MAPPING OF ECOSAIRILA PLANT ENERGY AND MATERIAL STREAMS FOR CONVERSION OF RENEWABLE POWER TO PRODUCTS

Lappeenranta–Lahti University of Technology LUT

Master's Programme in Chemical & Process Engineering, Master's Thesis

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ABSTRACT

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Mapping of EcoSairila plant energy and material streams for conversion of renewable power to products

Master’s thesis

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74 pages, 19 figures, 5 tables and 3 appendices

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Keywords: P2X, electrolysis, hydrogen, wastewater treatment, renewable energy

The main objective of this thesis was to research how effectively hydrogen could be produced and utilized from treated wastewater. This thesis was made for MetsäSairila Oy and was supervised by Ramboll Oy. The motive of this study for MetsäSairila was to map the potential of P2X-system to EcoSairila wastewater treatment plant. The goal of this thesis was to find a P2X-process, which could be used for MetsäSairila and perform rough evaluations for its feasibility.

The focus of this thesis was on the hydrogen production from alkaline electrolysis and map the potential uses for its product streams. The thesis was limited for focusing on the product streams and the side streams were only briefly discussed on theoretical level. The rough calculations were done in excel for mass balances, energy balances and cost estimations, and the data for the calculations were provided by EcoSairila and BioSairila.

Theoretical part discusses utilization of wastewater treatment plant as source for hydrogen production and how the products could be used effectively. Methanation was the best suiting process for hydrogen utilization. The practical part consists of mapping the starting values from literature and data from plant site. Calculations and analyzes of the results were performed from starting values. The main results of this thesis were that approximately 55 MW methane production is possible with 100 MW alkaline electrolyser. BioSairilas carbon dioxide outlet is not enough to achieve the demands of the electrolyser, which means that the rest of the CO_2 needs to be bought. Main operational expense is the cost of electricity, which can vary and impact feasibility of the researched process.

TIIVISTELMÄ

Lappeenrannan–Lahden teknillinen yliopisto LUT

LUTin insinööritieteiden tiedekunta

Kemiantekniikka

Tommi Tiainen

EcoSairilan massa- ja energiavirtojen kartoitus tuottamaan uusiutuvasta energiasta tuotteita

Kemiantekniikan diplomityö

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74 sivua, 19 kuvaa, 5 taulukkoa ja 3 liitettä

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Ohjaaja: DI Teemu Koskinen

Avainsanat: P2X, elektrolyysi, vety, jäteveden puhdistus, uusiutuva energia

Tämä työn päätavoitteena oli tutkia, miten tehokkaasti vetyä voi tuottaa ja hyödyntää käsitellystä jätevedestä. Työ tehtiin toimeksiantona MetsäSairila Oy:lle. Ramboll Oy oli työn ohjaaja. Tässä työssä oli tehtävänä kartoittaa mahdollinen P2X-järjestelmä EcoSairilan jätevesipuhdistamolle. Työssä oli tavoitteena löytää P2X-prosessi MetsäSairilalle ja tehdä karkeita arvioita prosessin toteuttamiseksi.

Työssä keskityttiin vedyn tuotantoon alkalisilla elektrolyyseillä. Työssä kartoitettiin mahdollisia käyttötarkoituksia vedyn tuotevirroissa. Työ rajoittui tarkastelemaan päätuotevirtoja ja sivuvirrat on käsitelty ainoastaan teoreettisella tasolla. Työssä tehtiin karkeat laskelmat massataseille, energiataseille ja kustannusarviolle taulukkolaskentaohjelmassa. Lähtötiedot laskelmiin saatiin EcoSairilanlta ja BioSairilalta.

Työn teoriaosassa käsiteltiin jäteveden puhdistamoa vedyn tuotannon lähteenä ja sitä, kuinka vedyn tuotannossa saatavia tuotteita voisi käyttää tehokkaasti. Tutkimuksen perusteella metanointi oli parhaiten sopiva prosessi vedyn tuotantoon. Simulaatiolaskelmien perusteella tämän työn keskeinen tulos on, että BioSairila ei pysty tuottamaan tarpeeksi hiilidioksidia 100 MW P2X-tuotantoprosessia varten. Prosessin kannattavuuteen vaikuttaa olennaisesti energian hinta.

SYMBOLS AND ABBREVIATIONS

Symbols

C	Concentration	g/mol
E	Energy	J
e^-	Electron	-
F	Faraday Constant	sA/mol
G	Gibbs free energy	J
H	Enthalpy	J
HHV	Higher heating value	MJ/kg
R	Gas constant	J/mol
S	Entropy	J/K
T	Temperature	K
U	Voltage	V
z	Number of moles of electrons transferred	
η	Efficiency	%

Abbreviations

AEL	Alkaline electrolysis
BOD	Biochemical oxygen demand
CAPEX	Capital expenses
CAS	Conventional activated sludge
CEDI	Continuous electrodeionization
CF	Cash Flow

CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
COD	Chemical oxygen demand
CSTR	Continuous stirred tank reactor
DAC	Direct air capture
H_2	Hydrogen
H_2O	Water
H_2S	Hydrogen sulfide
ICE	Internal combustion engine
ISO	International organization for standardization
KOH	Potassium hydroxide
MBR	Membrane bioreactor
NaOH	Natrium hydroxide
NCF	Net cashflow
O_2	Oxygen
O_3	Ozone
OPEX	Operational expenses
P2G	Power-to-gas
P2M	Power-to-methane
P2X	Power-to-X
PAC	Powdered activated carbon
PEM	Proton exchange membrane
PO	Pure oxygen

RO	Reverse osmosis
RWGS	Reverse water-gas shift
SOE	Solid oxide electrolyte
TDS	Total dissolved solids
TOC	Total organic carbon
TS	Total Solid
UPW	Ultrapure water
UV	Ultraviolet
WWTP	Wastewater treatment plant

Table of contents

1 Introduction

During the last few years, the global energy situation has changed significantly. The great recession in the late 2000's was the latest major shake-up in the economy, which caused energy prices to swing around drastically. After that, the energy economy has been in stable state for about 10 years with only one major oil price drop in mid-2010's. (European Central Bank, 2012) The corona virus pandemic (Covid-19), which started in March 2020, caused a rapid drop in energy prices due to the lockdown. Lockdown caused people to stay at homes and the movement over the borders of countries was minimized. Energy prices dropped, because the overall energy demand decreased, since online working in industries caused their energy consumption to decrease. Traveling and moving restrictions caused challenges in logistics, which caused countries like Finland to use more of its natural energy sources. This did cause concerns over the security of energy supply because an event that was unforeseen and sudden had such an impact on energy markets. (Alvik & Irvine, 2020), (Khan, et al. 2021)

Russia's invasion of Ukraine in February 2022 has made huge impacts on global energy landscape. Russia has been major oil and natural gas provider for Europe for years, and Europe has grown into being dependent on it. The sudden conflict has resulted on Europe not having access anymore for the fossil fuels provided by Russia causing energy prices to rise drastically (Eurostat, 2023). The war in Ukraine and the pandemic have caused a significant shake in energy markets, which has caused countries in Europe to improve their energy security. To avoid trading and traveling issues, which pandemic caused, countries want to become more self-reliant on energy production. The war caused European countries to find alternative sources of energy and the increase of using renewable energy was one of the solutions. (Besson, 2022), (International Energy Agency, 2023) Hydrogen as an energy source has been a popular talking point for future clean energy systems. Its flexibility to be used in heating and electricity makes it improve the energy security challenges and it can be produced without emissions, making it a green energy source. As an energy source, hydrogen is being currently researched heavily, but it has gained huge amount of interest over the past few years and progress has been accelerated. (International Energy Agency, 2019)

Wastewater treatment plants (WWTPs) play a crucial role in safeguarding the environment by ensuring effective protection. It is however quite an energy intensive process and has a significant carbon footprint. Humans consume water faster than nature can reproduce the resource, which means that recycling water is important to satisfy basic needs of normal life. As a result of, that means the countries must find solutions to minimize their environmental impacts. (Coromias, et al. 2013) Electrolysis process splits water into hydrogen and oxygen, which could be called Power-to-X (P2X)-process. It means that electricity is used to produce carbon-neutral synthetic fuels like hydrogen or liquid biofuels. They are useful in processes, which are hard to decarbonize. (Ramboll, 2024) WWTP could be another sector, which could benefit from this type of system. Producing hydrogen from treated wastewater could help to tackle these environmental issues and take big steps towards sustainable water treatment. Hydrogen has been steadily trending as a clean energy production method over the years. It is a very versatile and well researched component with different ways to produce, store, move and use. Oxygen is another interesting chemical element produced by electrolysis, which also has numerous potential end-uses available. In wastewater treatment, it could be used as recycled material for biological treatment or as heat source. (Hao, et al. 2019), (Ursua, et al. 2012)

This thesis research some of the important challenges in MetsäSairila. MetsäSairila is a waste management company in Mikkeli in southern Finland, whose main objective is to manage the waste produced by the population in Mikkeli and surrounding smaller areas. Its main jobs are maintaining the waste management center, improving the waste management of the area, and taking care of announcements and help regarding the area and waste. The company's Vision is to be a green economy operator and enabler of the area. (MetsäSairila, 2024)

EcoSairila and BioSairila are the main operators under Metsäsairila. Their main objectives focus on the treatment of waste. BioSairilas main job is to make biogas from biowaste. It has two biorefineries in the Mikkeli area. Main process in Sairila area has reception capacity of 13500 t biowaste and 6000 t wastewater sludge per year. Gas production is around 6,3 GWh and its main use is as vehicle fuel. (BioSairila, 2024) EcoSairila is an operator in charge of recycling and waste management. Its main attraction is its new and modern wastewater treatment plant, which is in Sairila. Its main unit is membrane bioreactor (MBR) which is the first in Finland and the most recent and advanced solution currently from the technological point of view. The WWTP has been built underground and the cleaned water is returned to lake Saimaa. (EcoSairila, 2024)

The motive of this thesis is to understand the possibilities with hydrogen production from treated wastewater via electrolysis. One of the main interests is whether hydrogen could be used with carbon dioxide to produce synthetic methane to enhance biogas production from BioSairila. Oxygen utilization is also another crucial point of interest, since it has multiple potential uses in waste management. Even though electrolysis consumes massive amounts of electricity, the potential to produce green hydrogen to boost the hydrogen economy is attractive to research. The effective utilization of by-products and using renewable energy sources like solar energy could also be used to balance the overall energy demand of the wastewater treatment plant and hydrogen plant.

1.1 Goals and Research Questions

Main objective of this thesis is to find a functional process for hydrogen production using treated wastewater as source for water electrolysis process using available streams from Eco- and BioSairila. The suitability of treated wastewater is investigated on theoretical level. Alkaline electrolysis process is the method used to produce hydrogen. The potential uses for hydrogen and by-products of electrolysis process, which are oxygen and waste heat, are researched and mapped. From these methods, a combined process of hydrogen production and product stream utilization is made. Rough simulations are made for the process, and then its sensibility is evaluated from an economical point of view. Thesis's research questions are:

- Is it possible to produce hydrogen with 100 MW sized electrolysis process from EcoSairila's streams?
- What is the potential uses for hydrogen, oxygen, and waste heat from the electrolysis process?
- Which of the product and by-product utilization methods are the most useful for the EcoSairila?
- How feasible is producing hydrogen from treated wastewater?
- What benefits does EcoSairila gain from the process?

Boundaries for this thesis are that it only focuses on hydrogen and oxygen utilization methods, which can be beneficial for waste management industries and Eco- and BioSairila. Simulations are only done for one chosen process. The chosen process is decided by comparing different options and choosing the process with the most potential. and the calculations are based on data provided by Eco- and BioSairila.

1.2 Research Methodology

This thesis is separated into two sections: literature and practical section. In the literature section, the main objective is to study different utilization methods for hydrogen, oxygen, and waste heat, which are produced from electrolysis process. In addition to this, the section handles background of this thesis from energy economy point of view, summary of wastewater treatment processes and basic principles of hydrogen production with focusing on electrolysis. Main use of material gathering was using LUT Primo, which is a LUT-library's search service for virtual material. It has access to many databases like Elsevier ScienceDirect, Scopus or Knovel. Used materials vary between articles, scientific research, books.

The practical section focuses on finding out the best combined process for electrolysis process and outlet stream utilization. Process is selected by doing rough calculations for mass- and energy balances and highlighting process features, challenges, or benefits from the literature, which could matter in the decision of the process. The chosen process is then put into a more detailed evaluation. Simulations of mass and energy balances for the chosen process are done by Excel and the results are then analyzed. The feasibility of the process is evaluated by performing rough cost and profit estimations.

2 Hydrogen Economy

This is the theoretical part of the thesis. It discusses various topics around wastewater treatment, hydrogen production and their potential connection together. Chapter 2 discusses briefly the current situation in hydrogen economy and its future potential. Chapter 3 discusses wastewater treatment and its current issues. Chapter 4 discusses hydrogen production via electrolysis and its viability to produce hydrogen from treated wastewater. Chapter 5 discusses of using the products and by-products from electrolysis to improve wastewater treatment plant and waste management in general.

The covid pandemic and Russia-Ukraine war has exposed a weakness in Europe's energy security. The dependency on energy sources from across the border has made the continent vulnerable to outside factors, that can cause problems with the country's economy. This has caused a lot of concerns in terms of future energy security, if global incidents like the pandemic and political disagreements with major trade partners can cause significant economic losses and issues in energy supply. (International Energy Agency, 2023) The research in terms of green technologies solving global warming can be slowed down by poor economic situation. Therefore, the subject of green energy production methods and becoming more self-sustaining in energy production has been getting more focus recently, and the implementation of green energy economy has been accelerated. For example, in Finland, there have already been made large investments on subjects like wind and solar power plants, low-carbon steel factories and battery cell production (Räisänen, 2023).

Hydrogen has been one of the main talking points of green energy economy. It has been researched and discussed for years already before the covid and Russia-Ukraine conflict. Hydrogen gas (H_2) has been seen as a light and reactive chemical compound with high energy content per unit of mass. It is also storable, flexible and has multiple potential end-uses. H_2 is also a green energy source, because it causes minimal emissions as fuel and has potential to be made using green production methods. It can be very critical in toppling some difficult environmental challenges because it has many applications in many sectors where emission reduction is challenging and slowing down countries to hit its environmental targets (Oliveira, et al. 2021), (Ball & Wietschel, 2008) Many countries all over the world like Japan, UK and USA have already included hydrogen in their plans of future energy economy. (International Energy Agency, 2019)

Hydrogen is already apparent in today’s economy as a chemical feedstock. Nowadays it is used to produce two important chemical compounds industrially: ammonia and methanol. In future, this will be expanded into other chemical processes like steel production, which produce a significant fraction of the world's carbon emission. It can be a direct replacement to fossil fuels as fuel for many sectors like transportation, buildings, and heating. Transportation has been the talking point for years and a suitable replacement for a gasoline based internal combustion engine (ICE) has yet to be found. It faces competition with other potential vehicle types like electric cars, but it has advantages in long-distance transportation and heavier vehicles, which are battery-based vehicles weaknesses. Another potentially useful aspect is its potential to strengthen energy security. (International Energy Agency, 2019) It can be used to produce electricity and vice versa, so it can be flexible tool to control energy usage and supply in areas where it is needed at the time. Hydrogen can also be a way to store energy, which can be helpful in situations like Russia-Ukraine war, where energy demand could potentially exceed energy production. (Oliveira, et al. 2021), (Ball & Wietschel, 2008) Figure 1 displays a potential future energy system with hydrogen in comparison with today’s fossil fuel system. (Oliveira, et al. 2021)

