Maija Ijäs

BIOMETHANATION POTENTIAL IN BIOGAS AND BIOETHANOL PLANTS IN FINLAND

Master's Thesis
Faculty of Engineering and
Natural Sciences
Associate Professor (tenure
track) Marika Kokko
Professor Jukka Rintala
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ABSTRACT

Maija Ijäs: Biomethanation potential in biogas and bioethanol plants in Finland
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Renewable energy sources and energy storages are needed to battle climate change. Biomethanation acts as a promising method of producing methane-rich biomethane by biologically combining H_2 with CO_2 stream. Biomethane is a renewable energy source which can be used for many purposes, like replacing natural gas as vehicle fuel.

The main objectives of this work were to find out the biomethanation potential in a typical case study and in the national level in Finland (including Finnish bioethanol plants) and to investigate potential biomethanation's significance in terms of case study's and Finland's biomethane production. The main research questions were following: What is the biomethanation potential of a typical case study of a biogas plant? What is the biomethanation potential of Finland as a nation?

Biomethane and CO_2 productions in biogas and bioethanol plants were investigated to find out the biomethanation potentials. The amount of additional energy retrieved from applying biomethanation to Finnish biogas plants was studied to find out the significance of biomethanation in Finland. In addition to the biomethanation potential, issues related to utilizing biomethanation in Finnish biogas plants were investigated by considering in-situ and ex-situ methods as biomethanation technologies. Finland's biomethanation potential was investigated in terms of the years 2020 and 2030, and case study's potential in terms of one year operation.

Methods included performing calculations based on initial data obtained from existing literature, along with information from companies involved. Parts of the research were conducted as literature review.

Continuous in-situ biomethanation potential in the case study corresponded to 46 % increase in the annual biomethane production. However, it is likely that the case study's operational parameters would be affected by in-situ biomethanation in a way which would lower the actual increase. Non-continuous in-situ biomethanation, which operates when sufficiently low electricity prices are available, could operate at 29 % of the full capacity. Integrating biomethanation to biogas plants was calculated to increase Finland's national methane production potential by 47 % in 2020, and by 40 % in 2030. Finland's biomethanation potential in comparison to Finland's energy sector (traffic energy consumption, heat production, electricity consumption and natural gas consumption) was found to be quite insignificant in 2020, but growing in importance by 2030, with the biogas and biomethane productions increasing.

Keywords: Biomethanation, biomethane, biogas, renewable energy

TIIVISTELMÄ

Maija Ijäs: Biokaasu- ja bioetanolilaitosten biometanointipotentiaali Suomessa
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Uusiutuvia energianlähteitä sekä energian säilytysratkaisuja tarvitaan ilmastonmuutoksen hidastamiseen. Lupaava metodi metaanirikkaan biometaanin tuottamisessa on biometanointi, jossa H_2 yhdistetään biologisesti CO_2-virran kanssa. Biometaani on uusiutuva energianlähde, jota voidaan käyttää moniin tarkoituksiin, kuten maakaasun korvikkeena.

Tämän työn tärkeimmät tavoitteet olivat selvittää esimerkkitapauksen avulla biometanointipotentiaali tyypillisessä biokaasulaitoksessa sekä Suomessa kansallisella tasolla (mukaan lukien suomalaisten bioetanolilaitosten biometanointipotentiaali), sekä tutkia biometanoinnin merkittävyyttä verrattuna esimerkkitapauksen ja Suomen biometaanin tuotantoon. Päätutkimuskysymykset olivat seuraavat: Mikä on esimerkkitapauksen, eli tyypillisen biokaasulaitoksen, biometanointipotentiaali? Mikä on Suomen kansallinen biometanointipotentiaali?

