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UTILIZATION POSSIBILITIES OF CO₂ FROM CEMENT INDUSTRY IN DIFFERENT PRODUCTS

Examiners: Professor Risto Soukka

                     Professor Jero Ahola

Supervisor: Professor Risto Soukka

ABSTRACT

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CO_2 can be considered as an abundant raw material and its utilization into a product provides a sustainable and profitable alternative to carbon storage. The objective of this work was to identify a feasible way for the utilization of CO_2 emissions from the Finnish cement industry into a valuable product. Based on the literature research, 31 potential products have been identified in 6 categories: fuels, inorganic carbonates, polymers, chemicals, gas, and solid carbon. The information about the identified products and technologies has been gathered from the literature using the IBM artificial intelligence language processing tool. Comparative assessment basing on the gathered data determines that the most promising options are carbon nanomaterials, construction aggregates and production of gaseous CO_2 for different purposes, such as greenhouses and concrete curing.

The detailed evaluation of the chosen option shows that none of the chosen technologies completely satisfy all the requirements. Although the carbon nanomaterials can utilize all of the emissions, the technology is on an early stage of development and cannot be implemented in the near future. Production of the construction aggregates requires a significant amount of the materials and there is a lack of the available feedstock in Finland. Profitability of gaseous CO_2 utilization highly depends on the capture technology and the transportation distance.

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In Lappeenranta, December 2018.

Mariia Zhaurova

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Abbreviations

ACT	accelerated carbonation technology
APR	air pollution residues
BAT	best available technique
BPA	bisphenol-A
CaL	calcium looping
CC	carbon capture
CCA	cellulose carbamate
CCS	carbon capture and storage
CKD	cement kiln dust
clk	clinker
CNF	carbon nanofibers
CNT	carbon nanotubes
CVD	chemical vapor deposition
DMC	dimethyl carbonate
DME	dimethyl ether
DPC	diphenyl carbonate
EU	European Union
FT	Fischer-Tropsch reaction
GCC	grounded calcium carbonate
GHG	greenhouse gases
HSE	health, safety, and environment
IEA	the International Energy Agency
IPCC	Intergovernmental Panel on Climate Change
LWA	light-weighted aggregates
MEA	monoethanolamine carbon capture
MF	melamine-formaldehyde
MSDS	material safety data shit
MTG	methanol to gasoline
MTO	methanol to olefins

PC   polycarbonate

PCC   precipitated calcium carbonate

POM   polyoxymethylene

PPC   polypropylene carbonate

RWGS   Reverse Water Gas Shift

TRL   technology readiness level

UF   urea-formaldehyde

VOC   volatile organic compounds

Variables

Q_{tot} total quantity of goods transported

Q_{load} maximum load of a single vehicle

N_s number of shipments

L_{tot} the total distance of shipment

L the distance between nodes

t_{tot} the total time of transportation

v speed of the vehicle

t_{load} loading time of the vehicle

N number of vehicles

t_{ava} availability hours of single vehicle

crf   capital recovery factor

capex capital expenditures

opex   operational costs

1. INTRODUCTION

Cement is an important material for building and civil engineering industries, and one of the main contributors to climate change accounting for around 5 % of the global anthropogenic greenhouse gases (GHG) emissions (CEMBUREAU, 2013) Due to economic development and rising world population, cement consumption for the last years has increased and this trend is expected to continue.

Clinker, the main component of cement, is usually produced by calcination of limestone. Carbon-based fuels burned during the clinker production release less than a half of carbon dioxide (CO_2) related to the cement production, whereas the majority of carbon dioxide comes from limestone decomposition (Habert, et al., 2010). This fact sets rather unique challenges for the cement production industry. Therefore, to comply with climate regulations, cement producers are forced to find methods to mitigate the industrial emissions and, at the same time, keep the low prices for the high-quality product.

The European Cement Association (CEMBUREAU) suggested three routes under the sector control, to achieve a significant reduction in CO_2 emission: resource efficiency, energy efficiency, and carbon sequestration and reuse. Based on its study (CEMBUREAU, 2013) the combination of all suggested routes can lead to 80% reduction in emissions.

Considering that a significant part of CO_2 emitted from the cement production cannot be avoided, implementation of carbon sequestration and utilization technology seems necessary for the industry in order to achieve emission targets. Although such technologies can capture up to 90 % of cement production emissions (CEMBUREAU, 2013) they are still on the early stage of development and requires considerable investments as well as an additional energy input to capture the gas. This can lead to higher prices for cement, which can significantly reduce the economic efficiency of cement production and cement competitiveness over new construction materials. However, utilization of captured CO_2 into a valuable product can compensate investment needed for carbon capture and storage (CCS) technology implementation and reduce expenses required for carbon allowances.

Carbon is a valuable component of many polymer materials, chemicals, and fuels. Carbon utilization from the emitted carbon dioxide can contribute to the mitigation of climate change by reducing GHG emissions. Thus, it is quite important for the development of the cement industry to find routes and opportunities to utilize and produce a valuable product from captured CO_2.

The aim of this work is to find efficient ways to utilize CO_2 emitted by the cement industry. In addition to economic efficiency and low environmental impact, the important requirement for technologies is the possibility to organize the production process near cement plants in Finland. For example, in Lappeenranta, Southern Karelia. For this purpose article review and machine analysis of the gathered information will be made.

The next chapter provides the description of the cement production technologies, including information about the amount and quality of CO_2 emitted during the production process, and possible ways to reduce it. In addition, the chapter contains an overview of the cement industry in Finland. Chapters three and four describe the existing carbon capture, storage, and utilization technologies. It contains a brief explanation and main characteristics of each technology, its ability to capture CO_2 and examples of technologies implementation. Chapter five describe the machine analysis of the information gathered in the previous chapters. The aim of the analysis is to find the best option for CO_2 utilization using the artificial intelligence of the IBM Watson service. Next chapters analyze the most promising options of carbon dioxide utilization in products and the possibility of their implementation on a local scale.

2. CEMENT PRODUCTION AND INDUSTRY OVERVIEW

Cement is a man-made inorganic powder material with complex composition. Its main components are lime (CaO), silica (SiO_2), aluminum oxide (Al_2O_3), and iron oxide (Fe_2O_3) (Cement Sustainability Initiative, 2015). When mixed with water, cement forms a plastic paste, which develops rigidity and increases compressive strength with time. This effect, which is called hydraulic hardening occurs due to the reaction of cement components with water and formation of calcium silicates. The ability to form solid material from plastic state allow cement to bind solid particles together, which makes it the basic material to produce concrete. (Bye, 1999, p. 1)

Different types of cement exist for different purposes. The European standard SFS-EN 197-1:2011 provides a specification for 27 types of common cement and 12 types of special cement (SFS-EN 197-1, 2011). In addition, several special types of cement, for example, supersulfated cement, and very low heat special cement, are covered by individual standards. Within the various cement types, the Portland cement is dominant on the market (Lehne & Preston, 2018). In the European Union (EU), the CEM I and CEM II types have 85% of market share (Tsupari, et al., 2017). However, the composition of Portland cement can also vary. For example, according to the SFS standard, clinker content in the Portland cement can be in a range from 65% to 100% (SFS-EN 197-1, 2011, p. 15).

2.1. Cement production technology

The cement production process includes three main stages: raw material preparation, clinker production, and grinding and blending clinker with other materials to make cement (**Figure *1***). (IEA, 2018) The clinker production process has four different options, such as: wet, semi-wet, semi-dry, and dry, which are distinguished by the moisture content of the raw materials in the kiln. In addition, there are several types of kilns used in the industry. (Schorcht, et al., 2013)
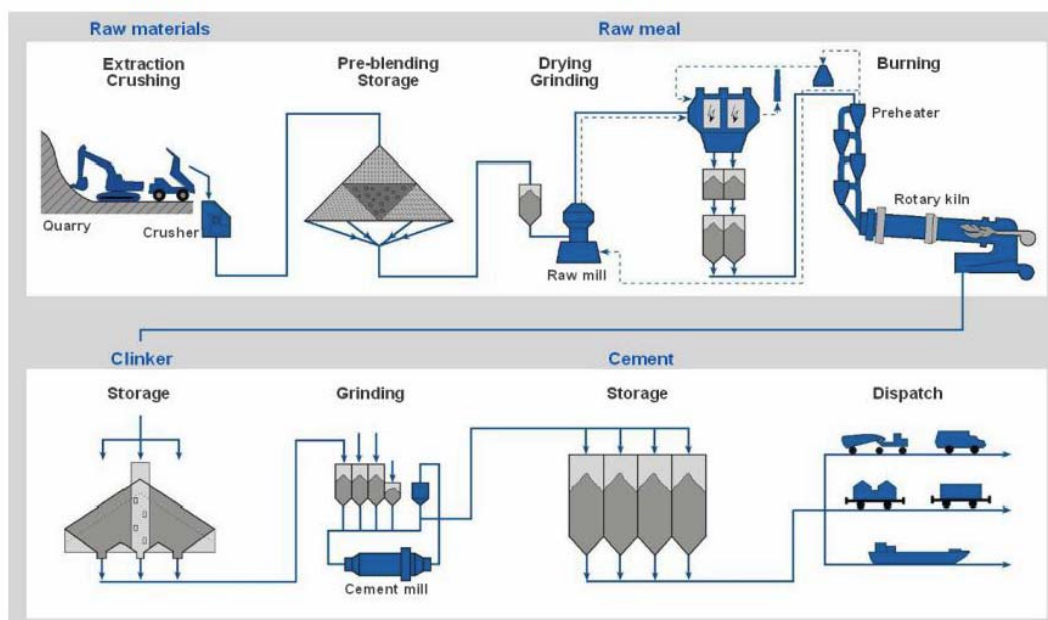

Figure 1 Cement manufacturing process (IEAGHG, 2013, p. 11)

Raw materials for cement are naturally occurring minerals containing calcium carbonate, usually limestone, marl or chalk extracted from quarries. Waste streams materials from other industries, such as mill scale, fly ash and slag, can be also utilized for cement production. (Cement Sustainability Initiative, 2015). Raw materials are blended and grinded in necessary proportions before the mix is fed to the rotary kiln. The preparation process, as well as all further operations, are different depending on the technology used. (Schorcht, et al., 2013).

There are 2 main types of technologies for clinker production: wet and dry processes. In addition, semi-wet and semi-dry processes can be utilized. Wet process is mainly used in Asia and practically not used in Europe, where only 2.5% of cement was produced using a wet process. Semi-dry and semi-wet processes are more common and their share in European cement production is 7.5%. (Supino, et al., 2016, p. 432.)

The dry process is the most common for the industry and over 90% of cement plants in Europe were equipped with dry kilns in 2007 (CEMBUREAU, 2013, p. 9; Moya & Boulamanti, 2016, p. 69). Worldwide, there is a trend towards a dry process and gradual reduction of wet-process plants (Moya & Boulamanti, 2016). The reason for the transition is the higher energy efficiency of the dry process, which consequently leads to the lower energy requirements and emissions from fuel burning (Kajaste & Hurme, 2016, p. 4048).

In the dry process, the raw material is preheated in calciner and then enters the kiln, where clinker is produced in temperatures about 1500 °C (Gerbelová, et al., 2017, p. 6142). The chemical process of clinker production from limestone called calcination (**Equation _1_**).

$$CaCO_3 \rightarrow CaO + CO_2$$
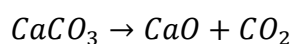
Equation 1 Calcination process

After the kiln, clinker is cooled, ground and mixed with additives to produce cement.

2.2. Cement industry

Economic growth increases the demand for concrete and cement because these are the only materials available in quantities enough to meet the growing demand of the construction sector. Growing faster than global fossil energy production, cement production increased more than 30-fold since 1950 and almost 4-fold since 1990 (Andrew, 2018, p. 195). In 2017 around 4100 million tons of cement was produced in the world (Statista, 2018). The main reasons for the cement industry's rapid development are global population growth, urbanization and, as a consequence, demand for the new buildings, infrastructure, and repair of existing constructions (IEA, 2018).

Since 1990 the main contribution to the industry growth was made by China, whose production rate in last decades has increased by a factor of almost 12 (Andrew, 2018, p. 195). Although there was a reduction in the cement production in China during the last years, the country still dominates the market (**Figure 2**) and the situation is expected to stay the same in the nearest future (van Ruijven, et al., 2016, p. 23).
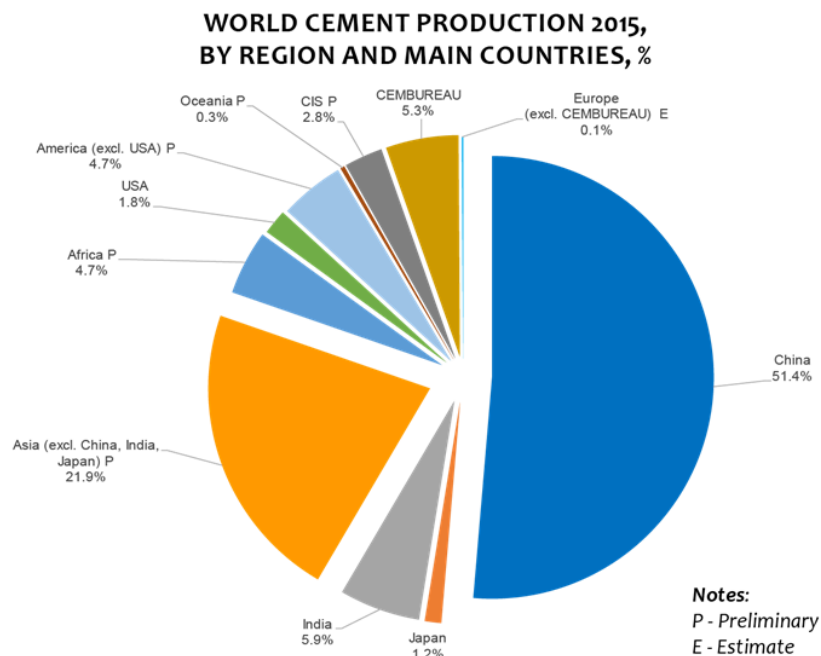

Figure 2 World cement production 2015, by region and main countries, % (CEMBUREAU, 2017, p. 8)

Despite the decrease in the cement production occurring in the last years, the long-term predictions expect the rise in the global cement production. Predictions of the cement production and demand in 2050 vary in different sources (IEA, 2018; Imbabi, et al., 2012; van Ruijven, et al., 2016). However, the main trends, such as the growth of the industry and increase in production efficiency, as well as the efficiency the concrete utilization are the same for all regions.

The International Energy Agency (IEA) is predicting a rise in the cement production of 12-23% by the year 2050 compared to 2014 level. Thus, the global cement production is expected to be around 4 682 Mt/year. The main increase in production is expected in Africa and Asia, where the current production level can be respectively tripled and doubled. Asia Pacific rate remains approximately on the same level because the triple growth in India and double in other Asia Pacific countries (Japan, Korea, Australia, etc.) will be compensated by the significant, more than 90% loss of the production in China. (IEA, 2018, p. 17.)

2.3. Carbon dioxide emission from cement production

Cement production is the second most CO_2 intensive industrial process, accounting for 2 Gt_{CO2}/year worldwide in 2007 (Kuramochi, et al., 2012, p. 92), which corresponds to about 5-8% of global anthropogenic emissions (CEMBUREAU, 2013, p. 3; Andrew, 2018, p. 195; Monteiro, et al., 2018). Approximately 80% of the construction sector's emissions come from the cement production (Habert, et al., 2010). However, estimation of global CO2 emissions from the cement production is challenging due to problems with data availability, changes in the production technology and reduction of the emissions. (Andrew, 2018, p. 199)

The cement production process has two main sources of CO_2 emissions: fossil fuel burning and process emissions, caused by the decomposition of raw materials, mainly carbonates, to oxides and carbon dioxide (**Figure *3***). CO_2 emissions from other processes are significantly smaller (Habert, et al., 2010) and the emissions from on- and off-site electric power production are not included in the CO_2 emissions related to the clinker and cement production. (Cement Sustainability Initiative, 2016, p. 18)
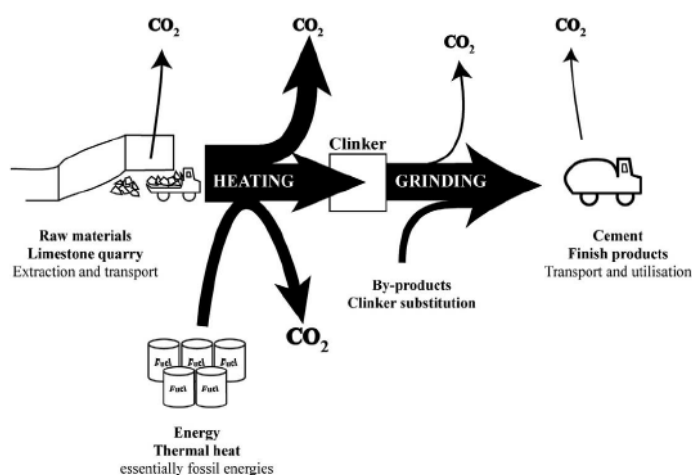
Figure 3 Simplified cement fabrication process, with a specific interest in CO2 emissions (Habert, et al., 2010)

CO_2 emissions per 1 ton of cement can vary significantly from plant to plant. The main factors determining the emissions from the production process are fuel used in the process, the efficiency of the kiln and the composition of raw material used for clinker (Habert, et al., 2010). Average emissions can be estimated based on the reference plant defined in the best available technique (BAT) standard. The reference BAT-plant has a capacity of 1Mt clinker per year, uses dry process with five stage preheater, precalciner, grate cooler, and vertical raw mill. The reference plant produces CEM I cement with 95% of clinker content. The fuel used is 100% petroleum coke with heat consumption 3 300 kJ/kg clinker. (Schorcht, et al., 2013, p. 44.)

The carbon dioxide emission of the BAT plant per 1 ton of cement is about 672 kg, of which 421 kg is from raw materials decomposition and 251 kg form carbon-based fuel burning (Schorcht, et al., 2013, p. 44). For 1 ton of the produced clinker, these numbers are 530 kg and 390 kg respectively (Habert, et al., 2010; Schorcht, et al., 2013, p. 69). The average CO2 concentration in the cement plant flue gas is 14- 33%, which can be considered as high compared to power plants (Kuramochi, et al., 2012).

Clinker burning perhaps the most important process in terms of CO_2 emission (Schorcht, et al., 2013, p. 26). It is not possible to completely avoid such emissions, but their reduction can be achieved by technological improvements and reduction of clinker-to-cement ratio. However, based

on the study made by Habert et al., these measures are not sufficient to reduce emissions to the required global goal level (Habert, et al., 2010).

2.4. Cement production in Finland

Cement industry in Finland is represented by the only cement producer - Finnsementti Oy. The company has two cement production plants with total capacity 1,6 Mt of cement or 1,3 Mt of clinker. The capacity of the plant in Parainen approximately 1 Mt_{cement}/year whereas the Lappeenranta plant capacity is 0.6 Mt_{cement}/year. The production rate has been growing for the last two years and in 2017 plants operated at almost full capacity producing 1,534 Mt of cement (1.18 Mt of clinker). (Finnsementti, 2018).

CO_2 emissions of Finnsementti plants in 2016 were 827 400 ton/year, of which process emissions were 553 200 ton (Finnsementti, 2018, p. 138). However, to estimate the possibility of carbon capture and utilization, it is important to know the emission level of each plant, since the transportation of captured carbon is quite challenging and expensive, therefore captured CO_2 should be utilized near the plant. The emissions of the plant can be estimated as 492 000 t_{CO2} in Parainen and 335 000 t_{CO2} in Lappeenranta. (Tsupari, et al., 2017). These values can be defined as the initial values for the estimation of different carbon utilization options.

The CO_2 emissions of the Finnish cement industry are constantly reducing due to the increased efficiency of the burning process and the growing share of alternative fuels, such as waste-derived fuels and car tires. The share of alternative fuels rapidly increased since 2000 and account almost 60% for the plant in Lappeenranta and 30% in Parainen. The total share of non-fossil fuels was 41% in 2017. (Finnsementti, 2018, p. 12) This share is planned to be increased to 50% in 2018 and the long-term goal is to replace up to 60% of fossil fuels by non-fossil fuels ones (Finnsementti, 2018, p. 23).

Total emission reduction since 2007 was about 11% and the emissions rate in 2017 was less than 700 kg/TEC (ton of cement equivalent). (Finnsementti, 2018, p. 8.) The emissions from fuel burning account for less than 300 kg/ton of clinker, whereas the emissions from limestone decomposition are approximately 500 kg/ ton of clinker. (Finnsementti, 2018).

An important issue to consider is the CO_2 emission allowances and carbon price. Carbon prices in Europe have rapidly been growing during the last 16 months. In May 2017 price for a metric ton of CO_2 was 4.4€/t, in October 2018 the price is already around 18.5 €/t and it is supposed to reach 25€/t by the end of the 2018. The growth is supposed to continue up to 50€/t during winters 2021 and 2022. (Watson, 2018). The penalty for exceeding the allowed limit is 100 €/t_CO2 (EU 2003/87/EC, 2003).

3. CONCEPT OF CARBON CAPTURE AND STORAGE

Carbon capture and storage (CCS) is a group of technologies for climate change mitigation by capturing CO_2 emitted by industrial processes, its transportation and permanent storage in an underground geological formation (EU 2009/31/EC, 2009). Often, CCS concept refers to a wider range of technologies and includes carbon capture from the air, different storage alternatives (e.g. geological and ocean), and application of CO_2 to different production processes. Intergovernmental Panel on Climate Change (IPCC) and IEA consider CSS as the key option for mitigation of CO_2 emission from the cement and other heavy industries, where emission come from technological processes (IEA, 2018). However, the industrial application of CSS is still limited and faces many challenges as for example, not developed business models, logistics, and gaps in regulations (IEA, 2018, p. 8).

3.1. Carbon capture technologies

Industrial emission is a mixture of different gases and different shares of CO_2. Separation of CO_2 from other gases and impurities, such as SO_2 and NO_x compounds is crucial for both storage and utilization. The process of CO_2 separation and capturing for further utilization is called carbon capture (CC) and the capture can be carried out using various technologies.

Existing CC technologies are on the different levels of the development and efficiency and their implementation depends to a large extent on the area of application. For example, CC technologies for large-scale power plants and oil-refineries are more developed than those for steel and cement industries (Cuellar-Franca & Azapagic, 2015, p. 83). Implementation of CC in cement and power

plants are different due to the differences in technological processes and flue gas characteristics. First difference is a higher CO_2 concentration in the cement plant flue gases. Second, cement plants do not have a low-pressure steam cycle, therefore post-combustion capture will require an additional energy source to produce steam. Finally, the exhaust gases from cement plants are used in the direct heat exchange to dry the raw material and carbon dioxide emissions have two different sources: fuel combustion and clinker production. (Maroto-Valer, 2010) As a result, the cost of carbon capture is different for cement and power plants.

CC technologies can be divided into three main groups: pre-combustion, oxyfuel combustion and post-combustion. Among them, post-combustion methods are most applicable to implementation in the cement industry (Kuramochi, et al., 2012). The oxy-fuel combustion is mainly studied as an addition to post-combustion calcium looping (CaL) capture. (Leeson, et al., 2017) Pre-combustion CC, despite being considered as the main technology for CC, is not efficient for the cement plants because the process emissions cannot be captured by this technology (Maroto-Valer, 2010, p. 474).

In the post-combustion capture technologies, the capture unit is installed in the tail-end separating CO_2 from flue gases of the conversion process. There are several methods that exist for the post-combustion carbon capture: absorption by chemical solvents or by solid sorbents, cryogenic separation, pressure/vacuum swing adsorption, and membrane separation. The main advantages of post-combustion CC technologies are their high efficiency, which can reach 90% (Monteiro, et al., 2018, p. 4). In addition, post-combustion capture technologies do not require fundamental modifications of cement kilns and could be applied to existing facilities provided there is enough physical space available on the site (IEA, 2018, p. 38)

Among the post-combustion CC, adsorption by monoethanolamine (MEA) and CaL are most studied for application on cement plants. Therefore, carbon capture by MEA and CaL can be assessed for the implementation in the cement plants in Finland.