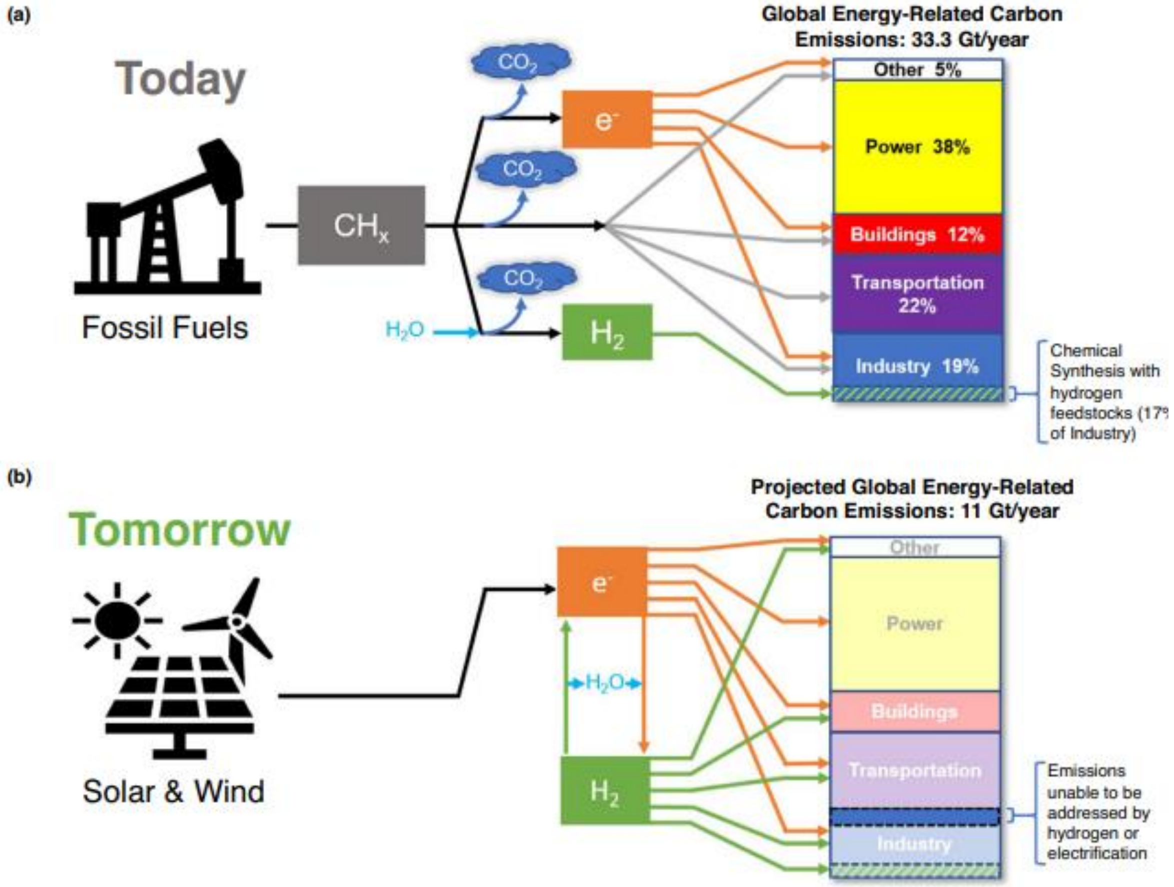

Figure 1. Visualization of current fossil fuel-based energy system (a) and future potential energy system based on hydrogen (b). (Oliveira, et al. 2021)

There are still some challenges with the future green hydrogen economy, which need to be solved. There is a lot of potential with hydrogen, but there are still a lot of unknown technological aspects. The green production methods are still under research. Hydrogen is produced currently via steam reforming or by gasification, where natural gas is used as feedstock. There are also challenges in long distance transportation and the formats in which the hydrogen could be delivered. Implementing hydrogen to the economy means that huge changes to infrastructure must be made, which will require heavy investments. Also, hydrogen’s flexibility can make the future infrastructure more complicated and harder to take full advantage of the whole potential. There are still some standards and regulations written that have not been made with green hydrogen methods in mind and some standards, which have not been agreed on yet like for example the safety measures or hydrogen vehicle refueling. (International Energy Agency, 2019), (Ball & Wietschel, 2008)

3 Wastewater treatment

This chapter discusses the basic principles of wastewater treatment and showcases two commercial methods used in present day. Two processes are commercial activated sludge (CAS) process and membrane bioreactor (MBR) process. Then, the environmental concerns of wastewater treatment are highlighted.

Water exhibits strong qualities in particle transportation due to its solvent properties, ability to dissolve various substances, and interactions with hydrophilic and hydrophobic particles. As a result of that, it functions well as a solvent, as cleaning material or in heat transport, and it is cheaper than other chemicals to use due to its massive nature reserves. It is then used in every sector in some way to achieve one’s needs. Naturally, production of waste is unavoidable in human activities. Since water is used in many applications, one of the most common forms of waste is wastewater. Wastewater comes from various sources, so it can be categorized into different wastewater types based on its origin, for example industrial wastewater or household wastewater. (Ghangrekar, 2023) Since wastewater has many sources, it also has unique characteristics. Physical characteristics of water include dark coloration, foul odor, the presence of solids, and factors which influence the temperature, conductivity, and turbidity. Some main chemical components in wastewater include various organic matter, metals, nutrients, and acids. There is some lively biological activity in wastewater usually like bacteria, viruses, or algae. (Sperling, 2007), (Shah, 2023b) Figure 2 shows some common characteristics of wastewater. (Sathya, et al. 2023)

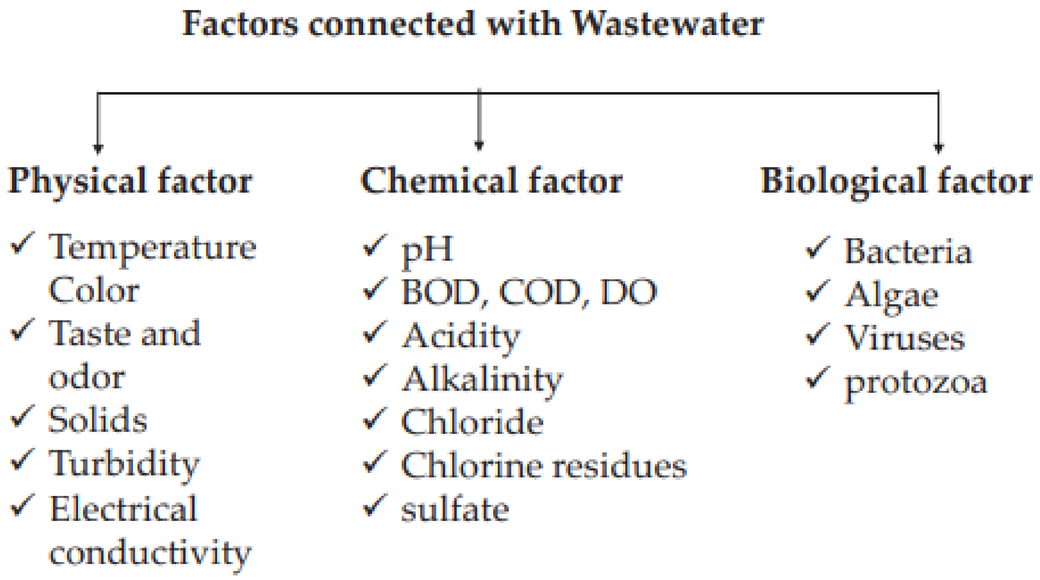

Figure 2. Physical, chemical, and biological characteristics of wastewater. (Sathya, et al. 2023)

Wastewater treatment needs careful planning and a solid understanding of the materials being handled. The different components in wastewater are usually categorized based on their features and removal methods. Solids, for example, can be categorized based on their size and their solubility. Visible and overweight sized solids like stones and dirt from rainwater can be easily and mechanically removed at an early phase of the process. Dissolved metal ions need some more dedicated chemical-based methods. Organic compounds can be categorized based on their biodegradability, overall oxygen demand and solubility, for example. Main idea of this classification is to put all similarly characteristic components into same categories so that planning of treatment system becomes more manageable and easier. (Innerebner, 2018), (Sperling, 2007)

The water treatment process itself is traditionally divided into various levels, where each of them has its own functions and removal objectives. The main idea is to have the similarly categorized components removed in specific levels of the process. In the early phases of the process, there are usually pre-treatment, mechanical removal methods and solid removals. As the process goes on, the focus starts to go more into harder to remove components and compounds, like organic removals and dissolved materials. At the later stages of the process, there are usually only specific toxic or non-biodegradable compounds left, which cannot be removed in earlier parts of the process. (Sperling, 2007), (Shah, 2023b)

Conventional process units can be divided into three distinct types: physical, chemical, and biological unit processes. Physical methods are methods using physical forces to remove pollutants from water. They can consist of a variety of methods, but some commonly used are, for example, screening, mixing, flocculation, flotation, and filtration. They are used to remove solids and easily removable organic matter and are apparent in earlier parts of the process. They can however be parted in later levels as just separation unit to separate reaction products from each other. Chemical process units are units using specific chemical reactions to remove pollutants. Adsorption is still a highly effective method in the removal of inorganic and organic pollutants. There are also other methods for more specific target compound removals like disinfection of bacteria and viruses and using precipitation in phosphor removal. (Innerebner, 2018), (Sperling, 2007)

Biological process units are methods which use microbes to remove contaminants in wastewater. Various methods exist in biological treatment, and they can be useful in removing many types of pollutants. Biological reactors are commonly used, and they are divided into aerobic and anaerobic units. Some organic matters are removed easily with oxygen and some without it. Aerobic systems are more suitable for low BOD/COD (Biochemical oxygen demand/Chemical oxygen demand) streams and are more effective in nutrient removal. Anaerobic systems are more suitable for streams with heavy concentrations of organic matter. Sedimentation ponds and land disposal areas are cost-saving alternatives for reactors, which lets biological activity occur in a more natural and un-controlled way. (Sperling, 2007) One common conventional biological process is CAS-process (Conventional activated sludge). It is a two stepped process, first starting with aeration step, where wastewater is treated with microorganisms to produce activated sludge and then the water and sludge is separated in sedimentation tank or secondary clarifier. (Al-Asheh, et al. 2021) Figure 3 shows the complete activated sludge process (Bhosale, 2015).

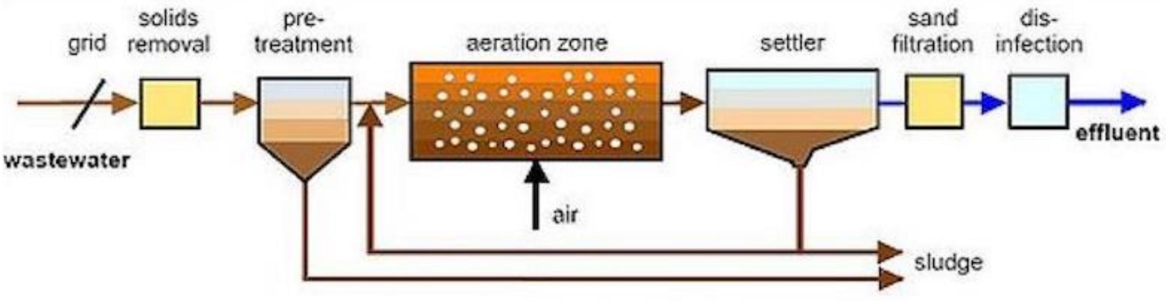

Figure 3. Standard active sludge process. (Bhosale, 2015)

3.1.1 MBR-Process

There are various technological advancements made from the conventional solutions. Membrane-based technologies have gained popularity in separation technologies. In wastewater treatment, it would use combined process of nanofiltration and reverse osmosis to remove organic materials from wastewater. It has several advantages over the traditional methods, like higher treated water purity, and it is good from operating and up-scaling perspective also. It is currently being used in food/beverage industries, in medical industries and for industrial effluent treatment. Membrane processes have been made into commercial scale like EcoSairila's MBR process. (Hills, 2000), (Shah, 2023a)

In WWTP, the membranes are a filtration system for solid-liquid separation. The membranes are answer for the low process performance of CAS-process. It replaces the secondary sedimentation tank in CAS-process to have a simple single-step process for the clarification and filtration. The process is called an MBR-process (Membrane bioreactor). MBR's can be used in both aerobic and anaerobic reactors and highly advanced systems do also combine these two. (Hai, et al. 2019) Figure 4 shows the flowchart of MBR-process. (Karim & Mark, 2017)

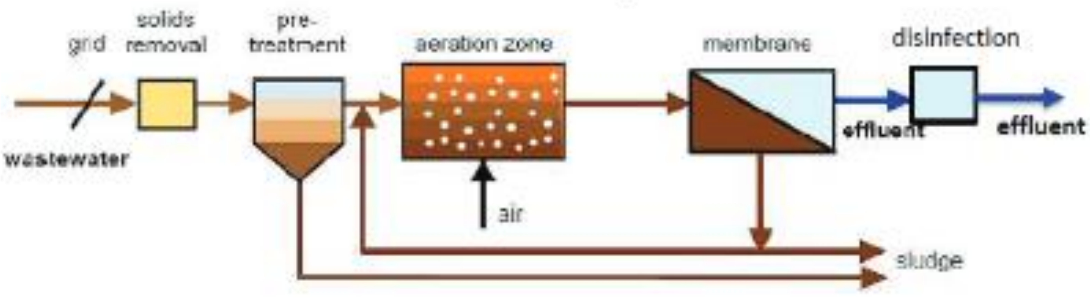

Figure 4. Standard MBR-process in WWTP. (Karim & Mark, 2017)

Compared to traditional CAS-process, the MBR has a lot of advantages. Size requirements for bioreactor is smaller than with CAS-process and the secondary sedimentation is left out completely, resulting a smaller footprint for the process. Other advantages are that waste is generated less and the process can produce high quality treated water. There are some disadvantages also. It has higher electricity consumption than CAS, and membrane fouling is a common issue in MBR-processes. Membrane fouling is a phenomenon where membranes' performance in process decreases over long-term operation (Chang, et al. 2019). It is commonly caused by particles either blocking the pores inside or larger particles not fitting the pores getting stuck on surface of membrane causing fluids to not get through the membranes. It has higher capital expenses, because of the antifouling mechanisms and membranes, and the higher electricity consumption causes operational expenses to be higher than the traditional CAS-process. Other issues in membrane-process in WWTP are that foaming propensity is higher, and the membrane process is more complex due to the cleaning and maintenance procedures of membranes. (Sameer, et al. 2021)

3.1.2 Wastewater treatment and environmental concerns

In the modern world, it is important to achieve sustainable and clean industries. Wastewater treatment is necessary for the removal of impurities and recycling of water. But there are some environmental concerns even if it helps the water stay clean. It produces greenhouse gases (mainly methane (CH_4) and nitrous oxide (N_2O)) and consumes enormous amounts of energy, which doesn’t make it sustainable. Clean water production is not something that can be abolished, because it is one of the basic needs of humans. As a result of that, the only possible way is to find improvements for the process to achieve more sustainable and green wastewater treatment. (Corominas, et al. 2013), (Hao, et al. 2019)

Some improvements have already been made, for example energy balancing and efforts to achieve a neutral carbon footprint. Thermal energy recovery is one interesting solution. Wastewater has good potential, and the heat it produces could be useful in various steps, for example, in sludge drying. (Hao, et al. 2019) Hydrogen is a potential center of the future green energy economy. That is why exploring its relationship with wastewater treatment is an attractive prospect.

4 Hydrogen Production

This chapter discusses hydrogen production via electrolysis. Electrolysis uses water and electricity as raw materials to produce hydrogen and oxygen. This chapter contains basic principles of hydrogen production and electrolysis process. Then, the suitability of treated wastewater is discussed and challenges in regards of up scaling the electrolysis process are highlighted.

Hydrogen is odorless, colorless, tasteless, and non-toxic gas, which is lighter than air. It is the simplest and the most common element in the whole universe. It is used in hydrogenation processes, which is used in various synthesis routes due to the reaction being highly selective and easy to operate. Some examples are methanol and ammonia production, but it is also used for specific chemicals in various sectors like in agrochemicals, fat hydrogenation in food industries and in pharmaceutical industry. Hydrotreatment and hydrocracking are commonly used in oil refining to break C-C bonds and for sulfur removal. Hydrogen's gravimetric energy density is 120 MJ/kg, so it has a high energy-to-weight ratio. Its combustion reaction with oxygen produces water, resulting in no production of greenhouse gases. Because of these aspects, hydrogen is considered to play a key role in the future energy economy. (Sankir, & Sankir, 2017), (Godula-Jopek, et al. 2015)

Because of hydrogen's simplicity, it has multiple production methods. They can be separated into four categories: thermal, electrochemical, biological, and photonic processes. Methane reforming is the most common thermal method currently used for hydrogen production, and it is also the most overall used method for hydrogen production. (Tak, et al. 2022) It commonly uses water vapor and natural gas as methane catalysts. Another common method is the gasification process, where a solid feedstock, usually coal, is split with incomplete combustion. It produces syngas as a product, which can then be refined into pure hydrogen. Issues with these processes are that they use fossil fuels as feedstock, and therefore produce greenhouse gases, so they cannot be relied on eternally as primary production method. Bio-based materials could be used to replace fossil fuels as feedstock. Biological feedstocks are more complicated and more expensive to use, so they are not reasonable to use right now. Anaerobic digestion is another alternative for biological processes, where micro-organisms like bacteria are used to break down organic matter into methane and carbon dioxide. Its stages acidogenesis and acetogenesis have hydrogen as product, so using that as for bio-hydrogen production is possible. There are still technical and economic challenges, which prevent its larger scale production. Electrochemical processes are processes using water and electricity for hydrogen production. Problems with electrochemical methods are that they consume enormous amounts of electricity and are not really used for large-scale production. Photonic methods like photocatalytic water splitting are researched to reduce the heavy usage of electricity. (Yukesh Kannah, et al. 2021)

4.1 Electrolysis process

Electrolysis is an electrochemical reaction, where water is split into hydrogen and oxygen. The principle of water electrolysis is to pass a direct current between two electrodes immersed in an electrolyte. Hydrogen is formed at the cathode and oxygen at the anode. The production of hydrogen is directly proportional to the current passing through the electrodes. More commonly, Michael Faraday’s laws of electrolysis state that (Jensen, 2012):

1. The mass of any substance deposited or dissolved is proportional to the absolute quantity of electricity that passes through the cell.
2. The masses of different substances deposited or dissolved by the same quantity of electricity are proportional to their electrochemical equivalent weights.

