis is the second phase where inputs and outputs of each step and processes are accounted. Planning and collection of data is also part of this step. The third step, impact assessment, helps visualize and understand environmental significance of all the product’s system. In this step, environmental impacts for chosen categories are calculated based on the inventory data. Interpretation is the final phase where results are summarized and concluded. This phase helps provide to recommendations and further decision options in accordance to the goal and scope definition (ISO 14040:2006). The interaction between different phases of the framework can be visualized in Figure 7.

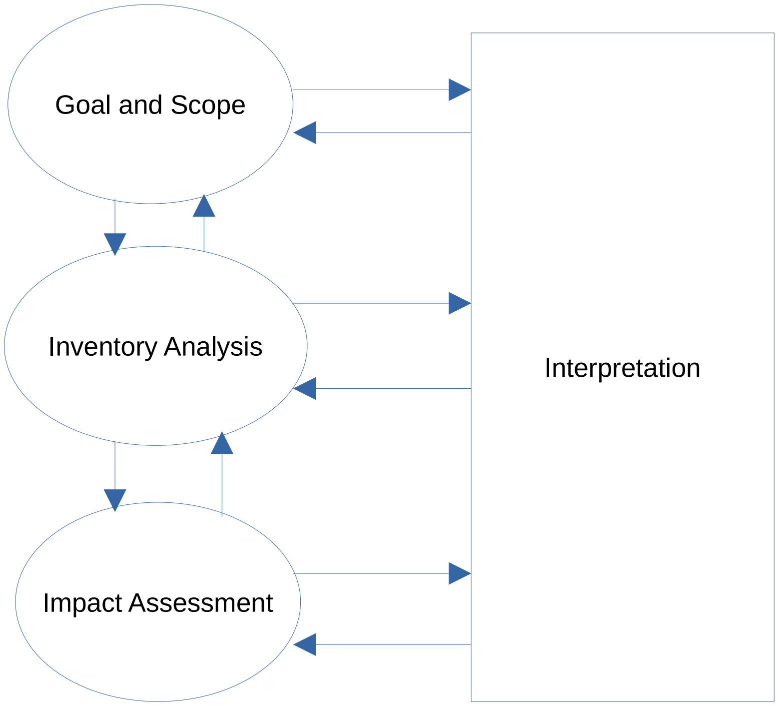

Figure 7: Stages of LCA, adapted from (ISO 14040:2006, 8)

GaBi was used in this report for Life cycle assessment. GaBi is a Life Cycle Assessment modelling and reporting software from Sphera (previously, Thinkstep). The Software can be used for modelling a product’s lifecycle and used for life cycle analysis, costing and reporting. The software comes equipped with a database which contains an inbuilt library of various processes. There are other options available for conducting life cycle assessment: excel or open sources alternative like LibreOffice, Umberto, SimaPro and Open LCA. GaBi was chosen due to familiarity and the available database which was also used as data source. GaBi Education Version 9.2.1 was used for this report. Example of GaBi models created for this research are presented in the Appendix.

4 CARBON FOOTPRINT OF POWER-TO-DIESEL

Carbon footprint analysis was conducted through LCA framework as seen on Figure 7. Global Warming Potential or GWP was the primary metric used for assessment. GWP is presented as unit of CO_2 equivalent mass (CO_2 e). GWP indicated is estimated potential for a period of 100 years. According to Kyoto protocol, different greenhouse gases have different global warming potential, and they are represented in relation to carbon dioxide. The weighted relationship between carbon dioxide and other GHG are presented in Table 2.

Table 2: Relative weight of GHG

Greenhouse Gas	GHG potential relative to CO_2
Carbon dioxide (CO_2)	1
Methane (CH_4)	25
Nitrous Oxide (N_2O)	298
Hydrofluorocarbons (HFCs)	124-14 800
Perfluorocarbons (PFCs)	7 390-12 200
Sulphur hexafluoride (SF_6)	22 800
Nitrogen triflouride (NF_3)	17 200

4.1 Goal and Scope Definition

The aim of the study was to conduct attributional LCA of synthetic diesel compared to traditional fossil fuel diesel as stated in chapter 1.2. Technologies in consideration are denoted in Figure 1. According to the different technologies five scenarios were created which can be observed from Table 3. Fossil fuel diesel was considered the base line scenario which was compared with four different pathways of H_2 and CO_2 production. All the scenarios were conducted using electricity from Finnish grid mix, German grid mix, and renewable grid simulated with wind and solar power.

Table 3: Description of different scenarios considered

Scenario	Details
1	Fossil Fuel Diesel production
2	AEC (H_2) + DAC(CO_2) + Fischer Tropsch Synthesis + Product upgrade
3	SOEC (H_2) + DAC(CO_2)+Fischer Tropsch Synthesis + Product upgrade
4	AEC (H_2) + Flue Gas Capture(CO_2) + Fischer Tropsch Synthesis + Product upgrade
5	SOEC(H_2) + Flue Gas Capture(CO_2) + Fischer Tropsch Synthesis + Product upgrade

4.1.1 Scope of the Study

A well to mile approach was taken for this study. The process from synthesis to conversion of fuel into distance is considered. Carbon footprint due to synthesis process is only considered and the footprint of setup is not taken into account.

4.1.2 Functional Unit

The functional unit for the study was one thousand km of distance travelled. To calculate the mileage of fuel, a mean energy demand of 2.1 MJ/km was used as the standard vehicle (VTT, 2017). Industry standard value of energy density were used for traditional diesel (IOR Energy Pty Ltd, 2010). The carbon footprint assessment is made with the GWP data acquired from the modelled vehicle after travelling 1000 km. The emissions, fuel required and the energy required for synthesis of the fuel are the main cause of environmental impact.

4.1.3 Data Quality

The research is conducted primarily based on secondary data. Previous studies and research papers were the source of data to model gas synthesis. Data for electricity grid and traditional diesel refineries were taken from GaBi database. As the market for synthetic diesel is new and only proof of concept prototypes are available (Sunfire; Vice News, 2018), real world data on performance is not available and hence most data were extrapolated from specifications available from research papers.

The data used represent the best available technology and methods with a functional prototype. Some technological specification were chosen as it represented a more efficient energy usage while some technologies were chosen as they were more established. Each case has been specified in life cycle inventory. Data from research papers and previous studies are taken directly when possible and estimated with assumptions when not available. Some processes are modelled from GaBi data base (Education Version 9.2.1).

4.1.4 Sensitivity Analysis

Two sensitivity analyses have been chosen. German Electric grid was used as a comparison to the Finnish one. Second sensitivity analysis was conducted by replacing the Finnish grid with wind electricity from wind and Solar Photo Voltaic to simulate future scenarios with 100% renewable grid. Grid usage of solar and wind were conducted separately to compare differences between the two different renewable sources.

4.1.5 Assumptions and Cut-offs

As data from prototypes are not publicly available due to proprietary intellectual property (IP), numbers and values are theoretical and based on data collected from previous studies, the best estimation based on specification of the prototypes and stoichiometric calculations. Carbon footprint due to raw material acquisition and construction of plants, energy used in running lights and other amenities as well as emissions due to transportation of fuels were all omitted from calculation. Cost was also not considered and the study was solely based on environmental impacts as denoted by carbon footprint.

4.1.6 Allocation

According to ISO 14040 : 2006, allocation is the partitioning of input or output flows of a process or a product system between the product system under study and one or more product system. During manufacture of the product, it can have multiple other products that are created simultaneously. Material and energy flows needs to be separated for different products based on the ratio of products created. For example When producing 1 kg of hydrogen from water, 8 kg of Oxygen is created. The energy and material needs to be divided between the products to correctly assign the environmental impacts.

In this study, allocation for oxygen is not conducted as it is assumed it is not collected and hence has no significance. Allocation is conducted in Fischer-Tropsch synthesis. During FT process, a mixture of diesel/kerosene(jet fuel)/and naphtha is obtained with a ratio of 65/25/15 by mass. Allocation is conducted to correctly portray the energy and material usage of different products. Synthetic diesel is only allocated its share in energy and material.

4.2 Life Cycle Inventory

Life cycle inventory contains the inputs and outputs of each process included within the system boundary. This chapter contains the technical details of modelled processes.

4.2.1 Traditional Diesel

Lifecycle data for fossil fuel data was taken from GaBi database. The process used was modelled as EU-28 diesel at refinery. The system boundary of the model can be seen in Figure 8.