3.1.1. Chemical absorption (MEA)

Monoethanolamine absorption is the most studied and developed method of post-combustion carbon capture (Cuellar-Franca & Azapagic, 2015). The principle of the technology is shown in

Figure *4*. Flue gas containing CO_2 is sent to the absorber where CO_2 reacts with 30 wt% MEA solvent. Then, a solvent with dissolved CO_2 is transmitted to the desorber, where the solution is heated to 120 °C. At this temperature, the reverse reaction takes place, so pure CO2 is released from the solvent. Pure CO2 can be further compressed and sent to a storage or for utilization. Regenerated solvent is recirculated back to the absorber and can be used again. (Anantharaman, et al., 2017, p. 21)
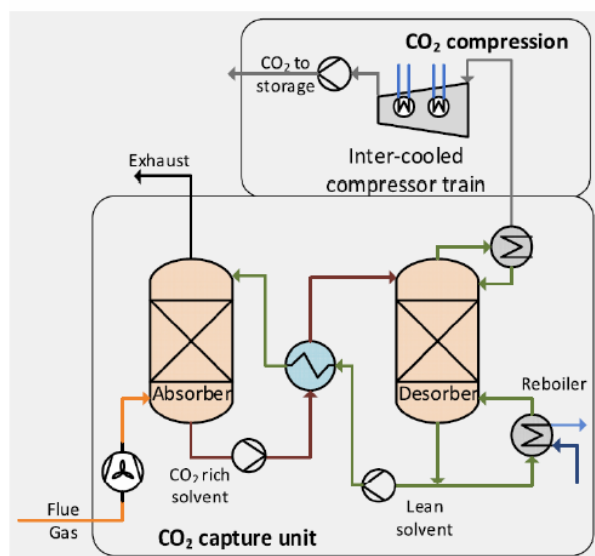
Figure 4 Principle of MEA absorption (Anantharaman, et al., 2017, p. 21).

MEA capture was designed for application on power plants and the technology is used at the first full-scale CC power plant in Canada. The possibility of MEA application on cement plant is studied to a lesser extent. (Cuellar-Franca & Azapagic, 2015, p. 84) Still, it is the most suitable option for cement plants because it can be implemented in a short-term with low technical risk (Kuramochi, et al., 2012, p. 101).

Although MEA technology is effective for flue gases with a low concentration of CO_2, it also has a number of disadvantages, such as high cost of the solvent production (1250 USD/ton), its degradation due to reactions with O_2 and SO_2, and finally, a high amount of waste solvent. (Dean, et al., 2011) These cause significant CO_2 emissions associated with MEA production and the

development of more sustainable sorbent is essential for CC based on chemical absorption (Cuellar-Franca & Azapagic, 2015).

The major issue for MEA technology implementation on the cement plant is the supply of low-pressure steam for solvent regeneration. Whereas power plants produce low-pressure steam, cement plants need either export it or install a boiler for steam production. (Reiter & Lindorfer, 2015) Some amount of steam can be generated by heat recovery from the cooler exhaust gas. Heat from the flue gas is not relevant because it is available approximately 2 hours/day when cement plant operates in the direct mode. During the interconnected operation of the cement plant, flue gas heat is needed in the raw mill. (Anantharaman, et al., 2015, p. 11). Waste heat is the cheapest option for steam, but it cannot cover the whole heat demand for solvent regeneration.

The source of imported steam strongly influences both the cost of CO_2 capture and its environmental impact. According to the scenario analysis made by Anantharaman et al., cost of captured CO_2 can vary from 41 to 65 €/t_{CO2} depending on the steam source and electricity price for the cases when steam is imported from CHP (Anantharaman, et al., 2015). The environmental impact is the lowest for the scenario with the use of waste heat available on the cement plant. For other cases, including natural gas boiler, external coal power plant and natural gas CHP, environmental impact was in the range 178-205 kg_{CO2}/MWh_{th}.

The cost of captured CO_2 varies from 41 to 65 €/t_{CO2} depending on the steam supply scenario (Anantharaman, et al., 2015). The comparative assessment made by (Kuramochi, et al., 2012) shows, that cost of CO_2 capture is the lowest in the case of steam import from the power plant (66 €/t_{CO2}). In a case steam is imported from boiler the cost will be 91 €/t_{CO2}. The highest cost is the onsite production of steam by coal CHP (131 €/t_{CO2}). However, in a long-term (20 years or more), these costs are supposed to decrease to 37 €/t_{CO2} and 52€/t_{CO2} for cases with steam imported from the power plant and boiler respectively. (Kuramochi, et al., 2012).

3.1.2. Calcium looping

Calcium looping (CaL) also known as carbonate looping is a second-generation post-combustion technology based on the reversible calcination and carbonation reactions of CaO and CO_2 (**Equation**

2). The technology has been rapidly developed in recent years because of its high efficiency and similarity to circulating fluidized bed reactor, which is a developed commercial technology.

$$CaCO_3 \rightarrow CaO + CO_2$$
$$CaO + CO_2 \rightarrow CaCO_3$$
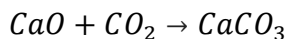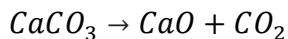
Equation 2 Calcination and carbonation reactions

The main principle of the technology is carbonation and regeneration of calcium oxide (**Figure 5**). Flue gas enters the carbonator, where carbonation reaction takes place and $CaCO_3$ is formed from CaO and CO_2. Then, clean flue gas leaves the carbonator and solid $CaCO_3$ moves to the calciner for regeneration (calcination) reaction. Next, the regenerated calcium oxide returns to the carbonator, and pure CO_2 is released during the $CaCO_3$ decomposition can be further compressed and utilized. (Martínez, et al., 2016, p. 273)
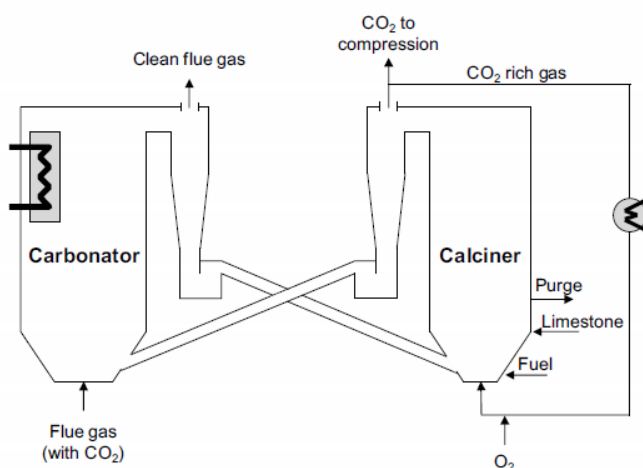
Figure 5 Schematic reactor layout of a post-combustion Ca-Looping process (Martínez, et al., 2016)

The carbonation process occurs at temperatures around 650 °C and due to the exothermic nature of the process, a significant amount of energy is released. This energy can be utilized for steam generation to increase the energy efficiency of the entire process. The regeneration process is endothermic and requires 900-950 °C for operations. (Martínez, et al., 2016, p. 273). Thus, to achieve high temperatures, additional fuel is has to be burned in the reactor with oxygen. (De Lena,

et al., 2017, p. 72) However, cement production produces large quantities of heat that also can be utilized for the calcination process (Kuramochi, et al., 2012, p. 101)

In a cement plant, CaL can be either integrated into the capture process or installed as a tail-end configuration. The key benefit of the tail-end installation is that no major change in the current cement plant is required, which significantly reduces investment for CC installation. The tail-end configuration requires higher fuel input than integrated unit and produces energy that exceeds the demand for cement production and capture process. (Spinelli, et al., 2017) The excess energy can be utilized and used either for the cement plant electricity consumption or it can be exported.

In the case of the excessed emissions' utilization, the equivalent emissions (direct and indirect) of tail-end configuration is lower than in an integrated plant (19.7 kg_{CO2}/t_{clk} and 200.1 kg_{CO2}/t_{clk} respectively) (Spinelli, et al., 2017). Finnsementti is already utilizing 30 GWh of excessed heat energy annually (Finnsementti, 2018, p. 11), therefore utilization of heat form CC can be integrated into the existing scheme.

The integration of CaL with preheater leads to the reduction of fuel demand but may cause the reduction of clinker quality due to the lower share of high-quality limestone used for clinker and a higher share of material used as sorbent (De Lena, et al., 2017, p. 87). In addition, it has many technical uncertainties associated with the effectiveness of raw meal usage as CO_2 sorbent and fluid dynamics issues might appear due to the higher solids to gas ration in precalciner. (Spinelli, et al., 2017)

One of the main advantages of implementing calcium looping in the cement industry is the synergy that might be achieved by using calcium carbonate both as sorbent and the material for clinker production. Thus, spent sorbent that cannot be used for carbon capture due to the degradation of its quality, can be used for cement production. This method can be effective being implemented together with carbon capture in power generation and provide an opportunity of partial decarbonization of both power and cement industry. (Dean, et al., 2011, p. 842)

Although the number of studies related to CaL has increased, the number of practical implementations of this technology is still limited. The technology was tested in small-scale experiments in a laboratory environment and its application was mainly tested for power plants. The first attempt to utilize CaL for the cement plant was made within the Horizon 2020 project CEMCAP. The pilot plant with a capacity 200 kWth was built based on two interconnected circulated fluidized beds. The CO_2 capture rate above 95% was achieved during the demonstration experiment with the CO_2 concentration in flue gases of 15vol.% (Hornberger, et al., 2017). Thus, the technology has been demonstrated at TRL level 6-7. (Martínez, et al., 2016, p. 273).

3.1.3. Oxy-fuel combustion

Oxy-fuel combustion is fuel burning in pure oxygen, so exhaust gas consists mainly of CO2 and water (**Figure 6**). Thus, the capture unit for chemical separation of CO_2 can be avoided. The technology requires less fuel because there is no need to heat nitrogen contained in the air and the higher temperature when burned with pure oxygen. However, pure oxygen is expensive and its production is energy intensive that leads to indirect environmental impact.
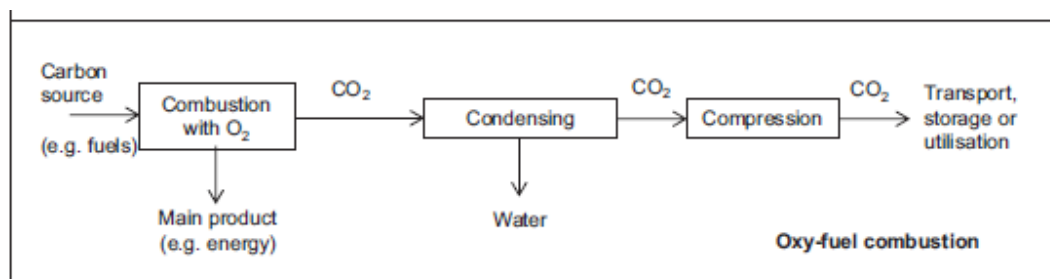
Figure 6 Oxy-fuel combustion (Cuellar-Franca & Azapagic, 2015, p. 84)

Implementation of oxy-fuel combustion on cement plants requires significant modifications of the plant configuration, burner design, and kiln. (Koytsoumpa, et al., 2018, p. 7) When the oxygen concentration in kiln is higher than 30-35% by volume the NOx compounds formation increases. Usage of oxygen also changes the temperature profile in a kiln that may cause a negative impact on clinker quality. Though currently, studies haven't reported any adverse effect on clinker quality, the issues related to oxy-combustion should be studied further on a large scale pilot testing. In addition, combustion in pure oxygen can cause damage to the kiln since it is designed to operate

in a certain temperature range. (Leeson, et al., 2017, p. 76) Currently, oxy-fuel combustion application for cement plants is on the development stage, but it can be a promising option for new plants because the possibility of oxy-combustion can be considered on the design stage. (Reiter & Lindorfer, 2015, p. 45)

3.2. Liquefaction, transportation, and storage.

Liquefaction is an intermediate step needed if CO_2 is not utilized directly after capture and should be transported to another location. Liquefied CO_2 can be transported by ship or road transport, such as trucks or trains. There are two main processes used for CO_2 liquefaction: external and internal. In the external process, ammonia or light hydrocarbons are used as refrigerants in a traditional refrigeration circuit. The condensation is carried out in the heat exchanger, so CO_2 is not in contact with refrigerant. In some cases, two external refrigerator circuits can be used. The internal method does not require additional refrigerant. In this method, CO_2 is compressed to a high pressure and then cooled down by air or water to the pressure necessary for the delivery. (Øi, et al., 2016)

The cost of liquefaction varies depending on the technology, electricity cost and scale. The simulation made by (Øi, et al., 2016) shows that the process based on ammonia refrigeration is the cost optimum for a CO_2 liquefaction plant with a capacity 1 Mt_{CO2}. The cost of electricity used in the modeling is 0.05 €/kWh. The investment for ammonia refrigeration process was estimated to 23 M€ and the operating costs to 4€/t. The investments and operational costs for internal refrigeration were estimated to 27 M€ and 4.13 €/t respectively. (Øi, et al., 2016, p. 510)

Transportation is the next additional step needed if CO_2 utilization is carried out in a place distant from the capture. There are several options for CO_2 transportation: pipeline, ships, train, and vehicle transport. Feasibility and effectiveness of each option depends on the scale of transportation, distance, final destination, and availability of the transport. For transporting large amounts of gas to a storage, the pipeline is the most developed and effective option. The pipeline is effective and most studied for CO_2 transportation from capture point to a storage. However, in the case of distributed end-points, vehicle transportation by truck or train might be the only option.

Cost of transportation is crucial for the cases when capture and utilization are carried out in different locations. Typically, in CSS systems, geological storages are located at some distance from capture points. In the case of CO_2 application to products, the utilization is expected to be implemented near the capture point (the cement plant). However, gas transportation is needed in the case of gaseous CO2 distribution for food and beverage industry or greenhouses.

4. CARBON UTILIZATION

Carbon utilization into products is an alternative to carbon storage, the option implies manufacturing of a valuable product from captured CO_2 and including carbon capture and utilization (CCU) in a company's business model. Although CCU is a promising option for CO_2 emissions reduction, it has many challenges that slow down development of technologies in this area. As a result, it is expected that in a short term the amount of CO_2 converted into a valuable products won't exceed 300 Mt/y with a current level of utilization of 200 Mt/y. (Monteiro, et al., 2018)

One of the factors slowing down the growth of CO_2 utilization is its high stability and necessity to use energy, co-reactants or both, for the conversion process. Therefore, the provision of high quantities of co-reactants or carbon-neutral energy might be an issue for the implementation and development of CO_2 utilization technologies.

Although the potential of CO_2 utilization is limited, it has a number of advantages. First is the revenue that can compensate the cost of CCS and transition of a company business model to a circular economy. Next advantage is a reduction of fossil feedstock usage and its substitution with captured CO_2. For example, substitution of fossil-derived CO_2 with captured in methanol or urea production. Considering the importance of carbon storage for climate change mitigation, utilization of CO_2 into a product helps to deal with the lack of geological storages needed for this purpose. Finally, fuel production from captured carbon contributes to the development of green energy in the energy system as well as its stabilization of energy grids via the introduction of stable energy sources. (Monteiro, et al., 2018, p. 1)

Although there is a wide range of products where CO_2 can be utilized to, there is no one ideal option. The feasibility and sustainability of utilization depends on many factors and highly depends on the local conditions, as well as resources and energy availability. Therefore, it is important to analyze all possibilities and find the most sustainable options for the exact case.

Utilization options can be classified either by production technology or by final product. Considering that the creation of a valuable product is the main purpose of CO_2 utilization in the scope of this work, the utilization options were classified based on the end-use possibilities. The possible products were divided into 6 groups: fuels, inorganic carbonates, polymers, chemicals, gaseous CO_2, and carbon (Table 1).

Table 1 CO_2 utilization into products.

Fuels	Inorganic Carbonates	Polymers	Chemicals	Gaseous CO_2	Carbon
Methanol	Calcium Carbonate	BPA Polycarbonates	Formic Acid	Food and beverage	Graphene
Dimethyl Ether	Magnesium Carbonate	Aliphatic Polycarbonates	Cyclic Carbonates	Horticulture	Nanofibers (CNFs)
Methane	Construction Aggregates	Polycarbonate Polyols	Dimethyl Carbonate		Nanotubes (CNTs)
Hydrocarbons	Carbonated Concrete	UF-resins	Isopropanol		
Ethanol		MF-resins	Synthesis gas		
Biodiesel		Cellulose Carbamates	Oxalic Acid		
		Polyoxymethylene	Urea		
			Formaldehyde		
			Melamine		

Based on the review articles and reports (Monteiro, et al., 2018; Müller, et al., 2015; Alper & Orhan, 2017; Mikkelsen, et al., 2010; Koytsoumpa, et al., 2018; CarbonNext, 2017), 31 possible options were identified. Next, it is highly important to determine the final use of the product, because it influences the fixation time, price or other parameters. Therefore, if a product has several

applications, its direct application has been evaluated. For example, although methanol is mainly used as an intermediate for other chemicals (e.g. formaldehyde, dimethyl ether etc,), its application as fuel was evaluated in the text. The products located further along the production chain have been evaluated as separate products. For example, although formaldehyde production does not require CO_2 directly, it is a valuable product that can be obtained from methanol, which in its turn produced from CO_2. Therefore, formaldehyde can be considered as an option for CO_2 utilization. The similar approach has been used for other options.

Next important factor is the technology used for the production since quite often there is more than one route to manufacture a product. The technologies can be on different stages of development, have different energy requirements and production costs. Thus, technology definition is the third important factor.

Summarizing, there are three main characteristics to be identified for each option before further comparison and evaluation: the final product, its applications and the technology used in the production process. In addition, the brief overview of possible options is important for identification of other characteristics might be important in further evaluation.

4.1. Fuels

The main source of anthropogenic CO_2 emissions is energy production, specifically power generation and energy for transportation, with shares 42% and 23% respectively. (Dutta, et al., 2017) In the future global energy demand is expected to reach 140 000 - 250 000 TWh in 2030. Although energy supply in many areas is expected to shift to renewable electricity sources (solar PV, wind or hydro energy), such areas as aviation, shipping, and some industries still require fuel, which cannot be substituted by electricity.

There are some issues common to all fuels produced from CO_2. All fuels described in this chapter are either gaseous or liquid, therefore they have short CO_2 fixation time, can be assumed as very short (< 1year). Thus, fuels cannot be considered as a long-term storage for CO_2. The longer fixation time is unlikely for fuels because it is unprofitable to store gaseous or liquid fuel for a

long time. Despite this, the growing demand for fuels and rapid development of CO_2-to-fuels technologies allow considering them as promising options for CO_2 utilization.

Next issue is the hydrogen required for many of the production processes in this group. Hydrogen production is very energy demanding, therefore sustainability and carbon neutrality of the hydrogen source is crucial since it can significantly reduce or even reverse the effect of carbon mitigation. For all technologies that require hydrogen, the hydrogen source is assumed to be sustainable. For example, hydrogen can be produced by electrolysis or biomass gasification. Finally, some of the production routes imply catalytic reaction, with catalysts sensitive to impurities. This introduces requirements to the quality and purity of CO_2 and consequently to the effectiveness of carbon capture technology. Commercial feasibility of catalyst is also an issue for some reactions.

4.1.1. Methanol

Methanol is a major intermediate for chemical production, therefore several products can be obtained from it. Around 32% of methanol produced worldwide is used for formaldehyde production, other products account for smaller shares, so acetic acid and diethyl ether account for 11% each, and methyl tert-butyl for 10%. Approximately the same share (11%) of methanol is used as a fuel for gasoline blending, and 4% for biodiesel production. (IGP Energy, 2014) This chapter describes methanol application as a fuel, whereas other major options, like formaldehyde, dimethyl ether and acetic acid will be analyzed in separate chapters.

The common way of methanol production is from syngas that is obtained from coal or natural gas. CO_2 utilization into methanol can be carried out in two ways, either by catalytic hydrogenation or by the Carnol process. The Carnol process is not effective in terms of CO_2 utilization because it requires methane and hydrogen. Considering that the main source of methane is natural gas, and methane production from CO_2 is not developed enough (chapter 4.1.3), this route won't be evaluated as an option for CO_2 utilization.

Hydrogenation of CO_2 into methanol is commercialized and implemented in several facilities (TRL 9). By its principle, the technology is similar to the conventional way of methanol production and it is based on the following reaction (Mikkelsen, et al., 2010, p. 59):

$$CO_2 + 3\,H_2 = CH_3OH + H_2O$$
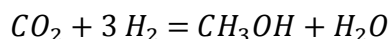
Equation 3 Catalytic hydrogenation of CO2 to methanol

The reaction takes place under the catalyst, the most widely used and commercially available catalyst is Cu/ZnO/Al2O3. The catalyst is very sensitive to sulfur compounds that can be contained in the flue gases of a cement plant, for example, hydrogen sulfide content should be less than 0.1 ppm (Müller, et al., 2015, p. 74) Therefore, the process imposes high requirements to CO2 quality. Despite the challenges, CO_2 hydrogenation to methanol is the most developed route of CO_2 utilization. (Monteiro, et al., 2018, p. 20)

4.1.2. Dimethyl ether

Dimethyl ether (DME) is the simplest ether that can be obtained from methane. Other names for DME are methoxymethane, wood ether or methyl ether. The product has several applications and can be used as a transportation fuel to substitute diesel, as a propellant in aerosols sprays, or as an extraction solvent. In addition, it can be used as a feedstock for the production of acetic acid.

DME has gained growing interest due to its good properties as an alternative fuel. Having a cetane rating of 55-60, which is higher than in methanol and conventional diesel (40-55), DME is non-toxic and non-carcinogenic and has lower NOx and SOx emission rates. (Matzen & Demirel, 2016, p. 1069). Also, DME can be easily stored and transported as a liquid in pressurized tanks. According to the International DME organization, DME is a fuel of the 21st century. (Monteiro, et al., 2018, p. 23)

DME can be produced via two routes: the direct synthesis from CO_2 and methanol dehydration. Taking into account that methanol can be produced from CO_2, both of these methods can be considered as CO_2 utilization routes. The catalysts used for the direct DME formation (Cu/ZnO/Al2O3) is the same that is used for methanol synthesis, therefore the DME synthesis

requires purified CO2 and consequently, installation of carbon capture and possibly additional purification unit in a cement plant. The conventional way of DME production (TRL 9) is its synthesis from methanol. (Monteiro, et al., 2018, pp. 22-24.)

4.1.3. Methane

Methane has two main areas of application, as fuel or as an intermediate for synthesis gas production. As a fuel methane is used in the Power-to-Gas technology that provides a possibility to store renewable electricity in the form of chemical energy. Thereby, CO_2 conversion to methane also fulfills the function of energy storage, which is one of the key challenges for renewable energy technologies development. In addition, methane can be stored and transported via existing infrastructure and can be mixed with the natural gas in natural gas grids.

The conventional way of methane production is the processing of natural gas, where methane is the main compound. Thus, substitution of fossil methane with the methane produced from captured carbon reduces the usage of natural gas, though it does not make the methane completely independent from fossil materials since CO_2 used in this case is also emitted from the fossil source. The two main technologies for methane production from CO_2 are catalytic hydrogenation and biological conversion. The technologies are very different in their nature (catalytic and biological) and both have high TRL level 8-9 (Monteiro, et al., 2018, pp. 29-30). However, they are not fully competitive with the conventional way of methane production from natural gas.

The catalytic hydrogenation of CO_2 to methane can be performed by different routes and the commercialized way is the Sabatier reaction. The catalysts for this process were extensively studied in last decades and the Ni-based catalyst can be considered as the most adequate. (Monteiro, et al., 2018, p. 29) . However, the design of the effective catalyst is crucial for the large-scale commercial application of catalytic CO2 methanation. In addition, hydrogen required as a co-reactant for the Sabatier reaction rises the problem of the sustainable hydrogen sources, as it was described above.

Bio methanation is anaerobic fermentation of CO_2 by methanogenic bacteria, which belong to domain Archae. The most important factor for the process is temperature and the optimal

temperature range depends on the type of bacteria. For mesophilic methanogens, the optimal temperature is typically in the range from 35-45 , for thermophilic is 55 °C, and for hyperthermophilic up to 65°C. Another important factor is pH, which optimal value typically is in the range 6-7.5. Finally, the availability of macro and micronutrients is crucial as well. (Zabranska & Pokorna, 2018) Thus, due to a narrow range of operational conditions, bio-methanation is a challenging process, despite the bacteria are being tolerant to impurities contained in CO_2 itself. (Götz, et al., 2016, p. 1380)

4.1.4. Hydrocarbons

Hydrocarbons are the most widely used fuels and their main source is fossil oil. Taking into account that fuels based on fossil-derived hydrocarbons are one of the main CO_2 emission sources, their substitution with hydrocarbons derived from fossil CO_2 can be beneficial for CO_2 emission reduction. The main products in the group of hydrocarbons are gasoline and diesel. In addition to the application as fuel, hydrocarbons can be used as a feedstock for the production of plastics, such as polyethylene and polypropylene, via ethylene and propylene respectively.