The electrodes should be resistant to corrosion, have good electric conductivity, exhibit good catalytic properties, and show suitable structural integrity. Furthermore, the electrodes should not react with the electrolyte. The overall chemical reaction of water electrolysis without required thermodynamic energy values can be written as (Equation 1) (Ursúa, et al. 2012), (Godula-Jopek, et al. 2015):

$$H_2O \rightarrow H_2(g) + \frac{1}{2}\, O_2(g) \;\; \Delta H^{o}_{298} = -285{,}83\; kJ/mol \tag{1}$$

Thermodynamics of water electrolysis can be described as change of enthalpy ΔH (Equation 2) (Ursúa, et al. 2012), (Godula-Jopek, et al. 2015):

$$\Delta H = \Delta G + T\Delta S \tag{2}$$

where	T	temperature
	ΔS	change of entropy
	ΔG	Gibbs free energy change

ΔG can be described as (Equation 3):

$$\Delta G = zFU_{rev} \tag{3}$$

where	z	number of moles of electrons transferred in the reaction (z = 2, for hydrogen)
	F	Faraday constant (96485 C/mol)
	U_{rev}	reversible voltage

U_{rev} means that it is the lowest required voltage for electrolysis. In the electrolysis of water, chemical energy is converted from thermal and electrical energy. (Ursúa, et al. 2012),

The electrolysis cell voltage U_{cell} can be described as (Equation 4) (Ursúa, et al. 2012):

$$U_{cell} = U_{rev} + U_{ohm} + U_{act} + U_{con} \tag{4}$$

where	U_{ohm}	overvoltage caused by ohmic losses,
	U_{act}	activation overvoltage
	U_{con}	concentration overvoltage.

There are energy and efficiency losses in the cell due to the overvoltage's and parasitic current. Therefore, the required cell voltage is higher than the minimum voltage. (Ursúa, et al. 2012)

Electrolyzer efficiency η_e is an effective way to evaluate the performance of the electrolyzer. It can be described as (Equation 5) (Ursúa, et al. 2012):

$$\eta_e = \frac{HHV(H_2)}{E_c} \tag{5}$$

where	$HHV(H_2)$	higher heating value of hydrogen (3,54 kWh/Nm^3)
	E_c	energy consumption (kWh)

Electrolyzer cells can be arranged into unipolar module, bipolar module, or mixture a of those. Uni- or monopolar module means that the electrolyzer cells are arranged into parallel connection and bipolar means that the cells are arranged into series connection. A mixture module is a mixed connection, with cells in series forming branches that are connected in parallel. (Ursúa, et al. 2012)

4.1.1 Alkaline electrolysis

Alkaline electrolysis is considered as the most developed technology for water electrolysis. Alkaline electrolysis cells are usually housed in a steel compartment. The two electrodes are separated by a gas-tight diaphragm, which is submerged in a liquid electrolyte. (Godula-Jopek, et al. 2015) Figure 5 shows the working principle of an alkaline electrolysis cell (Gallandant, 2017).

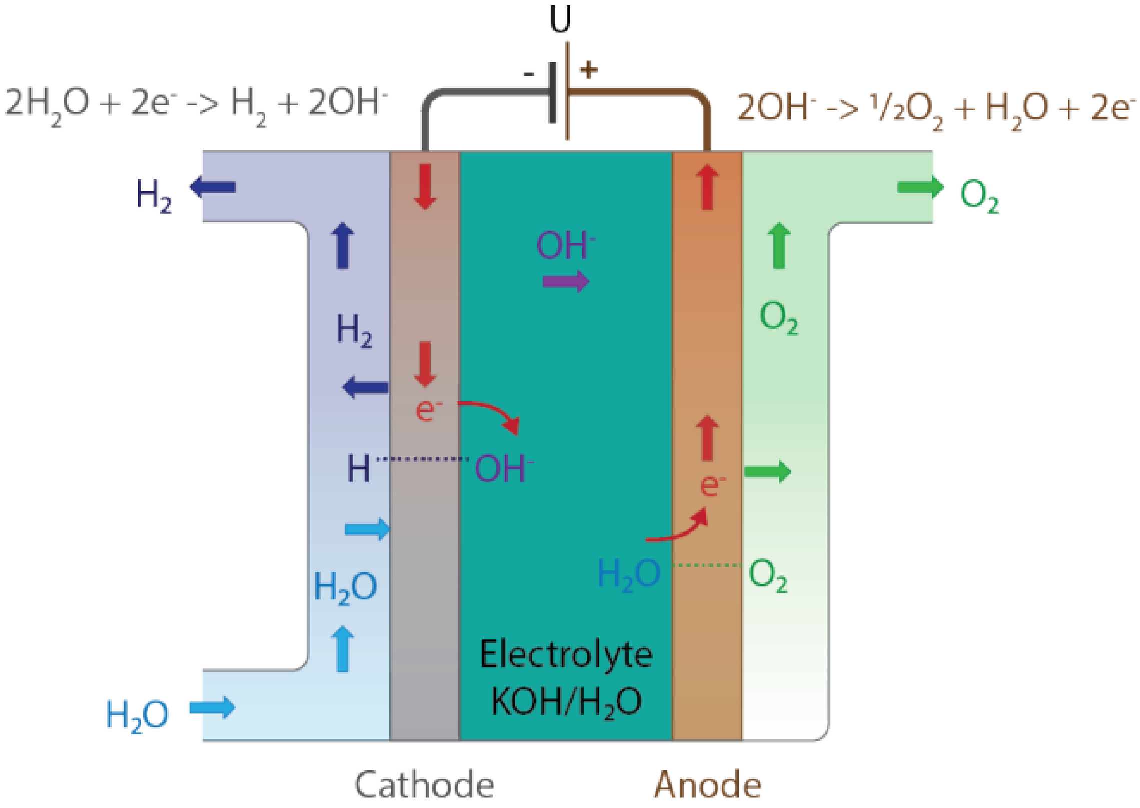

Figure 5. Working principle of Alkaline electrolyzer. (Gallandat, et al. 2017).

The electrolyte is usually an aqueous solution of potassium hydroxide (KOH) or sodium hydroxide (NaOH), which are due to their ionization capabilities strong conductors. Electrodes are usually made of materials which resist corrosion, like nickel. Chemical reactions taking place in alkaline electrolysis at the cathode and the anode, are as follows (Equations 6 & 7) (Ursúa, et al. 2012), (Godula-Jopek, et al. 2015):

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- \tag{6}$$

$$2OH^-(aq) \rightarrow \frac{1}{2}\, O_2(g) + H_2O\ (l) + 2e^- \tag{7}$$

Most conventional water electrolysis processes use some sort of alkaline process and system sizes vary to 1.8-5300 kW and production rate is between 0.25-760 Nm^3/h. There already exist commercial electrolyzers exceeding 100 MW production. A high purity levels of 99.5-99.9998% can be reached with hydrogen formation. The current density is usually around 0.2-0.4 A/cm^2. (Kumar, & Lim, 2022)

4.1.2 Proton exchange membrane electrolysis

Proton exchange membrane (PEM) electrolysis is a method where the density of the electric current is higher than in alkaline electrolyzer. (Godula-Jopek, et al. 2015) Diffusion overvoltage U_{diff} can be calculated according to the Nernst equation (Equation 8) (Marangio, et al 2009).

$$U_{diff} = \frac{RT}{zF} \ln \frac{C_1}{C_o} \tag{8}$$

where	R	gas constant
	C_i	concentration

In the process, a thin membrane in between the cathode and anode functions as electrolyte. (Godula-Jopek, et al. 2015) Figure 6 shows the working principle of PEM electrolysis (Gallandant, 2017).

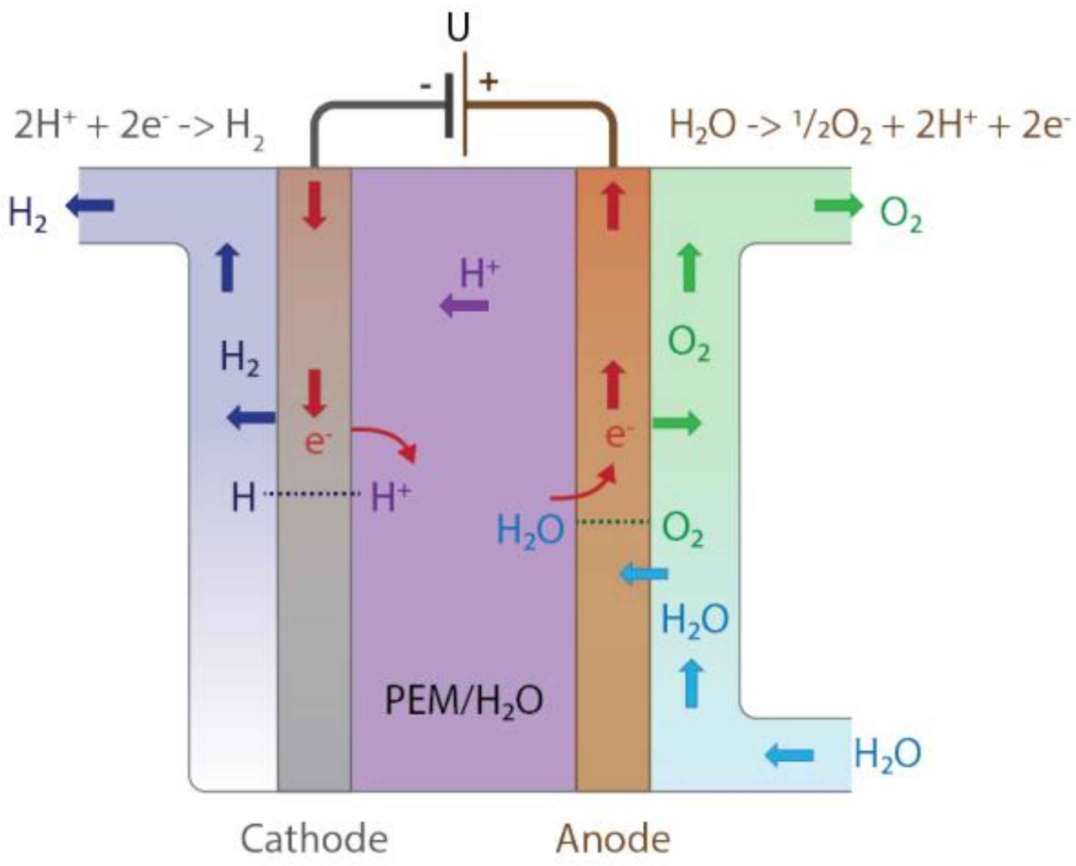

Figure 6. Working principle of PEM electrolyser. (Gallandat, et al. 2017).

The membranes are usually made from mechanically strong polymers with acidic qualities. Commonly they use sulphonated fluoropolymers. Chemical reactions taking place in PEM electrolysis at the cathode and the anode, are as follows (Equations 9 & 10) (Ursúa, et al. 2012), (Godula-Jopek, et al. 2015).

$$H_2O\ (l) \rightarrow \frac{1}{2}\ O_2(g) + 2H^+(aq) + 2e^- \tag{9}$$

$$2H^+(aq) + 2e^- \rightarrow\ H_2(g) \tag{10}$$

Commercial PEM electrolyzers usually operate around the current of 0.6-2.0 A/cm^2, which is significantly higher than the alkaline process. Production rates range from 0.01-240 Nm^2/h and system sizes are around 0.2-1150 kW. Higher hydrogen purity can be achieved with PEM than with alkaline. Over 99.9% purity can be achieved with it typically. (Kumar, & Lim, 2022)

4.1.3 Solid oxide electrolyte electrolysis

Solid oxide electrolyte (SOE) electrolysis is the third method existing besides PEM and alkaline. It uses high operating temperatures of typically between 700-1000 ˚C. It is steam-based electrolysis. Figure 7 shows the working principle of SOE electrolysis (Gallandant, 2017).

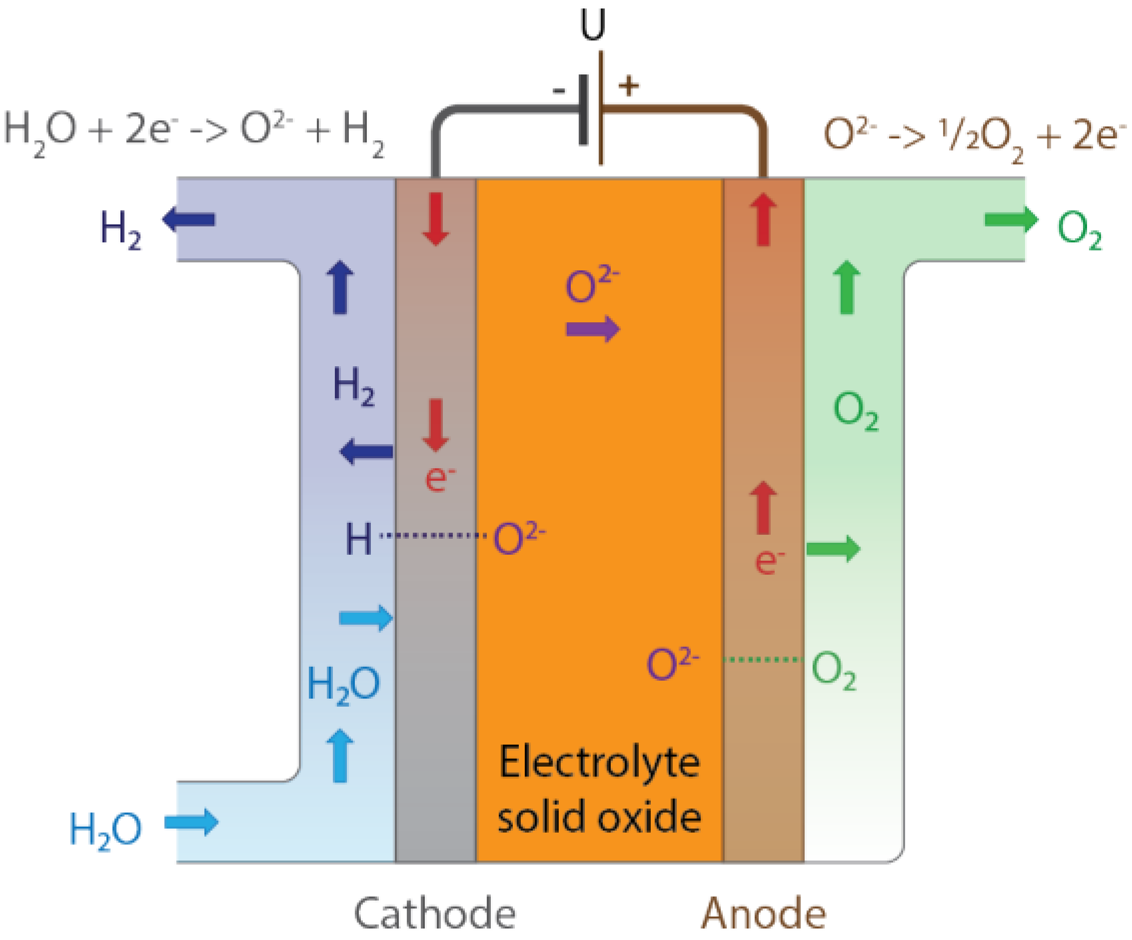

Figure 7. Working principle of solid oxide electrolyser. (Gallandat, et al. 2017)

It uses, like its name says, a solid oxide usually made from ceramic materials as membrane for the process. Chemical reactions taking place in SOE electrolysis at the cathode and the anode are as follows (Equations 11& 12) (Ursúa, et al. 2012).

$$H_2O(g) + 2e^- \rightarrow H_2(g) + O^{2-} \tag{11}$$

$$O^{2-} \rightarrow \frac{1}{2} O_2(g) + 2e^- \tag{12}$$

SOE electrolysis is currently in R&D stage, so there are not yet any conventional processes existing. Current density is kept around 0.3-0.6 A/cm^2. High hydrogen purity of 99.9% can be achieved with it. (Kumar, & Lim, 2022)

4.2 Hydrogen production from wastewater

To pursue net-zero emissions for wastewater treatment, it must solve its energy intensity challenges. Utilizing recycled water for energy production could lower the overall energy demands of the process and reduce carbon emissions. It also would negate water costs for hydrogen production and the process does not add any additional impurities to the water. (Donald, et al. 2023)

Various biological, electrochemical, photonic methods and mixtures of them have been investigated as potential methods for hydrogen production during wastewater treatments. The main advantages of biological methods are their clean and sustainable nature. Biological methods are also the cheapest options. Dark fermentation is the least expensive option among the potential candidates, and mixture processes like microbial electrolysis are also cheaper than their standard variations. Costs do vary from the scale of production. Expensive processes like electrolysis could be more efficient on a smaller scale. Photonic methods are still quite new and under investigation. They tend to have low energy and exergy efficiencies, which results that the future developments in research will impact the viability of these methods. (Yukesh Kannah, et al. 2021), (Tak, et al. 2022)