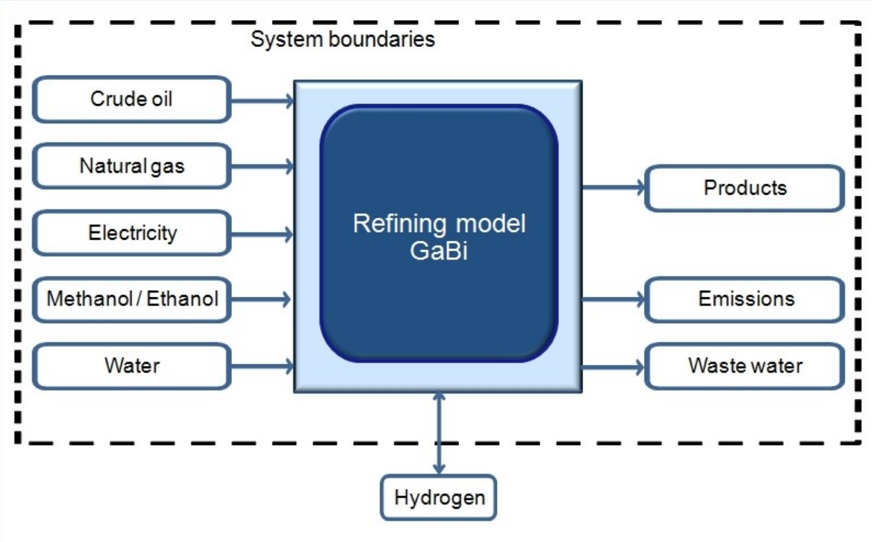

Figure 8: System boundary of diesel refinery (GaBi database).

Allocation for the process, according to final refinery products, were modelled by GaBi. The different products in the schematics considered by GaBi can be observed in Appendix I Energy density for diesel fuel was taken as 43.1 MJ/kg (Neste Corporation, 2016, 28).

4.2.2 Electricity

Electricity is the primary source of energy required for all the processes. Electricity supply was modelled after Finnish grid and German grid and the data were taken from GaBi database. The values found in GaBi are from 2015. Lifecycle analysis of the grid is available pre-modelled in GaBi and the system boundary of the modelled process can be seen from Figure 9.

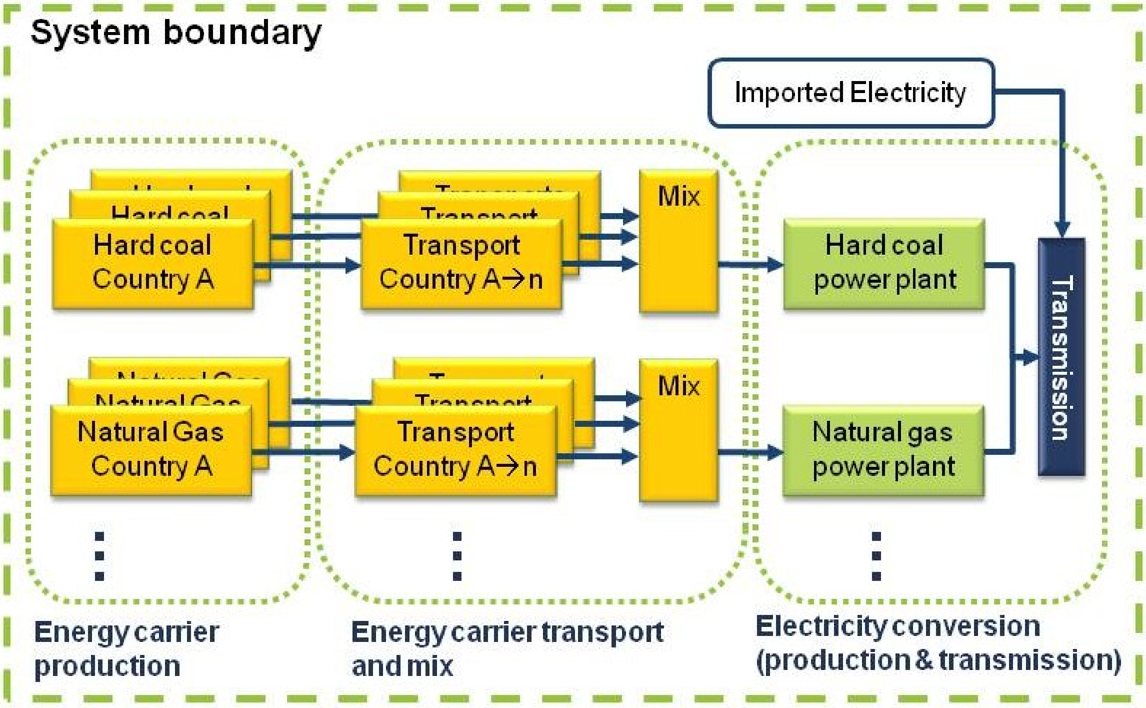

Figure 9: System boundary of electric grid LCA, GaBi database

Finnish Grid Mix

Grid electricity mix at consumer (FI) process was used from GaBi databae. The model is a lifecycle analysis of Finnish grid mix from 2015. Share of energy sources of the grid can be seen from Figure 10. In 2015; nuclear, hydro power and bio mass were the three main sources of electricity in Finland (75%). Fossil fuels and natural gas had a share of 16% (Finnish

Energy, 2016). The life cycle analysis was pre conducted with the system boundary seen on Figure 9.

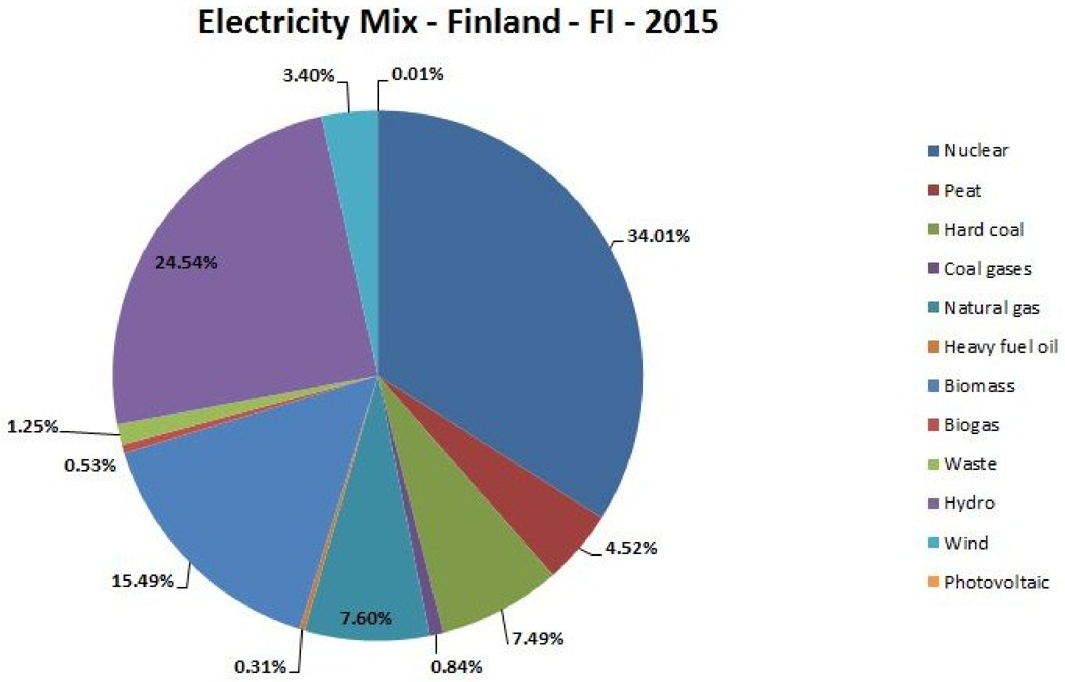

Figure 10 Finnish grid electricity composition in 2015 (GaBi database)

4.2.3 German Grid Mix

‘Grid electricity mix at consumer (DE-2015) ’ process available in GaBi was used to represent the German grid. The share of electricity in the model can be seen in Figure 11. Germany has a 23.95% share of lignite which is the single highest share among the energy source.

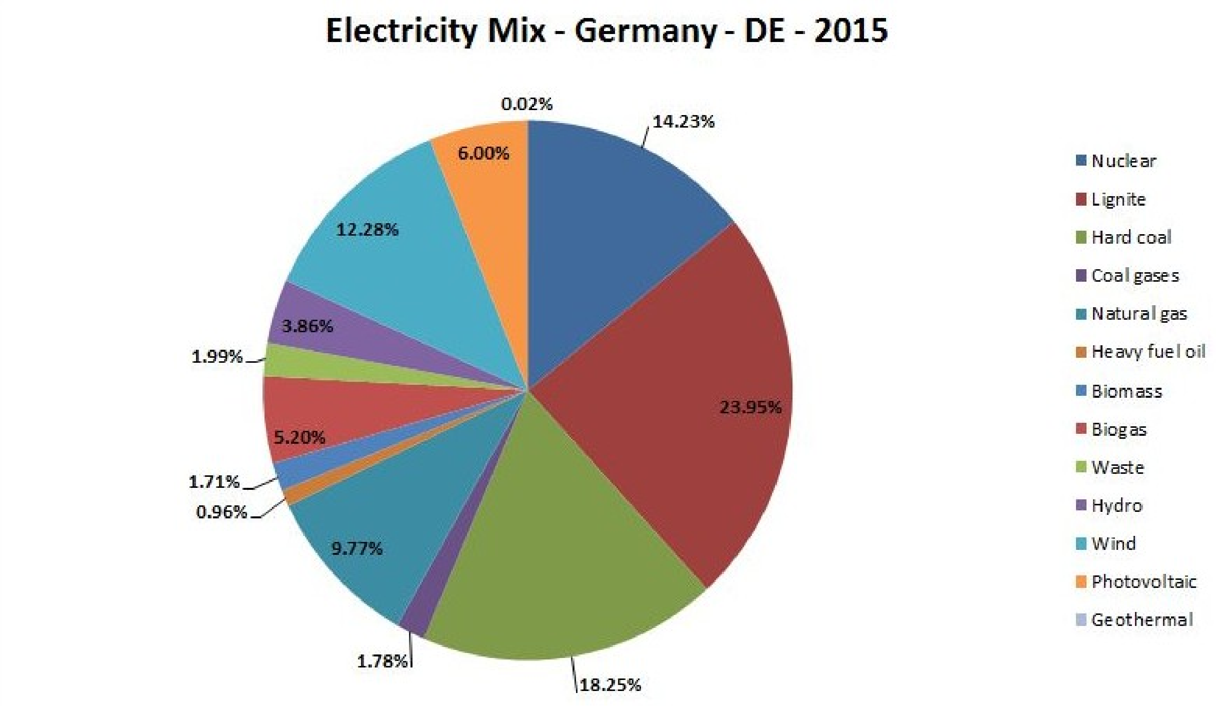

Figure 11: German grid electricity composition 2015 (GaBi database).