Biometaanin ja CO_2:n tuotantomäärät biokaasu- ja bioetanolilaitoksissa selvitettiin biometanointipotentiaalien laskemiseksi. Biometanoinnin merkitys Suomessa selvitettiin laskemalla biometanoinnilla biokaasulaitoksissa tuotettavissa olevan lisäenergian määrä. Lisäksi tarkasteltiin biometanoinnin aiheuttamia hyötyjä ja ongelmia suomalaisissa biokaasulaitoksissa tarkastelemalla in-situ- ja ex-situ-metodeja biometanointitekniikoina. Suomen kansallista biometanointipotentiaalia tutkittiin vuosien 2020 ja 2030 osalta, ja esimerkkitapausta yhden vuoden toiminnan osalta.

Tutkimusmenetelminä käytettiin laskentaa perustuen olemassa olevasta datasta sekä yhteistyöyrityksiltä saaduista tiedoista kerättyihin lähtötietoihin. Osa tutkimuksesta tehtiin kirjallisuuskatsauksena.

Jatkuvatoiminen in-situ-biometanointipotentiaali esimerkkitapauksessa tuottaisi vuodessa 46 % enemmän energiaa, kuin biokaasulaitos ilman biometanointia. On kuitenkin otettava huomioon, että H_2:n lisääminen suoraan biokaasureaktoriin todennäköisesti laskisi in-situ-biometanoinnin aiheuttamaa biometaanin tuoton nousua laitoksessa. Jos biometanointia toteutettaisiin esimerkkitapauksessa vain silloin, kun sähkön hinta on tarpeeksi alhainen voittojen mahdollistamiseksi, biometanointi olisi mahdollista vain 29 %:lla täydestä kapasiteetista. Suomen kansallista biometaanin tuotantoa biometanoinnin laskettiin nostavan 47 % vuonna 2020, ja 40 % vuonna 2030. Suomen kansallinen biometanointipotentiaali verrattuna Suomen energiasektorin energiantarpeisiin (liikenne, lämmöntuotto, sähkönkulutus ja maakaasun kulutus) oli melko merkityksetön vuonna 2020, mutta vuonna 2030 sen merkitys kasvaa, sillä biokaasun ja biometaanin tuotantomäärien uskotaan myös kasvavan.

Avainsanat: Biometanointi, biometaani, biokaasu, uusiutuva energia

PREFACE

This thesis was done as a part of ‘HYGCEL’ (Hydrogen and Carbon Value Chains in Green Electrification) project. I gratefully acknowledge the public financing of Business Finland for the ‘HYGCEL’ project, and all the people involved. I thank Gasum and St1 for the collaboration. I would like to give special thanks to Gasum’s Viljami Kinnunen and Matias Alarotu, as well as St1’s Anna Kankaanpää, for kindly co-operating and sitting in meetings with me. Your help and involvement added a lot of value to this thesis. Big thank you to my supervisors Marika Kokko and Jukka Rintala, your guidance throughout this work has been irreplaceable. Special thanks to Marika, I value greatly your time you have given me and the advice you have provided me with throughout the last 7 months.

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Hämeenlinna, 17.10.2022

Maija Ijäs

TABLE OF CONTENTS

ABBREVIATIONS

ρ	Density
a	Year
d	Day
E	Energy
g	gas
h	Hour
m	Mass
M	Molar mass
n	Amount of substance
P	Price
r_t	Hydrogen gas-liquid mass transfer rate
T	Temperature
V	Volume

CSTR	Continuously stirred tank reactor
H_{2g}	Gas phase concentration of H_2
H_{2l}	Liquid phase H_2 concentration
HRT	Hydraulic retention time
k_La	Gas transfer coefficient
L_{VR}	Reactor working volume
MER	Methane evolution rate
NADH	Nicotinamide adenine dinucleotide
NTP	Normal temperature and pressure (temperature: 219,3 K = 20 °C, pressure: 1 atm = 101 325 Pa)
OLR	Organic loading rate
P2G	Power-to-Gas
P2X	Power-to-X
PV	Photovoltaic
SAO	Syntrophic acetate oxidation
STP	Standard conditions for temperature and pressure
TBR	Trickle bed reactor
UASB	Up-flow anaerobic sludge blanket
VFA	Volatile fatty acid
VS	Volatile solids

1. INTRODUCTION

Climate change is forcing humankind to replace fossil fuels with energy derived from renewable energy sources. Efficient energy storages are also being needed because many renewable energy sources have fluctuating and not stable energy production styles.