4.2.1 Water quality requirements

Many electrolysis processes are quite sensitive to water quality. For alkaline electrolyzers impurities can cause significant effects on hydrogen production. Turbidity and dissolved solids are major challenges because they have free movement of ions. Organics and nitrogen are also observed to influence hydrogen production. Maximum TOC levels should be below 50 µg/L. The water conductivity ideally should be below 1 µS/cm. Impurities impact the process operation, performance and lifetime of electrolyzer. (Becker, et al. 2023) These values are usually quite high in common WWTP product streams. So, the water should be treated to achieve better results in electrolyzer. Pure water is separated into different grades or levels based on its impurity levels. Grading scales in ISO standards to 1-3, where grade 3 water is the least purified and grade 1 the most. Grade 3 water is produced by reverse osmosis (RO) process, and it is used in laboratory environments, pharmaceutical and food and beverage industries. It has a maximum conductivity of 5 µS/cm in 25 ˚C, which does not make it good enough for electrolyzer. Grade 2 (purified water) is water, which has gone through more treatment steps than in grade 3. After the RO process, the common method to achieve grade 2 water is deionization. It has maximum conductivity of 1 µS/cm at 25 ˚C and TOC levels of under 50 µg/L, and it has uses in laboratories, where more purified water is needed, for example some analyzers. It is commonly used in electrochemical processes, and it is suitable for electrolyzers. Grade 1 water is commonly known as ultra-pure water (UPW). It is produced from grade 1 water and goes through the polishing stage. It has a maximum conductivity of 0.1 at 25 ˚C and TOC levels of under 10 µg/L. It has more specific uses, like in advanced analytical procedures or some processes, where water purity is a critical factor. Water purity wise grade 1 water is the most suited for electrolysis. Figure 8 shows a descriptive image for different grades of water. (ELGA, 2021)

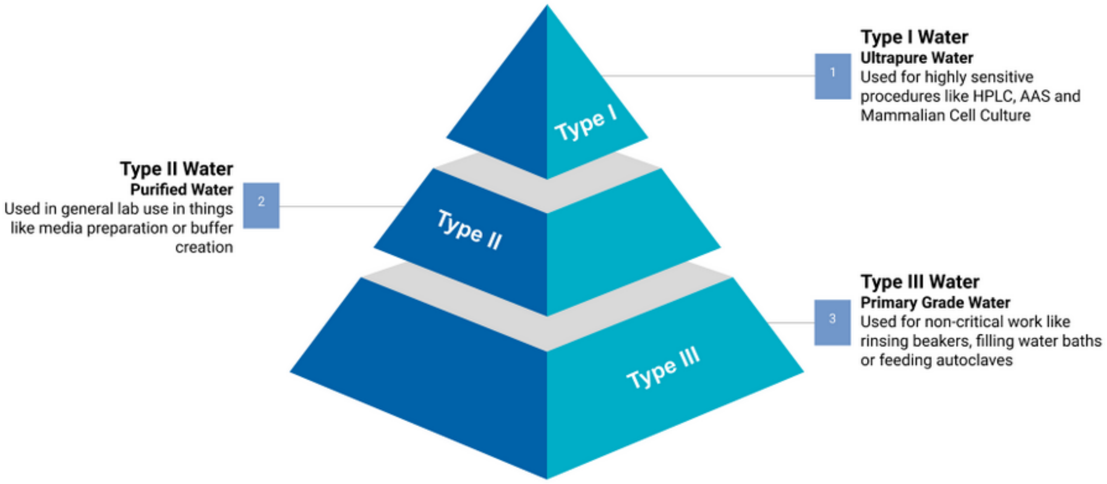

Figure 8. A diagram showing distinct types of purified water and where they are used in the laboratory environment. (ELGA, 2021)

Typical UPW goes first through a pre-treatment step, make-up step and finally a polishing step. Pre-treatment steps main point is to have water quality pure enough for the reverse osmosis. Its main objective is to remove suspended solids from the water. Suspended solids are problematic for later steps because they can, for example, foul RO membranes. The pre-treatment system varies based on its feedstock water quality. There is research done from MBR permeate straight to RO process without any pre-treatment and having positive results in terms of membrane fouling (Deng, H. et al. 2020). Make-up step is the desalting step. In modern days, reverse osmosis is the main process in the make-up step. It can remove most of the contaminations flowing through like total dissolved solids (TDS), particulates and TOC. The final polishing step's main purpose is to polish water quality to meet the requirements set by production purpose. There is an option for a reclamation step, where used UPW is then returned to process because producing UPW from high quality water is cheaper. (Yongxun, et al. 2018), (Hyunkyung, et al. 2016) Mixed bed polisher and continuous electrodeionization (CEDI) process are the main methods used in today's production. Membrane technology has made waves in the high-quality water production in recent years, replacing many traditional separation methods (Hyunkyung, et al. 2016). Figure 9 shows the general process for UPW production (Xuan-Tong, 2024).

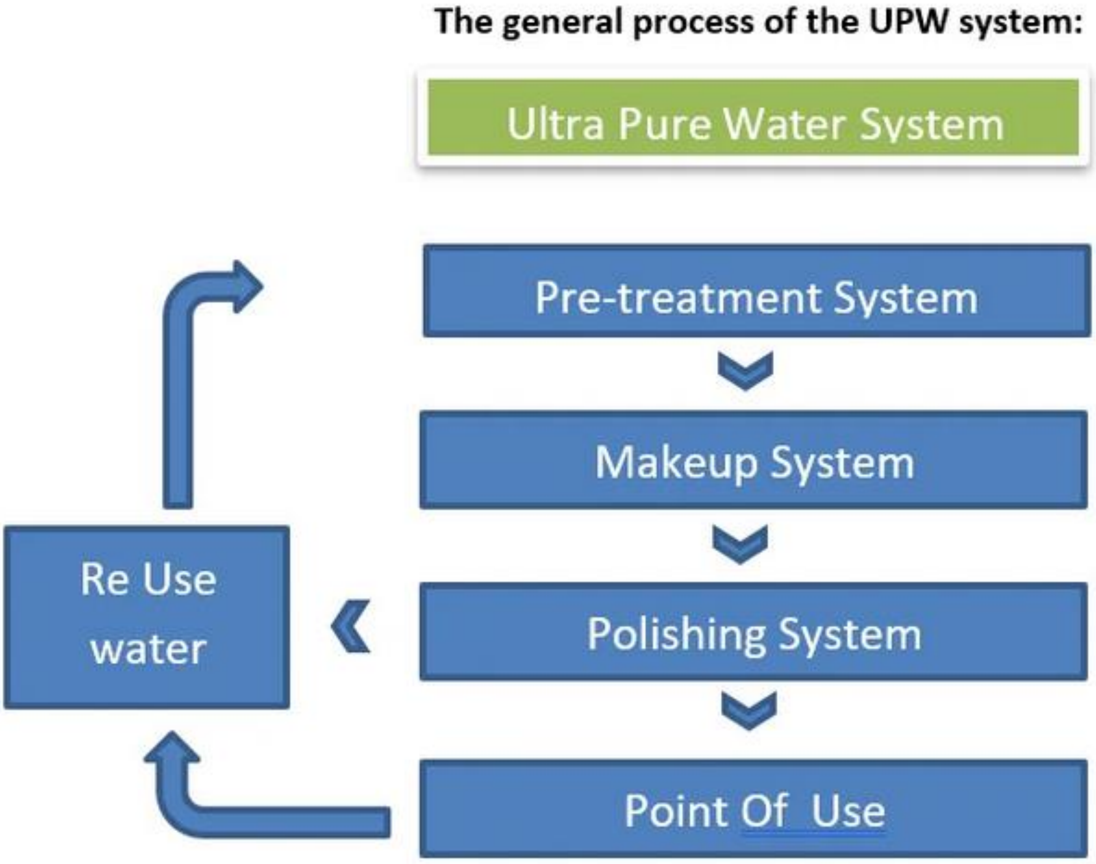

Figure 9. General process for making UPW. The point of use is the steps, where UPW is used in process and then it is recycled back into treatment. (Xuan-Tong, 2024)

4.2.2 Electrolyser sizing & units

Electrolyzers can be sized based on their power usage. 5 MW electrolyzers like HELA1000 electrolyzer use around 900 kg/h water and have hydrogen production of around 90 kg/h and oxygen production of 715 kg/h (Hygreen Energy, 2023). The capital expenses can vary between 875-1800 €/kWh in commercial units, but with large scale (100 MW and over) production, even values of 400 €/kWh can be achieved (Leeuwen et al. 2018), (Proost, 2018) . System efficiency is usually around 65%, but efficiency of 75% can be achieved with modern technology. Utilizing electrolysis process has proven to reduce carbon footprint of wastewater treatment process, because the produced hydrogen and by-products can be used to balance the energy intensity of the process. Research has been done, where a 10-year simulation was made to compare carbon emissions with traditional and hydrogen-included water treatment processes. Results were that a total of 320 CO_2 t equivalent emissions were saved over 10 years for water treatment system serving equivalent population of 26000 with solar power utilized. (Donald, et al. 2023) In this thesis, an electrolyzer size of 100 MW is used in calculations for it being commonly used size for large-scale production.

Apart from electrolysis cell and pre-treatment, there are other steps involved in conventional processes. To maintain stable process temperatures, cooling is a critical step to achieve that. The most common method is using liquid-based cooler using water. But also, in locations where availability of water is limited, air cooling methods are also used. The water demand is extremely high since in once-through cooling systems a 1 MW electrolyzer uses 25 L/s. In large scale like 100 MW electrolyzers can use 630 L/s of cooling water in once-through systems. So, cooling towers using evaporative cooling is preferred for its lower water consumptions. (Fius, 2020)

Hydrogen coming out of electrolyzer is not pure and needs to be purified before storing. Impurities in hydrogen consist of water, electrolyte, and oxygen. A simple gas-liquid separation vessel, like gas/liquid coalescer, is suitable for separating electrolyte-water solution from gaseous components. Excess oxygen is removed in deoxygenation step and water vapor is removed by drying the gas. Oxygen produced as side stream needs to be also treated similarly by removing excess liquid components by gas/liquid separation and then refined to remove other contaminants. Acquired Oxygen purity is around 99.0-99.5 %. (PALL, 2021) Figure 10 shows an electrolyzer with gas treatments. (International Renewable Energy Agency, 2020)

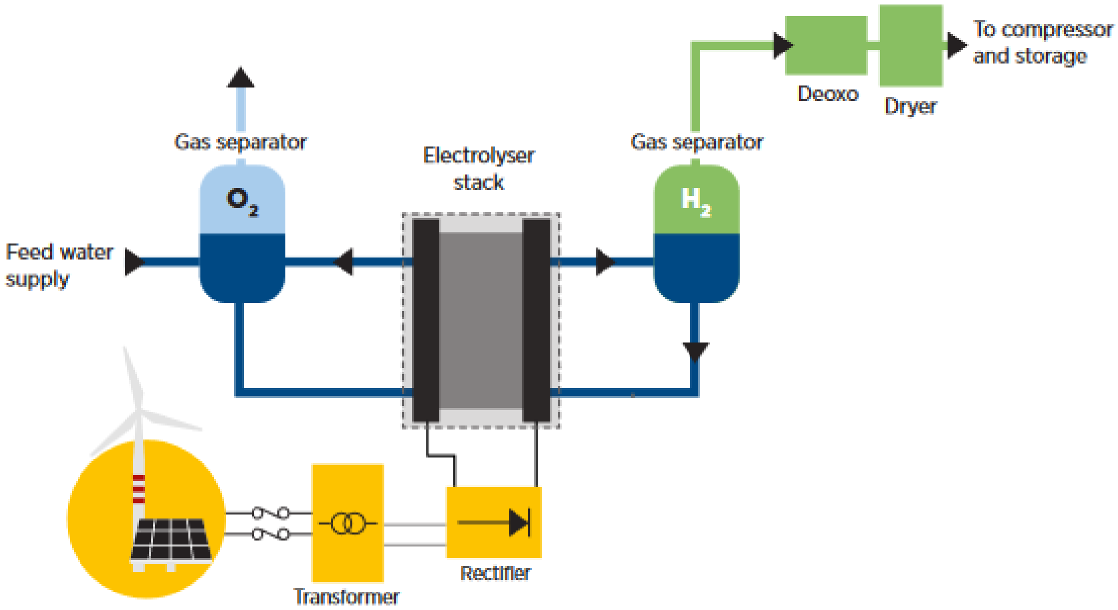

Figure 10. Flowchart of H_2 electrolyzer with gas treatments. (International Renewable Energy Agency, 2020)

5 Resource and material recovery

This chapter highlights the potential for electrolyzers products. Storing of gases and utilization of hydrogen as raw material for energy production is discussed. The potential of electrolysis by-products like oxygen and excess heat is discussed. There are few possibilities for utilizing electrolysis products in waste treatment. One simple option is to just sell it as a product. Hydrogen and oxygen have many uses in industrial applications, so they would have reasonable market opportunities. Waste heat could also be transported as district heat.

Hydrogen is the main product of the electrolysis process. Hydrogen, being a gas, needs to be treated in a storable state before it can be transported. There are multiple methods to store hydrogen and other gases. It can be stored in compressed form, liquid form, or material-based hydrogen storage. The containers need to be air-tight and thermally isolated to avoid gases to maintain their form and to avoid hazards. Transporting hydrogen would be done by trucks, where hydrogen would be stored into some sort of container. Transporting by pipelines would be more ideal, but in Finland there is a lack of proper infrastructure to perform gas transporting by pipes effectively (Vartianen, 2020). Hydrogen is a highly flammable gas so there are safety concerns and risks involved in storing and transporting hydrogen. According to the European Commission, selling green hydrogen is not currently profitable due to the high production costs of it. Green hydrogen production costs are estimated around 4-8 €/kg and its average selling price of hydrogen in general would be around 4-6 €/kg (Hydrogen Valley, 2023). Production costs of green hydrogen are around 2-3 times higher than traditional fossil fuel-based hydrogen. Even though it is not currently sensible, there is some potential for it in the future. (Longden, et al. 2022) Since the world is quite heavily going for hydrogen-based infrastructure, the high hydrogen demands, and safer transporting methods could make selling hydrogen more attractive. For now, using hydrogen for industry's own needs is a more sensible option. Hydrogen can be used as feedstock for a few synthesis processes like the well-known Fischer-Tropsch processes. But more interesting would be its potential in hydrotreatment steps of liquid biofuels made in pyrolysis processes. Utilizing "free" hydrogen as raw material would reduce the production costs for biofuel production, which is currently one of its major challenges. (Sankir & Sankir, 2018)

5.1 Carbon dioxide utilization

Carbon dioxide as raw material has gained interest in recent years. It has potential to reduce industry's carbon footprint, which is a challenge in waste management industries. Many industries produce CO_2 as a by-product, but it usually is not in pure form. It is released into the air as gas mixtures known as flue or exhaust gases. So, a process for capturing and storing CO_2 (CCS) might be required. Quite a common conventional method is using different solvents or sorbents to capture CO_2 from flue gas or directly from air. Sorption technologies and membranes have gained popularity in recent years for CO_2 capture. (Maroto-Valer, 2010) There are multiple ways of storing CO_2. Storage tanks are good for short-term storage, and it makes sense in methanation process since produced CO_2 is meant to be used as quickly as possible. On long term, CO_2 could be stored in underground or trapped in minerals by carbonation process. Figure 11 shows carbon capture process using CaO as sorbent. (Tregambi, et al. 2023)

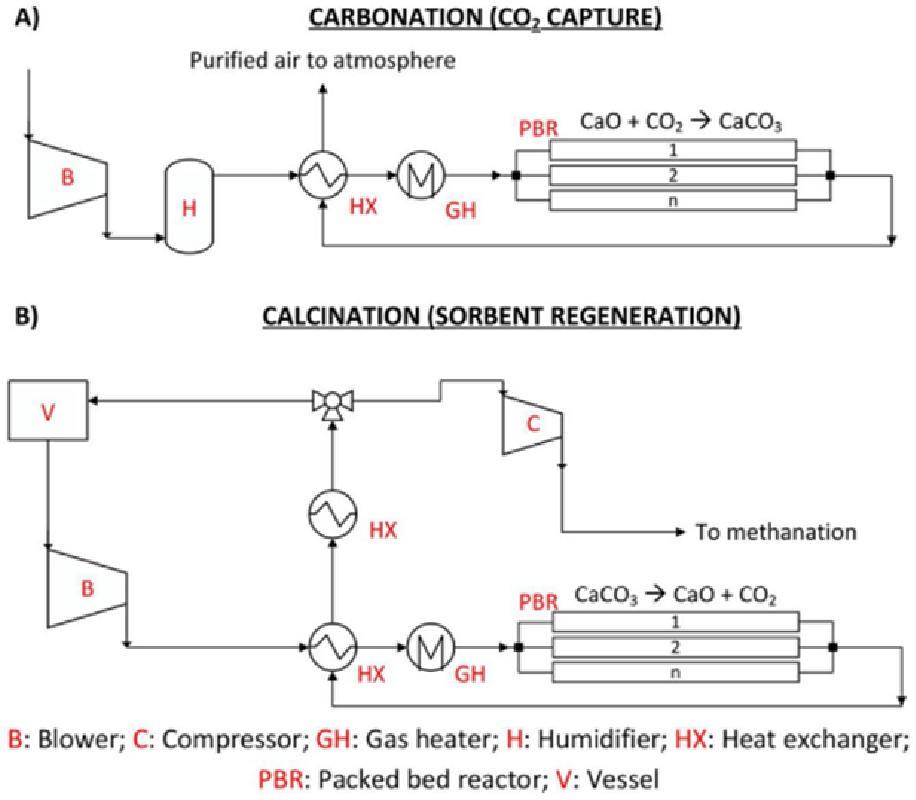

Figure 11. Examples of direct air CO_2 capture using calcination cycle and CaO as sorbent. A) is the capturing step using carbonation reaction. Calcium carbonate ($CaCO_3$) is produced from the reaction. B) is then the step, where $CaCO_3$ is converted back into CaO and CO_2, where CO_2 goes to methanation, and sorbent is reused in process. (Tregambi, et al. 2023)