Renewable Electricity Grid

Electricity form wind and electricity from solar (PV) was used to simulate renewable electricity grid. The process was taken from GaBi database. Used processes were modelled after Finnish electricity from wind and solar.

4.2.4 Hydrogen Synthesis

Alkaline Electrolysis Cell and Solid Oxide Electrolysis cell were chosen for modelling. The processes are described in detail below.

Alkaline Electrolysis Cell

The data for AEC was taken from research by Hänggi et al. (2019) and Lundberg (2019) both report data from similar range. The inputs for the process can be seen in Table 4.

Table 4: Input of Alkaline Electrolysis Cell per 1 kg of hydrogen produced

Input	Input per kg of hydrogen
Electricity	56 kWh
Deionized Water	10 litres

Solid Oxide Electrolysis Cell

Data for SOEC were taken from Häfele et al., (2016) and Lundberg (2019). The data reported are presented in Table 5.

Table 5: Input for Solid Oxide Electrolysis Cell per 1 kg of hydrogen produced

Input	Input per kg of hydrogen
Electricity	65 kWh
De-Ionized Water	9.1 litres

As discussed in chapter 2.1.3, SOEC has an operation temperature of 650-850°C which results in better reaction kinetics. It also allows optimization of setup which is capable of using operational heat from the process to replace the electricity required.

4.2.5 Carbon dioxide

From the different possible sources of carbon dioxide, Direct Air Capture (DAC) and Capture from Flue gas were chosen for this report, which are described in detail below.

Direct Air Capture

There were two prototypes available, one by Sunfire/Climeworks (Evans, 2017) and another by Carbon Engineering (Vice News, 2018). Climeworks data suggests the process requires 400kJ/mol of CO_2 thermal and 80 kJ/mol of CO_2 electrical energy. It would be possible to supply the thermal energy from FT synthesis process negating external thermal energy supply but the DAC system is required to be connected to the FT synthesis plant, which could not always be possible. Data from Gebald (2014) was taken which suggests the process takes 350 kJ/mol of CO_2 of electric energy for capture which uses a higher electrical energy than the alternative. Hence, 1 kg of CO_2 requires 2.21 kWh of electrical energy.

Flue gas Capture

Reiter and Lindorfer, (2015) report a mole of CO_2 requires 163kJ thermal and 10kJ electrical energy per mol of CO_2. Flue gas originates from chimneys from furnaces or kiln of processes such as power plants, steel industry and cement industry. Flue-gas is generally produced from exothermic reaction with available waste heat. Hence, thermal energy was omitted from the energy required as the waste heat from the main process can be used as discussed in chapter 2.2.3. Therefore, 0.0631kWh of electrical energy is required for 1kg of CO_2.

4.2.6 Reverse Water-Gas Synthesis

RWGS was modelled separately from Fischer-Tropsch process to visualize individual impacts and electricity usage. From equation 11, it was calculated the RWGS process requires 2.81kWh of energy per kg of 22 kg Carbon monoxide produced or 0.10kWh per 1 kg of CO. The energy was assumed to be electrical.

4.2.7 Fischer-Tropsch Synthesis

Fischer-Tropsch synthesis is a complex process and further refining and enrichment needs to be carried out before desired fuel can be obtained. Becker et al., (2012) reports the process consumes about 50 kJ of electrical energy for synthesis and about 30 kJ of electric energy for upgrade per a mole of -CH2- chain. van Vliet et al., (2009) suggests an 85% conversion of the obtained crude to diesel and the remaining 15% can be used to provide heat for the total diesel production heat demand. Due to lack of further corroborating data, the 85% of diesel synthesis model was discarded instead a 15/25/60 share for naphtha/jet fuel (kerosene)/ diesel as seen from Table 1 on chapter 2.5 was taken which provided some process data for corroboration.

Different types of fuels are obtained from FT synthesis and the properties of the products depend on the carbon number of the products. Carbon number of 5 and 6 are gasoline blends, C7 and C10 are Naphtha, C11 to C19 are diesel and C20 and above are gas which are further cracked down into the products according to the cracking method. (Becker et al., 2012)

As an average, Carbon 15 was taken to represent synthesis diesel. Due to the energy required available per -CH2- chain, calculation was done for the chosen carbon number. Table 6 represents the inputs for FT-synthesis and upgrade process.

Table 6: Entries of Fischer-Tropsch synthesis and fuel upgrade

Process entries	Amount
Carbon Monoxide In	420 kg
Hydrogen In	90 kg
Electricity In	23.9 kWh
Diesel Out	144 kg

Kurevija et al. (2007, 83) reports synthetic diesel has 8% lower density than conventional diesel and marginally higher heating value of 43.8 MJ/kg (traditional diesel = 43.1MJ/kg). Neste Corporation (2016, 28) provides heating values of 37 MJ/kg to 44 MJ/kg. A heating value of 37 MJ/kg was chosen for the model to represent reported lower values.

4.2.8 Diesel Passenger Vehicle

A euro 6 standard diesel car (2016 onwards) was used to represent a typical passenger diesel car. The car was modelled with emissions and energy data from VTT Technical Research Centre (2017). A mean energy demand of 2.1 MJ/km was used.

Since synthetic diesel produces less emission (DeHaan et al.; Alleman et al., 2005), modification to emissions data was made for diesel car when using synthetic fuel. The percentage reduction in emissions are presented in Table 7. This data was used to reflect the reduction in emissions when synthetic diesel was used as fuels. It should be noted that only carbon dioxide emission is significant in carbon footprint calculation.

Table 7: Reduced Exhaust Emissions with Synthetic Diesel compared to Traditional Diesel

Products	Reduction in emissions compared to fossil fuel diesel
Hydrocarbons	62%
Carbon monoxide	45%
Carbon dioxide	4%
NOx	13%
Particulate Matter	55%

4.3 Life Cycle Impact Assessment

Due to this study being a study of carbon footprint, Global Warming Potential (100 years) excluding Biogenic Carbon was chosen as the only impact category. Weighting and normalization was not conducted as there is only one impact category, hence comparison between different categories is unnecessary. CML 2001 impact assessment was utilized and the selected impact category was CML 2001-Jan 2016 Global warming potential (GWP 100 years), excluding biogenic carbon. The unit is equivalent kg of carbon dioxide or kgCO_2e. Total global warming potential (GWP) of each scenario planned in Table 3 is presented in Figure 12.

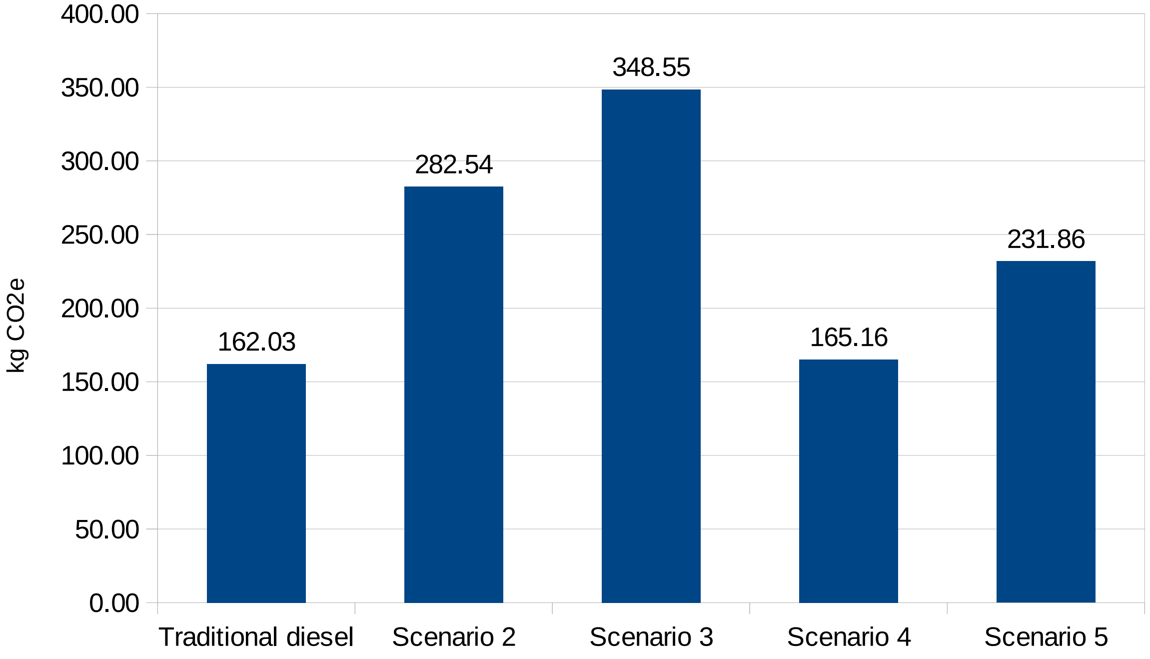

Figure 12 Global warming potential (100 years excluding biogenic carbon) of traditional diesel and synthetic diesel production scenarios

Comparing carbon footprint of synthetic diesel (e-diesel) and traditional diesel for a distance of 1000 km, it can be observed that traditional diesel has a lower carbon footprint than e-diesel production with Finnish grid electricity usage. From Figure 12, it can be seen that the carbon footprint of traditional diesel is comparable to scenario 4 (using AEC and flue gas capture) with e-diesel with a difference of +2%. Footprints from scenario 2, 3 and 5 are between 30% to 54% higher than traditional diesel.