Biogas, the gaseous product of anaerobic digestion of organic matter consisting of mostly methane (CH_4) and carbon dioxide (CO_2), has been used as a renewable energy source to create electricity and combined heat and power. Biogas usage has gained popularity in the world during the last decades. Biogas can be turned into biomethane, which is gas with high (over 90 %) methane (CH_4) content. Though biogas can be utilized as such, increasing biogas' CH_4 content to create biomethane has many benefits. Biomethane can be used as vehicle fuel, for heat and electricity production or for primary product for chemical industry, and it can be injected into natural gas grid and transported to where it is needed (Beil and Beyrich, 2013; Scarlat et al., 2018). Biomethane is storable, which could help with the storage problems related to fluctuating electricity. Biomethane's properties are also very close to natural gas, so it can act as a replacement of natural gas. (Rusmanis et al., 2019). At the time of writing this thesis, Europe's geopolitical situation has changed because of Russia's war with Ukraine, which has caused natural gas prices to increase. Because of this, biogas and biomethane's competitiveness is rising.

The process of producing biomethane through a biological method of combining H_2 with CO_2 is called biomethanation. Biomethanation can be carried out using CO_2 originating from a biogas plant, or from another CO_2 source. The basis of biomethanation is microbes, especially hydrogenotrophic methanogens. The two most common ways of conducting biomethanation are in-situ biomethanation and ex-situ biomethanation. In-situ biomethanation uses a biogas reactor with organic feedstock as the biomethanation reactor, into which H_2 is injected. Ex-situ biomethanation, on the other hand, uses an external biomethanation reactor, into which gaseous CO_2 and H_2 are injected. In-situ and ex-situ biomethanations and their advantages and disadvantages have been studied in the last years (Jensen et al., 2018; Luo and Angelidaki, 2012; Rachbauer et al., 2016; Savvas et al., 2017; Voelklein et al., 2019)

The objectives of this work were to find out the biomethanation potential in a case study of a typical biogas plant and in the national level in Finland and to investigate biomethanation's significance in terms of case study's and Finland's CH_4 production. The main research questions were following: What is the biomethanation potential of a typical case study of a biogas plant? What is the biomethanation potential of Finland as a nation? Biogas plants were considered as the main CO_2 source for biomethanation, and Finland's national potential was investigated for years 2020 and 2030. The amount of additional energy retrieved from applying biomethanation to Finnish biogas plants was determined. As for the case study, the research objectives were to calculate its biomethanation potential, to study impacts of integrating biomethanation into existing biogas plant, to investigate in-situ and ex-situ technologies as biomethanation possibilities, to investigate H_2 and renewable energy requirements in biomethanation and to conduct a techno-economic analysis of the case study biomethanation. In-situ option was studied in detail, and ex-situ option was investigated for comparative purposes. At Finland's national level, the objectives were to calculate Finnish biomethanation potential, and Finnish bioethanol plants' biomethanation potential and investigate H_2 and renewable energy requirements. Both in-situ and ex-situ biomethanation technologies were considered.

First, theory about anaerobic digestion, its process description and conditions are introduced. Theory behind biomethanation, its microbiology, process description of methane production and in-situ and ex-situ biomethanations are introduced. Materials and methods are described in three parts: case study of a typical biogas plant, Finland's national biomethanation potential and techno-economic analysis of the case study's biomethanation potential. Results and discussion are introduced firstly for the case study's calculations, and then for the Finland's national potential. Lastly, conclusions of the results and their meaning is discussed.

2. ANAEROBIC DIGESTION

Anaerobic digestion is a complex bio-chemical process, during which organic matter is degraded and converted into biogas. It happens in anaerobic conditions, has multiple steps and requires contribution of different micro-organisms. (Schnürer, 2016; Xu et al., 2020b) In nature, anaerobic digestion takes place in locations such as swamps and wetlands, lake bottom sediments and ruminant intestines (Lyu et al., 2018; Xu et al., 2020b). Humans take advantage of anaerobic digestion for example, when treating sewage sludge and biowaste (Deublein and Steinhauser, 2010). Anaerobic digestion happens due to humans also in places like rice fields and landfills (Lyu et al., 2018).