In WWTP the process does produce carbon dioxide as methane (CH_4) combustion and oxidation in bioreactors. There are also other impurities like Nitrous oxide (N_2O) and the CH_4. The issue with the capturing mechanisms is that they are expensive, because the CO_2 needs treatment before it can be utilized. (Campos, et al. 2016) Refining raw biogas into biomethane is another source for CO_2. Biogas composes mainly CH_4 and CO_2, so refining biogas into methane requires removal of CO_2 and other impurities. Acquired CO_2 from biogas plant has usually high CO_2 purities, so they might not need lot of treatment before storage. This would make them significantly cheaper than capturing flue gases from WWTP. (Li, et al. 2016) Another option would be buying CO_2 from third-party producer. Prices do vary on the source of where the CO_2 is obtained, but average price in Finland is about 105 €/t CO_2. Due the high costs of CO_2 capturing systems, good and cheap sources for CO_2 can be hard to come across. However, the market for CO_2 can increase in near future, because improvements of the carbon capture systems are researched. (Kiviranta & Linjala, 2023)

5.1.1 Methanation

Methanation is a chemical reaction, where CO_2 and H_2 are converted to methane gas and water. It is a hydrogenation reaction, where hydrogen is added to another compound. It is a 2-stepped reaction. First happens the reverse water-gas shift reaction (RWGS), where CO_2 and H_2 are converted into carbon monoxide (CO) and water. Then the hydrogen reacts with CO replacing the oxygen atom in it producing methane and water. Equation 15 shows the reaction for CO_2 methanation process, which is a combination of the CO methanation and reverse Water Gas Shift reaction (Equations 13 & 14) (Bassano, et al. 2019):

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad \Delta H_{298}^{o} = 41\ kJ/mol \tag{13}$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad \Delta H_{298}^{o} = -206\ kJ/mol \tag{14}$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \quad \Delta H_{298}^{o} = -165\ kJ/mol \tag{15}$$

Methanation can be done either by metal catalyst or biological catalyst. There are advantages and disadvantages to each of them. Biological methanation has lower reaction rates and lower volumetric mass transfer coefficient. It also has more tolerance for impurities (especially sulfides like H_2S) in input gas. Its operating temperatures (40-70 ºC) are quite a lot lower than with catalytic methanation (300-550 ºC). It does mean that biological methanation has lower operational expenses due to more tame operation conditions, but the catalytic methanation produces high temperature heat, which could have more applications in by-product utilization. Higher reaction rates in metal catalyst methanation means that the reactor volumes will be smaller, and it would be more suitable for large-scale production. Usually the catalyst is nickel-based catalyst in traditional catalytical methanation process and methanogens are used as biological catalysts. (Götz, et al. 2016)

The catalyst type determines which reactor types could be used in methanation. For catalytic methanation, the fixed bed reactor is the most common approach for its simple operation and easiness to build. It has uniform temperatures, which is positive in high temperature processes. Fixed-bed reactors are usually adiabatic reactors, but isothermal reactors are also a possibility. A fluidized bed-reactor is also a possibility for its more effective heat removal resulting that the number of used reactors is lower. It has drawbacks with catalyst deactivation, bubbling and its limitations in superficial gas velocity. There are other concepts also like three-phase fluidized bed reactors and structured reactors such as monolith reactors to tackle issues in more traditional reactor concepts. For average sized methanation plants the fluidized bed reactor is stated to be most effective and for large scale (over 100 MW) production the fixed bed reactor is the most suitable. Figure 12 shows the reactor options for both methane production with metal and biological catalyst. (Götz, et al. 2016)

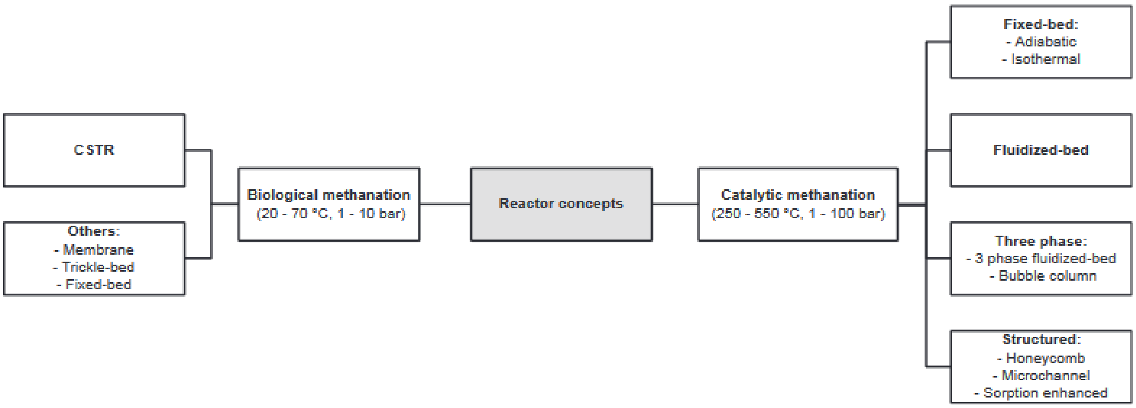

Figure 12. Reactor options for methanation. (Götz, et al. 2016)

Biological methanation has fewer options for reactors. The most common reactor is the continuous stirred reactor (CSTR), but other reactors are being researched like fixed-bed, trickle-bed, and membrane reactors. The interesting case for biological methanation is that it can be performed in in situ conditions instead of in separate reactors (ex situ). Its idea is that produced hydrogen from electrolyzer is fed straight into anaerobic digester in biogas production to convert the carbon dioxide into methane. It has some issues with getting high CO_2 conversion, but it could be a low-cost option to boost methane production rates in biogas production. Figure 13 shows the process of in-situ methanation. (Götz, et al. 2016)

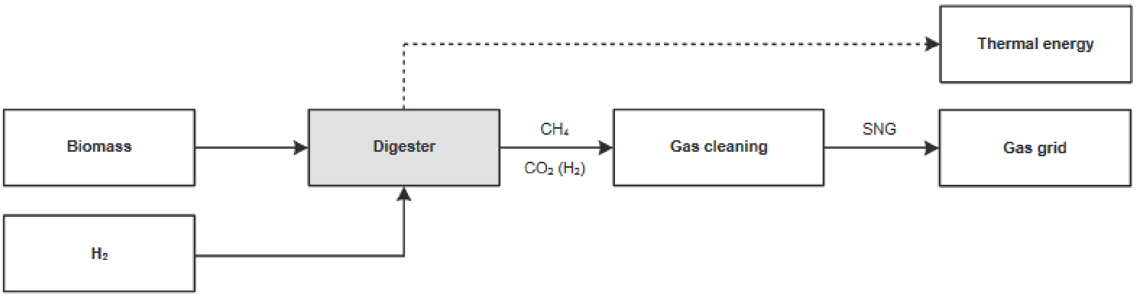

Figure 13. In-situ methanation process flowchart. (Götz, et al. 2016)

Utilizing electrolysis and methanation would make the process a P2G process. Water and electricity would produce green hydrogen, which would then be used to produce methane with CO_2. It is attractive from carbon footprint reducing point of view. There are some uncertainties in the process in terms of costs. Operating costs will depend on electricity prices, plant efficiency and CO_2 accessibility. Figure 14 shows the concept of utilizing electrolysis and methanation together. (Bassano, et al. 2019)

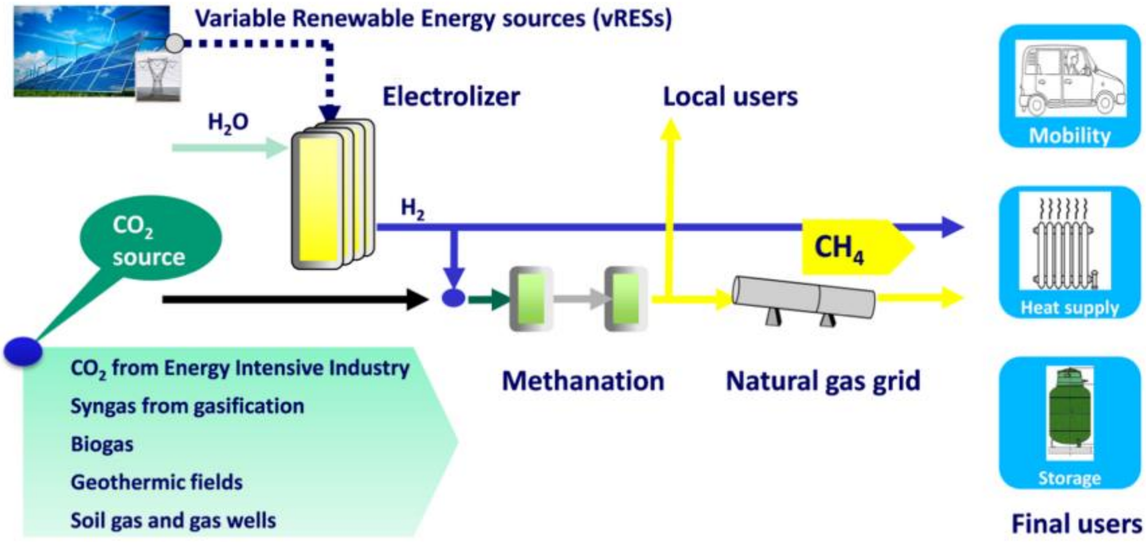

Figure 14. Concept of using methanation and hydrogen production process as power to gas method. (Bassano, et al. 2019)

5.1.2 Methanol production

Another option could be methanol synthesis using CO_2 as feedstock. Traditionally methanol is produced from syngas, which is acquired from processes using fossil fuels like natural gas reforming and coal gasification. Equations 16 & 17 show the two-stepped synthesis of methanol and equation 18 shows the combined reaction. (Borisut & Nuchitprasittichai, 2019)

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \Delta H_{300K} = 41{,}2\ kJ/mol_{CO_2} \tag{16}$$

$$CO + 2H_2 \leftrightarrow CH_3OH \qquad \Delta H_{300K} = -90{,}4\ kJ/mol_{CO_2} \tag{17}$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad \Delta H_{300K} = -49{,}2\ kJ/mol_{CO_2} \tag{18}$$

Methanol-process produces by-products, which would have to be removed. Main impurity is water in the synthesis process, so straightforward way to remove it would be distillation process. It also has potential to fit into the waste treatment industry, because it can get CO_2 from flue gases or from a biogas plant. Research for sensitivity of methanol production was made and the calculated costs of methanol production was around 517 € per ton produced methanol (Borisut & Nuchitprasittichai, 2019). Using “free” hydrogen and carbon dioxide does bring down the overall costs of the methanol process. Figure 15 shows the concept of the power-to-methanol (P2M) process. (Cui, et al 2022)

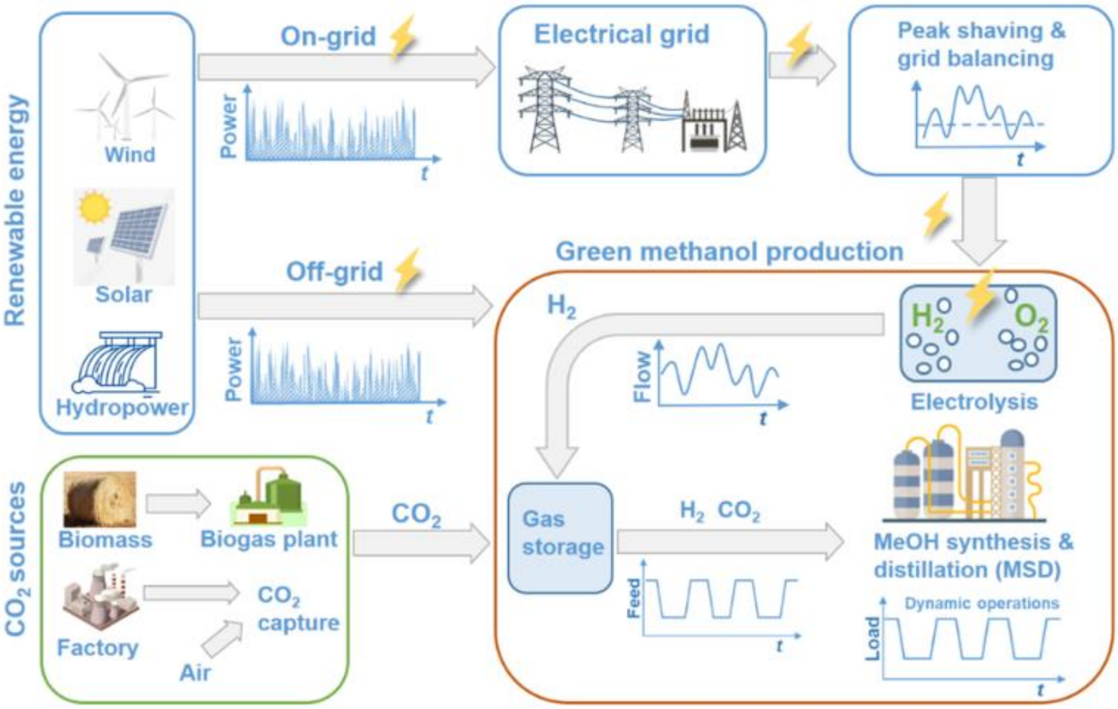

Figure 15. Power-to-methanol concept idea. (Cui, et al 2022)

5.2 Oxygen and heat utilization

By-products from the electrolysis process are oxygen and excess heat, and methanation also produces heat as by-products. From material and resource recovery point of view, utilizing by-products is a major step to optimize process and make it more profitable. A simple option for using by-products is just to sell them for pure profit, but if there is not a strong market for the products, it can be challenging to find potential customers. Oxygen has few uses in other industrial fields. It is used in chemical, steel and pulp and paper industries as material to enrich air's oxygen amount. Also, the medical field uses oxygen in medical treatment in oxygen therapy. Oxygen used in the medical field is referred to as medical oxygen. (TUKES, 2003) Oxygen could be sold at 46 €/t. Oxygen could also just be released to air, because just selling it would require investing in storage and transportation of the gas, giving additional costs. Waste heat of the process could potentially be sold as process heat. There is potential to connect waste heat to district heating network, but there are strict restrictions on the temperatures of the excess heat (Stack, et al. 2023). The selling price for the heat is 23 €/MWh. The heat could be used for heating various operations in plant site. Many processes use heat to maintain operation conditions of the process. The excess heat could be used to balance high energy demand of the electrolysis process.

5.2.1 Oxygen utilization in WWTP

There is potential in utilizing oxygen in wastewater treatment. Some biological processes like aerobic reactors, tanks and sludge activation processes utilize air as raw material, so utilizing recycled oxygen could give cost reduction benefits. As a result, air is changed into pure oxygen (PO) or oxygen enriched air. The aeration step is the phase where air circulates through the fluid causing water and air to make close contact with each other. Its main functions are promoting microbial growth and creating flocks on the surface. Main removals of aeration are compounds, which the microbes react with, like dissolved gases and metals, sulfides and volatile organic chemicals. It is a major step in the active sludge process. It has been researched to improve treatment rates, enzyme activity and less sludge and foam production. Pure oxygen is recommended when high strength wastewater is treated. The issues are that it is linked with pH drops and there is still quite little research about the impact of pure oxygen on wastewater treatment. (Skouteris, et al. 2020)

Oxygen can be converted to heat using various combustion processes. It can be used to enrich the air's oxygen concentration to increase productivity, energy efficiency and flame stability. It is used in metal heating and melting, glass melting and calcining, which have high flue gas temperatures and low thermal efficiencies. Burning waste with oxygen enriched air is one potential solution for waste treatment for oxygen utilization. It has been experimented in waste incineration process by influencing the temperature of combustion chamber, flue gas recirculation and concentration of oxygen in combustion air. Results showed that the O_2-enriched air could achieve higher exergy values and notable environmental benefits. Optimal oxygen purity for the enriched air was 60%. (Vilardi & Verdone, 2020)

Another use for oxygen would be production of ozone (O_3). Ozone is a strong oxidant used in various processes in WWTP and the food industry. Its main function is to act as disinfectant or as sanitizer. It has unique quality to produce secondary oxidants and free radicals in aqueous conditions to enhance its oxidizing power. Ozone is expensive to use, and its unstable nature makes it hazardous to transport. Being able to produce in the same facility as it is used would negate the drawback of the ozone. Ozone is produced when an oxygen atom reacts with oxygen molecules. There are few ways to create oxygen atoms. UV light can naturally split oxygen molecules into atoms, and this process occurs also in the ozone layer. Lighting can also generate ozone. A sudden electrical spark can momentarily split oxygen into atoms. During this brief period, the atoms react with nearby, still-intact oxygen molecules, resulting in the generation of ozone. Traditional commercial production methods are based on these phenomena, where either UV-light or electricity is used to split oxygen. Ozone could be produced in the same electrolysis process as hydrogen, but it would require a more advanced system to favor the oxidation into ozone for example capillary effect-based electrolysis or circulating water electrolysis system. (Okada, et al. 2019)

5.2.2 Sludge Treatment & Heat utilization

Sewage sludge is the by-product of the wastewater treatment process, where various categories of sewage sludge are obtained during wastewater treatment. The quantity and quality of sewage sludge depend on the source of wastewater and its treatment stage during wastewater treatment. Traditionally, sewage sludge has been considered a liability, the safe management of which is achieved through landfilling, which endures vast land requirements and operational costs prior to dumping. (Pöyry Finland, 2019)

Sludge pyrolysis is a method to produce biochar from sewage sludge. In the process, the sludge is pre-treated by removing water from the sludge by dehydration step. Drying is the most common method, and the main objective is to increase sludges' total solid (TS) content. Then there is the degradation step, where the sludge is split into char and into multiple smaller gases like hydrogen or methane. The moisture content of sludge before thermal treatement is recommended to be about 60% (Zhou, et al. 2023). The total heat demand for the process is around 550-800 kWh/ton sludge, if there is thermal drying included. (Pöyry Finland, 2019) (Naqvi, et al. 2019) Using waste heat from electrolyzer to maintain high operational temperatures of the process would decrease energy intensity and decrease operational costs of the process. Figure 16 shows the visualization of sludge pyrolysis process (ELIQUO, 2023).