From 13, it can also be observed that hydrogen production methods have the highest carbon footprint of all the processes. Alkaline electrolyser has approximately 16% lower electricity demand compared to Solid Oxide Electrolyser. After hydrogen production methods, vehicle running on traditional diesel has the next highest carbon footprint. Comparing only the carbon footprint of fuel usage in vehicles, traditional diesel has approximately 85% higher carbon footprint than synthetic diesel. Carbon capture methods have negative carbon footprint. Flue gas capture has lower carbon footprint than that of Direct Air Capture.

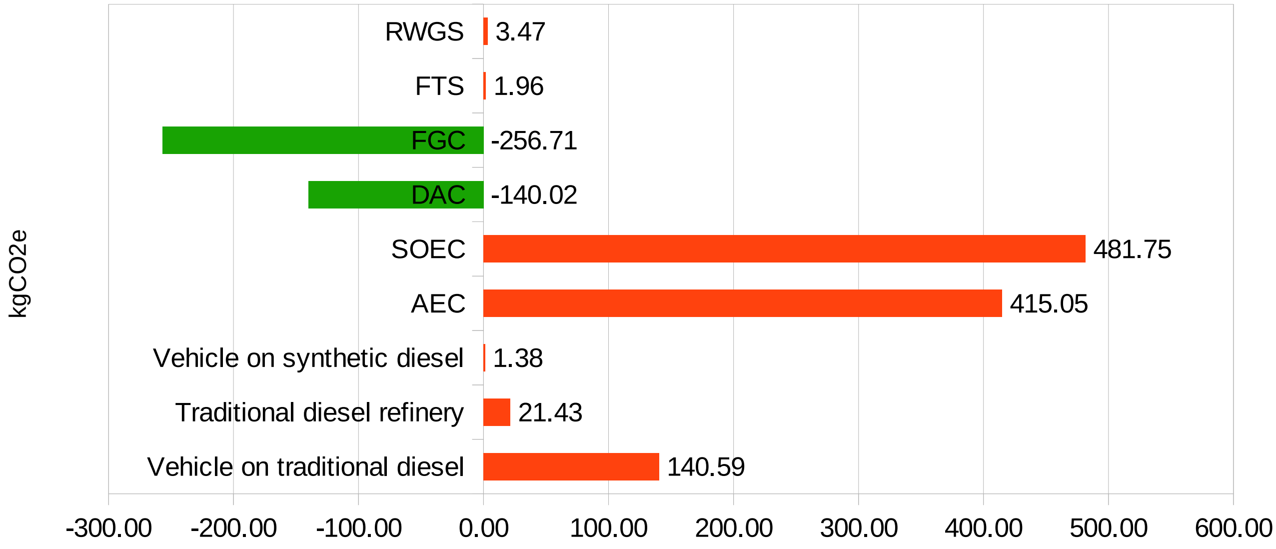

Figure 13: Global warming potential of individual modelled processes

When using German Grid instead of Finnish grid, a higher carbon footprint can be observed. The GWP due to German grid is about 75% higher than that of Finnish Grid as seen from Figure 14.

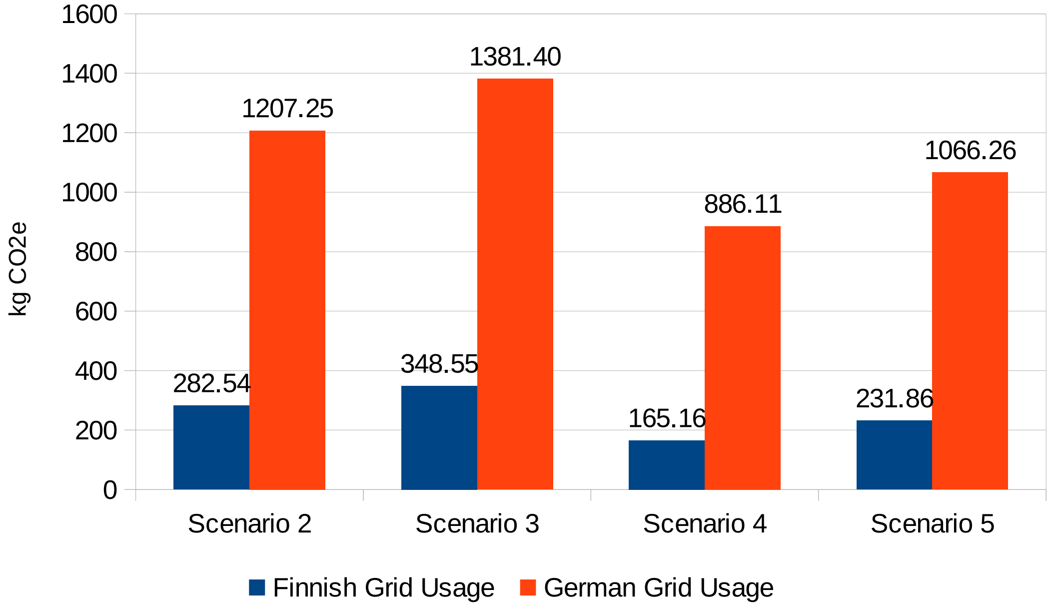

Figure 14: GWP comparison between Finnish and German grid in modelled scenarios

With a grid with 100% wind energy is used, all the scenarios with e-diesel have a negative carbon footprint. The results are similar with 100% solar energy grid as seen in Figure 15.

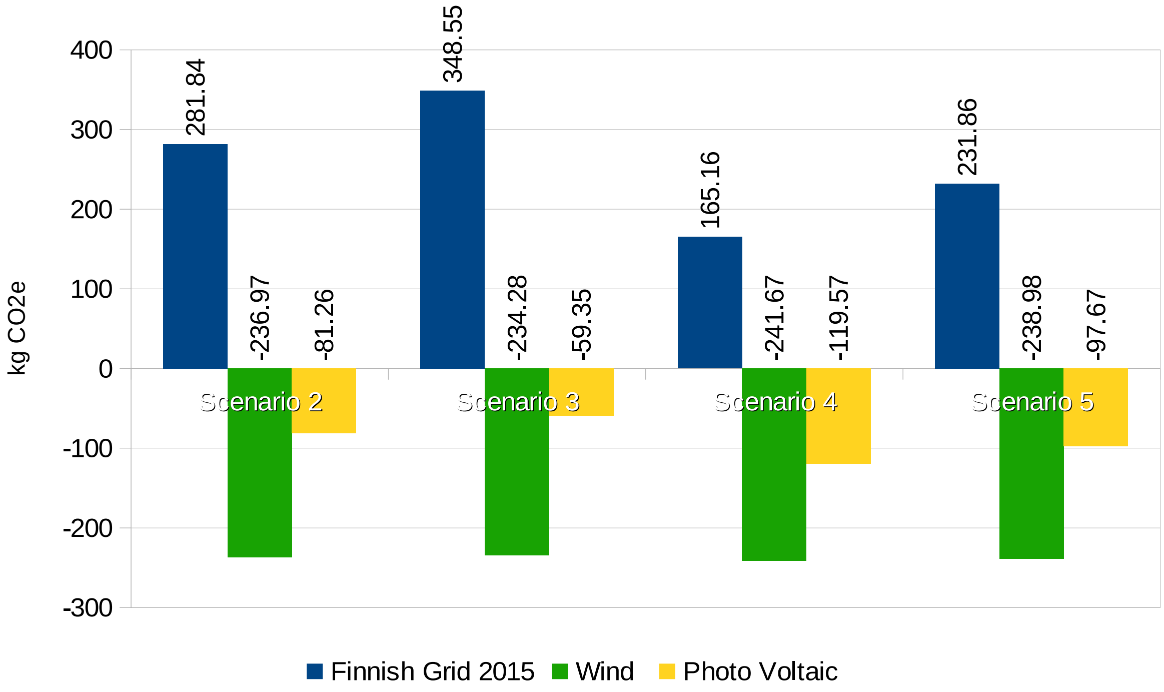

Figure 15: Carbon footprint comparison of synthetic fuel production scenarios with Finnish grid 2015 and 100% wind and solar (PV) grid

SOEC can be optimized as discussed in chapters 2.1.3 and 4.2.4. Optimization can result in a substantial reduction of carbon footprint from scenarios using SOEC as hydrogen source (scenarios 3 and 5). From Figure 8 it can be observed that after optimization, scenario using SOEC process has a negative carbon footprint with a reduction of 138% than before optimization. It is also possible to reduce energy required by Fischer-Tropsch synthesis by using heat from SOEC and also further optimize the system by conducting co-electrolysis of hydrogen and carbon dioxide (chapter 2.1.3). Further comparison of processes with SOEC optimization is presented in Figure 16.