Conventionally, hydrocarbons produced from fossil fuels – natural gas or crude oil. From CO_2 hydrocarbons can be produced by two routes: directly via Fischer-Tropsch (FT) process or indirectly either by multistage FT or via methanol. The direct and indirect FT are similar, and the main difference is that in the indirect method reactions occur in separate reactors. The FT technology is commercialized and widely implemented, however, most of the facilities use fossil feedstock (natural gas, coal) for hydrocarbon production. The CO_2 to hydrocarbon technologies are on the different stage of development and their TRL level can be ranged as 5-9 (Jarvis & Samsatli, 2018, p. 51; Monteiro, et al., 2018, p. 26).

Indirect route implies methanol synthesis and further methanol-to-olefin (MTO) or methanol-to-gasoline (MTG) processes. The methanol production from CO_2 is described in chapter 4.1.1. Further steps, MTO and MTG are commercially available, for example, ExxonMobil's MTG. The air-liquid Group combined the Lurgi's MegaMethanol technology with ExxonMobil's MTG and marketed the G2G technology for CO_2 utilization to hydrocarbons. (Monteiro, et al., 2018, p. 27) MTO technology is also commercialized, for example, Mitsui Chemicals is going to produce

olefins and aromatics from the methanol they already produce from CO_2. (Monteiro, et al., 2018, p. 26)

4.1.5. Ethanol

Ethanol is a simple alcohol that has many applications. Commonly it is used as a solvent, a component for chemical synthesis or even for medical purposes. However, it can be used directly as "drop-in" fuel or blended with gasoline and further used in the cars with a common internal combustion engine. Currently, all gasoline used in EU contains from 5 to 10 % of ethanol, in some countries gasoline with 85% of ethanol is available. However, the fuel with a high concentration of ethanol requires specific changes in vehicles that hinder growth of ethanol uptake. (Monteiro, et al., 2018, p. 33)

The conventional way of ethanol production is the hydration of ethylene obtained from fossil fuels. The alternative way to produce ethanol from renewable sources is fermentation of sugars contained in biomass, therefore the product often referred to as bioethanol. The biomass used for this purpose is mainly sugar cane or cornstarch, which are also used as food. The usage of food biomass has multiple disadvantages widely described in the literature and leads to the development of the technologies for ethanol production from cellulose or bio-waste. Thus, the possibility to use CO_2 methanol production can be important due to the growing demand for renewable fuels and issues related to the feedstock used for renewable ethanol production.

Ethanol can be produced by CO_2 hydrogenation via three routes: direct, indirect and biohydrogenation. The direct route is the reverse reforming, which has a very low conversion rate and selectivity to ethanol. Therefore, in practice, the two-step reaction is adopted (**Equation 4**). (Atsonios, et al., 2016, p. 796)

In the two-step hydrogenation, CO_2 is converted to CO via RWGS reaction to produce syngas. The next step is the ethanol synthesis from syngas via CO hydrogenation. Despite the reaction principle is being similar to methanol synthesis (**Equation 3**), there is no commercially available catalyst for ethanol production, which explains the relatively low level of the technology development (TRL 3-5) (Monteiro, et al., 2018, p. 32)

$$2CO_2 + 6H_2 \leftrightarrow C_2H_5OH + 3H_2O \quad (a)$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad (b)$$

$$2CO + 4H_2 \leftrightarrow C_2H_5OH + H_2O \quad (c)$$
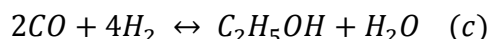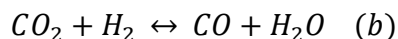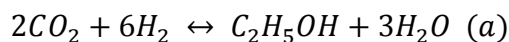
Equation 4 Reversed reforming of CO to ethanol (a) and two-step reaction based on RWGS (b) followed by CO hydrogenation (c)

Indirect route is the synthesis of ethanol via DME. Production of DME from CO_2 was described in chapter 4.1.2. Further, DME can be converted to ethanol via methyl acetate formation. The reaction is catalytic, has lower heating demand and therefore lower production costs compared to the direct route (Atsonios, et al., 2016, p. 804), but the technology is still on the early stage of the development and has TRL 3 (Monteiro, et al., 2018, p. 32).

Ethanol production via biohydrogenation was confirmed in the laboratory, but the technology is in the early stage of development and its TRL is 3. The conversion is made by a chimeric bacteria that contain recombinant DNA of different bacteria species. The metabolic process requires CO_2 and hydrogen as the main feed component. The other requirements are either oxygen or light depending on the bacteria type. (Monteiro, et al., 2018, p. 33). The overall efficiency of the process is rather low and the process suffers the problems similar to methane biological conversion: low solubility and poor mass transfer of hydrogen. (CarbonNext, 2017, p. 30) In addition, usage of the genetically modified bacteria can lead to problems with social acceptance of the technology.

4.1.6. Biodiesel

Biodiesel is fatty acid methyl esters (FAME) that can be used as fuel in conventional diesel engines. Due to the growing demand on the renewable fuels and good characteristics of biodiesels, the related technologies have been developed quite fast. Thus, global production of biofuels grows from less than 1Mt/y in 2000 to 20 Mt/y nowadays. (Monteiro, et al., 2018, p. 87) Compared to both conventional and renewable diesel, biodiesel has numerous advantages, such as non-toxicity,

biodegradability, and high flash point. Although biodiesel cannot be considered as carbon neutral, it produces lower emissions compared to petroleum diesel. (Ambat, et al., 2018) CO2 emissions from biodiesel production mainly relates to land use change that occurs during the growing of feedstock and its further conversion to fuel.

Depending on the feedstock used, different types of biodiesel can be classified by generations. The first generation of biodiesel produced from edible plants, such as rapeseed, soybeans or sunflowers. For the second generation of biofuel non-edible plants (e.g. Jatropha) or lignocellulosic materials are used. Although the first and second generation types of feedstock have their disadvantages, the biodiesel technologies are commercialized and implemented on a large scale. (Ambat, et al., 2018, pp. 358-359)

CO_2 utilized in the third generation of biofuels that are usually included fuels produced from algae, which use CO_2 in the metabolism. Biodiesel can be produced from the oil contained in algae via transesterification with methanol. The method is similar to traditional crops treatment. The amount of produced biodiesel depends on the oil content in algae and varies depending on the species. Oil content also defines the CO_2 utilization rate, and for different species, it can be estimated in range 1.25-2.5 t_{CO2}/t_{diesel}. Due to the higher productivity of algae compared to other biodiesel feedstock, the technology has a good potential. However, it is still on the early stage of development and has TRL 5. (Monteiro, et al., 2018, p. 35)

4.2. Inorganic carbonates

Mineral carbonation, or mineralization of carbon dioxide, is a naturally occurring process of silicate rocks' weathering. In nature, atmospheric carbon dioxide reacts with alkaline-earth oxides contained in rocks. The principle of the reaction can be defined as (Sanna, et al., 2014):

$$Metal\ oxide + CO_2 \rightarrow Metal\ carbonate + Heat$$

Equation 5 Carbonation reaction principle

Natural carbonation process is very slow, however, it can be accelerated by changing reaction conditions and the addition of catalysts. Thus, CO2 can be stored in a form of stable solid minerals

for a very long time, which makes carbonation a good option for CCS technologies. In addition to storage, carbonation also allows producing valuable materials that can be commercialized. This chapter describes several valuable products can be obtained via the carbonation process: calcium carbonate, construction aggregates, and carbonated concrete.

Despite the variety of products that can be obtained by carbonation, the technologies based on the process are similar and the main differences are due to feedstock used and final product obtained. The carbonation technologies can be divided into direct and indirect (**Figure 7**). The indirect route includes the additional step of Ca or Mg separation from the feedstock. Extraction can be made by the reaction with active chemicals, for example, HCl or acetic acid. Carbonation process can be either gas-solid or aqueous. The gas-solid process implies gaseous CO_2 introduction into the feedstock. In the aqueous process, CO_2 and Mg/Ca first dissolved in water, which increases the reactivity of components. The process is similar in both routes, but in the indirect route, it is carried out as a separate process, usually in a different reactor. (Olajire, 2013)
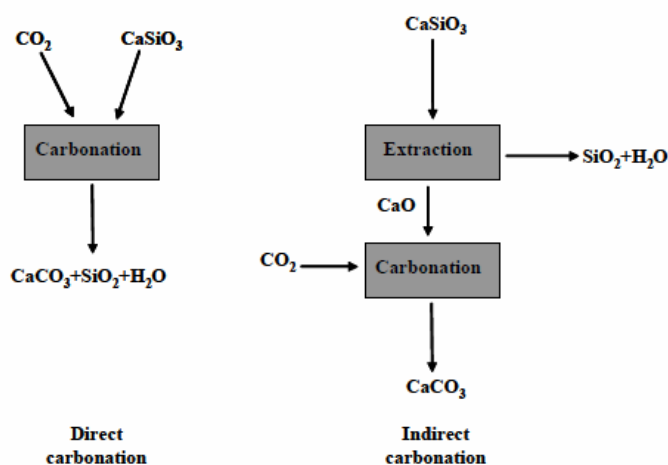
Figure 7. Basic principles of the direct and indirect carbonation methods (Eloneva, 2010, p. 28)

4.2.1. Calcium carbonate and magnesium carbonate

Calcium carbonate ($CaCO_3$) commercialized in two forms, ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC). Both forms have the same chemical composition, and the main difference is the purity of the substance, which defines the application of the product and its price. PCC is purer than GCC and has a lower content of silica, magnesium, and lead. The particle size, its distribution, and the physical properties such as brightness, opacity, and purity, are properties that mainly define the application of calcium carbonates. (Jimoh, et al., 2018, p. 332)

Calcium carbonates are mainly used as filler material, sealer, or adhesive. The main consumer of GCC and PCC is the paper industry (~40% of the global market) (Monteiro, et al., 2018, p. 10), where the product is used for filling and coating to improve paper consistency and increase the whitening level. PCC is also used in plastics (23%), sealants (17%), and paint (7%) industries (Jimoh, et al., 2018, p. 333).

Taking into account variations in the final application of calcium carbonate and the differences in the lifetime of different applications, the use of calcium carbonate has been evaluated for industries other than construction, namely paper, plastics, and paints and coatings. Thus, for PCC and GCC CO_2 fixation time can be assumed from very short (less than 1 year) for some application in the paper industry (e.g. newspapers and magazines) to medium (10-50 years) in uses as plastics fillers, paints and some paper application such as books. Application of calcium carbonates in the construction industry is described in chapter 4.2.2.

The conventional way of calcium carbonates production is re-carbonization of limestone, chalk or marble. Re-carbonization consists of two steps. The first step is calcination of raw material to obtain quicklime (CaO) and the next step is its carbonation to CaCO3. This process allows producing the high quality and purity calcium carbonate. The technology is mature and widely used, however, its implementation for CO_2 sequestration from cement plants seems unlikely due to limestone is used for the cement production process and CaO is the main component of clinker. Thus, as an option for PCC production, carbonation of silicate minerals (e.g. wollastonite, olivine, serpentine) can be considered. Due to the availability of resources and storage security, this is a

promising technology for carbon storage, though not economically feasible yet (Sanna, et al., 2014).

The third option is carbonation of calcium-rich waste materials, such as oil shale ash (Monteiro, et al., 2018, p. 9), slag from steel industry (Huijgen , et al., 2007), cement kiln dust, recycled concrete aggregate (Sanna, et al., 2012) or other waste streams contain calcium (Calera, 2018). This approach can be efficient from the point of view of waste utilization, and therefore either free or negative cost feedstock can be used. However, to produce PCC using this method, efficient separation of calcium carbonate from the waste stream is crucial. Thus, as an alternative to PCC production form silicate minerals, the production of GCC from waste stream will be evaluated as well.

One of the main advantages of mineral carbonation is tolerance to impurities in CO_2 and possibility of flue gas utilization in the process. Thus, carbon capture step can be avoided or captured gas can be lower quality, which can decrease the price of the final product. However, with no regards of feedstock used, additional purification might be necessary to obtain a high-quality PCC. This, in turn, leads to an increase in production costs.

It is important to mention the environmental impact of the mineral carbonation. The CO_2 uptake potential of minerals is rather small, for example, for wollastonite, the mass ratio of ore needed to carbonate one unit mass of CO_2 is 2.8, with the reaction efficiency 82% (Sanna, et al., 2014, p. 8056). Consequently, the extraction of big volumes of minerals can cause a significant impact on the environment.

Magnesium carbonate (magnesite, $MgCO_3$) production is similar to calcium carbonate, with a difference of Mg used to bond CO_2. The main disadvantage of this route lies in the utilization of magnesium carbonate, which main application is the production of magnesia (MgO). Thus, carbon stored in $MgCO_3$ will be released immediately (Monteiro, et al., 2018, p. 12). Considering the absence of a market this option was not evaluated in detail. However, a successful production of $MgCO_3$ was implemented on a pilot scale in Canada. The pilot plant was installed for a year in a

cement plant to test the technology in real conditions with flue gas a source of CO_2. (Kemache, et al., 2017)

4.2.2. Construction aggregates

Product. Construction aggregates are granular particular materials used for construction. The aggregates can be produced from a wide range of feedstock, such as gravel, sand, crushed stone, and construction or industrial waste. Based on the particle size, aggregates can be divided into two main groups, fine and coarse. Fine aggregates are usually produced from dust, sand, silt or clay and have a particle size in a range from 75μm to 9.5 mm. Coarse aggregates, produced mainly form gravel, cobbles or boulders and have a particle size from 9.5 to 37.5 mm. (Engineering basics, 2018)

The main use of aggregates is stabilization and reinforcement of constructions. For example, in the construction of roads and railways aggregates are needed for load bearing and distribution, and water drainage. As an essential part of concrete, aggregates are used in the construction of buildings, bridges, etc. In some cases, aggregates are used in sewage treatment for water filtration.

Aggregates produced by carbonation usually have relatively low density, so they can be classified as light-weighted aggregates (LWA). The application of LWAs is limited, but still wide, including lightweight structural concrete, low-density construction blocks, engineering fill, and horticulture growing mediums (Gunning, et al., 2009). The important limitation of carbonated aggregates is that they are not recommended to be used with still reinforcement (Jang, et al., 2016, p. 769).

Regardless of the constructions lifetime, CO_2 bonded in aggregates does not release in the atmosphere after the demolition. Therefore, CO_2 fixation time of the construction aggregates can be estimated as very long (>100 years).

Globally, the CO_2 utilization potential of aggregates is approximately 0.3 Gt/y. By 2025 it is expected to be extended up to 3.6 Gt by implementing strategic actions, such as support of technologies development, collaboration among the stakeholders and policy actions. (CO2 Sciences and The Global CO2 Initiative, 2016)

Feedstock overview. The conventional way of aggregates production is quarrying and crashing mineral deposits of limestone, granite, marble, etc. (**Figure 8**). Natural sand and gravel are the less preferable and utilized in the absence of better alternatives. An alternative to the quarrying is the production of aggregates from waste. Production of aggregates from waste decreases the amount of extracted natural material and the amount of waste sent to landfills. Both types of feedstock (minerals and wastes) can be carbonated to obtain carbonated aggregates. Carbonation improves aggregates wet-dry resistance, and compression and shear performance (Olajire, 2013). Utilization of captured CO_2 for carbonation makes the process also beneficial for the environment.
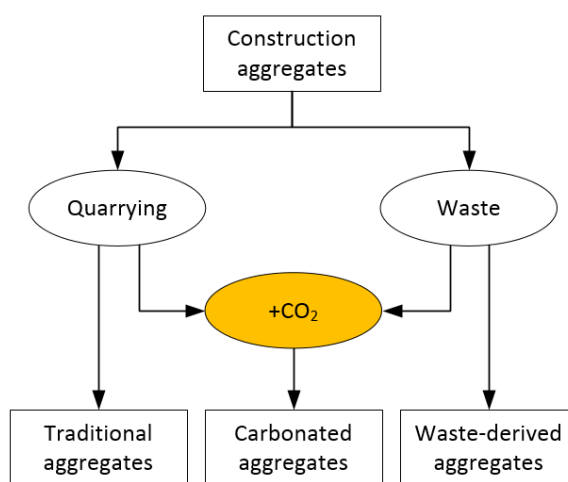
Figure 8 Types of construction aggregates.

There are two groups of feedstock that can be used for carbonation: calcium/magnesium reach minerals and waste streams. The CO_2 uptake potential of the feedstock strongly depends on its composition and on the technology used (Appendix I Table 1). The maximum theoretical uptake is in the range 0.08-0.55 $t_{CO2}/t_{material}$, but experimental values are usually lower and are in the range 0.07-0.24 $t_{CO2}/t_{material}$. (Jang, et al., 2016, p. 767)

Minerals suitable for carbonation are silicate rocks containing sufficient amount of Mg or Ca, such as serpentine, olivine, wollastonite and basalt. Minerals containing other metals can also be used for carbonation but they are either too valuable to be used for CO_2 sequestration (Fe, Ni, Pb) or form carbonates that are easily soluble in water (Na or K) (Monteiro, et al., 2018, p. 61). The main

challenges hindering the development of mineral carbonation technology are high energy intensity of the process, low reaction conversion and slow reaction kinetics (Sanna, et al., 2014, p. 8056).

The main environmental issue related to the mineral carbonation is the large-scale mining, which can cause land-use change, potential pollution of water, soil and air, and habitat degradation. The huge amount of raw material required for carbonation involves extensive mining and treatment of big volumes of material which leads to soil erosion, sedimentation and generates dust and particulate matter. Another important issue is the tailing management system, though in some cases tailings may also be used for carbonation. (Olajire, 2013, p. 384).

Waste streams used for carbonation can be divided into five categories: steel slags, cement-based materials, ash from power plants, municipal solid waste incineration residues (MSWIr), and water treatment sludge. Waste streams are less stable compared to quarried minerals and usually have fine particle size. Therefore their carbonation is faster, requires less energy and lower degree of pre-treatment before carbonation. In addition, wastes do not require mining and hazardous wastes can be reclassified through pH-neutralization. The challenges related to waste carbonation are their limited amount and possible legislative issues. (Olajire, 2013; Sanna, et al., 2014).

Steel slag is quite popular material and already has many applications, both direct and after treatment. For example, steel slag can be used as construction aggregate for road construction even without carbonation. The advantages of slags are their high CO_2 uptake rate and generation near CO_2 sources (still mills and power plants) (Sanna, et al., 2014). There are two types of slag: blast furnace slag and steel slag. Blast furnace slag contains mainly silicates of Ca, Al, and Mg. Steel slag consists of calcium silicates, calcium aluminoferrites, and fused oxides of calcium, iron, magnesium, manganese. Steel slag also includes free calcium oxide. Both types of slag can be used as aggregates for different construction applications. (Eloneva, 2010, p. 38)

Cement-based materials are cement kiln dust (CKD) and construction waste consisting of cement-based materials. CKD is a waste stream with a high content of CaO, which leads to better quality (stronger and more durable) and performance of aggregates produces from it. Furthermore, CKD is a potential hazardous waste, which may contain contaminants from fuel and raw material used

in the production processes. It is also a potential skin, eye, and respiratory irritator. Environmental and health risks associated with CKD can be reduced by stabilization of hazardous components by carbonation. The main advantages of CKD as a feedstock for aggregates production is its generation near the CO_2 source (cement plants) and the fine particle size that increase carbonation speed. The disadvantages are low CO_2 uptake capacity and quantities not big enough for sequestration of a cement plant emissions. (Sanna, et al., 2014).

Concrete and mineral waste is a fraction of construction and demolition waste (CDW). Finland produces over 1.6 Mt of CDW annually (2006-2012 data). Around 26% of CDW in Finland is recycled, which is lower than the average rate in EU (47%). (Dahlbo, et al., 2015) Around 250 000 tons of construction waste ended up at landfill sites (Deloitte, 2014). The share of concrete waste fraction varies between sites and there is no general composition that can be presented. The main advantages of CDW recycling to aggregates are the utilization of material that otherwise goes to landfill and substitution of natural resources with waste. A small share of CDW is currently used as construction aggregates without carbonation. In Finland in 2014, only 1% (1 Mt out of 81Mt) of the total amount of aggregates was produced from recycled materials. (UEPG, 2017, p. 12).

European Aggregates Association and Government Decree 591/2006 promotes the utilization of crushed concrete and the use of recycled aggregates, still, construction waste effective recycling is facing many challenges. First, is a disperse generation of CDW and consequently rising issues with long-distance transportation. Next is the low confidence of consumers in the recycling products due to the possible low quality of such aggregates. (Deloitte, 2014). Challenges arising from legislation and regulation will be discussed below.

Next category of possible waste feedstock is ash from fuel combustion and municipal solid waste incineration residues (MSWIr). Fuel combustion ash generates mainly on power plants, and its characteristics, availability, and possibility to be utilized for carbonation highly depend on the case. MSWI waste consists of three types of ash: bottom ash (MSWI BA), fly ash (MSWI FA), and air pollution control residues (APCr). APC is different from other combustion waste because it is considered as hazardous and have to be treated before landfilling. Ash from water treatment

sludge incineration can also be categorized as MSWIr and therefore the possibility of its utilization won't be considered separately.

The main advantage of MSWIr carbonation is the reduction of pH and leaching of hazardous components. Carbonation of hazardous wastes decreases their pH level below the hazardous threshold. Carbonation has been proved to be an effective treatment to reduce the leaching of lead and barium. Arsenic, copper, molybdenum, nickel and most anions were largely unchanged. Sulfate and chloride leaching were unaffected or even increased by carbonation. In general, carbonation treatment facilitated the reclassification of hazardous wastes. As a result, carbonation reduced the WAC classification of many of the wastes, but the mobility of some metals remained problematic. However, the effect on hazardous components should be assessed separately for each case. (Nielsen, et al., 2017).

The main challenges related to MSWIr utilization for aggregates production is low carbon uptake capacity and legislative issues. Use of incineration waste as a feedstock for the aggregates production might require an expensive test to prove that the final product is not harmful and obtain a permit for the process.

Technologies overview. In its principle, construction aggregates production is very close to the PCC and GCC production. The main difference is that for the construction aggregates production impurities containing in the feedstock should not be separated from calcium or magnesium carbonates, but contrarily, bounded by binding materials.

There are a number of technologies has been developed for accelerated mineral and waste carbonation. Usually the technologies designed to process the certain feedstock and to produce the certain type of the product (e.g. PCC from minerals, PCC from steel slag, construction aggregates from waste, etc.). The carbonation technologies are on the different stages of development, but only a few of them are commercialized. The most promising technologies will be described below.

Carbon8 developed and commercialized an accelerated carbonation technology (ACT), which can be applied to a wide range of waste materials containing calcium or magnesium, such as municipal

and paper incineration ashes, wood ashes, pulverized fuel ashes, steel slag, and air pollution residues (APRs). The combustion residues can be also used as CO_2-reactive binders in combination with quarry fines for the production of an accelerated carbonate aggregate. In addition to construction aggregates, the company produces light-weighted building blocks. (Gunning, et al., 2009) The Carbon8 facilities in Brandon, UK, and Avonmouth, UK utilize APC waste from the incineration facilities located approximately 120 km away. (Carbon8, 2017).