2.1 Biogas from anaerobic digestion

Biogas, which is the final product of anaerobic digestion, is a gas that is formed from organic matter in anaerobic conditions and consists mostly of methane (CH_4) and carbon dioxide (CO_2). Methane and CO_2 contents in biogas range typically between 55–75 % and 30–45 %, respectively (Hilkiah Igoni et al., 2008). Biogas also includes minor components such as water, hydrogen sulfide, oxygen, hydrogen (H_2) and ammonia (Liebetrau et al., 2017). Biogas is a renewable fuel, and it can be used for producing heat and power, but it can also act as raw material to biomethane. Upgrading biogas into biomethane means reducing biogas CO_2 content and its impurities. biomethane can be injected into gas grid. (Scarlat et al., 2018)

Using anaerobic digestion in order to generate biogas for electricity or combined heat and power has gained popularity over the last couple of decades. In 2021, the world's biggest biogas producer was China with more than 100 000 biogas plants and highest biogas production of 72 000 TWh (*IEA Bioenergy*, 2022). The most significant biogas producer in the European Union is Germany, with 10 000 biogas plants in 2021 which produce almost 120 TWh/a (*IEA Bioenergy*, 2022).

2.2 Microbial process in anaerobic digestion

The microbiological process of anaerobic digestion consists of four phases: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Figure 1) (Deublein and Steinhauser, 2010). It is possible to physically separate hydrolysis and acidogenesis from acetogenesis and methanogenesis (Liebetrau et al., 2017). In hydrolysis and acidogenesis, organic polymers are transformed into monomers and further into volatile fatty acids

(VFAs), such as butyrate, propionate, acetate and H_2. Then, in acetogenesis, VFAs are being converted into acetate, CO_2 and H_2. In the last step, methanogenesis, biogas that consists of methane and CO_2, is being produced from acetate or CO_2 and H_2. (Abdul-Sattar, 2011; Liebetrau et al., 2017; Schnürer, 2016; Xu et al., 2020b) Microbes present in anaerobic digestion are mostly bacteria and archaea, but also fungi may be present (Schnürer, 2016).