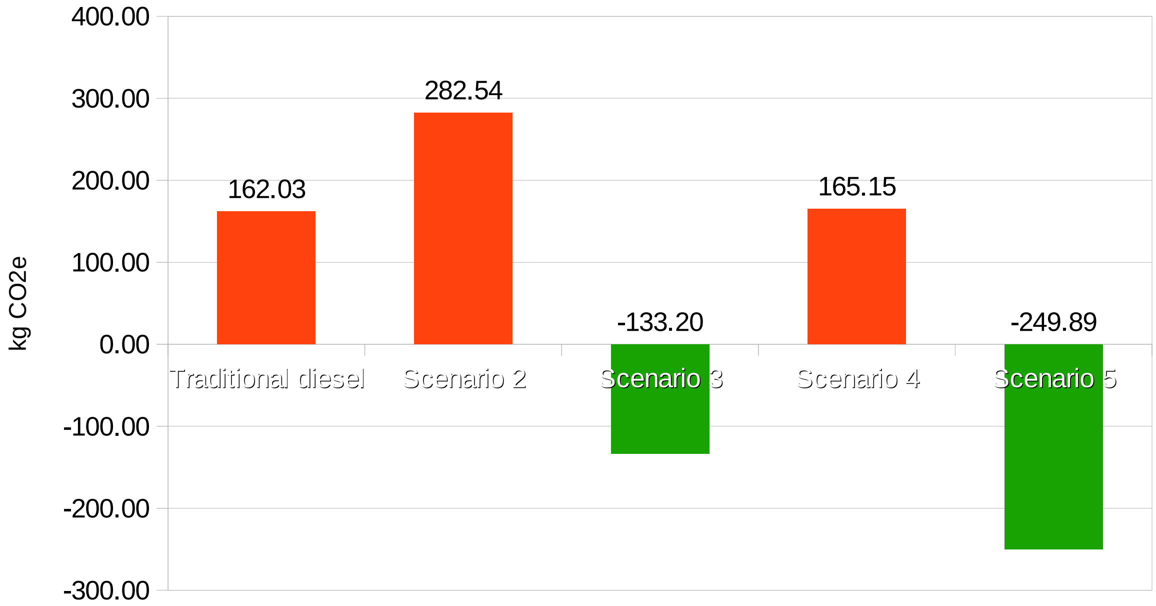

Figure 16: Global warming potential of modelled scenarios with SOEC optimization

With German grid usage, the percentage reduction in carbon footprint on scenarios 3 and 5 are similar to that of Finnish grid. However, only scenario 5 which uses SOEC and flue gas capture combination has a negative carbon footprint as seen from Figure 17.

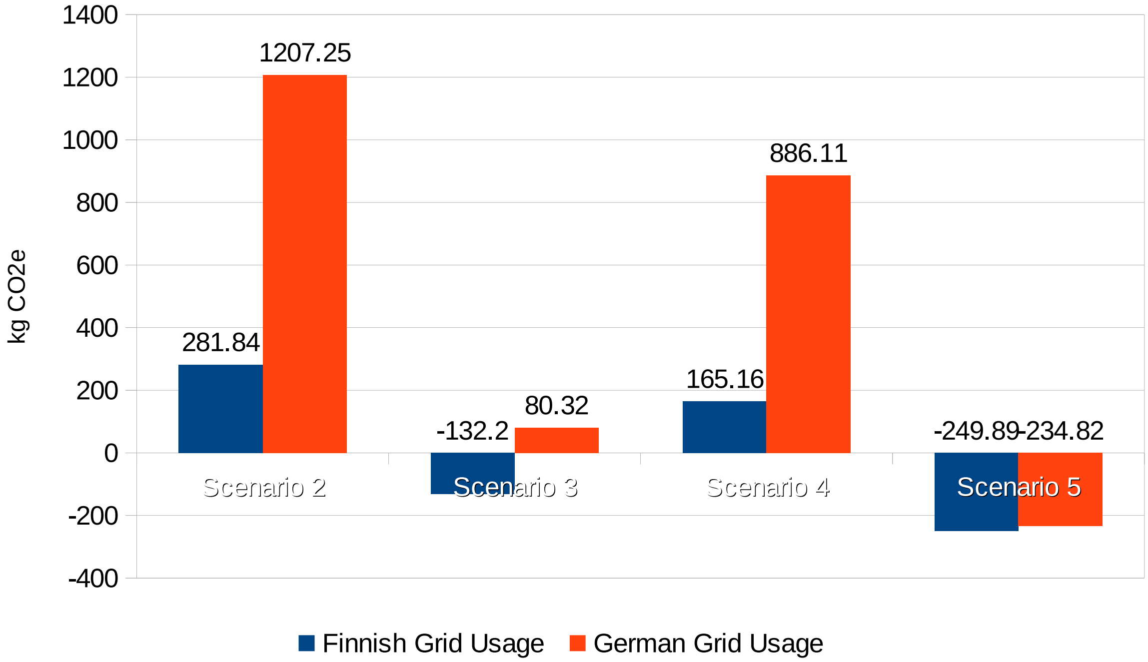

Figure 17: GWP comparison between Finnish and German grid in modelled scenarios after SOEC optimization.

4.4 Interpretation of Results

Comparing carbon footprint for the fuel needed for 1000 km with traditional diesel and different scenarios of synthetic fuel production with Finnish grid electricity, it was found that fossil fuel diesel had a lower carbon footprint. Among the synthetic diesel production pathways, scenario 4 which used alkaline electrolysis cell and flue gas capture as carbon and hydrogen sources had the least carbon footprint among the e-diesel pathways. The carbon footprint of scenario 4 diesel was approximately 2% higher than that of traditional diesel from refinery. Other scenarios had carbon footprint 30% to 40% higher than traditional fossil fuel. Scenario 3 had the highest carbon footprint which used Direct Air Capture and SOEC as carbon and hydrogen sources respectively.

Carbon capture processes have a net negative carbon footprint. This is due to carbon being removed from the atmosphere directly or from flue gas. Although both methods capture equal amount of carbon dioxide to produce fuel for 1000 km journey, direct air capture has a higher energy demand compared to flue gas capture which can observed from Figure 13. This is due to the fact that flue gas can use heat energy from its own process to reduce electricity requirement as discussed in chapter 2.2.3 and 4.2.5.

From Figure 13, it can be clearly observed that electrolysis has the highest amount of energy requirement. Solid oxide electrolysis cell has approximately 16% higher energy requirement than alkaline electrolysis cell. This is because of the high operational temperature needed for SOEC as discussed in chapter 2.1.3. When the energy is supplied from the Finnish grid, traditional diesel is still the better option in terms of carbon footprint. Emissions due to grid electricity are a major factor in carbon footprint of synthetic fuels. With a 100% renewable energy source, such as wind or solar energy, synthetic fuels yield a net negative carbon footprint as seen from Figure 16. It can also be observed that Fischer-Tropsch synthesis and RWGS reaction have negligible carbon footprint compared to the whole process. Similarly, if emissions from vehicle is only considered for a 1000 km journey, vehicle using traditional fossil diesel has approximately 85% more carbon footprint than when using synthetic diesel.

Usage of German grid electricity yields 75% more carbon footprint than that of Finnish grid. Comparing Figure 10 and Figure 11, it can be observed that while Finnish grid has the highest share of nuclear at 34% followed by bio mass and hydro electricity. Lignite, a type of coal, has the highest share in German grid. This explains the high disparity in carbon footprint between the two national grids. With the results in hand, a synthetic fuel production in the Finnish grid is clearly favourable to German grid in terms of carbon footprint.

Optimization of systems have been proposed such as by Fasihi et al. (2016) which is highly efficient with interconnected systems designed to use intermittent renewable resources. Also, discussed in chapters 2.1.3 and 4.2.2, designing the process to incorporate heat from SOEC which has a high operating temperature can completely replace electricity in other processes. Optimizing SOEC can result in the scenarios incorporating it to be carbon negative. Scenario 5 which utilizes Finnish grid 2015 with SOEC and flue gas capture can potentially cause a net negative footprint of (-)250 kg of CO_2 equivalent for e-fuel required for 1000 km of journey (56.8 kg of e-fuel). That is about 440 g of carbon dioxide equivalent removed from the atmosphere per 1 kg of e-fuel produced. The potential is even higher when 100% renewable sources are used as seen in Figure 18.