The Carbon8 Company is rapidly developing and currently operating three carbonation facility in the UK. The total capacity of the plants is 150 kt_aggregates per year, which allows utilizing of 15 kt_{CO2} annually. The main aim of the Carbon8 is not the utilization of CO_2 but rather the utilization of hazardous wastes. Therefore, currently, the company purchases CO_2 and CO_2 utilization potential is limited by the price of the gas. (Carey, 2018).
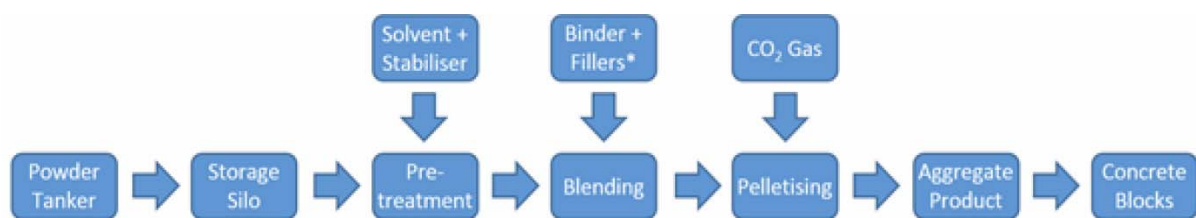
Figure 9 Carbon8 technology (Carey, 2018)

The technology of aggregates production is relatively simple (**Figure 9**) and does not require any additional reactants except CO_2. The reaction takes place at the ambient temperature and pressure, and the flue gas with a minimum CO_2 concentration of 20% can be used. Preferably concentration should be 50% and higher (Monteiro, et al., 2018, p. 13) Carbonation rate highly depends on the CO_2 concentration: at a concentration 70% significant reaction still takes place, and even at 10%, some level of treatment has been demonstrated. Application of CO_2 with higher concentrations leads to the extensive heat release and premature drying of the material. So usage of the diluted gas may be more economical. (Gunning, et al., 2010, p. 10)

The investment costs for a plant with a capacity 50 kt of aggregates per year is about 5.6 M€ (£5m). The construction time of a plant is about 6 months. The business model of Carbon 8 is based on favorable environmental regulation: landfill tax and aggregate tax. The main revenue streams are

gate fee for waste and price for aggregates. CO_2 is currently a cost but might be a revenue in the case of the captured CO_2 utilization. The gate fee for hazardous waste in the UK is quite high (~82 €/t). (Carey, 2018). The price for Carbon8 aggregates is about 9-16 €/t$_{CO_2}$. (CSLF Task Force, 2013, p. 42) Which is comparable with the average price for conventional aggregates, about 20 €/t (Monteiro, et al., 2018, p. 87)

Calera Technology. Another example of aggregates production is Calera Corporation, which has two operating pilot plants and are looking to license its technology (Monteiro, et al., 2018, p. 10). In the Calera technology calcium-rich alkaline waste is used together with CO2 transferred from the coal-fired power plant. The technology works on the next principle: in the scrubber, flue gas reacts with an aqueous alkaline solution that removes CO_2 (capture). Then captured CO_2 reacts with calcium source to produce calcium carbonate, which can be used in construction materials. The technology does not require a capture step, but the usage of brines is a limiting factor for the implementation of the technology on a significant level. In addition, usage of brines is potentially harmful to the water environment. (Sanna, et al., 2014)

As a material for carbonation Calera Technology uses industrial waste stream containing either alkalinity or calcium. Conventionally manufactured NaOH and CaCl2 are also used by Calera for building materials production (Jang, et al., 2016, p. 770). The main applications of Calera's products are supplementary cementitious materials for concrete, cement, and binder system for concrete products. (Jang, et al., 2016, p. 770) Calcium carbonate produced by Calera can be used as a supplementary cementitious material, can replace a portion of Portland cement, or used for the production of cement board products. (Calera, 2018)

Mineral Carbonation International. An Australian company developing magnesite carbonation technology. The company was named Resource Innovator of the Year in Berlin in June 2018. They've built 3 carbon reactor systems and a semi-continues research pilot plant built in 2017 to test a commercial potential. Now they're aiming to design a pilot plant that can process 5-10 kt of CO_2 per year and scale it every 3 years to a further 10 fold scale to increase in capacity. The goal is the capacity of 1Mt of CO_2. The technology has been patented, but much of the know-how is

not disclosed. Including economic evaluations. The technology is developed under research commercial secrecy. Though they are open to communications and cooperation.

The technology uses crushed serpentinite rocks that contain magnesium to produce building and construction materials, such as cement, paving stones and plasterboard. Their aim is to get the price low enough to make the process economical. Short description: serpentine (lizardite) mined, crushed and heat activated (milled mineral heated to 630 C). Then it mixed with water and sodium bicarbonate (source of alkalinity). Then the mixture is heated to 225 C and stirring is started.

Sky Mine Technology. Also uses brines (NaOH) for carbonation, but final products obtained via SkyMine technology are sodium bicarbonate (Na_2CO_3, baking soda) and hydrochloric acid (HCL). A joint venture namely Skyonic Corporation, which includes BP and Conoco-Phillips, has started the construction of a commercial CO_2 capture plant to remove 83 000 t_{CO2} per year from a cement plant (130 000 t_{CO2} taking into accout the reduced emissions in producing baking soda). Despite the fact that the reliability of the process has been proved and large investment has been received ($128 million), a comprehensive cost assessment is not publically available. Also, it has to be noticed that the market for HCl and sodium bicarbonate is not large for a wide application of this technology. (Sanna, et al., 2014)

Market overview. The aggregates production is the largest non-energy extractive industry with the global market of 53 200 Mt/y, of which more than a half are crushed stones. (Monteiro, et al., 2018, p. 13) According to European Aggregates Association data for 2014, the major producers of aggregates in Europe are Germany (more than 550 Mt/y), Russia, and Turkey.

In Finland 567 companies are producing around 80 Mt of aggregates per year from 2530 quarries and pits. The consumption of aggregates per capita in Finland is one of the highest in Europe, around 15 Mt/capita. The two main types of aggregates produced in Finland are crushed rock (~47Mt) and sand & gravel (~32Mt). (UEPG, 2017, p. 10). According to Finland's National Mineral Strategy, the demand for aggregates is supposed to grow with the growth of the national economy and construction volumes. At the same time, sand and gravel will be more difficult to

obtain in the future, which should increase the share of recycled aggregates, demolition waste, and waste rock from mining. (GTK, 2010)

The market for aggregates is usually very local because the transportation costs can double the price of aggregates every 30 km. Further, it leads to possible depletion of aggregates near the developed areas. Thus, transportation is a crucial parameter for aggregates production.

4.2.3. CO_2 concrete curing

Concrete is the most widely used man-made material in the world. Due it its characteristics, such as durability, good mechanical properties, and long lifetime, it can be used for a various applications in construction. Constructions made of concrete undergo the process similar to mineral rock weathering (chapter 4.2.1), when CO_2 in the air reacts with calcium contained in concrete. This process of passive concrete carbonation is beneficial for non-reinforced concrete because it decreases concrete porosity and consequently increases its strength.

However, carbonation is unfavorable for steel reinforced concrete, because carbonation decreases its pH. Concrete with low pH can no longer work as active protection against steel oxidation, which leads to the corrosion of steel. Cement carbonation is a complex process and its influence on the concrete properties is ambiguous and requires further study. Still, active carbonation can be considered a promising option to store CO_2 for a long period. (Šavija & Luković, 2016) Taking into account that bonded CO_2 will not release after the demolition of a cement construction, the CO_2 fixation time can be defined as very long (more than 100 years).

Mixing of the solid component of concrete with water starts the hydration reaction, which causes the hardening of concrete. Through the proper hardening process concrete acquires its strength and durability. Curing of concrete is a maintenance of adequate temperature and moisture conditions during concrete hardening to achieve a desired quality of the construction. The adequate humidity ($\sim 90\%$) and temperature (50-70°C) is needed during the whole curing period that can last up to 28 days for the concrete made of Portland cement. The addition of accelerators can shorten the curing process to 24 hours. (Monteiro, et al., 2018, p. 14; Zhang, et al., 2017 b)

The conventional way to maintain the moisture and temperature is using steam. However, steam generation is an energy-intensive process, thus as an alternative to steam, use of CO_2 for curing was suggested already in the 1970s. The idea was not feasible those times because of the high cost of CO_2 production, but the necessity of carbon utilization and the development of carbon capture technologies lead to the further development of this technology. Concrete curing with CO_2 causes complex structural changes in the concrete structure, which leads to higher strength and improved durability of the material. (Šavija & Luković, 2016) The time required for curing using CO_2 is comparable to the steam curing with accelerators (Monteiro, et al., 2018, p. 15) or in some cases even shorter (Zhang, et al., 2017 b, p. 127)

Implementation of concrete carbonation is on the stage of pilot plants constructed by the Carboncure technologies and the Solidia Technologies. The Carboncure Technologies Inc. injected CO_2 into concrete mixing in mixing truck. Addition of optimal dose of CO_2 shortens initial settings of concrete and improves its strength up to 14% after the first day. (Monkman, et al., 2016). Another example of the carbonated cement production is Solidia Technologies. In addition to carbonation curing, Solidia produces low-lime calcium silicate based cement (CCSC), which can consume around 240 kg CO_2 per ton of cement. (Lehne & Preston, 2018, p. 104) The CCSC's can be produced in the same kilns as Portland cement but using another material.

The important advantages of carbonation concrete curing are relatively low energy consumption and no additional requirements for chemicals in the process. (Jang, et al., 2016) In addition, curing with CO_2 leads to the lower (~80%) water usage (DeCristofaro, et al., 2017) that is beneficial from the environmental point of view. However, carbonation curing has also some disadvantages. First, as it was already mentioned, carbonated concrete increases corrosion of steel used for constructions' reinforcement. Considering that only 25% of concrete used with steel reinforcement (UN Environment, 2017), there is still a potential for carbonation curing due to the size of the concrete market.

4.3. Polymers

Due to the unique properties and relatively low price of polymers, they are used in many areas from everyday home appliances to medicine and space industry. Yet, as in the case of fuel, polymers production requires fossil-derived hydrocarbons and possibility to produce polymers from renewable materials is an important issue on a global level. There are many types of polymers that can be produced using CO_2 in combination with other feedstock. Moreover, in some cases, there is more than one technology to obtain the same product. Therefore, it is important to classify and clearly define which products will be analyzed. The classification of polymers described in this chapter presented in **Figure *10***.
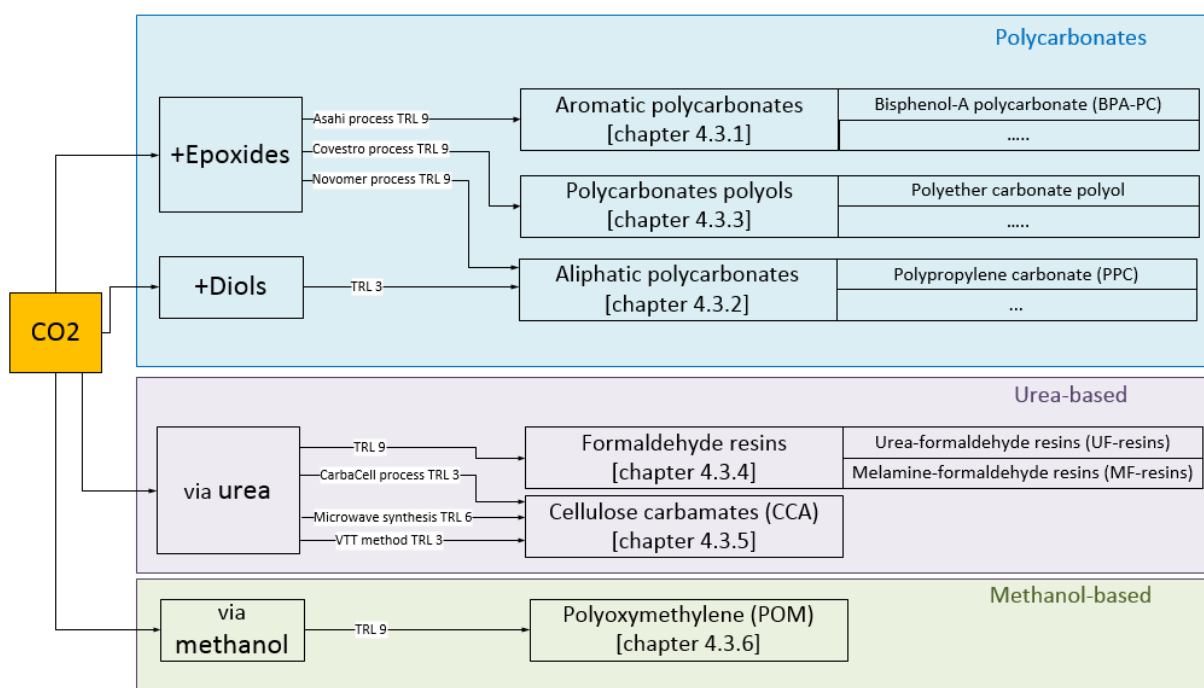
Figure 10 Polymers produced using CO2

Polymers can be divided into three main categories: polycarbonates (PCs), urea-based polymers, and methanol-based polymers. Polycarbonates can be divided into two main groups: aromatic and aliphatic. Aromatic carbonates contain an aromatic ring in their structure, and the most important and widely used product in this group is bisphenol-A polycarbonate (BPA-PC). Aliphatic are polycarbonates that do not contain an aromatic ring. This group presented by linear polymers:

polypropylene carbonate (PPC) and polycarbonate polyols. Considering that CO_2 can be used for urea production, it can also be considered as a feedstock for urea-formaldehyde (UF) resins and melamine-formaldehyde (MF) resins. Further, urea and cellulose can be used for the production of cellulose carbamates, a product that potentially can replace viscose. Finally, there is an option to produce polyoxymethylene (POM) from CO_2 via methanol and formaldehyde. Moreover, POM can be produced from technically fixated CO_2 (Müller, et al., 2015, p. 74)

It is important to mention, that although polymer synthesis process requires high purity CO_2, usage of captured waste CO_2 in the commercial polycarbonate production process was reported by the Econic Technologies and Covestro. (Poland & Darensbourg, 2017, p. 5006).

4.3.1. Polycarbonates

Bisphenol-A polycarbonate (BPA-PC, commonly referred as polycarbonate PC) is a lightweight transparent polymer with high resistance to heat and impact, and good mechanical properties (Monteiro, et al., 2018, p. 36). BPA-PC is thermoplastic that can be molded to a variety of shapes. Due to its unique properties, BPA-PC is one of the most important engineering plastics and it is used many areas, such as domestic appliances, power tools, automotive parts, medical devices, electronic equipment, safety glasses, construction, packaging, etc. Although BPA-PC is not easily degradable and potentially can store CO2 for a long period, usually the lifetime of the BPA-PC based products does not exceed several decades or even a decade. Taking into account that it is not possible to define the exact lifetime of the product, the CO_2 fixation time for BPA-PC products can be assumed as medium (10-50 years).

Industrial route of BPA-PC production is from bisphenol-A and diphenyl carbonate (DPC), which in turn is produced from phenol and phosgene (**Figure 11**). Development of alternative production routes was stimulated by the environmental harm and high toxicity of phosgene, large amount of sodium chloride obtained as side-product, and industrial importance of BPA-PC (Ang, et al., 2015). The most developed and commercialized alternative route was developed by Asahi Kasei Chemicals.
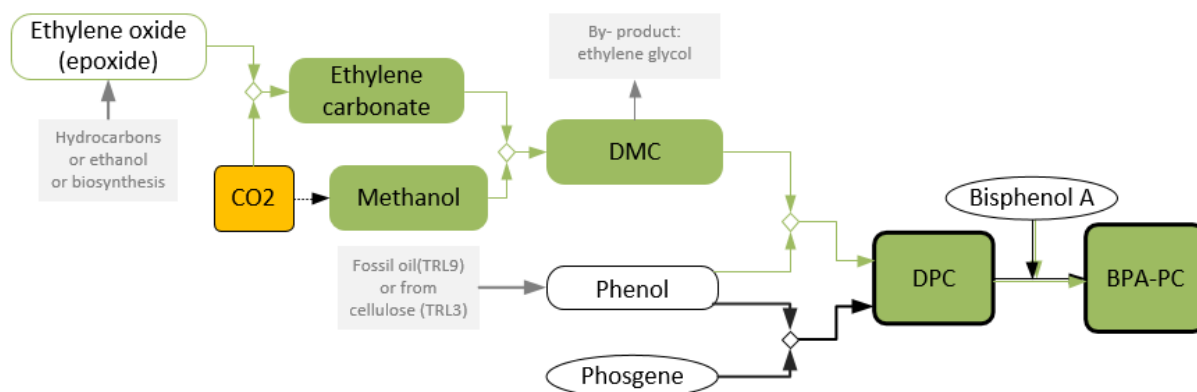
Figure 11 BPA-PC production routes: traditional (black) and Asahi Kasei (green)

Asahi Kasei process uses CO_2 and ethylene oxide as feedstock. BPA-PC is produced through a four-step process via ethylene carbonate, dimethyl carbonate (DMC) and DPC. Ethylene glycol as a valuable by-product can be considered as an additional advantage of the process. In 2010, Asahi Kasei route amounts to 15% of global BPA-PC production (Mikkelsen, et al., 2010, p. 50). Currently Asahi Kasei is commercializing more effective process, which bypasses DMC production, and uses CO_2 and alcohol as feedstock.

Despite the non-phosgene process of BPA-PC production, the polycarbonate is potentially harmful to health and environment due to the possible release of BPA during the contact with water. In addition, production of epoxides used for polymer production is highly energy intensive, which may diminish the effect of carbon sequestration.

Polypropylene carbonate (PPC) is an alternating copolymer of propylene oxide and CO_2 with high molecular weight and high carbon content (up to 50%) (Monteiro, et al., 2018, p. 38). PPC is biodegradable, has low oxygen permeability, poor processability, and mechanical performance. Such properties reduce possible applications of the polymer. Until recent PPC was used mainly as a binder in ceramics, adhesives, and pyrotechnics, but due to its good biodegradability, it is an emerging material for food packaging. (Luinstra & Borchardt, 2012, p. 30; CarbonNext, 2017, p. 19) Thus, it can be assumed that CO_2 sequestration period of PPC is short (< 10 years).

The commercialized route of PPC synthesis using CO_2 was developed by Novomer. The Converge polymer is PPC polyol designed to be used in polyurethane hot melt adhesives applications. The process is based on the reaction of CO_2 with epoxides (e.g. propylene oxide) under zinc-based catalysts. (Monteiro, et al., 2018, p. 38) The main disadvantage of this process is a high energy intensity of epoxides production, and therefore their high price. However, fossil-based epoxides can be replaced with bio-derived and production of PPC has a potential to be completely renewable (Machado, et al., 2018). The lifetime of PPC polyol used for polyurethane is longer than those for biodegradable packaging, and in some cases can be above 10 years (Monteiro, et al., 2018, p. 40). However, the more realistic sequestration period is still less than 10 years.

The alternative route of PPC production is CO_2 reaction with diols. This route is mainly used for cyclic carbonates synthesis, but direct copolymerization of CO_2 with polyols was demonstrated by (Tamura, et al., 2016). The reaction can be performed at low pressure with has a high yield (97%). Thus, this route can be developed to a green and low-cost process of PCs production. (Tamura, et al., 2016). The third route existing for polycarbonate synthesis is via reaction of CO_2 and oxetanes. Although it was demonstrated in the laboratory, this route is less thermodynamically favorable than others and therefore it is not considered as an option in literature. (Omae, 2012; Darensbourg, et al., 2010)

Polycarbonate polyols are polymers containing multiple hydroxyl groups. Commonly they are used as co-monomers for polyurethanes production. Polyurethanes have a wide range of applications, such as insulation, furniture, footwear, automotive industry, coatings, etc. The commercially produced from CO_2 PC polyol Caryon is used for the production of polyurethane foam for mattresses. Thus the sequestration period for CO2 fixated in polyurethanes can be assumed as 10-50 years.

The conventional way of PC polyols production is the reaction between epoxides and alcohols, for example, ethylene glycol and ethylene oxide. (Monteiro, et al., 2018) These components are usually obtained from petroleum-based hydrocarbons (e.g. ethylene). The alternative route of polyols production is via the reaction between CO_2 and epoxides. The process is similar to PPC synthesis, but different catalysts allow it to obtain a different structure of the polymer. On the

industrial scale PC polyol (commercial mane Caryon) is produced by Covestro process. The production of Caryon polymer was launched in 2016 in Belgium.

Despite PC polyols on average contain 20 wt% of CO_2, the production process cannot be considered as a carbon sink for all cases, but the GHG emission reduction up to 11-19% can be achieved. The reason is the epoxides (propylene or ethylene oxides) used in the synthesis, which production is petroleum-based and high energy intensive. (Monteiro, et al., 2018, p. 40)

4.3.2. Urea-based polymers

Urea can be used as a feedstock for the production of resins and cellulose-based materials (**Figure 12**.) The possibility of CO_2 utilization into urea-based resins is completely dependent on the possibility to produce urea and/or formaldehyde from the fixated CO_2. Such are valuable products with a wide range of applications and developed production technology, therefore it is important to consider them as an option.
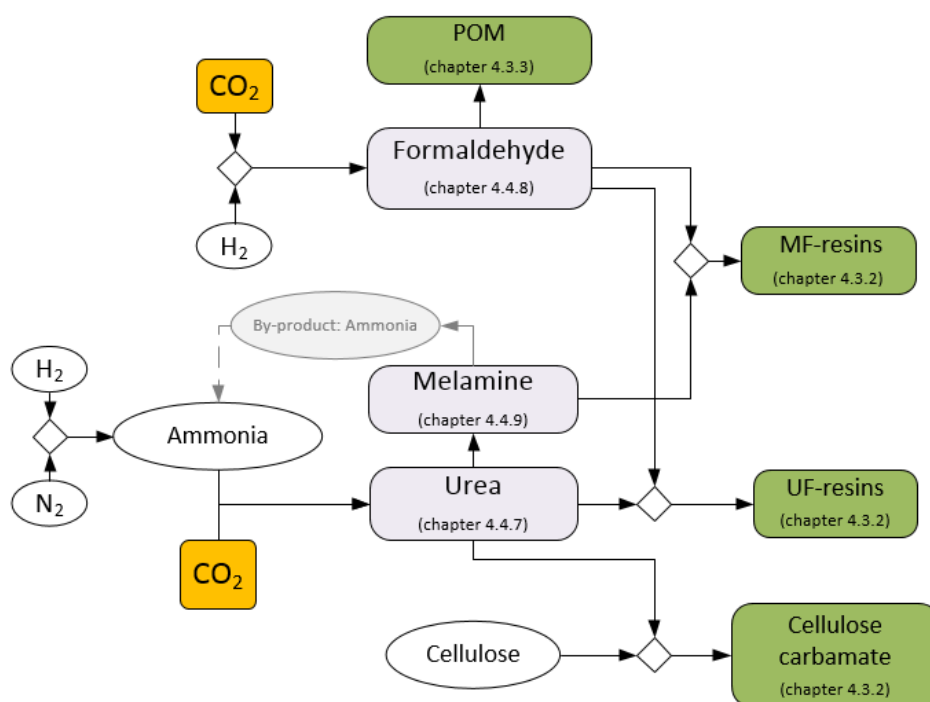
Figure 12 Polymers and other chemicals produced based on urea and formaldehyde

Urea-formaldehyde (UF) and melamine-formaldehyde (MF) resins are amino plastics obtained from urea and formaldehyde. The main applications of UF-resins are binding agents for wood materials (plywood and lightweight boards), glues, varnishes, and foams. MF-resins are more expensive, but due to their unique properties (transparency and water-resistance), these polymers used in construction for panels, surface coating, kitchen furnishing. Thus, CO_2 can be fixated in the plastics for decades. (Müller, et al., 2015, p. 72.)

The conventional way of urea-based resins production (**Figure** *12*) can be used for CO_2 sequestration in cases than either one or both components are produced from captured CO_2. Thus, there is a possibility to produce a resin with carbon fraction completely built from technically fixated CO_2 (Müller, et al., 2015, p. 79). The advantage of this option is that both urea and resins synthesis does not require catalysts (Müller, et al., 2015, p. 72). This reduces the quality requirement to CO_2 though does not allow to completely avoid the capture step. The main disadvantage of UF- and MF-resins is the formaldehyde emission that poses potential health risks. However, the addition of particular additives helps to reduce the emissions to an acceptable level (Müller, et al., 2015, p. 74).

The third urea-based polymer can be produced using CO_2 is **cellulose carbamate (CCA)**, which might be considered as the most promising alternative to viscose in fiber production. Although CCA is biodegradable, it has relatively long storage period due to the high stability at room temperature. (Willberg-Keyriläinen, et al., 2018, p. 195.) The main application areas of the material are fibers and films industries, high-absorbents in nonwoven industry, filter manufacturing, hollow fibers and sponges (VTT, n.d.; Guo, et al., 2009). In addition, cellulose carbamate can be used for manufacturing foams for insulation or soundproofing (Müller, et al., 2015, p. 73). Thus, based on the application described above, CO2 fixation time of cellulose carbamates can be assumed as short (< 10years).