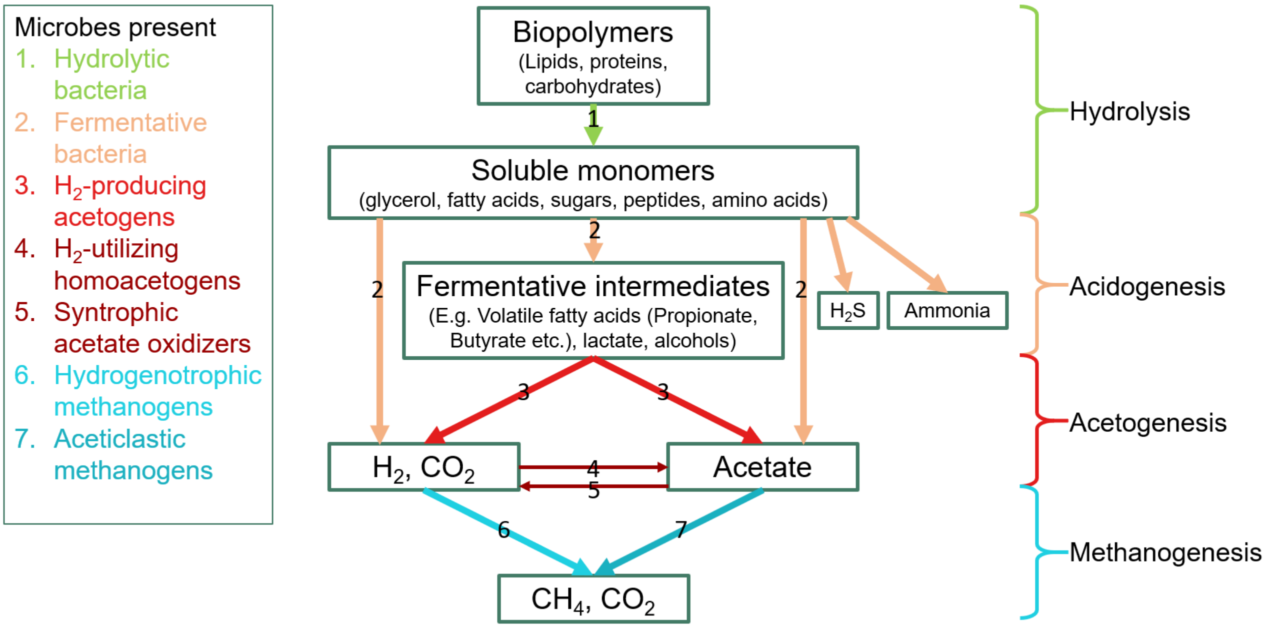


Figure 1 *Anaerobic digestion. Four phases, their main products and microbes present in each phase are displayed. Adapted from* (Abdul-Sattar, 2011; Schnürer, 2016; Xu et al., 2020b).

The CO_2 and CH_4 contents of biogas are dependent on mostly feedstock and the level of feedstock degradation. Theoretically, fats produce the most methane-rich biogas, whereas carbohydrates produce the least methane-rich biogas. (Al Seadi et al., 2008; Xu et al., 2020b)

2.2.1 Hydrolysis

During the first phase, hydrolysis, insoluble and complex biopolymers are broken down into smaller compounds, monomers. Hydrolysis itself is a chemical reaction, during which a compound is being broken down into smaller pieces (Katyal and Morrison, 2007). Without being hydrolyzed into smaller parts, these polymers would be too large to fit through cell membranes. Carbohydrates, proteins and lipids are hydrolyzed into soluble monomers such as sugars, long chain fatty acids, amino acids, peptides and glycerol. Hydrolytic bacteria are present at this phase and secrete enzymes like lipase and protease, which catalyze hydrolysis. (Lester and Birkett, 1999; Schnürer, 2016; Xu et al., 2020b)

Hydrolysis is considered to be the rate-limiting step in anaerobic digestion, because some particles take a long time to degrade (Schnürer, 2016). The rate at which biopolymers are being broken down depends on the feedstock. For example, hydrolysis of proteins can be up to several days longer than hydrolysis of carbohydrates. (Xu et al., 2020b)

2.2.2 Acidogenesis

After hydrolysis, soluble monomers are used as substrate by fermentative bacteria and turned into different fermentative intermediates, such as acetate, butyrate, CO_2 and H_2 (Deublein and Steinhauser, 2010). The most important reaction of acidogenesis by quantity is acidogenic fermentation, which is the formation of acetate (Lester and Birkett, 1999). Sugars are converted into pyruvate, which works as an important intermediate. Pyruvate acts as an electron acceptor for oxidation of NADH (nicotinamide adenine dinucleotide), which leads to the formation of VFAs like acetate, butyrate, propionate, and other compounds like CO_2, H_2 and lactate. (Lester and Birkett, 1999; Schnürer, 2016)

Amino acids are degraded via two pathways: the Stickland reaction and another pathway. In the Stickland reaction, pairs of amino acids are oxidized and reduced, resulting in the production of VFAs and CO_2. The other pathway happens, when H_2 partial pressure is low enough. This leads to oxidation and electrons being released as H_2. The amino part in amino acids is released as ammonia, regardless of the degradation pathway. (Schnürer, 2016; Xu et al., 2020b)

Long chain fatty acids are degraded through β-oxidation, which results to production of acetate and H_2. H_2S is produced via cysteine degradation. (Schnürer, 2016; Xu et al., 2020b)