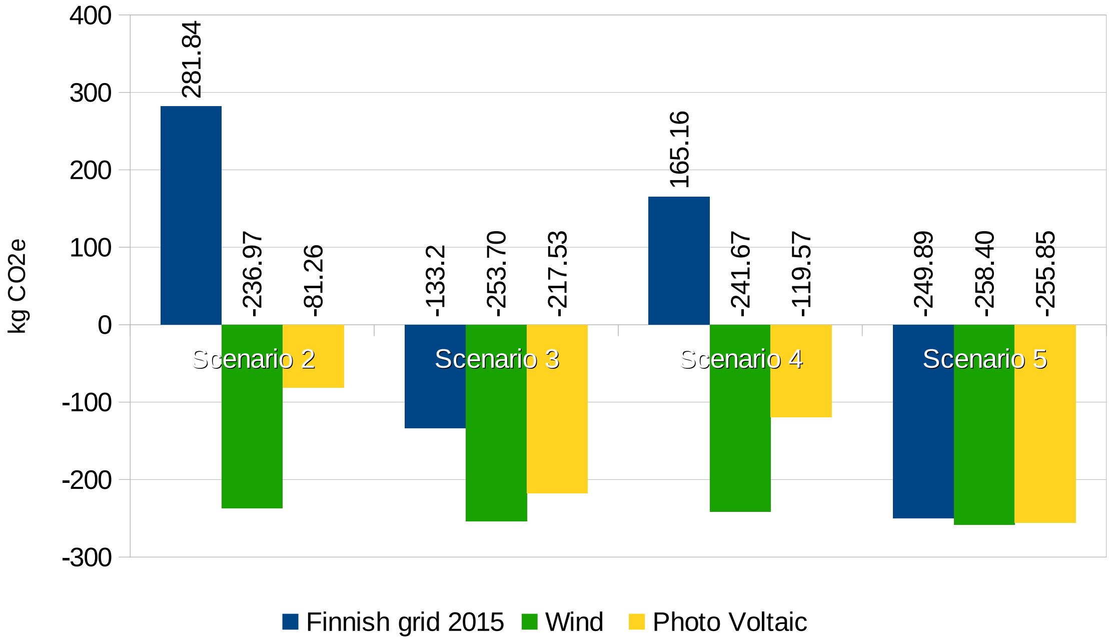

Figure 18 Carbon footprint comparison of synthetic fuel production scenarios with Finnish grid 2015 and 100% wind and solar (PV) grid after SOEC optimization.

5 DISCUSSION

Previous studies have been conducted for synthetic diesel by Spath and Dayton (2003), van Vliet et al. (2009), Larsson et al., (2015) and Hänggi et al. (2019). Spath and Dayton (2003) focus on biomass–derived syngas, whereas van Vliet et al. (2009) discuss on the possibility to use other feeds like natural gas, coal, biogas or mixture for Fischer-Tropsch synthesis. Those studies comment on the energy conversion of different fuels and pathways. Hänggi et al. (2019) also discuss energy conversion rate and further demonstrate the energy return of fuels per energy invested. Larsson et al., (2015) conducted a techno-economical assessment of synthetic fuels in the Swedish market and concluded methane produced from electricity to be the most competitive alternate fuel source.

Nikolas Hill et al. (2020) in their publication report on the future of all types of fuels for transportation including synthetic diesel and gasoline. The report was conducted to provide policy-maker insights on the significance and relevance of transportation in climate change. A total and extensive LCA analysis was conducted with various types of power trains, fuel types and energy sources until 2050. The study concludes e-fuels or synthetic fuels will still have far greater GWP impact even in 2050 when using grid electricity mix. The study concluded synthetic gasoline to have a carbon footprint of more than 100 gCO_2 e per 1MJ of fuel while synthetic diesel to have about 500 gCO_2 e per MJ of fuel. Their projection for impact for the grid in 2050 is still 27.02 gCO2e/MJ three times that of renewable electricity usage. The report recognizes using renewable or very low-carbon electricity as the key in achieving environmental benefits from the use of e-fuels.

Comparing with the findings of this report, synthetic diesel was found to have a carbon footprint of 80 – 165 gCO_2e per 1 MJ of fuel using the Finnish grid which has a 58 gCO_2e/MJ (2015) carbon footprint and 420-660 gCO_2e/MJ when using the German grid which has a carbon footprint of 157 gCO_2e/MJ (2015). Simulating the processes with a wind energy based grid with a grid footprint of 2.34 gCO_2e/MJ, synthetic diesel had an average negative carbon footprint of (-)110 gCO_2e/MJ. With solar based grid with a carbon footprint of 19.1 gCO_2e/MJ, the processes had a negative carbon footprint between (-)30 to (-)60 gCO_2e.

However, with optimization to SOEC for hydrogen synthesis and using flue gas capture as carbon source, the impact was found to have a negative carbon footprint of up to (-)120gCO_2e per 1MJ of synthetic diesel on the 2015 Finnish grid, up to (-)110gCO_2e/MJ on the German grid, (-)112 to (-)125 gCO_2e/MJ with wind based grid and (-)40 to (-)120 gCO_2e/MJ with a solar based grid.

5.1 Answers to Research Questions

Comparing the Carbon Footprint of traditional fossil diesel and synthetic diesel from four different production pathways, following are brief answers to the research questions defined in chapter 1.1.

5.1.1 Which pathway of synthetic fuel manufacture has the least carbon footprint?

Hydrogen production has the highest carbon footprint followed by carbon dioxide capture. Alkaline Electrolyser has less carbon footprint than Solid Oxide Electrolyser by approximately 16%. If SOEC setup is optimized to supply thermal energy to other processes like Fischer-Tropsch synthesis and possibly utilize waste heat from exothermic industries such as steel industries, or combined heat and power plants, then SOEC can have a net zero carbon footprint and hence lower footprint than AEC.

Similarly, DAC uses more energy as it is depended on electricity whereas flue gas capture uses little electricity compared to DAC due to the fact that flue gas can utilize thermal energy from its own process negating the need of electricity.

Hence, using AEC for hydrogen synthesis and flue gas capture for carbon source has the lowest carbon footprint when optimization of SOEC is not possible. With optimization, SOEC is clearly the better option with flue gas capture, which results in the process to have a negative carbon footprint of up to (-)440 gCO_2e/kg or (-)120 gCO_2e/MJ with the 2015 Finnish grid. The footprint is even lower with renewable energy sources.

5.1.2 What is the difference in carbon footprint between fossil fuel and synthetic fuel?

Fossil fuel diesel was calculated to have lower carbon footprint compared to synthetic diesel by 2-40% using the Finnish grid mix. However, with SOEC optimization, synthetic diesel had a 250% less carbon footprint than traditional diesel with a net negative carbon footprint. The values are even lower when renewable energy sources are used.

5.2 Future

Energy is the major investment required for the manufacture of synthetic fuels, and electricity is the main supply of energy. There are many alternative modes of transportation for the future that rely solely on energy from renewable, zero carbon or minimal carbon emissions sources. Electric vehicles are arguably the best future as they produce zero emissions during operation. Electrical vehicles have more flexibility as they can also be connected to smart grids to manage future power supply and demand. The main problem with renewable is that they are intermittent and hence not always available. There are models proposed by Fasihi et al., (2016) which demonstrates efficient methods to incorporate available and future technologies for efficient and reliable synthetic fuels production. One of the suggested examples is using PEMEC technology with renewable energy sources for hydrogen production as it has lower startup time.

It is possible to overproduce energy when possible and store for later use. Optimal storage management is required for absolute grid coverage. Electric vehicles can provide a storage option when connected to smart grids. But one of the problem is availability of materials. Batteries require raw materials which are needed to be mined, and recycling previously mined elements cannot realistically be sufficient. There are roughly about a billion personal vehicles in the planet that use fossil fuels. Fifty trillion euros of investment is required to replace them with an average cost of fifty thousands per new alternative vehicles. Future studies should also include land usage as metric to visualize climate change.

Other modes of energy storage are hydrogen or Fischer-Tropsch products like methane, DME, syngas and synthetic gasoline/diesel. Hydrogen production and storage omits the need of carbon synthesis but usage of hydrogen requires hydrogen fuel cell vehicles or hydrogen to energy plants. Methane, DME and Synthetic diesel not only provides alternative energy storage mode but also a cleaner transportation option and a transitional bridge for a zero emission future. Methane can be used in syngas vehicles and power plants and DME can be used in existing diesel vehicles with some adjustment. Synthetic diesel can be used in existing diesel vehicles without any modification. Fischer-Tropsch fuels can also be utilized as carbon sequestration method.

New research from Randers and Goluke (2020) suggests a chain reaction caused by self-sustained melting of permafrost which is caused by methane release which results in lower surface albedo which in turn causes higher atmospheric humidity. This causes a continuous rise in temperature even if GHG emissions due to human activities reach zero by 2100. The research even concludes that the cycle will continue even if GHG emissions reached zero by 2020. The simulation projects global sea level rise of 3 m by 2500 and temperature increase up to +2°C by 2500. This cycle is predicted to initiate just at +0.5°C above pre-industrial levels. This suggests that Paris agreement of 2015 to reduce global temperature and maintain it within +2°C is not sufficient for climate change mitigation. The research concludes that global temperature needs to be kept under +0.5°C to prevent climate change. This is not possible by only reducing GHG emissions. GHG needs to be taken out of the atmosphere to prevent climate change. Capturing carbon from air or flue gas and converting it to synthetic fuel for storage could be required to prevent climate change and to maintain temperatures at +0.5 °C above pre-industrial conditions. Synthetic diesel production is a good option as seen from this research, it has the potential to remove up to 440 gCO_2e/kg of fuel or 120 gCO_2e/MJ of synthetic diesel produced.