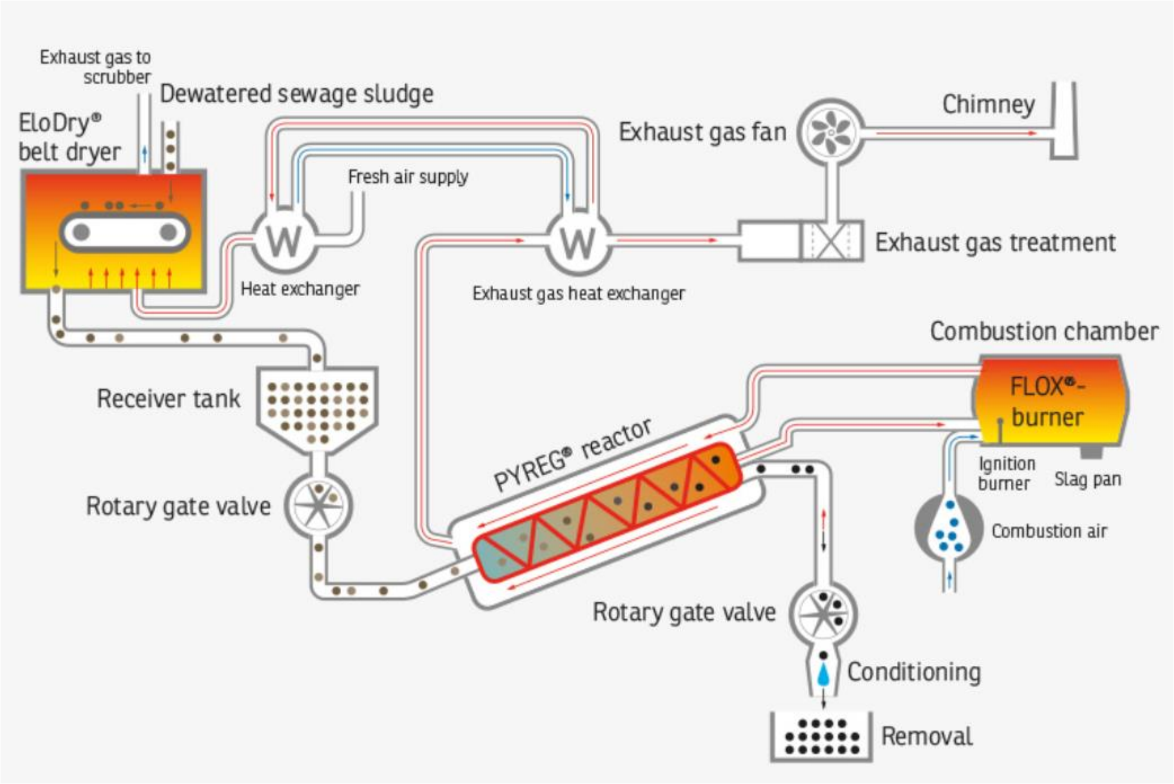

Figure 16. Sludge pyrolysis process using PYREG reactor and EloDry dryer. (ELIQUO, 2023)

Thermal hydrolysis is a process for treating waste and sewage sludge. It is thermal treatment of wet waste at a high temperature and pressure to make it more biodegradable. Heat cuts down the big and complex polymers, enzymes and bacteria into simpler monomers or oligomers, which makes them faster to compost. This is generally used as pre-treatment method for waste in biogas production. It increases reaction rates of the process because the simpler components in waste will react faster. It operates in temperatures between 120-200 ºC and is usually operated at a pressure of 7 bar, so the process has high energy consumption but like in pyrolysis the excess heat could be utilized in heating the thermal process and it would also increase in biogas production over time. (Barber, 2020)

5.3 Conclusions for theoretical part

This subchapter summaries the theoretical part and its main takeaways. Chapter 2 discussed the current situation and future potential of hydrogen economy and chapter 3 discussed the basic principles of wastewater treatment and its current situation. Wastewater treatments main ecological issue is its high energy consumption. The process is vital to human life, because it recycles water. As a result of that, the only solution for wastewater treatment is to find solutions to reduce its carbon footprint. Hydrogen is discussed for its future potential as green energy source for its high energy content and flexibility in use. It has potential in reducing carbon footprint in areas, where reducing emissions are challenging. The potential of hydrogen in WWTP is to balance its energy intensity.

Chapter 4 discussed hydrogen production via electrolysis and technological challenges of using treated wastewater as water source for electrolysis. Water electrolysis is an electrochemical method using water and electricity to produce hydrogen, oxygen and heat. Impurities in water has an impact on electrolysers performance. Treated wastewater has high conductivity and total organic carbon (TOC) values, which makes pre-treatment of water necessary before electrolyser. Commercial alkaline electrolysers does vary usually between 1 kW and 5 MW, but there exists already plants with over 100 MW total power input. Cost of electricity is a problem with large scale plants, but using renewable energy sources like solar energy and utilizing products and by-products can be used to mitigate the problem.

Chapter 5 highlighted the potential utilization of electrolyzer products and carbon dioxide. Electrolyzer produce hydrogen as main product and oxygen and excess heat as by-products. Hydrogen in synthesis route with CO_2 was researched utilization method for hydrogen. Methane and methanol productions are two synthesis routes, where hydrogen and CO_2 are raw materials for the process. Methane production seems more sensible route for EcoSairila, because BioSairila already has methane production from biowaste. The infrastructure and market for methane already exists in EcoSairila, so the role of the methanation process would be a boost for methane production and decrease of carbon emission from BioSairila.

Oxygen and excess heat has few potential utilization methods in aeration and sludge treatment, but also has potential in just reducing energy demand of processes in WWTP and biogas production. The potential process of methanation and electrolyzer does produce gases like hydrogen and methane in various parts of the process. Gas storage and transportation becomes important factor for feasibility of the process. For a temporary storage of light gases like hydrogen a compressed tank is a reasonable choice. Liquid storage is quite commonly used in gas transporting, so a methane, which needs to be transported, and carbon dioxide, which comes in liquid form when bought, does require liquid storage.

6 Materials & Methods

In this thesis, mass and energy balances are used to do rough simulations for the wastewater treatment plant, hydrogen production and hydrogen utilization. Equations used for balances do differ from unit to unit and process to process, because there are distinct factors, compounds, and chemical reactions in them. Rough and simplified cost estimations were done from mass and energy balances and the process feasibility was evaluated.

6.1 Mass Balances

Mass balances are a distribution of inlet and outlet streams that flow in the system, and they can be used to determine quantities of raw material and products produced. Mass balances are the basis of process design. Balances over individual process units set the process stream flows and compositions and provide the basic equations for sizing equipment. Mass balances are also useful tools for understanding plant operations and finding problems in the process. They can be used to check performance against design, to extend the often-limited data available from the plant instrumentation, to check calibrations, and to find material loss sources. Material balances are essential to obtaining high-quality data from laboratory or pilot plants. Mass balance has been discussed in detail in literature (Equation 19). (Paoletti & Nastri, 2021), (Towler & Sinnott, 2007)

$$Material\ out = Material\ in + Generation - Consumption - Accumulation \tag{19}$$

Material inlets and outlets can be described as a unit of mass, concentration, or volume. For a steady-state process, the accumulation term is normally zero, because the objective is to have the same amount of material flowing in and out of the process. In most chemical processes, chemicals are generated and consumed. When chemical reactions occur, a particular chemical species may be formed or consumed in the process. If there is no chemical reaction, the steady-state balance reduces to that material outlet is equal to material inlet. Many separation units are an example of this. (Paoletti, I. & Nastri, M. 2021), (Towler, G. & Sinnott, R. 2007)

6.2 Energy Balances

There is a relation between energy and mass as stated in one of the most famous principles of Physics by Albert Einstein, the mass-energy equivalence. Because of that, there exists a balance for energy also. It can be used to determine the energy requirements of the process: the heating, cooling, and power required. In plant operation, an energy balance (energy audit) of the plant will show the pattern of energy use and suggest areas for conservation and savings. Energy balance for a unit mass of material is stated in as (Equation 20) (Paoletti & Nastri, 2021), (Towler & Sinnott, 2007):

$$Energy\ out = Energy\ in + Generation - Consumption - Accumulation \tag{20}$$

Inlet and outlet streams for energy are the amount of heat the streams carry in and out of system, visible as the stream's temperature. Accumulation in the energy balance means how much energy is stored in the process. In steady state processes, the mass flow in and out of the process is supposed to be equal even if there is chemical reaction occurring. With energy this, however, is not always the case because chemical reactions can either release or consume energy based whether they are exothermic or endothermic reactions. It is caused by chemical bonds breaking and forming. Energy can exist in several forms, including chemical energy, heat, mechanical energy, and electrical energy. The total energy is conserved, but energy can be transformed from one kind of energy to another. Energy balances can be quite massive and complicated at times, if there are multiple variables, energy types and reactions in the system at same time. (Paoletti & Nastri, 2021) (Towler & Sinnott, 2007)

6.3 Cost Estimations

Cost estimations are an important way to evaluate the process. The processes' main function is to make profit, which means it is important to know what is achievable with the process before building it. A simple way to calculate the profitability of a process is by calculating net cash flow (NCF). Equation 21 is the NCF of the process (Towler & Sinnott, 2007):

$$NCF = CF_{in} - CF_{out} \tag{21}$$

where CF_{in} Cash flow inside of company

CF_{out} Cash flow outside of company

Cash flow can be divided into three categories: investments, operations, and financing. Investments consist of primarily the capital expenses (CAPEX) and other fixed assets like property and equipment. CAPEX in process costs consists of investment in process equipment's like reactors, piping & etc. There exists an estimation for process CAPEX from literature like for alkaline electrolyzers it is usually around 500-1000 €/kW depending on the scale of the process (Proost, 2018). There are also fixed investments expenses like workforce & engineering, they can be calculated as % of equipment costs. Operations mainly consists of operational expenses (OPEX) of the process. There are two OPEX values: fixed and variable. Variable OPEX is mainly the cash flow of the input and output streams of the process. Meaning how much profit is made by selling the products and costs of the raw materials, additive chemicals, and energy. Fixed OPEX are the costs which go to maintaining the process like salaries, maintenance & etc. There exists a % of CAPEX values for these fixed costs in literature. Financing is the company's cash impacts financing activities like debts and shares. (Leeuwen, et al. 2018), (Al-Breiki & Bicer, 2023)

The processes' payback time can be calculated by dividing investments with annual cashflow. Equation 22 shows the formula for payback time. (Towler & Sinnott, 2007)

$$Payback\ time = \frac{Investement}{Annual\ cashflow} \tag{22}$$

Payback time tells the required time when the process turns from losses to profit. It doesn't take account of building time but can be used to calculate buyback time from the start of the operation, so it is quite simple calculation to evaluate process performance.

7 Case EcoSairila

This chapter discusses the relevant procedures before process simulations. It highlights the processes of EcoSairila, BioSairila, chosen electrolyzer and hydrogen utilization method. The mass and energy balances are calculated for the processes and then the suitability is evaluated and briefly explained potential by-product utilization locations.

7.1 Process Showcases

In this subchapter, the processes of EcoSairila WWTP (wastewater treatment plant) and BioSairila biomethane production plant are displayed and explained. The processes are based on data from the MetsäSairila plant site. Then, the mass and energy balances from the plants are showcased to highlight the available streams to use in fitting the P2X method into the process.

7.1.1 EcoSairila WWTP

EcoSairila WWTP uses wastewater from Mikkeli and its surrounding municipalities. Daily wastewater consumption is around 8000-24000 m^3/d depending on the time of season. Maximum capacity for wastewater consumption is 33000 m^3/d. Firstly, the water goes through a three-stepped mechanical preliminary treatment process. Main idea is to remove undissolved and visible contamination like grit and remove random debris, which can damage the process equipment. First, it goes through bar screens, which removes large objects and debris from the water like plastics and cloths. After bars, ferric sulfate is added for phosphor removal. The second pre-treatment step is sand separator, which removes heavy gritty substances by using high speed turbulent water flow to separate the heavy substances from lighter ones. After grit removal, the wastewater goes through fine screens to remove smaller contaminations, which the first two steps could not remove, and can cause problems and damage to the main process itself.

Pre-sedimentation is the next phase after pre-treatment. It is the primary treatment method which main purpose is to remove solid matter and parts of the organics from the water before biological treatment. Sludge is generated from pre-sedimentation and is collected by pumping it from the bottom of the tank. It is mechanically dried using a spin-dry mechanism. EcoSairila produces daily about 17800 kg of sludge. Dried sludge from EcoSairila is delivered to BioSairila biomethane plant to produce biomethane.

Before the next step, there is an inlet for sodium hydroxide (NaOH) to improve phosphor removal. The secondary treatment method is the membrane bioreactor (MBR) step. It uses six chambers with some of them being aerated and some without oxygen. Air is used as oxygen source for the aerated process and air stream is about 5-6 kg/d. The main target removals are nitrogen-based components like ammoniums and organic matter. After that comes the MBR-filters, which replaces secondary sedimentation, polishing and UV-disinfection steps from traditional process. Powdered activated carbon (PAC) is added to decrease membrane fouling. It has lower pressure drops, it does not consume as many chemicals and its energy consumption is lower than traditional processes. Energy consumptions in MBR-processes are around 0.79 kWh/m^3. Treated wastewater is then released to lake Saimaa. Bioreactors does produce CH_4 and N_2O emissions, but the direct emissions are usually quite minimal from WWTPs. Figure 17 shows the flowchart of EcoSairila WWTP.

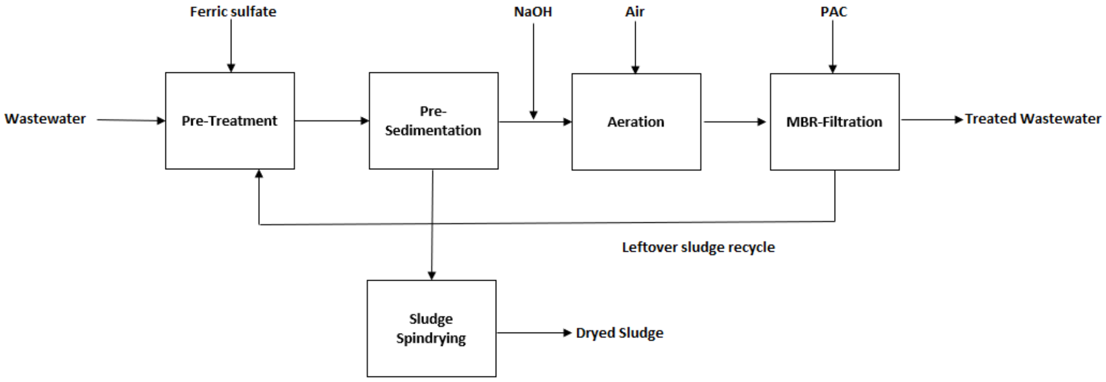

Figure 17. EcoSairila WWTP block flowchart.

7.1.2 BioSairila Methane Plant

BioSairila biomethane plant uses dried sludge from EcoSairila and various packed and unpacked biowaste to produce biogas, which is then refined into methane. Firstly, they are pre-treated by pre heating the biowaste and sanitization of sludge. After pre-treatment the plant uses three mesophilic reactors to produce raw biogas with anaerobic digestion in low temperatures. Each reactor is sized 535 m^3. One of the three reactors uses sludge as raw material and the other two focuses on biowaste. Reactor temperatures are about 35-40 ˚C and biogas production rates average around 230 m^3/h. It also produces digestate as by-product, which is unreacted biowaste and sludge. It can be separated into liquid and solid digestates. There is a separator for dividing these two phases into solid and liquid outlet streams. They are then transported to another location for use.