2.2.3 Acetogenesis

In the third phase, acetogenesis, VFAs formed in acidogenesis, are converted into mostly acetate, CO_2 and H_2 (Lester and Birkett, 1999). Acetate is produced by two pathways: either by H_2-producing acetogenic bacteria, or H_2-utilizing homoacetogenic bacteria, which in addition to H_2, also utilize CO_2 and organic acids. (Xu et al., 2020b)

In the pathway of acetate production by H_2-producing acetonic bacteria, acetate is being produced by fermentation. Products from acidogenesis are used by H_2-producing acetogenic bacteria, and catalyzed into acetate, CO_2 and H_2. This pathway has two important requirements: H_2 partial pressure needs to be sufficiently low, and formed H_2 needs to be removed from the process. Accumulation of H_2 in acetogenesis inhibits the functions of acetogenic bacteria. To prevent this issue, usually H_2-utilizing bacteria called hydrogenotrophic methanogens, are present for the next phase, methanogenesis. (Liebetrau et al., 2017; Xu et al., 2020b) This symbiosis between H_2-producing acetogenic bacteria and H_2-utilizing hydrogenotrophic methanogens is called syntrophy (Xu et al., 2020b).

The other pathway of producing acetate is performed by H_2-utilizing homoacetogenic bacteria. These bacteria use H_2 to not only produce acetate, but also to reduce CO_2. This reaction releases energy and reduces H_2 partial pressure. (Xu et al., 2020b) Homoacetogenic bacteria operate in so called Wood-Ljungdahl pathway. Acetate can also be oxidized to H_2 through Wood-Lungdahl pathway; this process is carried out by syntrophic acetate oxidizers. (Angelidaki et al., 2018; Mulat et al., 2017)

2.2.4 Methanogenesis

The last phase of anaerobic digestion is called methanogenesis. This is the step where methane is finally produced. (Lester and Birkett, 1999; Liebetrau et al., 2017; Schnürer, 2016) There are two main pathways of producing methane in methanogenesis: hydrogenotrophic and aceticlastic methanogenesis. (Liebetrau et al., 2017; Lyu et al., 2018) In hydrogenotrophic methanogenesis, H_2 is used as energy to reduce CO_2 to methane. In aceticlastic methanogenesis, acetate is used as substrate to produce methane and CO_2. (Liebetrau et al., 2017) Aceticlastic methanogens are said to produce most (up to 70 %) of the methane in anaerobic reactors (Alvarado et al., 2014; Lyu et al., 2018), especially in conditions where there are low levels of ammonia (Schnürer, 2016). However, it has been proved that hydrogenotrophic methanogens are also very common, and in some cases dominate the methane production (Alvarado et al., 2014).

2.3 Anaerobic digestion conditions

Anaerobic digestion requires certain conditions. Some important parameters that affect the process of anaerobic digestion include temperature, retention time, organic loading rate and mixing (Lester and Birkett, 1999). There are also multiple other parameters that have an effect on the process, such as pH and H_2 partial pressure (Xu et al., 2020b).

Temperature is a significant factor in anaerobic digestion. It is crucial for the microbes present to have a suitable temperature, so their growth and reproduction can be optimal. Anaerobic digestion usually takes place in mesophilic conditions, between 25 and 40 °C (Lester and Birkett, 1999), or in thermophilic (45–60 °C) conditions (Weiland, 2010). Different microbes in the phases of anaerobic digestion process favor slightly different temperatures, even if the microbes are all mesophiles. Acetogenic mesophilic bacteria favor temperature of ca. 25–35 °C and mesophilic methanogens' optimal temperature can be around 32–42 °C. However, temperature changes during the process of anaerobic digestion should not exceed 2 °C, because larger changes will decrease the biogas yield. (Xu et al., 2020b)

In nature, temperature conditions are more versatile than in a man-made reactor. For example, some methane producing methanogenic microbes can live in extreme temperatures, minimum being under 0 °C and maximum over 120 °C (Lyu et al., 2018; Xu et al., 2020b). For biogas reactors, however, it is said that temperatures under 20 °C might be too cold for optimal biogas production (Lester and Birkett, 1999).