6 CONCLUSION

In this study, carbon footprint of synthetic diesel was calculated with different pathways and compared to that of traditional fossil fuel diesel. Finnish grid was primarily used to provide required power in the processes. The carbon footprint was calculated for 1000 km travelled by standard diesel passenger vehicle with the chosen fuels. The assessment demonstrated that using Finnish grid electricity, synthetic diesel produced would have a higher carbon footprint than that of fossil fuel diesel when process optimizations are not considered.

It was also seen that electrolysis had the highest footprint. SOEC had higher footprint than AEC due to its operating parameter. However, designing the processes to utilize waste heat showed significant reduction in carbon footprint with SOEC which was less than that of traditional fossil diesel. It was also observed that electric grid composition was the main factor that affected the carbon footprint. Synthetic diesel using German grid had considerably higher footprint than Finnish grid usage and in both cases still had higher footprint than traditional diesel. Usage of a renewable sources such as wind or solar PV results in a sizeable footprint reduction even before process optimization. Further optimization of processes and development in energy sources can lead to synthetic fuel to have even lowered carbon footprint.

Mitigating climate change is the primary challenge of our generation. Coalition of countries have joined together and set goals to limit climate change by limiting global temperatures to +2 °C compared to pre-industrial conditions. However, newer research has suggested the temperature needs to be maintained well below +0.5°C than pre-industrial conditions to prevent a chain reaction causing temperature increase of +3°C and sea level rise of +3 m. Limiting the usage of fossil fuels, which is the major contributor to GHG emissions and global warming, is not sufficient. Removal of GHG from the atmosphere is required to realistically maintain temperatures under the threshold. Carbon sequestration is essential. Planting trees and limiting biomass usage should also be prioritized when possible to prevent additional GHG in the atmosphere. Producing synthetic fuels with optimized processes using renewable energy sources with net zero or minimal carbon footprint results in a high amount of carbon dioxide removal from the atmosphere. The removed carbon, however, escapes back to the atmosphere once the fuel is burned. Although economically unfeasible, synthetic fuel can be stored in oil wells which could permanently remove carbon dioxide from the atmosphere. This could be necessary in the future to maintain global temperature to level below 0.5°C to prevent the chain reaction that leads to global temperature rise of +3°C by 2050.

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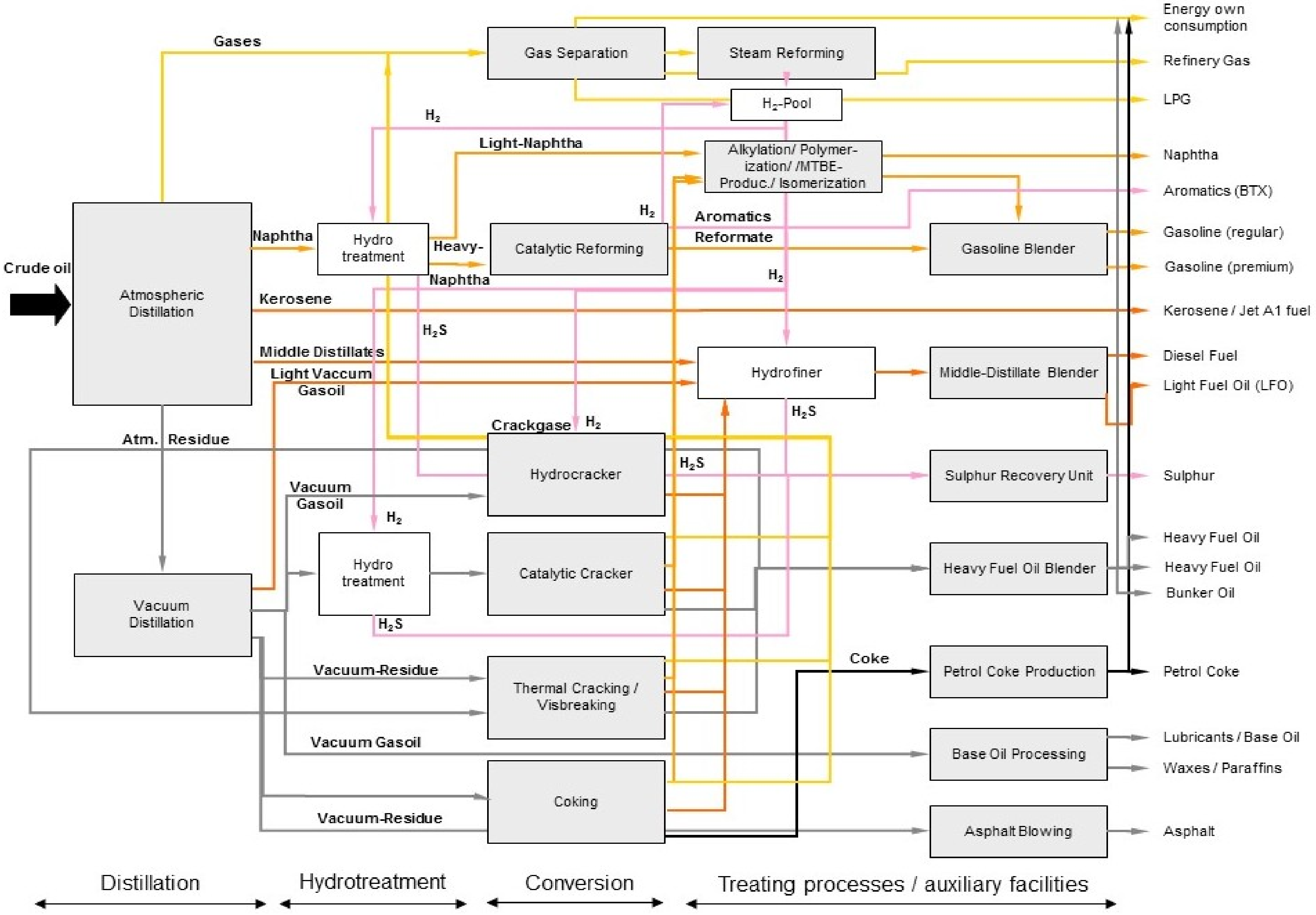
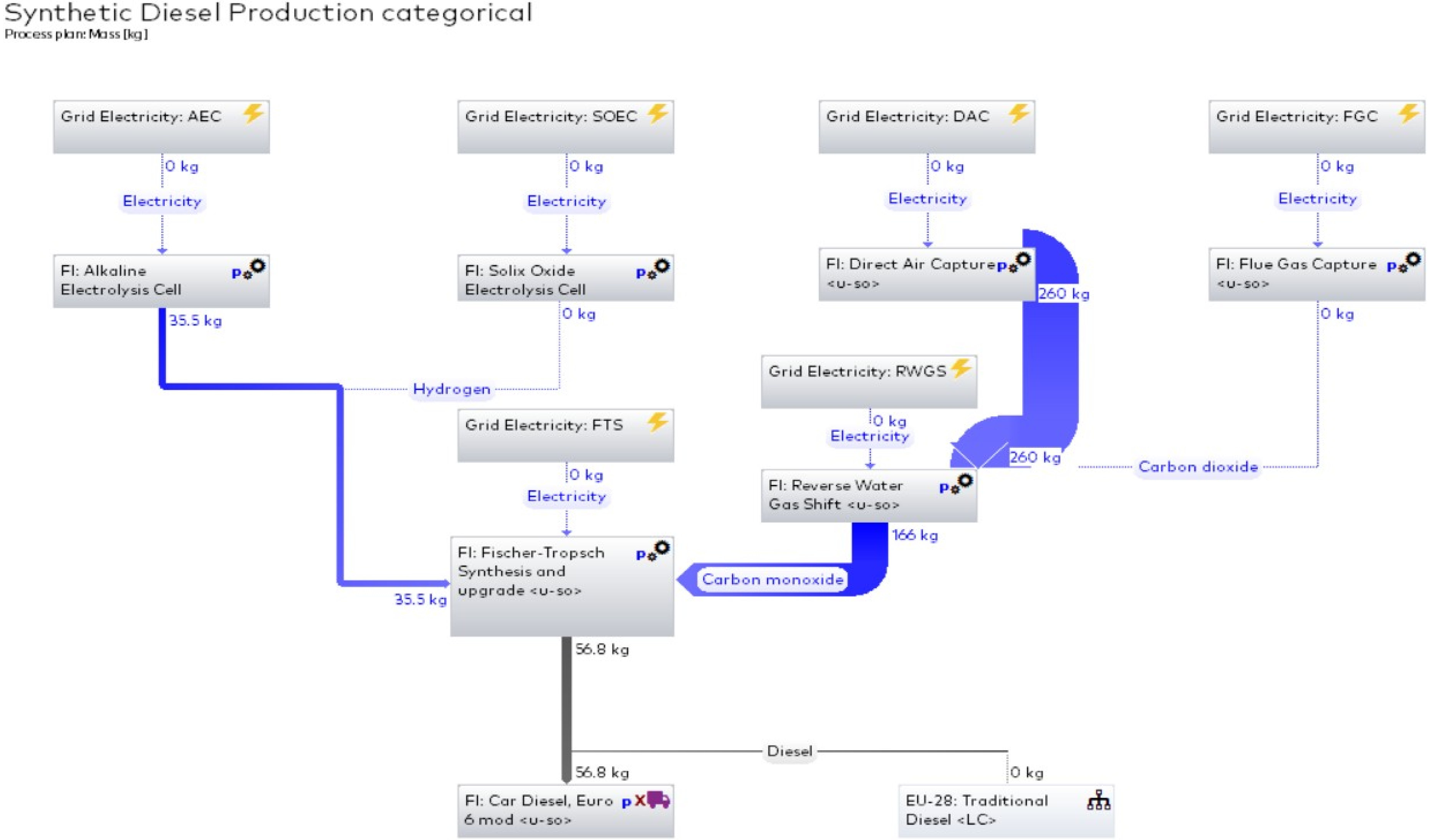
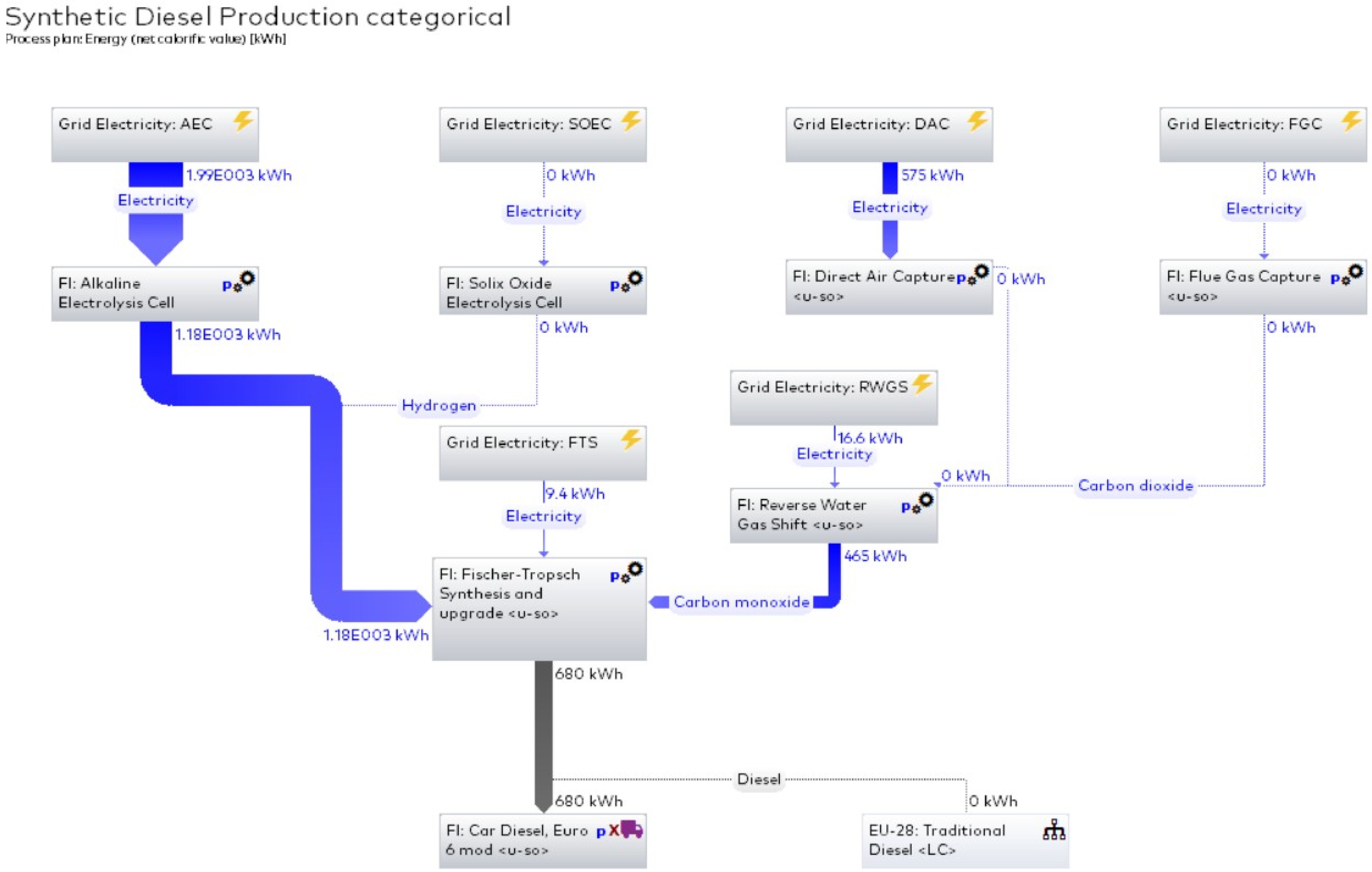
Appendix I GaBi Schematic of Diesel from Refinery