The importance of this option lies in the possibility to close the gap appearing due to the growing demand for fiber, which cannot be meet with current materials. The additional advantage is that viscose spinning machines can be used in the CCA production process (Qi, 2017, p. 13). Cellulose carbamate can be produced via three different methods from urea and cellulose. The most

developed one is the production by microwaves irradiation. The advantages of this processes are the solvent-free and catalyst-free conditions, and the low conversion time (few minutes). The method was demonstrated on a pilot scale. (Fu, et al., 2014; Qi, 2017)

The patented CarbaCell process is similar to viscose production. The main difference is the utilization of urea in CCA synthesis instead of carbon disulfide (CS_2) used in the viscose production. The CarbaCell method can be used on the industrial level, though it has not been implemented yet due to certain requirements to catalyst, solvent and the process (reaction time and temperature). (Qi, 2017, p. 13.)

The third option is the method developed by VTT. The method does not require a solvent or other components except urea and cellulose, has high efficiency and can be scaled-up and commercialized. (VTT, n.d.).

4.3.3. Methanol-based polymers (Polyoxymethylene)

Polyoxymethylene (POM, polyacetal, polyformaldehyde) is a formaldehyde-based thermoplastic with established production technology. POM has the highest elasticity among the existing large-scale thermoplastics (Müller, et al., 2015, p. 74) and has better mechanical properties than polyethylene and polypropylene (Alper & Orhan, 2017, p. 118). Because of its good mechanical properties, POM is used for the production of different mechanical parts (gears, wheels and other moving elements), vehicle construction, electrical engineering, furniture industry, household devices, etc. Thus, the fixation time can be assumed as relatively short (< 10 years).

The industrial route of POM production is from formaldehyde, which in turn can be produced from CO_2 via methanol or formic acid production (**Figure** *12*). This route provides a possibility to produce POM completely from captured CO_2 and replace fossil-based carbon (Müller, et al., 2015, p. 88).

4.4. Chemicals

CO_2 can be used directly or indirectly for the production of a wide range of bulk and fine chemicals. The most important options will be described below. It is important to mention, that

CO_2 is used for the production of a wide range of fine chemicals, which were not evaluated in this work. Fine chemicals are usually produced in a small amount and therefore their CO_2 utilization potential is very small.

4.4.1. Formic acid

Formic acid (HCOOH), is liquid colorless acid with a pungent odor. Formic acid is a high-value product, which is mainly used as a preservative and antibacterial agent. In 2013, around 34% of formic acid produced worldwide was used in animal feed. Leather tanning and textile dyeing accounted for 32 % and 13% respectively. (Pérez-Fortes, et al., 2016, p. 16445.) Thus, CO_2 fixation time can be assumed from very short (<1 year) to short. (<10 years) (Monteiro, et al., 2018, p. 43.)

Alternatively, formic acid can be used as fuel due to being an effective hydrogen carrier. The conversion of CO_2 to formic acid requires only 1 molecule of hydrogen, which makes it the most thermodynamically favorable route from all the fuel options. However, high toxicity and possible mutagenic properties of formic acid, make its large-scale production as fuel questionable. (Monteiro, et al., 2018, p. 43.) CO_2 fixation time in the case of formic acid utilization as fuel can also be assumed as short.

The conventional way of formic acid production is via methyl formate. The process consists of two reactions. Frist is carbonylation of methanol (methanol reaction with carbon monoxide) to methyl formate and further hydrolysis of methyl formate to formic acid. The alternative routes for formic acid production via CO_2 are hydrogenation and electrolysis.

The hydrogenation route implies the thermocatalytic conversion of CO_2 and hydrogen. The reaction takes place in the presence of catalysts and requires methanol as a solvent for formic acid. The TRL of the hydrogenation technology is 5 and the route is considered as the most likely technology to be commercialized. The CO_2 utilization potential of the hydrogenation is limited by higher energy consumption compared to other routes. (Jarvis & Samsatli, 2018, p. 53). Next route is the electrochemical reduction that has TRL 3. The process combines hydrogen production by hydrolysis and subsequent CO_2 hydrogenation. (Monteiro, et al., 2018, p. 43.) This technology is

also seen as an effective option, but still have not been commercialized. (Jarvis & Samsatli, 2018, p. 53).

4.4.2. Cyclic carbonates

Cyclic carbonates is a group of organic chemicals that includes three commercialized products: ethylene carbonate, propylene carbonate, glycerol carbonate. Ethylene and propylene carbonates are usually used as solvents, components for synthesis of other cyclic compounds, and as electrolytes in lithium ion batteries. Propylene carbonate can be also used as a plasticizer. Glycerol carbonate is an emerging chemical, which is used as a solvent and a component for manufacturing polycarbonates and different intermediates. Also, glycerol carbonate is an important component in cosmetic and pharmaceutical industries. (CarbonNext, 2017, p. 16.) CO_2 fixation time for these applications can be considered from very short (<1 year) to short (<10 years) (Monteiro, et al., 2018, p. 42).

The state of art technology for the production of cyclic carbonates is by the reaction of CO_2 with epoxides. Although the conventional route utilizes CO_2 in the production process, the CO_2 emissions from cyclic carbonates production are higher than the amount of the utilized CO_2 (Monteiro, et al., 2018, p. 41). Besides, epoxides are usually produced from hydrocarbons. This makes the state of art technology for the production of cyclic carbonates being dependent on fossil materials. Unfortunately, all alternative routes also require fossil-derived components, such as diols or olefins.

An alternative route for cyclic carbonates production is via CO_2 and diols reaction. The route requires further development because of the challenges with equilibrium, side reactions, and process conditions. etc. The technology has been investigated within the CyclicCO2R project and has a TRL level of 3. (Monteiro, et al., 2018, p. 41.) Other alternatives are via CO_2 and monohalohydrins reaction and via CO2 and olefins. The technologies also require further development and have TRL 4-5 for monohalohydrins and TRL 1-3 for olefins. (CarbonNext, 2017, p. 17.)

Cyclic carbonates is a niche product with quite a small market (40 kt/y), so currently the CO_2 utilization potential of this options is low. However, growing demand for lithium ion batteries makes the production of cyclic carbonates a promising options. In addition, from the thermodynamic perspective, cyclic carbonates are the most favorable CO_2 utilization option. (Monteiro, et al., 2018, p. 42.)

4.4.3. Dimethyl carbonate

Dimethyl carbonate (DMC) is an alkyl carbonate with good miscibility with water, non-toxic and readily biodegradable in the atmosphere. The main applications of DMC are an intermediate for polycarbonate production and a solvent. Also, DMC can be used as a substitute for toxic compounds, such as phosgene. (Pyo, et al., 2017, p. 61.) An important application of DMC is an intermediate for BPA-PC production (chapter 4.3.1). Thus, depending on the application, CO_2 fixation time of DMC can be assumed from very short (<1 year) to short (< 10 years).

Historically DMC was produced by the reaction of phosgene and methanol. However, because of the high toxicity of phosgene, currently the main share of DME is produced by methanol carbonylation (reaction of methanol with CO and O_2). The alternative route of DME production is the direct electrochemical synthesis from CO_2 and methanol. The main limitation of this route is the high energy requirements and low conversion of DMC. Based on the life-cycle assessment, at the current stage of development, the commercial route is more sustainable than electrochemical conversion. (Garcia-Herrero, et al., 2016, p. 2088.)

The direct synthesis of DMC from methanol and CO_2 can be also performed using membrane reaction technology. The pilot plant with a capacity utilizing this route for DME production has been built by Akzo Nobel.

4.4.4. Isopropanol

Isopropyl alcohol, commonly called isopropanol, is a colorless liquid with strong odor. Isopropanol mainly used as solvent in various industries, from cosmetics and personal care products to paints, resins, and pharmaceuticals. The electronics industry uses isopropanol as

cleaning and drying agent. Besides, isopropanol can bused as intermediate in manufacturing of ketones. Based on the applications, the CO2 fixation time of isopropanol can be assumed from very short (<1year) to short (<10 years). (Monteiro, et al., 2018, p. 44.)

The most common industrial route of isopropanol production is the direct synthesis from propylene. Thus, the development of alternative routes for isopropanol production allow the industry to reduce the share of petroleum-based fossil materials. The existing alternatives to the state-of-art technology are biological production and bioelectrochemical conversion. Both methods are on the early stage of development and have TRL of 3. Biological production implies genetically modified bacteria *Escherichia coli* or cyanobacteria *Synechococcus elongates* that can use light and CO_2 to produce isopropanol. (Monteiro, et al., 2018, p. 44.) In bioelectrochemical conversion, electricity is playing role of CO_2 redundant, which is used by a mixed microbial community for the production of multicarbon compounds, including isopropanol (Arends, et al., 2017).

Isopropanol is a valuable alcohol. Although its market is relatively small and mature, the price for the chemical is quite high (1200-1700 €/t). Thus, potential profitability makes isopropanol an attractive option for CO_2 utilization. However, usage of genetically modified bacteria might arise a public acceptance issues, which can be a barrier for the technology implementation. (Monteiro, et al., 2018, p. 44.)

4.4.5. Synthesis gas

Synthesis gas (syngas) is a mixture of hydrogen and carbon monoxide (CO), with a small share of carbon dioxide (Mackaluso, 2007, p. 98). Syngas can be used as fuel or as a building block for a wide range of chemicals from hydrogen to ammonia, methanol and ethanol. An important application of syngas as intermediate is for the production of synthetic petroleum via Fischer-Tropsch process. (Amin & Tahir, 2011, p. 44.; CarbonNext, 2017) Based on the applications, CO22 fixation time of syngas can be assumed as short (<1 year).

The industrial route of syngas production is by reforming of natural gas. Alternatively, syngas can be produced by electrolysis from water and CO_2. The electrolysis can be carbon neutral if

renewable energy sources will be used for electricity production. There are several routes exist for this purpose, but none of them is developed enough. Still, two routes are potentially suitable for the implementation on an industrial scale. First technology is the simultaneous co-electrolysis of H_2 and CO_2, and the second is the separated electrolysis. CO_2 electrolysis to produce CO and water electrolysis to produce hydrogen. The advantage of the second option is than CO and H_2 can be mixed after electrolysis at any desired ratio. However, both the technologies are on the early stage of development (TRL 3). (Liu, et al., 2016).

4.4.6. Oxalic acid

Oxalic acid ($C_2H_2O_4$) is the simplest dicarboxylic acid and a secondary product of formic acid (Müller, et al., 2015, p. 76; CarbonNext, 2017, p. 13). The acid is used as a fixation agent in fabric dyeing process, for separation of rare earth metals, and as a removal agent for bleaching, cleaning and rust removal. In addition, oxalic acid can be used in the pharmaceutical industry for the antibiotics production and in chemical industry for the production of fine chemicals. (CarbonNext, 2017, p. 13) The period of CO2 fixation oxalic acid can be assumed as very short (<1 year) (Müller, et al., 2015, p. 89).

In nature oxalic acid is found in many plants (Müller, et al., 2015, p. 89). On the industrial scale the acid can be produced either by heating sodium formate (Müller, et al., 2015, p. 89) or by the oxidation of carbohydrates, ethylene glycol or propylene glycol (CarbonNext, 2017, p. 13). The last route implies the use of environmentally harmful nitric acid as an oxidation agent (CarbonNext, 2017, p. 13). Therefore, more sustainable routes of oxalic acid production are important.

An alternative method for the oxalic acid production is the electrochemical reduction of CO2 in a water-free media that cannot donate hydrogen (aprotic media). The process shows a relatively high yield (85%), The TRL of the technology is 3-4 and for the future scale-up it requires improvements in the reactor design. In addition, development of non-degradable and easily recyclable electrolyte is also needed. (CarbonNext, 2017, p. 13.)

4.4.7. Urea

Urea or carbamide is an organic compound, which main application is agricultural fertilizers. In addition, urea is widely used for the production of melamine (chapter 4.4.9), and urea-based resins (chapter 4.3.2). A small share of urea is used as moisturizer in the pharmaceutical industry, as an additive to tobacco in the cigarette industry, and for the production of fine chemicals, such as urea-hydrogen peroxide complex. (Müller, et al., 2015, p. 89.) Taking into account that melamine and polymers have been evaluated separately, CO_2 fixation time for other urea applications can be assumed as very short (<1 year) (Müller, et al., 2015, p. 72).

The conventional industrial way of urea production is direct hydrogenation of CO_2 with ammonia (**Figure *12***). Currently, the main source for ammonia and CO_2 for the urea production is natural gas. Reforming of natural gas produces hydrogen, needed for the ammonia production, and by-product CO_2. Thus, urea plants are often built near the ammonia production plant to utilize this CO_2. (CarbonNext, 2017, p. 9.) Considering that CO_2 utilized for the urea production otherwise would be waste, utilization of another CO_2 source seems unreasonable. However, if sustainable hydrogen from another source is available, the utilization of CO_2 captured from flue gas makes sense.

4.4.8. Formaldehyde

Formaldehyde is a colorless gas with a strong odor. The main application of formaldehyde is the production of paints and polymers, such as amino resins (chapter 4.3.2) and polyoxymethylene (POM) (chapter 4.3.3). Resins industry with share of 55%, is the biggest consumer of formaldehyde (Franz, et al., 2016, p. 21). Besides this, formaldehyde is used in over 50 industrial processes, including pharmaceuticals, cosmetics, and disinfectants (Franz, et al., 2016, p. 1; Bahmanpour, et al., 2014, p. 2). Considering that the main application of formaldehyde is intermediate for plastics production, its CO_2 fixation time has been assumed equal to the POM (<10years). The reason for this choice is that POM has the lowest CO_2 fixation time among the formaldehyde-based plastic considered in this report.

On the industrial scale formaldehyde is produced from methanol, either by its dehydrogenation or partial oxidation (Bahmanpour, et al., 2014, p. 3). In the case of methanol being produced from

captured CO_2, the industrial route of formaldehyde production can be considered as an option. However, there is an alternative route for the formaldehyde production directly from CO_2 bypassing the methanol production stage. This can be achieved by hydrogenation to the intermediate formic acid (chapter 4.4.1) and it subsequent reduction to formaldehyde. However, this technology is on the very early stage of development, TRL 1-3. (CarbonNext, 2017, pp. 10-11; Heim, et al., 2017, p. 2350.)

4.4.9. Melamine

Melamine is the most important downstream product of urea and the important component in the production of MF-resins (**Figure *12***, chapter 4.3.2). Beside the resins production melamine is used for the production of foams, adhesives, molding compounds, and flame retardants. However, as in the case of formaldehyde, the main application of melamine considered in the evaluation, is the feedstock for the resins production, therefore its CO_2 fixation time can be assumed as medium (10-50years).

The conventional way of melamine production is from urea and ammonia. Often melamine production facilities are located nearby the urea production plants. (Müller, et al., 2015, p. 72.) Because the urea production process utilizes CO_2 (chapter 4.4.7), melamine can also be considered as an option for CO_2 utilization. In addition to the developed production technology (TRL 9), melamine is a very valuable product, which price is Europe can reach 1175 €/t (ICIS, 2016). Considering that the price of urea is less than 300 €/t (IndexMundi, 2018), the high price for melamine can compensate the costs for hydrogen production from the sustainable source and the cost for carbon capture. However, more detailed evaluation is needed in this case.

4.5. Gaseous CO_2

In all processes described above, CO_2 has been used as a feedstock and during the production process, it was transformed into another substance. This chapter describes direct applications of captured CO_2. The technologies used for carbon capture described in chapter 3.1. The conventional way of CO_2 production is its purification from CO_2 rich streams (>95 mol%) (Monteiro, et al., 2018, p. 115) In Europe about the half of food grade CO_2 sourced from ammonia production. The

situation in Finland is different due to the lower ammonia production. The only ammonia plant in Oulu operated by Kemira Oyj has a capacity of 75 kt/a. (Perez, 2017).

There are several plants producing purified CO_2 in Finland. The two main companies capturing CO_2 from the air: AGA Ab and Oy Polargas Ab (AirLiquid). In addition, there are plants producing CO_2 as a byproduct from industrial processes, such as hydrogen production (Fortum Oy in Sköldvik), alcohol production (Primalco Oy in Koskenkorva), and calcium chloride production (Kemira Oy in Kokkola). The total installed capacity in 2000 was 70 kt_{CO2} and 62 kt_{CO2} was produced. (Koljonen, et al., 2002)

Gaseous CO_2 is used in the food industry, horticulture (for greenhouses), water treatment, power to gas (PtG), and concrete curing. With the exception of concrete curing, CO_2 fixation period for all direct applications can be assumed as very low (less than 1 year).

The main companies producing beer and soft drinks in Finland are Oyj Hartwall (Helsinki, Lahti, Tornio, Karijoki), Oy Sinebrykoff Ab (Kerava and Pori) and Olvi Oy (Iisalmi). Some of them produce CO_2 for their own use. For example, Hartwall has capture plants in Lahti and Tornio, which production capacities are 350 kg/h and 400 kg/h respectively. Thus, the demand for CO_2 from other sources is rather low for the beverage industry and in the year 2000 the total amount of CO_2 purchased for the beverage industry was 14.6 kt. (Koljonen, et al., 2002, p. 72).

The total annual usage of CO_2 in greenhouses is unknown and mainly depends on the type of crop grown in greenhouses. However, it can be estimated based on the consumption of 100-300 kg_{CO2} per hectare per hour. (Mikunda, et al., 2015, p. 11) The greenhouse cultivation area in Finland in 2017 was about 389 ha (Luke, 2018). Thus, the total CO_2 demand for greenhouses may be estimated in the range 0.3-0.9 Mt/y. However, the sparse distribution of greenhouses may lead to higher transportation costs and therefore unaffordable CO_2 price for greenhouses.

In water treatment, CO_2 is used for lowering the pH of alkaline water. However, the demand for the gas is rather small. In Finland, water treatment plants use approximately 4 kt of CO_2 annually. The biggest of them are in Helsinki, Tampere, and Turku. (Koljonen, et al., 2002, p. 72)

4.6. Carbon

There are four main products that consists of pure carbon and can be obtained from CO2: amorphous carbon, graphene, nanofibers (CNFs), and nanotubes (CNTs). The last three products are more valuable than carbon black. Carbon black (amorphous carbon) is not considered as an option due to main development and research is conducting towards the structured carbon nanomaterials. The main difference between carbon products is the structure, which strongly influences on material's characteristics and consequently on its value and possible applications.

Carbon nanomaterials are emerging materials with superior strength, flexibility and durability characteristics. Therefore they can be used for reinforcement of lightweight, high strength building materials and production of composites and synthetic materials. Another area of application is the production of electrodes for Li-ion batteries and capacitors. In addition, carbon nanomaterials can be used in nanoelectronics and as an adsorptive material for water. (CarbonNext, 2017; Mao, et al., 2017; Licht, 2017) Considering that carbon does not release to the atmosphere after the product lifetime, the CO2 sequestration period for these materials can be assumed as very long (>100 years).

Commercial production of graphene, CNTs, and CNFs is based on chemical vapor deposition (CVD) technology. This method allows producing high-quality nanomaterials from carbon-containing gases, for example, methane. Due to high chemical stability and energy required for its conversion, CO_2 has not been considered as a raw material for CVD. Despite graphene and CNTs have been synthesized from CO2 via CVD (Allaedini, et al., 2015; Allaedini, et al., 2016), this route requires more research and has many disadvantages such as high temperature (1100 C) and high purity of required materials.

An alternative route for graphene synthesis from CO_2 was invented by the Graphene Technologies. The process is based on burning magnesium metal in a dry ice CO_2 environment. The technology has relatively low heat and electricity demand but also some issues, such as problems with the synthesis control and pure magnesium used in the process. However, the technology was patented and is supposed to be implemented on the commercial level. (Chakrabarti, et al., 2011)

The most developed alternative route for CNFs and CNTs production is the C2CNT technology that implies electrocatalytic conversion in molten salt (Li_2CO_3). The C2CNT technology has been designed for utilization of CO_2 from cement plants. The technology is based on CO_2 splitting into pure oxygen gas and solid carbon. The process is carried out in the electrolysis chamber with nickel anode and steel cathode. The equations of processes are presented below. (Licht, 2017).

$$Dissolution: CO_2(gas) + Li_2O \ (soluble) \rightarrow Li_2CO_3(molten)$$

$$Electrolysis: Li_2CO_3(molten) \rightarrow C(CNT) + Li_2O_3(soluble) + O_2(gas)$$

$$Net: CO_2(gas) \rightarrow C(CNT) + O_2$$
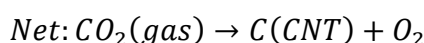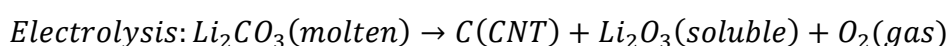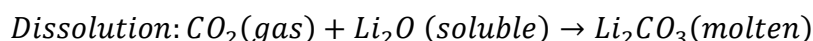
Equation 6 Electrocatalytic conversion of CO_2 in molten salt into CNTs (Licht, 2017).

During the process electrolyte (Li_2CO_3) is not consumed and CO_2 is used as the main reactant. The process requires a temperature of 770 °C. However, dissolution of CO_2 is exothermic and heat released during this reaction can compensate part of the heat requirements. Moreover, when integrating the process with a cement plant, part of the plants process heat can be recovered. Thus, the process does not require other sources of the external heating, though the preheating to molten state is needed in the beginning to start the reaction. Furthermore, in the case of the C2CNT integration with the cement plant, oxygen produced as by-product can be used for partial oxy-combustion in the cement production process. (Ren & Licht, 2016; Licht, 2017)

The C2CNT process has relatively low energy requirements and can utilize renewable energy to drive the electrolysis. The process shows 80-100% coulombic efficiency (formation of each mole of solid carbon requires four moles of electrons) and requires 7 MWh of electric energy to produce 1 t of CNTs. The important advantage is that flue gases from cement or coil power plant can be used for synthesis without additional capture step. The process is tolerant of the impurities containing in the flue gases, such as sulfur and nitrogen compounds and does not require pure carbon dioxide either. At the moment the technology has been implemented on pilot scale and has been patented. (Licht, 2017).

In addition to a number of advantages, there are some issues requiring further development. First is the metal resistivity, which is insignificant on a smaller scale, but can be an issue on a larger scale. Thus, a bigger electrode can have a large voltage drop, which can lead to energy losses. Further, the morphology of CNMs synthesized on the electrolytes depends on many parameters, such as temperature, electrolyte, potential, and current deposition. (Licht, 2017). Thus, the process requires precise control of the reaction and maintaining optimal reaction conditions on a large scale is an issue for the further development of the technology.

5. ANALYSIS OF CARBON UTILIZATION OPTIONS

Evaluation of different options for CO_2 utilization can be performed based on many criteria, including technological, economic, environmental, social acceptance, and risks related to all categories. However, there is no standardized methodology for the techno-economic and sustainability assessment suitable for all areas. Different approaches suggested for carbon capture and utilization assessment mainly focused on macro scale systems and optimization of one criterion, usually either economic or environmental. In addition, the studies are mainly concentrated on geological carbon storage Such an approach does not imply further recycling of carbon and its introduction into a circular economy, as it can be done, for example, in the case of fuels. (Karjunen, et al., 2017, p. 34).

The modeling tools, such as life-cycle assessment (LCA), techno-economic process evaluation tool (TEPET), or carbon source nodal network (CARSON) provide more precise assessment, but at the same time require detailed information about the processes and a significant amount of time for the building of complex models. Thus, detailed modeling methods cannot be implemented in the timeframe of this work to assess all the possible options. Therefore, the evaluation was made in several stages (**Figure *13***).