Raw biogas is stored in gas storage, which is used to control gas inlets to gas refining step and combustion. Around 10-20% of biogas is recycled into heat by burning it in combustion. Heat is used to maintain temperatures in pre-heating of biowaste and in bioreactors. The main use for biogas is that it is refined into biomethane by removing excess gases and impurities from it and therefore increasing methane purity. The other main component in biogas, aside from methane is carbon dioxide (CO_2) and it is the focused removal in the gas reforming step. Gas reforming is a multi-stepped and quite complicated process, but the end-product is biomethane and by-product gas mostly consisting of CO_2 and its purity is always over 95% and is usually quite close to 99%. The impurities in the gas are considered methane. Figure 18 shows the flowchart of BioSairila biomethane plant.

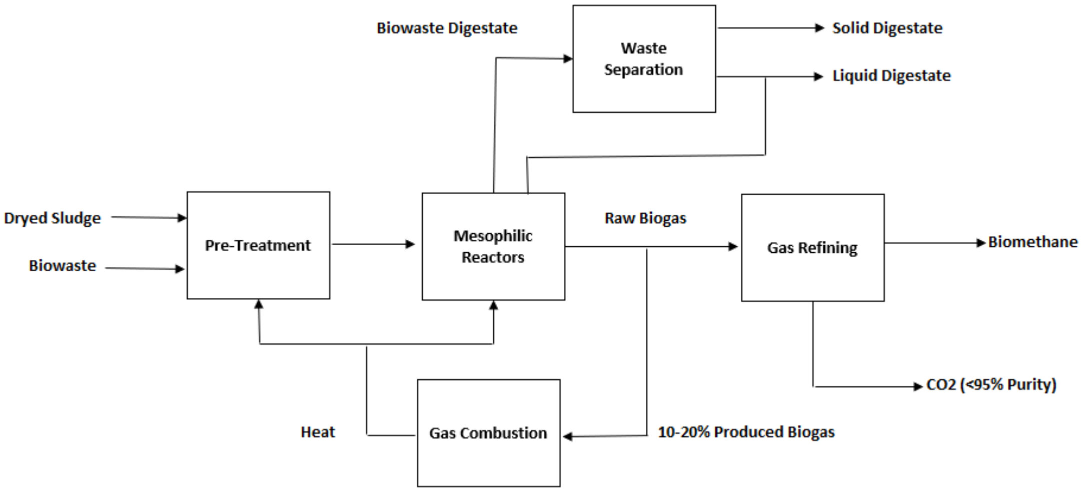

Figure 18. BioSairila block flowchart for methane production.

7.1.3 Available Streams

In this thesis, the outlet stream of treated wastewater is used in simulations. EcoSairila aims to keep inlet and outlet streams flow rates similar to each other, so the outlet streams daily flows are similar 8000-24000 m^3, which should be easily enough to satisfy electrolyzer even, when taking account the potential water losses in pre-treatment unit. Carbon dioxide stream from BioSairila is used as synthesis route for chosen P2X- method. BioSairila states that the carbon dioxide production from gas refining is around 115 m^3/h, which is about 5400 kg/d. With CO_2:H_2 conversion of 1:4, the required hydrogen amount would be around 1000 kg/d. It is a pretty low number compared to how much hydrogen 100 MW electrolyzer can produce, which is around 40000-45000 kg/d. As a result of that, it can be assumed that rest of the needed carbon dioxide is bought.

7.2 Chosen P2X method

In this subchapter, the chosen P2X method for electrolysis and hydrogen utilization is chosen. The unit parameters used in simulations are also shown in this subchapter. The chosen process was Alkaline electrolyzer combined with carbon dioxide (CO_2) methanation unit to produce methane as power to methane process.

7.2.1 Alkaline Electrolyzer for P2X-Process

In this thesis a 100 MW alkaline electrolyser was used to produce hydrogen from treated wastewater. Treated wastewater needs to be first diluted into Ultrapure water (UPW) as pre-treatment to lower water conductivity and total organic carbon (TOC) levels. The random ions can hamper electrolyzers performance, so they need to be removed. Reverse osmosis (RO) causes some water losses in water stream, and in case of treated wastewater, the losses are about 33%, meaning that water inlet to pre-treatment unit needs to be about 1,5 times the water demand for electrolyzer. In this thesis the pre-treatment unit was not the focus, but a standard RO + CEDI unit is taken into account, when making cost estimations. Proosts (2018) economic evaluation of alkaline electrolyser does have taken account the water deionizer in capital expenses. Electricity consumptions for CEDI and RO are 0.26 & 5-13 kWh/m^3 produced water, which means that RO-process has major impact on electricity consumption of pre-treatment unit (Wood & Buzzell, 2020).

Alkaline process was chosen for this thesis as the method for producing hydrogen. The reasoning for choosing the alkaline over more efficient PEM was the maturity of alkaline technology and the low costs used for large scale production. Chosen unit size is 100 MW, because there are already some commercial units available for this sized electrolyzers like HELA1000 by SinoHy Energy. HELA1000's stated water demand is 480 m^3/d, which is enough to satisfy from EcoSairila treated wastewater streams even, when taking the water losses from the pre-treatment into account. HELA1000 starting values are used as starting values for mass balance calculations. De Groot et al (2022) made research for optimal operating conditions for alkaline electrolyzers. The results were that temperature window of 80-100 ˚C and pressure of 5 bars were optimal for large-scale electrolyser systems, where waste heat and footprint of plant is important. Commercial alkaline electrolyzers usually uses 30 wt% KOH solution as electrolyte and it is the chosen electrolyte. Alkaline electrolyzers expected stack lifetime is around 7-10 years, which would be target for the buyback time of entire process. (SinoHy Energy, 2023)

Electrolyzer needs a cooling method to keep operation temperatures stable. Cooling water demand is 100320 m^3/d in HELA1000 electrolyzer, so that means the EcoSairila treated wastewater cannot be used in the cooling system (SinoHy Energy, 2023). For large scale electrolyzers cooling towers are commonly used as the cooling method and there are two options for that, the wet and dry methods. The dry cooling methods' advantage is that it does not use any water and is often the only option available when water is not available. It is though more sizeable and needs more capital expenses than the wet method. In MetsäSairila there is lake Saimaa as a potential available water source for cooling water nearby, where the treated wastewater normally is returned. So, in theory, the water demand for wet cooling tower could be satisfied, and therefore it is the chosen method for this thesis work. It doesn't have a huge impact on simulations, but in cost evaluation it is taken into account.

For hydrogen, a storage method between electrolyzer and methanation unit is recommended for process control. There exist hydrogen storages, which can store hydrogen at 100 bars, where hydrogens density is 7.8 kg/m^3. So, for approximate 42 t daily hydrogen production, a 5000 m^3 sized storage would be able to store most of the days production because it is only a temporary storage for methanation and in normal circumstances, there should always be a steady flow in and out of the tank. Oxygen is not utilized in this thesis other than calculated as outlet stream. To reduce costs, oxygen is just released into the air. In Table 1, the parameters for 100 MW electrolyzer unit are shown, which are then used in simulations and in cost evaluation.

Table 1. Working parameters for Electrolyzer

Unit/Component	**Explanation/Value**	**Source**
Electrolyzer	**100 MW power output, 20000 L/h water demand, 80-100 ˚C, 5 bar**	SinoHy Energy, 2023, De Groot, et al 2022
CAPEX	500 €/kW	Proost, 2018
FIXED OPEX	4% of CAPEX	Leeuwen, et al. 2018
Hydrogen	**Storage 5000 m^3, 100 bar**	-

CAPEX	100 €/m^3	Leeuwen, et al. 2018
FIXED OPEX	1.5 % of CAPEX	Leeuwen, et al. 2018
Oxygen	**Released in atmosphere**	-

7.2.2 Hydrogen utilization for P2X

There are two synthesis options to use hydrogen and CO_2. Both methanol and methane can be produced with these raw materials. The chosen method was the methanation route, because BioSairila already has the infrastructure ready for methane utilization, so the aim of this thesis would be to boost methane production rates in MetsäSairila concern.

CO_2 is one available resource from the Gas refining step of BioSairila's biomethane production. Since CO_2 s purity is somewhere between 95-99 % and the rest of it is estimated to be pure methane, the carbon dioxide only needs to be compressed and stored from the gas refining step and then just directed to methanation reactors. 5400 kg/d CO_2 production in BioSairila is around 0.22 t/h, which is quite limited in amount so the rest of the carbon dioxide should then be either bought or captured directly from the air. Prices of carbon dioxide vary from the sources they are acquired. The average selling price of carbon dioxide in Finland 105 €/t CO_2 was used for cost calculations. Usually, carbon dioxide is sold in liquid form in Finland, so it would also be used as storage method. A 200 m^3 liquid storage is used in cost estimations for this thesis.

In the theoretical part, it was stated that methanation with metal catalyst would be more suitable for average and large-scale production of methane. The carbon dioxide coming from BioSairila is of high quality to not have many issues with metal catalysts, which makes catalytic methanation the better option. The scale of methanation plant would be approximately 50-60 MW production, so the fluidized bed reactor or the three-step fluidized bed reactor would be suitable for the process. Methane can be stored in liquid form to save the required space for storage. There exist storage tanks, which can store liquid carbon dioxide and methane. The price for 200 m^3 storage would be 28 000 € for piece. The price of the catalyst is not taken into account because it does not have a huge impact on operational costs. In Table 2, the parameters for methanation units are shown, which are then used in simulations and cost evaluation.

Table 2. Parameters used in methanation calculations.

Unit/Component	**Explanation/Value**	**Source**
Methanation	**0.01 MW power output,** **Nickel Catalyst,** **250-550 ˚C, 1-100 bar**	Wai, S. et al. 2020 Götz, M. et al. 2016
CAPEX	400 €/kW	Leeuwen, C. et al. 2018
FIXED OPEX	10% of CAPEX	Leeuwen, C. et al. 2018
Carbon Dioxide	**Storage 200 m^3**	-
CAPEX	28 000 €	Alibaba, 2024
FIXED OPEX	3.5 % of CAPEX	Leeuwen, C. et al. 2018
Synthetic Methane	**Storage 200 m^3**	-
CAPEX	28 000 €	Alibaba, 2024
FIXED OPEX	2 % of CAPEX	Leeuwen, C. et al. 2018

7.3 Side stream utilization

One of the objectives of this thesis is to map the potential uses for electrolysis by-products and try to highlight a few areas where they could potentially be utilized. There are few areas where EcoSairila and BioSairila processes could be improved. One of the main weaknesses of wastewater treatment is its energy consumption, since it uses multiple large units with most of them needing to be operated in set temperatures and pressures. Electrolysis process also consumes massive amounts of electricity so, utilizing the by-products in energy generation has the potential to energy savings and balancing the energy intensity of process. BioSairila uses its biogas to heat its heat-demanding reactors and pre-treatment, so if the by-products like the waste heat would be used in heating the reactors, then all the produced biogases could be used in biomethane production therefore increasing productivity of the process. Sludge treatment in WWTP's side is only done with mechanical drying. Although it is enough to satisfy BioSairilas needs, there are some questions about whether it could be improved on.

Both electrolysis and methanation produce waste heat as by-products so it could be used in areas, which were previously stated. It could simply be used as a heat source to replace the gas combustion in BioSairila or decrease energy demand of wastewater treatment. There exist various sludge treatment processes with high energy intensity, which could benefit from free heat source. For example, pyrolysis process for biochar production and thermal hydrolysis as alternative pre-treatment of sludge could be attractive options for utilizing waste heat. Connecting waste heat to district heating is also an option, but temperatures with waste heat stream and district heating network might not be compatible making it not sensible.

Oxygen has a bit more variety, with its utilization potential. It could be used in combustion to improve efficiencies in combustion of biological fuels, with quite low combustion efficiencies. So, it could be another alternative heat source along with waste heat if needed. Aeration in WWTP uses air as oxygen source for its free cost and unlimited availability. There are articles experimenting with higher oxygen purity streams in aeration causing positive impacts on production efficiency. The issue with that is that buying oxygen for that purpose is not worth it, but if the source would be free, it would be worth experimenting with mixture streams or even with pure oxygen. Oxygen could also be used in producing ozone with on-site production, which would be more beneficial than buying ozone. Ozone is an expensive gas, because of it being unstable and naturally decomposes to oxygen, making transporting it challenging. There are articles on how ozone could be used to reduce membrane fouling in MBR-process. Table 3 shows the utilization potential of oxygen and excess heat.

Table 3. Potential use for Oxygen and excess heat.

Oxygen	**Potential uses**
Pure Oxygen	Sold as profit, Ozone production
Enriched Air	Aeration air stream, Combustion
Excess heat	**Potential Uses**

Process heating	Decrease energy consumption for various units e.g. biogas reactors in BioSairila
Sludge Treatment	Sludge pyrolysis, Thermal Hydrolysis

8 Simulations

In this chapter, the simulations of power to methane with alkaline electrolyzer combined with methanation with biological catalyst are shown. Rough cost estimations are also made based on capital (CAPEX) and operational expenses (OPEX). This chapter also shows some analysis of the results and has some discussion on positives and some potential improvements.

8.1 P2M Process simulations

In this subchapter, the process flowchart for the simulated process is shown and then the results are shown. Figure 19 shows the simplified flowchart of the combined process. Treated wastewater is firstly pre-treated into ultrapure water (UPW). About 33% of the water is lost during pre-treatment, so then the water inlet into pre-treatment needs to be 1.5 times the water inlet into electrolyzer. Electrolyzer is then used to produce hydrogen with the rate of 43 t/d. It produces waste heat and oxygen as side streams, which could be utilized effectively to lower the costs of the process. Hydrogen is separated and stored before reactors. Methanation reactors use all the produced hydrogen with enough carbon dioxide. It can produce 3.6 t/h methane with high conversion rates, which are achievable in CO_2 methanation. The production size is approximately 55 MW in heating value, when calculated from higher heating value of methane. Appendix 1 shows the calculations for the balances.

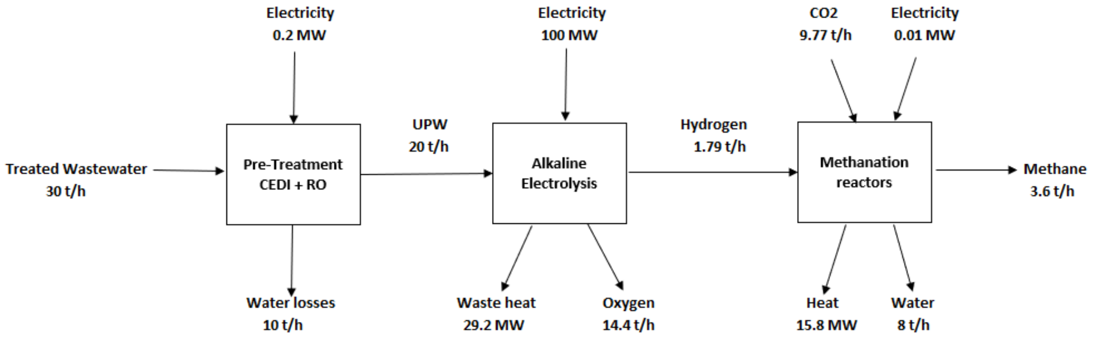

Figure 19. Flowchart of Power-to-methane system for EcoSairila.

Carbon dioxide demand is around 9.77 tons per hour, so that means the BioSairilas around 0.22 tons hourly production of CO_2 is clearly not enough. It only consists of 2.2 % of the total carbon dioxide demand. The rest of carbon dioxide captured directly from air would be hugely expensive, because energy consumptions would be enormous. Low temperature solid sorbent-based DAC would require 250 kWh/t CO_2 electricity and 1750 kWh/t CO_2 heat demand, which would mean that it would use about 57 MW of electricity and over 400 MW of heat. It would be more sensible to buy carbon dioxide from another supplier.

8.2 CAPEX/OPEX

There already exist evaluations of capital expenses (CAPEX) values based on production rates or sizes of the plant. These values include all the fixed variables included in CAPEX like engineering costs. The installation, planning and other fixed investments are estimated to be 28% of equipment costs. (Leeuwen, C. et al. 2018) Table 4 shows the capital expenses of the process. Appendix 2 shows the calculations for capital expenses.

Table 4. Capital expenses of the process calculated from starting values. (Leeuwen, C. et al. 2018)

Equipment	**Size**	**Value**
Electrolyzer	100 MW	50 000 k€
Hydrogen Storage	5000 m^3	500 k€
Methanation Reactor	55 MW	22 000 k€
CO_2 Storage	200 m^3	28 k€
CH_4 Storage	200 m^3	28 k€
Installation, Planning & Design	28% of equipment	20 320 k€
Total		92 871 k€

Operational expenses (OPEX) are separated into two categories: variable and fixed OPEX. Variable OPEX's are prices and costs of the streams in this process. Fixed OPEX are the operational costs of the process units and are stated as % of CAPEX of the unit. The yearly production is expected to be 8000 h (333.33 days). Electricity price is set to a 40 €/MWh and the price of selling heat is set to 23 €/MWh. Table 5 shows the production costs of the process. Appendix 3 shows the calculations for operational expenses.