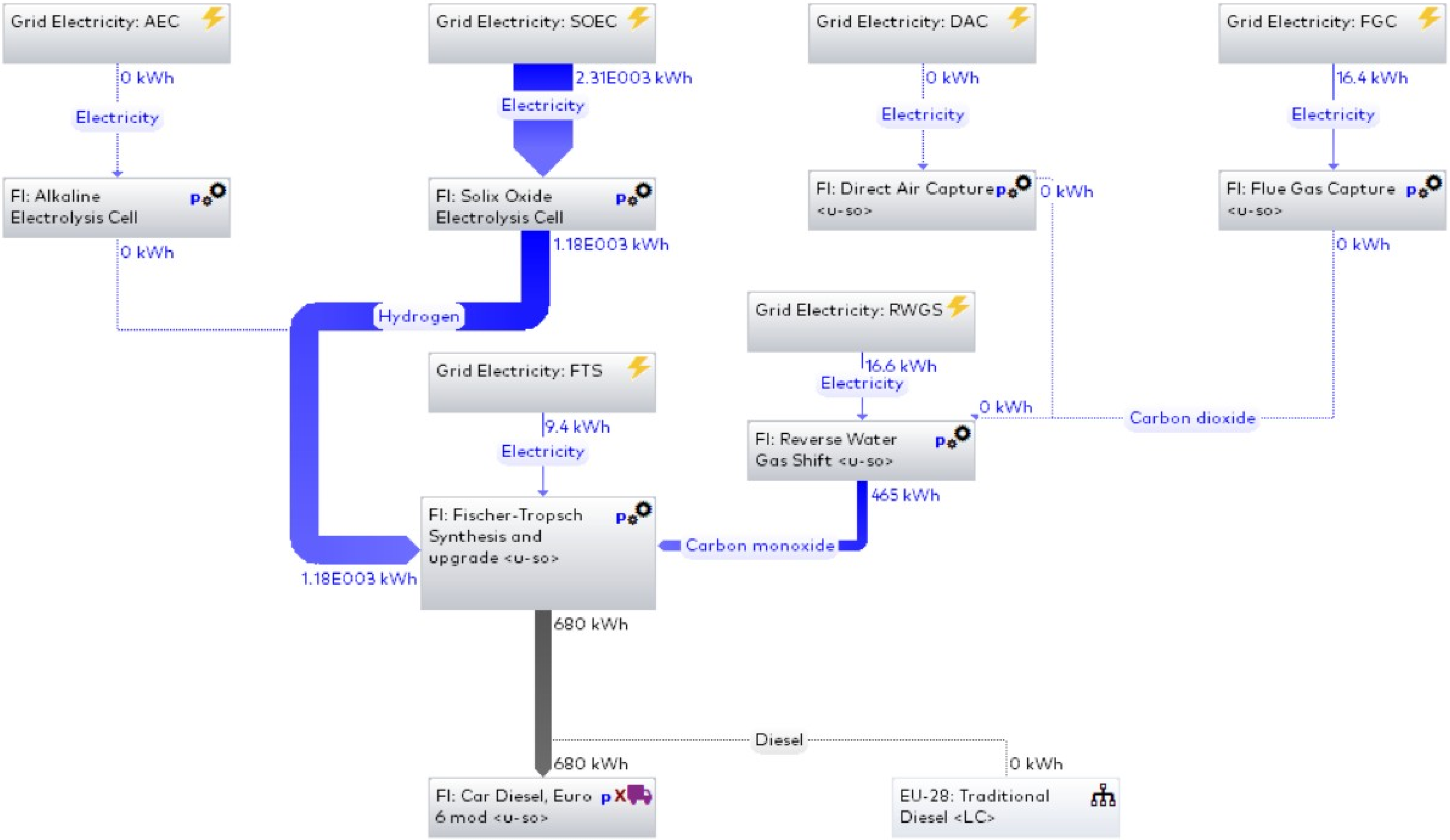
Appendix II Example GaBi model with mass of flows. Scenario 2 active.



Appendix III: Example GaBi model with net energy of flows. Scenario 2 active.



Appendix IV Example GaBi model with mass of flows. Scenario 5 active.



Appendix V Example GaBi model with net energy of flows. Scenario 5 active.