First, the key assessment criteria were identified based on the objectives of the assignment and literature research. Then, IBM Watson Service were used for gathering the information that is necessary for the assessment. Next, all options were evaluated based on the key criteria and the three most promising options were chosen. Further, the detailed techno-economic and

sustainability assessment of the most promising options were made based on the assessment criteria identified below. This chapter describes the methods and tools used in the assessment.
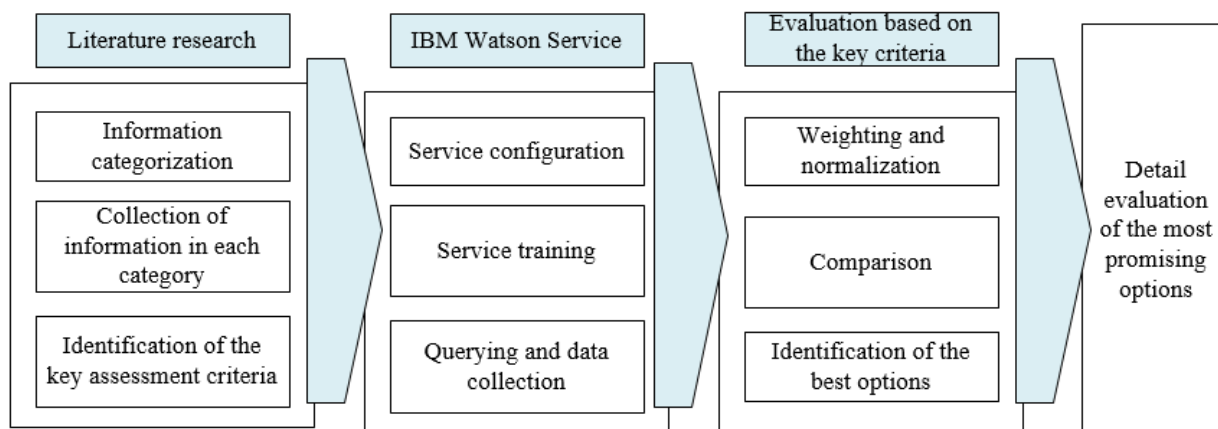
Figure 13 Assessment of CO_2 utilization options

5.1. IBM Watson Discovery service

Evaluation of possible CO_2 utilization options requires a multidisciplinary approach and selection of proper indicators to evaluate different aspects and risks related to each option. Considering the big amount of sources and a wide range of data needed for the evaluation, the IBM Watson Discovery service was used for the analysis of gathered data. The service can analyze a big quantity of unstructured data using AI and to find hidden patterns based on language processing.

Data analysis procedure with the Discovery service consists of several steps: configuration of the service, data uploading, training, and querying. Configuration is needed to define the parameters related to the documents conversion and text processing. The IBM Watson service allow it to upload documents in .doc, .pdf, and .html formats, but further, the service converts them to .json format. For the correct conversion, it is important to set the characteristic of the converted

documents, such as font type and size of headings, titles, and main text. Configuration related to text processing is the customization of the information enrichment process. The enrichment categories are standardized and include such fields as keywords, entities, relations, concept, and semantic roles. The enrichments are needed for the AI algorithms to process the text. The information can be uploaded after the service has been configured.

An important point related to data uploading is to supply the service with a complete information set. In order to collect the data set that covers all issues related to the topic, the area of research has been divided into several categories (Appendix II Table 1). The first category includes information about the cement industry, its CO_2 emissions, and CCS technologies. This category has been defined to support the IBM Watson system with the background data. Next category includes information about the possible utilization options and it has been divided into 6 sub-categories: fuels, inorganic carbonates, polymers, chemicals, gaseous CO_2 and carbon. Further, each sub-category includes the CO_2 utilization option (a product). For each option at least 5 articles related to the product were gathered. The last category of the collected data includes documents related to different technologies, reviews, comparisons, etc. The reason for the separation of this category is that in most cases, CO_2 utilization options divided and analyzed based on a technology rather than a product. The last category of documents that have been collected but does not upload to the IBM service, is the Material Safety Data Sheets (MSDS). These documents are crucial for the health and safety issues assessment, but cannot be analyzed effectively in the IBM service due to the service limitations.

The documents were searched from LUT library database, Elsevier Science direct database, Google patent database, and Google search engine. As a result, 356 articles selected based on the titles and abstracts have been collected for the analysis in the IBM Watson Discovery. The selection of articles might be a limiting factor for the analysis because it is quite challenging to estimate the data distribution and to be sure that all the necessary information is included. However, in the case of lack of information, additional documents can be uploaded to the system. Another possible limiting factor is the inability of the IBM Watson to process schemes, tables, and chemical equations.

After the information has been uploaded to the IBM Watson Discovery, the next step is the training. The training is needed to improve language processing algorithms and increase the relevancy of the answers given by the system. The training involves a set of queries (minimum 50) and rating the relevancy of the answers. Based on the training results, the AI teaches itself to return answers more relevant to the case study. After the training, the IBM Watson can be used for querying.

5.2. Assessment based on the key criteria

The first step of the evaluation is the definition of key criteria. Taking into account the challenges facing the cement industry, the objectives set during the meeting with industry representatives, and the results of the literature research, the next key criteria have been chosen and weighted based on their importance (**Table 2**). In addition, an important characteristics influences the choice of a key criterion is a possibility of the criteria numerical assessment and comparison.

Table 2 Key assessment criteria and their weights

Criteria	Weight
CO_2 uptake potential	2
Fixation time	3
Usage of fossil materials	2
Technology readiness level (TRL)	1
Health, Safety, and Environment (HSE)	2

The first two criteria were chosen due to the decrease in CO_2 emissions being the main objective of this work. Taking into account that process CO_2 emissions cannot be avoided, their capture and storage is the only option of the emission reduction. Therefore, CO_2 uptake potential shows the effectiveness of capture and fixation time shows the effectiveness of storage. Technology readiness level (TRL) indicates whether the technology can be implemented in a short time period. This criteria is important due to the expected decrease in emission allowance in the near future. Usage of fossil materials indicates the CO_2 emissions may occur during the production process. This indicator does not take into account the amount of the materials or emissions, but only the presence

or absence of them. Comparison of the emissions from different processes and materials may be incorrect at this stage.

The weighting has been done according to the next principles. The most important criteria with the highest weight (3) is the fixation time. Considering the main aim of the emission reduction is to reduce and maintain low level of CO_2 in the atmosphere, process emissions have to be captured in the product for as long as possible, preferably forever. Introduction of CO_2 into a circular economy is an option, but it does not applicable to the process emissions from the cement industry, due to the constant input of CO_2 from the decomposition of raw materials.

The lower rating (2) has been given to the criteria which lower performance can be compensated or justified. CO_2 uptake potential has lower importance because the low uptake potential can be compensated by a large amount of the manufactured product. Usage of fossil materials can be justified if the amount of captured CO_2 is still lower than net CO_2 emissions from the production process. HSE issues are highly important because some products are potentially hazardous to health (e.g. carbon nanomaterials), but in the most cases, special guidelines and frameworks are existing to prevent or minimize possible risks.

Finally, the lowest rating has the TRL because the technologies are constantly developing and this criteria can changes quite fast within the few years. However, the TRL is still an important criteria because of the possible reduction in the CO_2 emission allowances after 2012, when the next trading period in the EU emissions trading system will start.

Possible risks to health, safety, and environment (HSE) is a composite criteria basing on material safety data sheets MSDS for each product (Appnedix III Table 1). Three main aspects have been taken into account in this criteria: human health, environment, and content of hazardous compounds. Risks were rated from 1 to 3 based on the principle that the more dangerous the substance, the lower its rank (**Table *3***).

Table 3 HSE risk assessment

Human health	Value	Environment	Value	Hazardous materials	Value
Toxic or carcinogenic	1	Hazardous to the environment	1	Highly hazardous	1
Minor irritations	2	Low risks, may be harmful	2	Possibly hazardous	2
No risk	3	No risks	3	No risks	3

For the further assessment with the key criteria, the HSE aspects were weighted and normalized. The highest weight (3) was given to the human health risk because the health risks are mainly related to the usage of the product and it is difficult to manage and mitigate them. Environmental risks importance was weighted as (2) because they are mainly related to the production process and easier to manage. Hazardous materials have the lowest importance (1) because the hazardous materials are used during the production process and there are guidelines for such risk management and mitigation. After the weighting, the HSE parameters were normalized and scaled based on the principles described below. The constructed composite score was further used for the evaluation with other parameters.

It is important to mention, that economic parameters have not been included in the first step of the evaluation. The reason is the impossibility of their comparison on the basis – the higher score, the better. For example, a big market for the product cannot be considered as an advantage if the production is not profitable. Alike, a high price for a product does not make sense if there is no market for the product or the production costs is higher than price.

The second step, after the key criteria have been defined, is the evaluation based on the key criteria value and importance. Criteria value was scaled from 1 to 5 based on the formula:

$$X_i = \frac{X_i'}{X_{max}'} \cdot 5 \qquad\qquad (1)$$

Where, X_i' - a criterion value before scaling; X_{max}' the maximum value of the criterion; X_i – the criterion value after scaling.

Next, the indicator value for each key criterion can be calculated based as follow:

$$I = \frac{\sum_{i=1}^{N}(X_i W_i)}{W_{max} \cdot 5 \cdot N} \tag{2}$$

Where,

I indicator value;

N number of criteria, N=5 in this case;

X_i value of the evaluation criteria;

W_i the weight of the evaluation criteria;

W_{max} the maximum value of evaluation criteria;

Finally, based on the indicators' values, the best options can be chosen for the evaluation.

5.3. Detailed evaluation

The final step of the evaluation is the detailed assessment based on the assessment matrix. The assessment matrix was developed based on the sustainability parameters (environmental, economic, and social), the challenges facing the industry, and utilization technologies' characteristics. Suitable assessment criteria were identified in the next categories: characteristics of the product and utilization technology, economic aspects, HSE (health, safety, and environment) aspects, legislation, and social acceptance.

Product characteristics.

1. *CO_2 uptake potential.* Although the CO_2 uptake is one of the most important parameters, it takes into account only the CO_2 bonded in the final product and does not take into account carbon emissions during the manufacturing of the product or other components needed for the production. In some cases, these emissions can exceed the amount of utilized CO_2 and makes the whole utilization process useless. During the literature review, this issue was considered and mentioned for the cases where it might happen.

2. *Fixation time.* Probably the most important parameter for the purpose of carbon storage.

3. *Health, safety, and environment (HSE).* Health and safety issues were assessed based on the material safety data shit (MSDS) for each product.

Technology characteristics

4. *CO_2 quality required for the process.* Most of the options require relatively pure CO_2, which makes it necessary to use an intermediate carbon capture step. Processes that do not require CC and can utilize flue gas are preferable due to the lower cost of production.

5. *Usage of fossil materials.* Considering that many of the CO_2 utilization technologies require co-reactant for the production process (e.g. hydrogen, epoxides, methanol), it is important that the usage of co-reactant does not lead to larger CO_2 emissions than those that were captured. This indicator does not take into account energy emissions.

6. *Energy consumption of the process.* Energy consumption influence possible CO_2 emissions of CO_2 utilization process and the final price of the product.

7. *Other resources needed.* This parameter takes into account feedstock, co-reactants, and catalysts needed for the process. Due to a lack of resources, the implementation of the technology might be impossible. For example, the sustainable hydrogen source is an issue for many CO_2 utilization technologies.

8. *Technology readiness level (TRL)*

9. *Emissions to the environment.* Possible air and water pollutions, land use change, and other environmental risks might appear during the production process.

Economic characteristics.

10. *Market size*. This parameter is needed to estimate the demand on the product. The possibility to utilize product on a local market is more preferable than its export.

11. *Investment and operational costs*. Although investment costs are an important factor for a techno-economic assessment, it is quite challenging to estimate it briefly due to their dependence on many factors, such as the maturity of the technology and the type of a plant (first of a kind or N:th of a kind), business model and final product. Moreover, for the cases of technologies with a low TRL level, estimation of the investments cost is very uncertain due to the gaps of knowledge presently and a possible breakdown in the technology in the future (Martínez, et al., 2016). Therefore, this indicator won't be included in the first stage of assessment and the investments costs will be evaluated only for the most promising options.

12. *Production cost*. It is probably the most challenging parameter to estimate because in most cases there is no available information on the production costs, especially for the concepts or technologies implemented on a pilot scale. Therefore, this parameter has not been included in the first step of estimation.

13. *Price of the final product* is a parameter estimating the profitability of the CO_2 utilization. However, this parameter can be assessed only in conjunction with production costs and market size. For example, high price on a product cannot be considered as an advantage if there is no market for the product. Vice versa, a cheaper product with a big market might be more profitable due to the higher sales. Therefore, the influence of the price will be assessed in the second part of the evaluation.

There might be other parameters important for the evaluation, as for example legislative issues, taxes or public acceptance. These parameters were not included in the evaluation matrix but will be taken into account during the second step of evaluation. Furthermore, taking into account that evaluation was made based on the data contained in the literature, different options were evaluated with different accuracy, depending on the availability of information.

5.4. Economic evaluation

The main parts of economic assessment are an estimation of investment costs, fixed and variable operation and maintenance costs. Considering the lack of information, it is not possible to estimate all the parameters. In such cases, possible assumptions have been made. The basic parameters used for the economic assessment: economic lifetime 20 years, discount rate 8%.

Investment costs (capex) highly dependent on the scale of production. Thus, to take into account difference in scale between case study and capacities used in literature, capital costs were scaled according to the next formula

$$\frac{Cost_A}{Cost_B} = \left(\frac{Scale_A}{Scale_B}\right)^{SF} \qquad (3)$$

Where

$Cost_A$ the required cost of the facility with capacity $Scale_A$;

$Cost_B$ the known cost of the facility with capacity $Scale_B$;

CF a scaling factor for the technology;

Operational costs (opex) can be divided into fixed and variable. Fixed variable costs include maintenance costs, labor costs, insurance, taxes, etc., and can be calculated as a percentage of capex. Variable costs depending on the material and energy used for the production and can be assumed independent on the scale. Based on the investment and operational costs, the levelized cost can be estimated as follow:

$$Cost = \frac{capex \cdot crf + opex_{fix}}{Annual\ production} + opex_{var} \qquad (4)$$

Where,

$capex$ capital investments;

crf capital recovery factor;

$opex_{fix}$ fixed operational costs;

$opex_{var}$ variable operational costs;

Capital recovery factor can be calculated by the formula:

$$crf = \frac{i \cdot (1+i)^n}{(1+i)^n - 1} \qquad (5)$$

Where

n facility lifetime

i discount rate

For all calculations, facility lifetime was assumed 20 years, and discount rate 8%.

Transportation. Cost of transportation by trucks can be calculated by the methodology described in the research made by Karjunen et al. (Karjunen, et al., 2017). The methodology takes into account the costs of investment, fuel, labor, maintenance, and general expenses. Initial data for transportation costs by vehicles presented in **Table 4**

Table 4 Transport costs for vehicles (Karjunen, et al., 2017, p. 38)

Variable		Truck	Train	Unit
Availability	t_{ava}	6570	4380	h/a
Investment		374.321	487.577	€/unit
Fuel costs		0.57	1.34	€/km
General expenses		3788	31.57	€/a
Hourly cost		27.55	27.55	€/h
Loading time	t_{load}	2	12	€/trip
Maintenance		0.133	0.0886	€/km
Capacity	Q_{load}	22	80	t_{CO2}/trip
Speed	v	55	45	km/h
Interest rate		10	10	%
Lifetime		1(	10	a

The cost of transportation can be calculated as follow:

- Dividing the total quantity of goods transported Q_{tot} by the maximum load of a single vehicle Q_{load}, the number of shipments N_s can be found. The total quantity of goods is equal to the amount of CO_2 captured on the plant

$$N_s = \frac{Q_{tot}}{Q_{load}} \qquad (6)$$

- The total distance L_{tot} is the number of shipments multiplied by the distance between nodes and doubled due to trucks needs to return after each trip.

$$L_{tot} = 2 \cdot L \cdot N_s \qquad (7)$$

- Further, the total time of transportation t_{tot} can be calculated based on the total distance L_{tot}, vehicle speed v, loading time of the vehicle t_{load}, and the number of shipments N_s

$$t_{tot} = \frac{L_{tot}}{v} + N_s \cdot t_{load} \qquad (8)$$

- Next, the number of vehicles can be obtained by dividing the total time of transportation t_{tot} by the availability hours of a single vehicle t_{ava}

$$N = \frac{t_{tot}}{t_{ava}} \qquad (9)$$

Investments for transportation $capex_{transp}$ can be calculated by multiplying the number of vehicles by the cost of one vehicle.

Operational cost $opex_{transp}$ is the sum of general expenses, hourly costs, fuel, and maintenance

- Finally, the cost of transportation per ton of CO2 can be calculated as

$$Cost_{transp} = \frac{capex_{transp} * crf + opex_{trans}}{Q_{tot}} \qquad (10)$$

6. EVALUATION OF THE RESULTS

The results of data gathering and calculations of key indicators for CO_2 utilization options presented in Appendix IV and the best 10 options are in **Table 5**.

Table 5 CO_2 utilization options with the highest ranks based on the key criteria evaluation

№	Product	Technology	Rank
1	Nanotubes (CNT)	Electrocatalytic conversion in molten salt, C2CNT	61.3
2	Nanofibers (CNF)	Electrocatalytic conversion in molten salt	60.0
3	Graphene	burning Mg metal in a CO2 dry ice	60.0
4	Carbonated concrete	Direct mineral carbonation	56.0
5	Construction aggregates	CO2 mineralization	53.3
6	Melamine	From urea	52.0
7	Methane 1	Sabatier reaction	48.0
8	Methane 2	Biological conversion	48.0
9	Calcium carbonate GCC	Carbonation of waste	48.0
10	POM	methanol->formaldehyde	48.0

According to the evaluation, carbon nanomaterials (CNTs and CNFs) produced by the electrocatalytic conversion in molten salts are the best options (**№1** and **№2**). Although the CNTs production technology is more developed, both technologies are on the early stage of development. The main difference between the first two options is the reaction conditions and materials used for electrodes because these are factors influencing the final product structure. Considering a very low TRL of the both options, they can be evaluated together as CNMs.

Despite graphene production technology by burning Mg metal in CO_2 dry ice **(№3)** has higher total scoring, it seems reasonable to give a priority to the following options with lower rank for the following reasons. The TRL level of carbonated concrete and construction aggregates are much higher than those of graphene (TRL 9 and TRL 3 respectively). Considering that the TRL level of the first two option is also low (TRL 3-4), it might be important to analyze the alternative that can be implemented in the shorter time period. In addition, it will expand the range of the evaluated options. Thus, graphene production won't be analyzed.

Next two options (№4, №5) are based on the same technology – mineral carbonation, but the final products are completely different. Evaluating carbonated concrete production by the cement industry, it seems reasonable to assume that the final product, in this case, will be either gaseous CO_2 or carbonation as a service. The reason for this assumption is that the carbonation process takes place during the concrete hardening, which is the responsibility of the construction company. Thus, further evaluation of this option will be focused on the carbon capture and transportation. Such an approach might be also useful for the evaluation of other options because carbon capture is a necessary step in most of the utilization options. In addition, gaseous CO_2 can be utilized in other industries (e.g. food and beverage, greenhouses).

Summarizing the result, the three most promising options that have been chosen for the further assessment are carbon nanomaterials, gaseous CO_2 and construction aggregates.

6.1.   Carbon nanomaterials (CNMs)

Product. Carbon nanomaterials is an emerging product with a wide variety of application. Production of CNMs is very efficient in terms of CO_2 uptake and fixation time. CNM's CO_2 uptake of 3.67 t_{CO2}/t_{CNM} (CarbonNext, 2017, p. 43) is the highest among all the options considered in this evaluation. The CO_2 fixation time of CNMs is also one of the longest among the other options because this form of carbon is very stable. Moreover, it can be assumed, that carbon will stay in the form of CNMs until it is transformed intentionally.

There are two main forms of CNMs: carbon nanotubes (CNTs) and carbon nanofibers (CNFs). The main difference between them is their structure. Otherwise, they have similar areas of application and production technology. However, CNTs is more valuable than CNFs, thus further evaluation will be made mainly for CNTs production.

Probably the main disadvantage related to CNTs is the possible carcinogenic effect on humans. The major concern is the possible inhalation of dry powder during manufacturing and processing steps. The exposure during the later stages of the product lifecycle is also an emerging concern. Although there is no epidemiological data for humans, CNTs can be compared to asbestos due to

their small size. Therefore CNTs may have similar behavior and consequently cause similar damage to lungs. (Kane, et al., 2018)

Technology. Currently, the most developed technology for the production of CNMs is C2CNT described in chapter 4.6. The technology is rapidly developing, but currently its TRL is still low for the implementation on an industrial scale. The important advantage of C2CNT is that it has been developed for the implementation on the cement plants and utilization of the low quality CO_2. Considering the cement plant flue gas has relatively high concentration of CO_2, it can be used directly without the capture step. This is undoubtedly a big advantage because it leads to the reduction of the final product's cost.

Another important advantage of the technology is that CO2 is used as a main reactant and the technology does not require other feedstock but electricity only. Electricity consumption for 1 ton of CNTs is about 7MWh (Licht, 2017). Comparing to other options, the energy consumption is rather high even considering the amount of CO_2 utilized per ton of a product (**Table 6**). However, the technology is on the very early stage of the development, so it can be assumed that energy consumption can be reduced during the technology development.

Table 6 CO_2 uptake potential and energy requirements for different utilization options

Product	CO2 uptake potential, $t_{CO2}/t_{product}$	Source	Energy requirements, $MWh/t_{prodcut}$	Source
Methanol	1.37	(Jarvis & Samsatli, 2018)	0.4-0.55	(Jarvis & Samsatli, 2018)
Formic acid	0.96	(CarbonNext, 2017)	4.07	(Pérez-Fortes, et al., 2016)
Dimethyl carbonate	0.49-1.47	(Otto, et al., 2015; Al-Saydeh, et al., 2018)	0.27-0.37	(Garcia-Herrero, et al., 2016)
Urea	0.73	(CarbonNext, 2017)	0.2	(Pérez-Fortes et al., 2014)
CNTs	3.67	(Licht, 2017)	7-9	(Licht, 2017; Ren & Licht, 2016)

Because of the high energy requirements, the choice of the energy source is crucial for CNMs production. Considering the importance of carbon sequestration, CO_2 emissions from the energy source should not be higher than the amount of CO_2 utilized for the production. Thus, for the purpose of the effective CO_2 utilization, a renewable energy source should be used for electrolysis.

The market for CNMs is quite small, with CNTs production is about 1000 t/y (Shah & Tali, 2016), but it is rapidly expanding with the technology development. The price for the material highly depends on the grade of the material - its purity, length and surface functionality. Industrial grade CNTs costs from 200 000 to 400 000 UDS/ton (Ren & Licht, 2016). However, with the technology development, the price is expecting to go down. The investments costs are not possible to estimate due to the early stage of the technology development, and the production cost can be estimated approximately 2000 USD/t of CNT, that is much cheaper than 25 000 USD/t for conventional production via CVD (Ren & Licht, 2016).

6.2. Gaseous CO2.

Product. Fixation period of CO_2 in gaseous form strongly depends on the application. In the case of carbonated concrete production, the fixation time will be very long (>100 years). Fixation time of gaseous CO_2 in other applications will be much shorter (less than 1 year). Despite the short-fixation period, utilization of captured CO2 for beverage industries and greenhouses to substitute fossil-derived CO_2 can be beneficial. Production of gaseous CO2 is basically a carbon capture process. Therefore the uptake potential of this option can be considered as $1 t_{CO2}/t_{product}$.

Technology. Both of the most applicable cement industry CC technologies MEA and CaL can be installed in tail-end configuration to the existing plants. The capture efficiency is quite high in both cases (~90%). The comparative assessments of different CC technologies for cement industry (Kuramochi, et al., 2012; Leeson, et al., 2017) show that CaL is the most efficient from technological and economic points of view. The MEA capture is almost half less energy efficient than CaL considering the same capture efficiency (85%). The most energy demanding part of MEA capture technology is the regeneration of the solvent, though there are new types of solvents with lower energy demand are under development. (Leeson, et al., 2017, p. 75).

In addition to high energy demand for regeneration, the solvent used in MEA capture undergoes degradation. The degradation rate of MEA is approximately 1.4-2.1 kg_{MEA}/t_{CO2}. Thus, MEA capturing of all CO_2 emissions from Finnsementti plants will produce around 1.14-1.71 kt of waste solvent. The necessity of waste utilization will lead to additional costs and possible impact on the environment. Limestone used in the CaL as a sorbent can be used for cement production and does not require utilization as waste material.

The main advantage of MEA is the higher TRL level, thus the implementation of this technology has lower risks due to a higher level of technology development. (Leeson, et al., 2017, p. 75). However, considering the rapid development of CaL, this advantage may be lost in the future.