Table 5. Operational expenses of the process calculated from staring parameters. (Al-Breiki & Bicer, 2023), (Kiviranta & Linjala, 2023), (Leeuwen, C. et al. 2018)

Mass Balances	**Price**	**Cost/Profit per year**
CH_4	1 840 €/t	53 050 k€
CO_2 Bought	-105 €/t	-8 034 k€
Energy Streams	**Price**	**Cost/Profit per year**
Electricity Electrolysis	-40 €/MWh	-32 000 k€
Electricity Methanation	-40 €/MWh	-3.9 k€
Electricity Pre-Treatment	-40 €/MWh	-64 k€
Heat Electrolysis	23 €/MWh	5373 k€
Heat Methanation	23 €/MWh	2870 k€
Fixed OPEX	**% from CAPEX**	**Cost/Profit per year**

Electrolyzer	4	-2 000 k€
Hydrogen Storage	1.5	-7.5 k€
Methanation Reactor	10	-2 200 k€
CO_2 Storage	3.5	-0.98 k€
CH_4 Storage	2	-0.56 k€
Total OPEX		16 900 k€

The simple payback time by dividing capital investments with profit from process would make 5.5 years, which would be before to electrolyzer stacks expected lifetime (7-10 years). It is sensible to electricity price, however. With electricity price of over 61 €/MWh the process starts to make losses if other base values are same. In a modern world, where the price of electricity can have a huge variance, some problems may occur with processes with high electricity consumption. These are only rough calculations with a lot of financial aspects like debts, capital, loans and interest rate for the investment being left out from calculations to simplify it.

8.3 Results Analysis

From the mass balances a 55 MW hourly production of methane can realistically be achieved from 100 MW alkaline electrolyzer. There was research made by Al-Breiki & Bicer (2023) with 10 MW PEM electrolyzer, where 6.6 MW worth of methane was achievable. In their work the Capital expenses for the PEM process was about 43000 k€, but the 23600 k€ was from equipment costs of the solar energy system for it. Excluding solar energy, the CAPEX would be about 19400 k€ and when excluding the building and construction of solar field it would be even lower. With our 55 MW alkaline methane production and almost 100000 k€ capital investment, it looks that the rough calculations are on similar level to research of Al-Breiki & Bicer (2023), where a more detailed cost estimations were performed. BioSairila can however only produce the fraction of required carbon dioxide for CO_2 methanation, which would mean that rest of it would be needed to be bought. It is a big expense from operational expense-wise and the lack of available carbon sources might be an issue. The market and availability for carbon dioxide is expected to increase, because storing, capturing, and transporting it is becoming more manageable. The in-situ process, where the hydrogen from electrolyser is forwarded straight to bioreactors, seems interesting if smaller electrolyser would be used. If the hydrogen would be performed in BioSairilas mesophilic reactros, the costs would be lower compared to similar sized ex-situ process, because the methanation reactors aren’t needed anymore. It would be solid option if there isn’t available carbon sources to perform larger scale methanation.

The cost of electricity is the main operational cost sink in the process, which was also highlighted in the research performed by Al-Breiki & Bicer (2023) when evaluating P2M sensitivity. About 25% of the cost of electricity in electrolyzer could be recovered if all available heat is recovered and used as reduction for energy costs. The price of electricity is not stable in the current economy and can result in net losses if the price is high enough. Solar fields are commonly found in research articles as power sources for electrolyzer. With 1 ha of solar panels with 1 kWh/m^2/d power generation, the panels could satisfy 10 % of the required daily power output of electrolyzer. Winters are an issue in Finland with solar panels, because usually electricity prices tend to be higher at that time and the sun is up for only a short amount of time, but the production can be limited in winter season if the prices are too high and bigger maintenances could be tactically scheduled into this time window.

Overall, when considering the payback time of 5.5 years, this process has potential to make profit before electrolyzer stacks need to be replaced. This thesis focused on the overall view of power-to-x process’ potential in wastewater treatment. There is room to improve the process with better side stream utilization, energy balances, carbon sources and sizing of process. Further research topics could be focusing on the process side stream management, optimization of process and more detailed evaluation.

9 Conclusions

In this thesis, the primary objective was to find if it was possible to produce hydrogen from EcoSairilas treated wastewater. A rough calculation for mass and energy balances was made for the P2X-process and its feasibility was evaluated with rough cost estimations. Also highlighting the potential utilization areas for by-products was made. The first research question was how manageable it was to produce hydrogen with 100 MW alkaline electrolyzer using EcoSairila streams. From the theoretical research and data from plant site, the water requirements for electrolysis is possible, if the treated wastewater is pre-treated by reducing TOC and conductivity of water before electrolyser. EcoSairila also produces enough treated wastewater to satisfy 100 MW electrolyzers water demands expect the cooling water. There is a close water source in lake Saimaa, which can be used for cooling.

The second research question was how the electrolysis products can be utilized and third question what the potential for EcoSairila is. From calculations, a 55 MW worth of methane was feasible to produce from 100 MW alkaline electrolyser. Side streams of the process are oxygen and excess heat and in theoretical part it was researched the potential utilization methods for EcoSairila and BioSairila. Oxygen enriched air is one option to utilize oxygen. Aeration in WWTP could benefit from more oxygen rich air and waste combustion with lower carbon concentrations would improve the efficiency of combustion process. Oxygen could also be used as raw material for on-site ozone production or sold to other companies. Waste heat of the process could be used to balance energy demands of the whole MetsäSairila concern. Excess heat could be used in heating BioSairilas mesophilic reactors for example. BioSairila uses part of their produced biogas to produce heat for reactors, so replacing that with the heat from P2X-process would increase methane production. There exist sludge treatment processes with high heat intensity like sludge pyrolysis or thermal hydrolysis, which could benefit from free heat source.

Fourth and fifth research questions were how feasible the process is and what benefits does the process have. Calculations for the process told that, BioSairilas carbon dioxide can only produce a small fraction of the required carbon dioxide for the methanation. Rest of the CO_2 would be sensible to buy from third-party supplier. Availability of carbon sources can be an issue for the methanation process. Good alternative for lack of carbon dioxide would be in-situ methanation in bioreactors. In this thesis, it was determined that we use 100 MW electrolyzer for the simulations, but for the required methanation process, vast amounts of carbon dioxide are required. Electricity is the main cost for operations, and it can determine if the process does profit or losses. With 40 €/MWh electricity price, the process simple buyback time would be around 5.5 years. The process has huge electricity consumption, because of electrolysis. In many research articles of electrolysis, solar energy is used to reduce energy consumption of electrolysis-process with positive impact. It would balance the energy intensity of the process and reduce the dependency of electricity prices. Overall benefits of the process is the increase of methane production and reduction of BioSairilas carbon dioxide generation.

This process has potential for further research. This thesis has only rough calculations whether the process has any hope for production. Further research topics would be side stream utilization, more detailed research on electrolysis or methanation, potential carbon sources for the process or more detailed economic evaluation of the P2M- process.

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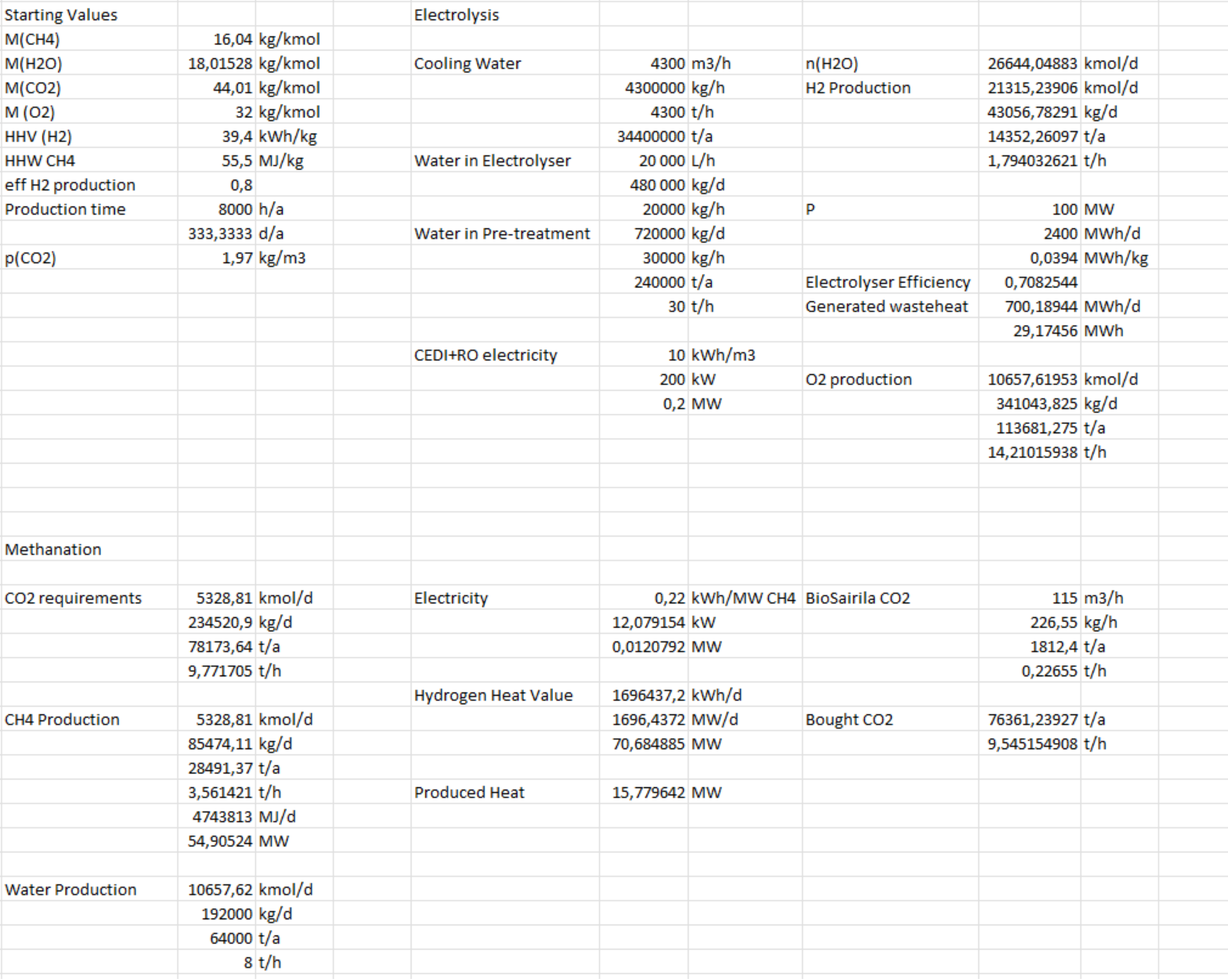
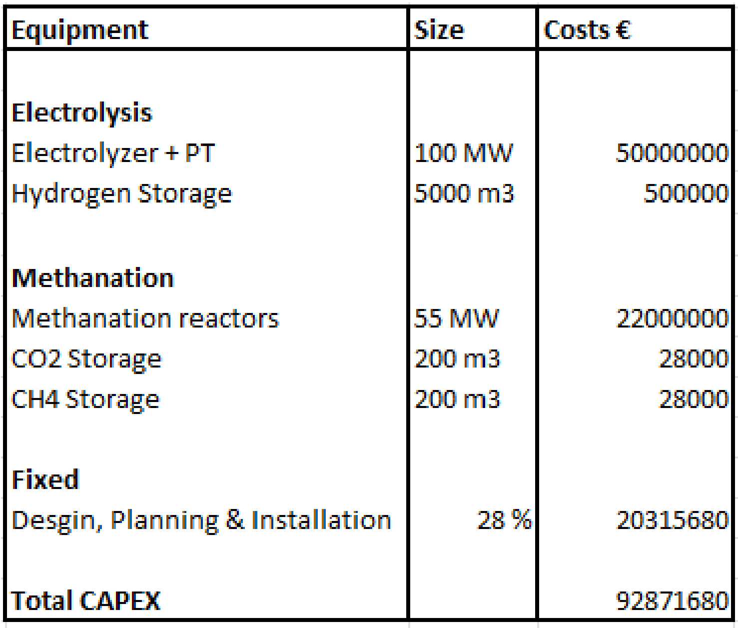
APPENDIX 1 (Mass & energy balances of P2M plant)



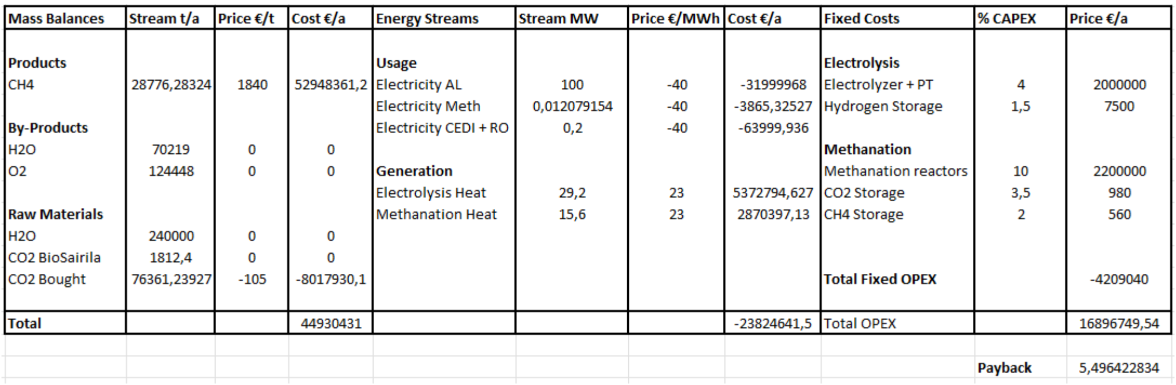
Starting Values			Electrolysis					
M(CH4)	16,04	kg/kmol						
M(H2O)	18,01528	kg/kmol	Cooling Water	4300	m3/h	n(H2O)	26644,04883	kmol/d
M(CO2)	44,01	kg/kmol		4300000	kg/h	H2 Production	21315,23906	kmol/d
M (O2)	32	kg/kmol		4300	t/h		43056,78291	kg/d
HHV (H2)	39,4	kWh/kg		34400000	t/a		14352,26097	t/a
HHW CH4	55,5	MJ/kg	Water in Electrolyser	20 000	L/h		1,794032621	t/h
eff H2 production	0,8			480 000	kg/d			
Production time	8000	h/a		20000	kg/h	P	100	MW
	333,3333	d/a	Water in Pre-treatment	720000	kg/d		2400	MWh/d
p(CO2)	1,97	kg/m3		30000	kg/h		0,0394	MWh/kg
				240000	t/a	Electrolyser Efficiency	0,7082544	
				30	t/h	Generated wasteheat	700,18944	MWh/d
							29,17456	MWh
			CEDI+RO electricity	10	kWh/m3			
				200	kW	O2 production	10657,61953	kmol/d
				0,2	MW		341043,825	kg/d
							113681,275	t/a
							14,21015938	t/h
Methanation								
CO2 requirements	5328,81	kmol/d	Electricity	0,22	kWh/MW CH4	BioSairila CO2	115	m3/h
	234520,9	kg/d		12,079154	kW		226,55	kg/h
	78173,64	t/a		0,0120792	MW		1812,4	t/a
	9,771705	t/h					0,22655	t/h
			Hydrogen Heat Value	1696437,2	kWh/d			
CH4 Production	5328,81	kmol/d		1696,4372	MW/d	Bought CO2	76361,23927	t/a
	85474,11	kg/d		70,684885	MW		9,545154908	t/h
	28491,37	t/a						
	3,561421	t/h	Produced Heat	15,779642	MW			
	4743813	MJ/d						
	54,90524	MW						
Water Production	10657,62	kmol/d						
	192000	kg/d						
	64000	t/a						
	8	t/h						

APPENDIX 2 (Capital expenses of the plant)



Equipment	Size	Costs €
Electrolysis		
Electrolyzer + PT	100 MW	50000000
Hydrogen Storage	5000 m3	500000
Methanation		
Methanation reactors	55 MW	22000000
CO2 Storage	200 m3	28000
CH4 Storage	200 m3	28000
Fixed		
Desgin, Planning & Installation	28 %	20315680
Total CAPEX		92871680

APPENDIX 3 (Operational expenses + Payback time)



Mass Balances	**Stream t/a**	**Price €/t**	**Cost €/a**	**Energy Streams**	**Stream MW**	**Price €/MWh**	**Cost €/a**	**Fixed Costs**	**% CAPEX**	**Price €/a**
Products				**Usage**				**Electrolysis**		
CH_4	28776,28324	1840	52948361,2	Electricity AL	100	-40	-31999968	Electrolyzer + PT	4	2000000
				Electricity Meth	0,012079154	-40	-3865,32527	Hydrogen Storage	1,5	7500
By-Products				Electricity CEDI + RO	0,2	-40	-63999,936			
H_2O	70219	0	0					**Methanation**		
O_2	124448	0	0	**Generation**				Methanation reactors	10	2200000
				Electrolysis Heat	29,2	23	5372794,627	CO_2 Storage	3,5	980
Raw Materials				Methanation Heat	15,6	23	2870397,13	CH_4 Storage	2	560
H_2O	240000	0	0							
CO_2 BioSairila	1812,4	0	0							
CO_2 Bought	76361,23927	-105	-8017930,1					**Total Fixed OPEX**		-4209040
Total			44930431				-23824641,5	Total OPEX		16896749,54
									Payback	5,496422834