Market. As it was already mentioned, main markets for gaseous CO_2 utilization are beverage production, greenhouses, water treatment, and cement curing. The additional possibility of gaseous CO2 utilization may be a Power-to-Gas system. However, due to the scale of the cement plants in Finland, this option might be profitable only as a part of a bigger system. Taking into account that there is no such a system yet, this option won't be evaluated in detail.

The market of carbonated concrete is quite small nowadays, but it is expected to grow by 2030 to 6.5 Gt in a pessimistic case and to 16.5 Gt in an optimistic case (CO2 Sciences and The Global CO2 Initiative, 2016, p. 27). According to the study, one of the main barriers in the development of the carbonated concrete is the availability of the CO_2 for curing. (CO2 Sciences and The Global CO2 Initiative, 2016, p. 28) Thus, the availability of CO_2 on the market may stimulate the development of carbonation curing. The market for carbonated concrete is supposed to be very local, due to the high cost of transportation and rather sparsely distributed customers.

There is a similar situation with the horticulture industry, where gaseous CO_2 can be used for greenhouses. Greenhouses provide the possibility to utilize 0.3-0.9 Mt_{CO2}/y, which accounts for 34-103% of the cement plants emissions. However, the sparse distribution of greenhouses may lead to excessively high transportation costs, which can make the price for CO_2 unaffordable for greenhouses.

Food and beverage market in Finland is limited and therefore there might not be a demand for CO_2. The beverage industry still can be considered as a utilization option due to the growing demand for beverage and consequently CO_2 in the summer period. The effect of climate change causing the growing number of extreme temperature events and an increase in average temperature can lead to the shortage of CO_2 from traditional sources.

Although the beverage industry is not so spatially distributed as in the previous cases, the beverage facilities are relatively far from the cement plants. The shortest routes to supply CO_2 for beverage are Lappeenranta-Lahti (150 km) to the Hartwal facility and Parainen-Pori (168 km) to the Sinebrykoff facility. In addition, CO_2 purity is especially important for the beverage industry and for the production of food grade CO_2 additional purification might be needed, which will lead to a further increase in the CO_2 price.

Costs. First, it is important to mention that the majority of studies related to carbon capture and utilization in the cement industry have been made for the BAT reference plant (Anantharaman, et al., 2015; Kuramochi, et al., 2012; De Lena, et al., 2017; Hills, et al., 2016). Both Finnsementti plants have lower capacity and therefore the costs for the CC facility construction will be higher. Cost of carbon capture via MEA technology will be evaluated based on the guideline provided by the CEMCAP project (Anantharaman, et al., 2015; Anantharaman, et al., 2017)

Investment costs for MEA CC unit with 90% efficiency for a reference cement plant is 107 M€ (Anantharaman, et al., 2015, p. 18) Using the scaling formula (**Error! Reference source not found.**) and the data from the guidelines, investment and operational costs for the cement plants can be calculated (Table 7).

It is important to mention that the cost of MEA strongly depends on the steam cost. In this evaluation, the steam sources have been chosen similar to the suggested in the CEMCAP guideline: partial steam recovery from the cement plant and natural gas boiler. Based on their scenario evaluation, the lower cost for captured CO_2 can be achieved by importing steam from a CHP plant.

For the cement plant in Lappeenranta, Kaukaan Voima power plant might be a source for a cheaper steam.

Table 7 Costs of CO_2 capture using MEA technology

Parameter	Unit	Reference plant	Lappeenranta	Parainen
Emissions	Mt_{CO2}/y	0,85	0,34	0,49
Capex	M€	107	57	74
	€/$t_{CO2capt}$/y	7,0	9,3	8,4
Opex fixed	M€/y	8,6	5,1	5,8
	€/$t_{CO2capt}$	11,2	16,7	13,2
Opex var	€/$t_{CO2capt}$		32,6	
Cost of CO_{2capt}	€/$t_{CO2capt}$	63,2	69	65

For CaL it is not possible to make a detailed cost estimation due to the low level of technology development. The investment costs for CaL vary from 147 M€ (Rodríguez, et al., 2012) to 253 M€ (Cormos & Cormos, 2017). The spread of CO_2 capture costs is not so significant and vary in range 18.4 €/t_{CO2} to 30.1 €/t_{CO2} (Rodríguez, et al., 2012; Leeson, et al., 2017). Considering that the capture costs per ton of CO_2 increase as the scale decreases, cost of CO_2 captured for the case study plants can be assumed higher than for the reference plant. (**Table 8**).

Table 8 Costs of CO2 capture using CaL technology

Parameter	Unit	Reference plant	Lappeenranta	Parainen
Capex	M€	147-253	79-136	102-175
Cost of CO2capt	€/tCO2capt	18-30	30-40	

The liquefaction costs can be calculated by scaling the numbers given in (Øi, et al., 2016) to the case study plants scale. Thus, the cost for liquefaction based on the ammonia refrigeration can be estimated at 8.6 €/t_{CO2} for the plant in Lappeenranta and 7.2 €/t_{CO2} for the plant in Parainen.

Costs of the transportation by trucks are depending on the distance and the volume of transported CO_2. Thus, the costs were calculated for different distances. The results are very close for both plants, therefore the average numbers are presented in the table below. It is worth mentioning that although transportation cost per ton of CO_2 is expectedly growing with increasing distance, transportation cost per km is simultaneously decreasing.

Table 9 Costs of CO2 transportation

Distance	km	50	100	150	200
Cost	$€/t_{CO2}$	8	13	18	23
	$€/t_{CO2}/km$	0.16	0.13	0.12	0.115

Summarizing the numbers calculated above, the price of gaseous CO_2 can be calculated, taking into account liquefaction and transportation (**Table 10**).

Table 10 Cost of gaseous CO_2 ($€/kg_{CO2}$) depending on the transportation

		Transportation, km			
		50	100	150	200
LPR	MEA	87	92	97	102
	CaL	57	62	67	72
PRN	MEA	80	85	90	95
	CaL	45	50	55	60

Based on the calculated results, the cost of captured CO_2 for utilization as a product can be compared to the market price for CO_2. The market price for food-grade CO_2 in Europe is around 80-150 €/ton (Monteiro, et al., 2018, p. 47). Thus, using CaL technology, gaseous CO_2 might be a profitable product even considering the transportation for a long distance. MEA capture is more expensive, but still can be considered for a short distance (50-100 km) transportation.

There are two more factors that should be taken into account. First, production of food-grade CO_2 might require additional purification, which increases the cost of the gas. Second, for the long-

distance transportation, the transport emissions should be considered, to avoid the case when emissions from capture, liquefaction, and transportation exceed the amount of CO_2 captured.

6.3. Construction aggregates.

Feedstock used for the production of carbonated construction aggregates determines the production technology and the characteristics of the final product. Therefore, it is important to assess availability and carbon uptake potential of the materials for aggregates production.

Feedstock. The most suitable option for mineral carbonation in Finland is wollastonite, which occurs mainly as an impurity in limestone. The two main mines quarrying carbonated rocks (wollastonite in particular) are Ihalainen (Lappeenranta) and Parainen. The deposit of the Ihalainen mine is about 10 Mt and the similar deposit has been found in Savitaipale. The production rate of the mine in Lappeenranta is 18 kt/a (Teir, et al., 2005, pp. 2958-2959).

The CO_2 uptake rate of wollastonite is 0.35 t_{CO2}/t_{mat} (Tier, 2008, p. 38). Thus, to utilize the emissions only from the Lappeenranta cement plant, about 1 Mt of wollastonite should be mined, which is incomparable to the production rate of Ihalainen mine (about 18 kt). Taking into account also the deposit of the mine in the Lappeenranta (~10 Mt) (Teir, et al., 2005, pp. 2958-2959), wollastonite utilization can be considered not effective for the production of carbonated aggregates.

Another option is magnesium silicate minerals whose deposits are located mainly in central and eastern Finland. The most common mineral is serpentinite, which has deposits in eastern Finland occupy an area about 121 km^2. The magnesium silicates content in these deposits varies in a different formation, but on average about 2.5-3 ton of the mineral is required to utilize 1 ton of CO_2. (Tier, 2008, p. 12) Although usage of quarried minerals is not limited by legislation and usually minerals can be produced in bigger amounts than wastes, the minerals as a feedstock have some drawbacks. The most important of them are the high energy intensity, low reaction conversion, and slow reaction kinetics. These factors can be named as the main barriers for the commercial implementation of mineral carbonation. (Sanna, et al., 2014, p. 8056) Furthermore,

the extensive mining required for the utilization of cement plants' emissions can cause a higher environmental impact than benefits of CO_2 utilization.

Waste streams are more available in Finland, though their amount is also limited. The suitable waste streams for carbonation are slag from iron and steel industries, cement-based materials, municipal solid waste incineration ash, and wood ash. These materials are usually alkaline, inorganic and rich in Ca/Mg (Olajire, 2013, p. 383), therefore they can be carbonated as minerals. The table below shows the waste streams that might be available for the utilization in Finland (**Table *11***) and the distance from the feedstock source to the cement plants. Sources for the CO_2 uptake data can be found in Appendix I Table 1. The distances by land are indicated in cases when they are less than 200 km.

The closest to the cement plants source of feedstock for carbonation is cement kiln dust. Although CKD is generated in limited amounts and already utilized in cement production, its utilization for aggregates production might be more effective than current utilization. However, more detailed analysis and life-cycle assessment are needed for such an evaluation.

Table 11 Waste streams available for the construction aggregates production in Finland

Material		CO_2 uptake	Location	Amount of waste	CO_2 utilized	Distance		
						Lappeenranta	Parainen	
		t_CO2/ t_mat		Mt	Mt	land, km	land, km	sea, km
Steel mills waste	Steel slag	0.25	Raahe	0.302	0.076	-	-	800
		0.25	Tornio	0.047	0.012	-	-	1000
	BF slag	0.25	Raahe	0.571	0.143	-	-	800
		0.25	Imatra	0.036	0.009	40	-	-
Cement based materials	CKD	0.2	LPR	0.08	0.016	0	-	-
		0.2	PRN	0.16	0.031	-	0	-
	Construction waste	0.11	Finland	1.3	0.143	-	-	-
Thermal waste	Wood ash	0.08	South Karelia	0.071	0.006	100	-	-
	MSWI BA	0.24	Riihimäki	0.06	0.014	200	200	
		0.24	Kotka	0.03	0.007	110	-	-
		0.24	Oulu	0.03	0.007	-	-	800
		0.24	Vaasa	0.03	0.007	-	-	500
		0.24	Vantaa	0.05	0.012	-	180	-

		0.24	Lahti	0.04	0.010	150	-	-
		0.24	Tampere	0.03	0.007	-	200	-
		0.24	Leppävirta	0.03	0.007	220	-	-

Despite a relatively high amount of construction and demolition waste (CKD) generated in Finland, such feedstock is not efficient for CO_2 utilization due to several reasons. First, CKD has low CO_2 uptake potential, which can vary significantly from site to site and the prediction of the CO_2 amount can be utilized in the carbonation process is very uncertain. Estimation described in literature shows quite low carbonation efficiency compare to other waste sources. Furthermore, generation of CKD in Finland is dispersed due to the large and sparsely populated areas. Thus, transportation of construction wastes to the carbonation facility and further transportation of aggregates to the construction area might be unprofitable. In addition, generation of CKD is unstable and can vary significantly from year to year depending on the construction projects in the region. Finally, the quality of the recycled aggregates might be an issue of concern for the customers in Finland. According to the stakeholder's survey made by Deloitte (Deloitte, 2014), the quality of recycled aggregates is often poor in cases which do not require a permit and therefore have not been controlled by authorities. Considering all the issues described above, for the further estimation, 5% of the total CKD generated in Finland is assumed to be available for the construction aggregates production.

Steel slag is generated in bigger amounts (~1.2 MT/y), but the slag is quite popular material and already has many applications, both direct and after treatment. In Finland, steel slag is mainly utilized in road construction and earthworks. Less usual products made from steel slag in Finland are insulation and aggregates produced by Outokumpu and fluidized bed material produced by Fescon. The blast furnace slag (BFS) produced at Raahe is a certified product that is already used in road construction, earthworks, and cement industry. Converter steel slag from Raahe is used as asphalt filler in road construction. (Watkins, 2014).

Furthermore, the steel industry is a large source of CO_2 emissions, therefore production of aggregates from steel slag and CO_2 can be more efficient near the steel plants. However, the demand for the final product might be an issue for the steel plant due to their location (**Figure 14**).

The two biggest steel plants are located in the northern part of Finland, in Raahe and Tornio, whereas the most intensive construction takes place in the southern part of the country. Thus, the low demand for construction aggregates near the steel mills and high transportation costs for the aggregates utilization in the south may make carbonated aggregates production near steel mills economically unprofitable. Transportation of steel slag by sea to the Parainen cement plant and the
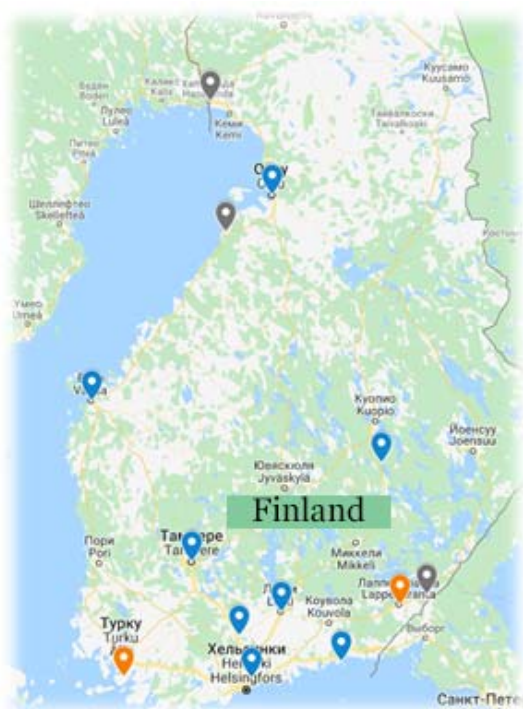
production of aggregates closer to the construction areas can be more economically feasible due to the aggregates weight and volume is higher than those of steel slag. However, a more detailed evaluation is needed in this case.

Figure 14 Location of steel mills (grey marks), MSWI plants (blue marks) and cement plants (orange marks)

Next possible feedstock for carbonation is a thermal waste, ash generated fuel or waste incineration. MSWI residues in Finland generated by 9 waste incineration plants located in Riihimäki (I and II), Kotka, Oulu, Vaasa, Vantaa, Lahti, Tampere, and Leppävirta. In **Figure *14***, the locations of waste incineration plants are marked with blue signs. Considering transportation by land, the farthest from the cement plants is the incineration facility in Leppävirta, which is located ~220 km away from Lappeenranta. Transportation by sea can be suggested for the MSWIr

generated in Oulu and Vaasa. Thus, basically, all sources of MSWIr may be available as feedstock suppliers for the carbonated aggregates production.

The amount of ash per generated per ton of waste and its CO_2 uptake capacity depends on the waste composition and incineration technology used, so it can vary from case to case. By fairly rough estimations, the average amount of MSWI BA generated by waste incineration plant in Finland is 30-40 kt/t (Sormunen, 2017, p. 35). The total amount of APC residues generated in Finland in 2009 was 10-15 kt (Hjelmar, et al., 2009, p. 45). Considering the small amount of APC residues and the lack of detailed data available, this type of waste will not be considered in the further evaluation.

Thermal waste from power plants is another suitable source. However, due to the lack of information, availability of this feedstock has been estimated only for the cement plant in Lappeenranta. The average amount of ash and slag generated in South-East Finland is 101,7 kt (Deviatkin, et al., 2016, p. 19). Mainly the ash is generated by wood, peat, and waste incineration. Considering the MSWIr has already been taking into account, the available amount of thermal waste can be assumed as 71 kt.

Pulp and paper ash is also an option for the construction aggregates production. Currently, the amount of available ash is quite low (~0.4 kt) due to the high rate of utilization (64-87%). However, the demand for the pulp and paper ash is limited by road construction (Deviatkin, et al., 2016, p. 22). Thus, utilization of pulp and paper ash for construction aggregates production might be a question for the further research.

Concluding the information above, the amount of CO_2 can be utilized by waste carbonation is about 76 kt and 302 kt for the cement plants in Lappeenranta and Parainen respectively (Table 12).

Taking into account the economic feasibility of Carbon8 technology that utilizes the waste located in the distance approximately 120 km away (Carbon8, 2017), it can be assumed, that production of aggregates from waste will be profitable and allow the cement industry to utilize at least 14% of CO_2 emissions from the cement plant in Lappeenranta and 6% in Parainen. Transportation of

waste on longer distances might also be profitable but requires more detailed analysis. The cement plant in Parainen might have a possibility to utilize steel slag and MSWIr transported by sea, which allows it to utilize 50% of CO_2 emissions. As it was mentioned above, estimation of the construction waste availability is challenging, but a small share of construction waste can be assumed as available for carbonation.

Table 12 CO_2 emissions can be utilized from the cement plants by the carbonation of wastes

		LPR		PRN	
		Mt	% of CO2	Mt	% of CO2
CO2 emissions		0.335		0.492	
By land					
	< 150 km	0.04748	14 %	0.0312	6 %
	150-200 km	0.0216	6 %	0.0192	4 %
By sea		-	-	0.2444	50 %
Total without construction waste		0.06908	21 %	0.2948	60 %
Construction waste 5%		0.00715	2 %	0.00715	2 %
	Total	**0.07623**	**23 %**	**0.30195**	**61 %**

Technology. Considering the lack of minerals suitable for carbonation, the Mineral Carbonation technology cannot be considered as an option due to it using magnesium minerals as feedstock. The Carbon8 technology might be considered the most suitable option for waste carbonation. In addition to waste utilization and replacement of quarried material with aggregates produced from waste, Carbon8 technology has other advantages. First, it does not require additional reactants like Calera and SkyMine technologies. The technology is developed and implemented on the commercial scale. Possibility to produce building blocks using the same technology is also an advantage because it increases possible routes of the product utilization. However, the leaching of hazardous components, especially sulfates and chlorides, might be problematic. In addition, implementation of technology in Finland can differ due to Finland's waste legislation being stricter than those in the UK. Thus, the requirements to obtain a permit for waste utilization into a product can significantly decrease the profitability of the technology.

The business model of Carbon8 is profitable with gate fee for waste about 82€/t_{waste} (Carey, 2018). Considering the Finnish gate fee for waste around 70 €/t_{waste} and possibility to utilize free CO_2

containing in the cement plant flue gases, the Carbon8 business model should be also profitable in Finland. Due to the lack of information about the economics of the process, more detailed research is needed to evaluate the economic feasibility of the technology in Finland. However, some rough estimations can be done based on the data from the Carbon8' presentation (Carey, 2018).

Before the estimation, next assumptions have to be made:

- the weight gain during the waste carbonation is maximum 8% (Li, et al., 2007, p. 1203)
- the CO2 uptake is 0.177 $t_{CO2}/t_{aggregate}$ (Carey, 2018, p. 11)
- the gate fee is 82€/t_{waste}
- cost of CO_2 is 80 €/t_{CO2}
- price of aggregates is 20 €/$t_{aggregates}$
- all values given in GBP and USD was converted to EUR

First, based on the assumptions above, it can be calculated that the production of 1 ton of aggregates requires 0.93 t_{waste}. In addition, it requires 0.177 t_{CO2}, which costs 14.16€/$t_{aggregate}$. Next, considering the profit of ~333€/t CO_2, the profit per ton of aggregate can be calculated as 58.9€/$t_{aggregate}$.

Based on the revenue streams diagram (Carey, 2018, p. 10), the revenue stream of the company consists of the gate fee and aggregate sales. CO_2, which is currently a cost was not taken into account. Thus, the revenue gained from 1 ton of aggregates can be calculated as follow

$$Revenue = waste\ input * gate\ fee + aggregate\ sales *$$
$$price\ of\ aggregates = 0.93 * 82 + 1 * 20 = 95\ €/t_{aggregates} \qquad (11)$$

Based on the principle that the profit of a company is equal its revenue minus expenses, the cost of the carbonation process can be estimated as revenue minus profit. Thus for the Carbon8 process, operational costs are approximately

$$Costs = Revenue - profit = 95.9 - 58.9 = 37\ €/t_{aggregates}. \qquad (12)$$

The operational costs for the process using flue gas CO2 can be estimated as

$$Operational\ costs = Costs - price\ for\ CO2 = 37 - 14.16$$
$$= 22.84€/taggregates$$

<div style="text-align:right">(13)</div>

Based on the estimations, it can be assumed that without the gate fee for waste utilization, the process most likely won't be profitable because the cost for natural aggregates is around 20 €/t. However, it is worth mentioning that these estimations are not accurate and their main purpose in a comparison with other options.

Legislation issues.

Production and use of aggregates in Finland are regulated by European standards for concrete EN 206-1 and the guideline Betonin kiviainekset 2008 BY 43. The guideline sets high standards for aggregates and requires an evaluation of recycled aggregates in every particular case. The evaluation is needed for a number of parameters, such as compressive strength, carbonation, freeze/thaw, corrosion factor caused by chlorides, and other chemical content (Sorato, 2016). Although it is not clear whether the carbonated aggregates fall under the requirements of the assessment in every case, the high requirements for the quality of aggregates should be met.

Waste legislation is another important influence factor. There are four main acts regulating the waste utilization: Waste Act (646/2011), Waste Tax Act (2010/1126), Chemical Act (744/1989), and the Environmental Protection Act (86/2000). According to legislation, a company should obtain a permit for each project where waste-derived aggregates are used. The permit is very narrow and granted for a specific waste from the specific demolition area.

However, the Finnish Government Decree 591/2006 (rev. 403/2009) significantly simplifies usage of waste-derived aggregates for certain types of earthworks, such as the construction of roads,

parking areas, sports grounds, railway yards, etc. These cases do not require a permit, but only notification of authorities. Thus, taking into account that road construction can be defined is one of the main areas of carbonated aggregates production, the legislation won't be a barrier. However, production of building blocks most likely does not fall under the Decree. (Sorato, 2016)

The important point that should be taken into account is the differences between waste and by-product defined in the legislation. For example, waste falls under the Decree 591/2006 and utilized for road construction is classified as a product, but in all other cases, it is classified as waste. (Sorato, 2016) Thus, the legislation regulated the production of carbonated aggregates from waste should be studied in more detail.

7. CONCLUSION

The specific challenge facing the cement industry is the process emissions that cannot be completely avoided by a substitution of the emissions source, as it can be done for fuel emissions. Therefore, CCS or CCU are the only options available for the mitigation of the process emissions. However, the possibility to offset the costs of capture and utilization processes makes the CCU a preferable option.

The nature of the process emissions does not allow it to be included in a circular economy, because it will require a constant increase in the utilization capacities. Thus, the main aim of the CCU process is capture of the emissions and reduction of the CO_2 level in the atmosphere. Based on the above, CO_2 fixation time can be assumed as the most important requirement for the emissions utilization technology. Therefore, despite the options with a very short or short sequestration time can be more effective and profitable, their implementation does not solve the main problem but rather postpones it. Considering the growing number of innovative technologies and its rapid development, implementation of an effective CCU technology with a short or medium sequestration period might be considered as a temporary option.

An important factor for an effective CO_2 sequestration and utilization by any technology is the choice of the energy source. CO_2 is a stable substance and its transformation requires energy.

Therefore it is important to consider that the net emissions are negative, i.e. the emissions from the capture and utilization processes is lower than the amount of CO_2 being utilized. Otherwise, process of CO_2 utilization will be rather harmful than beneficial for the environment. Use of the renewable energy sources can be a suitable and effective options for this purpose, though the detailed analysis might be required for each case.

Based on the evaluation made in this work, from the all variety of options, there is no single option that can be implemented immediately and utilize all emissions from the cement industry into a profitable product. There are multiple barriers for an effective and profitable utilization: lack of the feedstock, low level of the technology development, small demand for the product, low utilization time, etc. An important barrier is a carbon capture step, which is necessary for the most CCU options. Although CC technologies are not developed enough to be implemented cost-effectively, capture and utilization of CO_2 as a valuable product still can be an effective and sustainable option.

Probably the biggest consumer for gaseous CO_2 is greenhouses, which estimated market is big enough to utilize all CO_2 emissions from the cement industry. Concrete curing by carbonation is also a very promising option because of a very long CO_2 fixation time. Although currently there is no demand for the carbonation curing, the development of the market is hindered mainly by the absence of cheap CO_2. It is impossible to estimate the potential market for the concrete curing because the number of construction sites in a region can vary significantly from year to year. The low requirements to CO_2 purity is an additional advantage of the carbon utilization for concrete curing in comparison to greenhouses and beverage industries. This allows the producers to reduce the cost of CO_2 production.

The main factors that influence the cost of captured CO_2 are the carbon capture technology and transportation costs. There are two main CC technologies suitable for cement plants: MEA and CaL. Despite CaL has lower TRL, it is rapidly developing and more effective for cement plants because the synergy can be achieved. The price of CO_2 capturing by CaL ($\sim$30 €/t_{CO2}) estimated to be much lower than using MEA ($\sim$70€/t_{CO2}). The main advantage of MEA compare to CaL capture is a higher TRL.

Transportation is one of the main barriers for sustainable utilization of gaseous CO_2. Considering the spacious distribution of the main consumers (greenhouses and construction sites), optimization of transportation routes is important for the reduction of both the CO_2 emissions and the cost of the product. Finally, the environmental benefits of CO_2 utilization as gas can be questionable because of CO_2 emissions related to capturing, transportation, packaging, etc. These emissions can vary significantly and therefore a detail estimation, for example, life cycle assessment is needed for each case.

Although the production of food-grade CO_2 from captured CO_2 might not be profitable at the moment, such factors as the development of capture technologies, growing prices for the emissions, and taxes, can change the situation in the near future.

Production of the construction aggregates is one of the most effective options for the process emissions utilization. However, this option also has challenges and the main of them is the low CO_2 sequestration capacity and therefore a high amount of feedstock needed. Although the aggregates can be produced from several types of minerals and a wide range of waste, availability of the material for carbonation can be an issue.

Based on the estimations made in this work, production of carbonated aggregates from minerals might be not very efficient for Finland due to the lack of material, their location at a considerable distance from cement plants and the environmental impact of large-scale mining. Waste as a material for carbonation is more available than minerals, though the additional challenge, in this case, is the spatial distribution of waste sources. The most available waste streams for the aggregates production are steel slag and MSWIr. Estimations show that the sources of the wastes are located on the accessible distance, but a more detailed assessment is needed because the transportation emissions can be higher than CO_2 utilization potential.

Production of aggregates from CO_2 and waste feedstock is beneficial from the environmental point of view because two waste streams are utilized. Moreover, a carbon footprint of the aggregates produced from waste should be lower than the footprint of aggregates produced from natural stone.

However, the level of possible environmental impact and options for its minimization and prevention should be assessed for each case.

Carbon8 technology for the construction aggregates production from waste can be considered for CO_2 utilization from the cement industry. The technology has a number of advantages and can utilize flue gas without CO_2 capture. However, the optimal CO_2 concentration in flue gas is ~50%, thus the possibility to use CC with low efficiency might be considered. The business model of Carbon8 is based on the high landfill taxes. For a profitable implementation of the business model in Finland, more detail evaluation including costs of permits, taxes, and cost of CO_2 capture, is needed. In addition, Finnish waste legislation can be a barrier for the aggregates production from the waste stream. In some cases, waste (e.g. steel slag) can be considered as a by-product and therefore there are no legislative barriers for its utilization into a product. However, regulation of MSWIr utilization should be further assessed.

Utilization of CO_2 for the production of carbon nanomaterials is the most effective option in terms of CO_2 uptake and the fixation time. CNMs are emerging materials in many areas due to their unique properties. The most developed route of CNTs production utilizing CO_2 (C2CNT process) is on a very early stage of development (TRL 4) and a lot of development is needed before it can be implemented. However, the technology has a number of advantages. Probably the most important advantage of the technology related to this work is that the process has been designed for the utilization of CO_2 emissions from the cement plant. In addition, the process does not require CC and can utilize flue gas and waste heat from the cement plant. If the renewable energy source is used in the process, the CNMs production can be carbon negative.

In conclusion, it is worth mentioning the limitations of this work. First, the numerical estimations have been made based on the literature data. Therefore the result of the data applied to a real case may be uncertain. Next, some sources that have been used are not scientific articles, but companies' presentations or internet sources. It also increases the uncertainties of the final results. Finally, more detail estimation of the environmental impact is important for each option to calculate the net CO2 emissions and the effectiveness of CO2 sequestration.

8. SUMMARY

Reduction of process emissions is a unique challenge facing the cement industry. Due to the nature of the process emissions, the most suitable route of their reduction is sequestration and utilization of CO_2 into a valuable product. This allows the industry to offset the costs of CO_2 utilization and keep a low price and the high quality of the cement. Moreover, CO_2 emissions from the burning of fuel can be utilized along with the process emissions. In this study 31 products have been identified as possible options for CO_2 utilization. Based on the defined key indicators, the most suitable options were chosen and analyzed in detail. These are carbon nanomaterials, construction aggregates, and gaseous carbon.

Production of carbon nanomaterials is probably the most effective option because of the highest CO_2 uptake potential, very long fixation time, and high estimated profit. Production of carbon nanomaterials by electrocatalytic conversion in molten salt can be carbon neutral if a renewable energy source is used for electrolysis. However, the technology requires further development and cannot be implemented in the near future. In addition, possible carcinogenic properties of CNMs require special attention and further study.

Production of the construction aggregates is a commercialized technology with very high CO_2 fixation time. The limitation of this technology is a low CO_2 uptake potential and therefore a significant amount of material needed for utilization. Based in the estimations made in this work, around 20% of CO_2 emissions from the cement plant in Lappeenranta and around 60% of CO_2 emissions from the plant in Parainen can be utilized for the production of aggregates. The most available material for the aggregates production is waste. Waste utilization into a product brings additional environmental benefits to this options, but the option may also encounter legal barriers due to the strict waste legislation in Finland.

Utilization of gaseous CO_2 is the third option assessed in the details in this work. Depending on the application, gaseous CO_2 has different fixation time. The profitability of the option depends on the capture technology used and the transportation distance. Based on the estimations, usage of

CaL may be profitable on the distances up to 200 km, whereas MEA capture may be profitable on the short distances (~50 km).

This study presents a rather general analysis of the evaluated options. The final results have some degree of uncertainty due to the different quality of data being used in the study. To get more accurate results the detailed evaluation of the environmental impact and economic efficiency for a more specific case might be needed.

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Appendix I. Table 1. CO_2 uptake potential of the materials suitable for carbonation

Type	Material	Composition	Theoretical uptake capacity g/g_CO2	CO2 uptake	Source
Minerals	Calcium oxide	CaO	1.27		(Monteiro, et al., 2018)
	Slaked lime	Ca(OH)2	1.68		(Monteiro, et al., 2018)
	Brucite	Mg(OH)2	1.33		(Monteiro, et al., 2018)
	Olivine/Forsterite	Mg2SiO4	1.6		(Monteiro, et al., 2018)
	Wollastonite	CaSiO3	2.64-3.5		(Monteiro, et al., 2018), (Tier, 2008)
	Serpentine	Mg3Si2O5(OH)4	2.1		(Monteiro, et al., 2018)
	Enstatite	MgSiO3	2.28		(Monteiro, et al., 2018)
	Talc	Mg3Si4O10(OH)2	2.87		(Monteiro, et al., 2018)
	Basalt(Plagioclase/Feldspar)	Na0.5Ca0.5Si3AlO8	12.3		(Monteiro, et al., 2018)
Steel mills waste	BF Slag				(Zappa, 2014),(Jang, et al., 2016), (Sanna, et al., 2014)
	Steel slag		0,31-0,52	0,06-0,17-0,24	(Zappa, 2014),(Jang, et al., 2016), (Sanna, et al., 2014)
	Ferrochrome slag				(Jang, et al., 2016), (Sanna, et al., 2014)
Cement based materials	CKD		0.29-0.43	0.11-0.26	(Jang, et al., 2016), (Gunning, et al., 2009), (Sanna, et al., 2014)
	Waste concrete		0.2	0.01-0.16	(Jang, et al., 2016), (Sanna, et al., 2014)
	Construction waste*			0.11	(Pasquier, et al., 2018)
Ash from power plants	Ash from coal PP	contains CaO	6-9	0.02-0.07-9,7	(Nielsen, et al., 2017),(Jang, et al., 2016), (Carey, 2018)
	Wood ash		50	0.08	(Jang, et al., 2016), (Sanna, et al., 2014)
	Biomass ash**		0.386	0.161	(Gunning, et al., 2009), (Carey, 2018)
MSWI	Bottom ash MSWI-BA	contains CaO	0.16	0.03-0.24-0,32	(Nielsen, et al., 2017), (Gunning, et al., 2009),(Jang, et al., 2016)
	Fly ash MSWI-FA	contains CaO		0.07-0.1-0,12	(Gunning, et al., 2009),(Nielsen, et al., 2017),(Jang, et al., 2016)
	APC residues		0.343	0,114-0,167	(Ecofys, 2017)
Water treatment	Sewage sludge ash SSA		0.235	0.032	(Carey, 2018)

*Construction waste consisting of cement-based materials.
**Fine ash residues from the incineration of plant matter from agricultural processes

Appendix II. Table 1. Classification of the information for data gathering

Category 1	Background data	
		Cement industry
		CO2 emissions from the industry
		CCS technologies
Category 2	Utilization options	
	Fuels	
		Methanol
		DME
		Methane
		Hydrocarbons
		Ethanol
		Biodiesel
	Inorganic carbonates	
		Calcium carbonate
		Magnesium carbonate
		Construction aggregates
		Concrete curing
	Polymers	
		Polycarbonates
		Polyols
		Resins
		Cellulose carbamates
		Polyoxymethylene
	Chemicals	
		Formic acid
		Cyclic carbonates
		DMC
		Isopropanol
		Syngas
		Oxalic acid
		Urea
		Other chemicals (formaldehyde)
	Gas	
		Food and beverage
		Horticulture
	Carbon	
		Graphene
		CNMs
		Polymers
Category 3	Technologies, reviews, etc.	

Appendix III. Table 1. HSE parameters value and weighting. Green cells – top 10 with highest rank, red cells – bottom 10 with lowest rank

			Final product	Human health	Rank	Environment	Rank	Hazardous ingredients	Rank	Normalized result
Fuels	1	Methanol	Fuel	Acute toxicity, specific target organ toxicity	1	None	3	None	3	44.4
	2	Dimethyl ether	Fuel	None	3	None	3	None	3	66.7
	3	Methane	Fuel	None	3	None	3	None	3	66.7
	4	Hydrocarbons	Fuel	Specific target organ toxicity,	1	Hazardous to the env.	2	None	3	37.0
	5	Ethanol	Fuel	Minor eye irritation	2	None	3	None	3	55.6
	6	Biodiesel	Fuel	Minor eye irritation	2	Low	2	None	3	48.1
Inorganic carbonates	7	Calcium carbonates	All purpose	Minor eye irritation	2	None	3	Waste	2	51.9
	8	Magnesium carbonate	All purpose	Minor eye irritation	2	None	3	None	3	55.6
	9	Construction aggregates	All purpose	Irritation (eye, respiratory)	2	None	3	Waste	2	51.9
	10	Carbonated concrete	All purpose	Irritations: skin, eye, respiratory	2	None	3	None	3	55.6
Polymers	11	Poly(bisphenol-A carbonate)	For plastics production	Indirectly	2	None	3	BPA	1	48.1
	12	Aliphatic polycarbonates	For plastics production	Serious irritation, carcinogen (indirectly)	1	None	3	None	3	44.4
	13	Polycarbonate polyols	For plastics production	Irritation (eye, respiratory, skin)	2	None	3	None	3	55.6
	14	Urea-formaldehyde resins	For plastics production	Health risk, carcinogen, irritation	1	None	3	CH2O	1	37.0
	15	Melamine-formaldehyde resins	For plastics production	Health risk, carcinogen, irritation	1	May be harmful for aquatic life	2	CH2O	1	29.6
	16	Cellulose carbamates	For plastics production	None	3	None	3	None	3	66.7
	17	Polyoxymethylene	For plastics production	None	3	None	3	None	3	66.7

			Final product	Human health	Rank	Environment	Rank	Hazardous ingredients	Rank	Normalized result
Chemicals	18	Formic acid HCOOH	Chemical	Severe damage (skin, eyes), toxic	1	haazardous for water,	2	None	3	37.0
	19	Cyclic carbonates	Chemical	Irritation: eyes	2	None	3	None	3	55.6
	20	Dimethyl Carbonate	Chemical	None	3	None	3	None	3	66.7
	21	Isopropanol (IPA)	Chemical	Serious damage : eye, specific organ toxicity	1	None	3	None	3	44.4
	22	Synthesis gas	Intermediary	None	3	None	3	None	3	66.7
	23	Oxalic acid	Chemical	Acute toxicity, damage: eye	1	None	3	None	3	44.4
	24	Urea	Fertilizer, intermediary	Not hazardous, irritating (eye, skin, respiratory)	2	None	3	NH3	2	51.9
	25	Formaldehyde	Intermediary	Acute toxicity, skin corrosion, mutagenic, carcinogenic, cause damage to organs	1	None	3	HCOOH	2	40.7
	26	Melamine	Plastic, intermediary	Serious irritation: eye, respiratory, oral tocixity	1	None	3	NH3	2	40.7
Gas	27	Food and beverage	Gas	None	3	None	3	None	3	66.7
	28	Horticulture	Gas	None	3	None	3	None	3	66.7
Carbon	29	Graphene	All purposes	Irritation: eye, respiratory, may cause cancer	1	None	3	None	3	44.4
	30	Nanofibers (CNF)	All purposes	Irritation: eye, respiratory, may cause cancer	1	None	3	None	3	44.4
	31	Nanotubes (CNT)	All purposes	Irritation: eye, respiratory, may cause cancer	1	None	3	None	3	44.4

Appendix IV. Table 1. Utilization options and key parameters

			Final product	Technology	Uptake t/t_product	Fixation time	Fossil material	TRL	HSE
Fuels	1	1	Methanol	Fuel, intermediary	Hydrogenation (RWGS+F-T)	1.4	<1y	-	9	44.4
	2	2	DME 1	Fuel	Direct synthesis	1.9	<1y	-	3	66.7
		3	DME 2		via MeOH	1.9	<1y	-	9	66.7
	3	4	Methane 1	Fuel	Sabatier reaction	2.8	<1y	-	9	66.7
		5	Methane 2		Biological conversion	2.8	<1y	-	8	66.7
	4	6	Hydrocarbons 1	Fuel	Fischer-Tropsch synthesis	2.4	<1y	-	6	37.0
		7	Hydrocarbons 2		MTO/MTG	2.4	<1y	-	9	37.0
	5	8	Ethanol 1	Fuel	Catalytic hydrogenation	1.9	<1y	-	5	55.6
		9	Ethanol 2		via DME	1.9	<1y	-	3	55.6
		10	Ethanol 3		Biohydrogenation	1.9	<1y	-	3	55.6
	6	11	Biodiesel (fatty acids)	Fuel	Photobioreactor	0.5	<1y	-	5	48.1
Inorganic carbonates	7	12	Calcium carbonate PCC	PCC	Carbonation of silicates	0.3	10-50y	+	3	51.9
		13	Calcium carbonate GCC	GCC	Carbonation of waste	0.4	10-50y	-	7	51.9
	8	14	Magnesium carbonate	Magnesium carbonate	Carbonation of silicates	0.4	<1y	+	5	55.6
	9	15	Construction aggregates	Aggregates	CO2 mineralization	0.1	>100y	-	9	51.9
	10	16	Carbonated concrete	Concrete	Carbonation	0.1	>100y	-	9	55.6
Polymers	11	17	Poly(bisphenol-A carbonate)	Plastic	Asahi route	0.2	10-50y	+	9	48.1
	12	18	PPC 1	Plastic	CO2 and diols	0.3	<10y	+	3	44.4
		19	PPC 2		CO2 and epoxides	0.3	<10y	+	9	44.4
	13	20	Polycarbonate polyols	Feedstock for polyurethanes	Covestro process	0.4	10-50y	+	9	55.6
	14	21	UF-resins	Plastic	UF-resins	0.9	10-50y	+	9	37.0
	15	22	MF -resins	Plastic	MF-resins	0.9	10-50y	+	9	29.6
	16	23	Cellulose carbamates 1	Fiber	CarbaCell process (patented)	0.5	<10y	-	3	66.7
		24	Cellulose carbamates 2		Synthesis by microwave irradiation	0.5	<10y	-	5	66.7
		25	Cellulose carbamates 3		VTT method	0.5	<10y	-	3	66.7
	17	26	POM	Plastic	methanol->formaldehyde	0.4	<10y	-	9	66.7

			Final product	Technology	Uptake t/t_product	Fixation time	Fossil material	TRL	HSE
Chemicals	18	27	Formic acid 1	Chemical	CO2 hydrogenation (Power-2-FA)	1.0	(<1y) -(<10y)	-	5	37.0
		28	Formic acid 2		CO2 electrolysis (Power-2-FA)	1.0	(<1y) -(<10y)	-	3	37.0
	19	29	Cyclic carbonates 1	Chemical	CO+diols	0.4	(<1y) -(<10y)	+	5	55.6
		30	Cyclic carbonates 2		Monohalohydrin route	0.4	(<1y) -(<10y)	+	5	55.6
		31	Cyclic carbonates 3		Olefin route	0.4	(<1y) -(<10y)	+	3	55.6
	20	32	DMC	Chemical	Direct synthesis	0.5	(<1y) -(<10y)	-	7	66.7
	21	33	IPA 1	Chemical	Biological produciton	1.2	(<1y) -(<10y)	-	3	44.4
		34	IPA 2		Bioelectrochemical CO2 conversion	1.2	(<1y) -(<10y)	-	3	44.4
	22	35	Syngas	Intermediary	Co-electrolysis of CO2/H2O	0.6	<1y	-	3	66.7
	23	36	Oxalic acid 1	Chemical	Electrochemical reduction of CO2	0.9	<1y	-	4	44.4
	24	38	Urea	Fertilizer, intermediary	The conventional route	0.7	<1y	-	9	51.9
	25	39	Formaldehyde	Intermediary	Formic acid formation and its reduction	1.5	<10y	-	2	40.7
	26	40	Melamine	Plastic, intermediary	From urea	1.0	10-50y	-	9	40.7
Gas	27	41	Food and beverage	Gas	Direct utilization	1.0	<1y	-	9	66.7
	28	42	Horticulture	Gas	Direct utilization	1.0	<1y	-	9	66.7
Carbon	29	43	Graphene	All purposes	burning Mg metal in a CO2 dry ice	3.7	>100y	-	3	44.4
	30	44	Nanofibers (CNF)	All purposes	Electrocatalytic conversion in molten salts	3.7	>100y	-	3	44.4
	31	45	Nanotubes (CNT) 1	All purposes	C2CNT process	3.7	>100y	-	4	44.4

Appendix IV. Table 2. Utilization options weighted and normalized. Green cells – top 10 with highest rank, red cells – bottom 10 with lowest rank

			Final product	Technology	Uptake t/t_product	Fixation time	Fossil material	TRL	HSE	Rank	Result
					Scaled	Scaled	Scaled	Scaled	Scaled		
Fuels	1	1	Methanol	Fuel	Hydrogenation (RWGS+F-T)	2	1	5	5	4	30.0	**40.0**
	2	2	DME 1	Fuel	Direct synthesis	3	1	5	2	5	31.0	**41.3**
		3	DME 2		via MeOH	3	1	5	5	5	34.0	**45.3**
	3	4	Methane 1	Fuel	Sabatier reaction	4	1	5	5	5	36.0	**48.0**
		5	Methane 2		Biological conversion	4	1	5	5	5	36.0	**48.0**
	4	6	Hydrocarbons 1	Fuel	Fischer-Tropsch synthesis	4	1	5	4	3	31.0	**41.3**
		7	Hydrocarbons 2		MTO/MTG	4	1	5	5	3	32.0	**42.7**
	5	8	Ethanol 1	Fuel	Catalytic hydrogenation	3	1	5	3	5	32.0	**42.7**
		9	Ethanol 2		via DME	3	1	5	2	5	31.0	**41.3**
		10	Ethanol 3		Biohydrogenation	3	1	5	2	5	31.0	**41.3**
	6	11	Biodiesel (fatty acids)	Fuel	Photobioreactor	1	1	5	3	4	26.0	**34.7**
Inorganic carbonates	7	12	Calcium carbonate PCC	PCC	Carbonation of silicates	1	4	3	2	4	30.0	**40.0**
		13	Calcium carbonate GCC	GCC	Carbonation of waste	1	4	5	4	4	36.0	**48.0**
	8	14	Magnesium carbonate	Magnesium carbonate	Carbonation of silicates	1	1	3	3	5	24.0	**32.0**
	9	15	Construction aggregates	Aggregates	CO2 mineralization	1	5	5	5	4	40.0	**53.3**
	10	16	Carbonated concrete	Concrete	Carbonation	1	5	5	5	5	42.0	**56.0**
Polymers	11	17	Poly(bisphenol-A carbonate)	Plastic	Asahi route	1	4	1	5	4	29.0	**38.7**
	12	18	PPC 1	Plastic	CO2 and diols	1	3	1	2	4	23.0	**30.7**
		19	PPC 2		CO2 and epoxides	1	3	1	5	4	26.0	**34.7**
	13	20	Polycarbonate polyols	polyurethanes	Covestro process	1	4	1	5	5	31.0	**41.3**
	14	21	UF-resins	Plastic	UF-resins	2	4	1	5	3	29.0	**38.7**
	15	22	MF -resins	Plastic	MF-resins	2	4	1	5	3	29.0	**38.7**
	16	23	Cellulose carbamates 1	Fiber	CarbaCell process	1	3	5	2	5	33.0	**44.0**
		24	Cellulose carbamates 2		Microwave irradiation	1	3	5	3	5	34.0	**45.3**
		25	Cellulose carbamates 3		VTT method	1	3	5	2	5	33.0	**44.0**
	17	26	POM	Plastic	methanol->formaldehyde	1	3	5	5	5	36.0	**48.0**

			Final product	Technology	Uptake t/t_product	Fixation time	Fossil material	TRL	HSE	Rank	Result
					Scaled	Scaled	Scaled	Scaled	Scaled		
Chemicals	18	27	Formic acid 1	Chemical	CO2 hydrogenation (Power-2-FA)	2	2	5	3	3	29.0	**38.7**
		28	Formic acid 2		CO2 electrolysis (Power-2-FA)	2	2	5	2	3	28.0	**37.3**
	19	29	Cyclic carbonates 1	Chemical	CO+diols	1	2	1	3	5	23.0	**30.7**
		30	Cyclic carbonates 2		Monohalohydrin route	1	2	1	3	5	23.0	**30.7**
		31	Cyclic carbonates 3		Olefin route	1	2	1	2	5	22.0	**29.3**
	20	32	DMC	Chemical	Direct synthesis	1	2	5	4	5	32.0	**42.7**
	21	33	IPA 1	Chemical	Biological produciton	2	2	5	2	4	30.0	**40.0**
		34	IPA 2		Bioelectrochemical CO2 conversion	2	2	5	2	4	30.0	**40.0**
	22	35	Syngas	Intermediary	Co-electrolysis of CO2/H2O	1	1	5	2	5	27.0	**36.0**
	23	36	Oxalic acid 1	Chemical	Electrochemical reduction of CO2	2	1	5	3	4	28.0	**37.3**
	24	38	Urea	Fertilizer, intermediary	The conventional route	1	1	5	5	4	28.0	**37.3**
	25	39	Formaldehyde	Intermediary	Formic acid formation and its reduction	2	3	5	2	4	33.0	**44.0**
	26	40	Melamine	Plastic, intermediary	From urea	2	4	5	5	4	39.0	**52.0**
Gas	27	41	Food and beverage	Gas	Direct utilization	2	1	5	5	5	32.0	**42.7**
	28	42	Horticulture	Gas	Direct utilization	2	1	5	5	5	32.0	**42.7**
Carbon	29	43	Graphene	All purposes	burning Mg metal in a CO2 dry ice	5	5	5	2	4	45.0	**60.0**
	30	44	Nanofibers (CNF)	All purposes	Electrocatalytic conversion	5	5	5	2	4	45.0	**60.0**
	31	45	Nanotubes (CNT) 1	All purposes	C2CNT process	5	5	5	3	4	46.0	**61.3**