In anaerobic digestion process, pH influences the growth and metabolism of microbes. It should be noted, that a pH too low or high can deactivate or even kill the important microbes in the process. (Weiland, 2010; Xu et al., 2020b) Acetogenic bacteria can grow in quite a wide range of pH, 4.5–8. Methanogens, however, favor pH of 6.7–7.5. If a single-phase reactor is used, usually pH is kept at around 6.5–7.5 (Schnürer, 2016; Xu et al., 2020b).

Organic loading rate (OLR) means the mass of feedstock's volatile solids (VS) fed to the digester in a day per digester volume (Bachmann, 2013; Mattocks, 1984). Volatile solids are organic, degradable portion of the feedstock (Mattocks, 1984). OLR can be calculated with Equation 1 (Bachmann, 2013):

$$OLR\ \left(\frac{kg\ VS}{m^3\ d}\right) = \frac{VS\ input\ \left(\frac{kg}{d}\right)}{Digester\ volume\ (m^3)} \tag{1}$$

Hydraulic retention time (HRT) expresses the average time period that the feedstock input stays in the digestor (Equation 2). HRT must be long enough to achieve adequate degradation of substrates and to avoid washout of the microbes. Usually HRT should be more than 10 days in waste-utilizing reactors (Bachmann, 2013).

$$HRT\ (d) = \frac{Net\ digester\ volume\ (m^3)}{Feedstock\ input\ (m^3/d)} \tag{2}$$

H_2 partial pressure needs to be kept very low in anaerobic digestion's acetogenesis stage (Rusmanis et al., 2019). This is because accumulation of H_2 in acidogenesis stage can cause the inhibition of acetogenic bacteria, and thus inhibition of VFA degradation (Rusmanis et al., 2019; Weiland, 2010; Xu et al., 2020b). If H_2 partial pressure increases and H_2 starts to accumulate, it causes digestion process to slow down, pH decrease and results in acidification (Xu et al., 2020b).

3. BIOMETHANATION

The terms “biomethanation” and “biomethane” can mean different things in literature. Biomethanation can simply refer to the process of turning biomass into methane (Ferry, 2011), but the same term is also used when talking about the process of upgrading CO_2 into methane-rich biomethane (Scarlat et al., 2018; Weiland, 2010). This thesis follows the example of many articles (Beil and Beyrich, 2013; Liebetrau et al., 2017; Rusmanis et al., 2019; Scarlat et al., 2018; Weiland, 2010) and thus the term “biomethanation” is used to describe the latter option; using microorganisms in upgrading CO_2 into methane-rich biomethane.

Biogas upgrading has been a traditional way of increasing CH_4 content, which consists of many techniques, such as water scrubbing, pressure swing adsorption, membrane separation and using organic solvents (Beil and Beyrich, 2013). Another approach to increase the CH_4 content is to aim at reducing biogas’ CO_2 content by turning it into methane, which ultimately increases biogas CH_4 content (Liebetrau et al., 2017). There are a few ways to turn CO_2 into methane: biomethanation, which is a biological method of combining H_2 with CO_2 stream (Luo et al., 2012), electromethanogenesis (Cheng et al., 2009) and different chemical catalytic processes (Rönsch et al., 2016). Chemical catalytic methanation techniques have been studied more than biological ones, and catalytic methanation has already been applied in large scale (Dannesboe et al., 2020), whereas biomethanation has been studied mainly in laboratory-scale (Jensen et al., 2021b). In this thesis, biomethanation methods are discussed.

3.1 Biomethanation as power-to-gas technology

Biomethanation process utilizes specific microbes from anaerobic digestion, which can convert H_2 and CO_2 into methane and water by Sabatier reaction (Equation 3) (Lecker et al., 2017; Rusmanis et al., 2019; Thauer et al., 1977):

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{3}$$

Reaction is exothermic, and it results in a chemical energy potential loss, if compared with input H_2. Nevertheless, biomethanation process is still attractive, due to the many usage possibilities of biomethane. (Jensen et al., 2021b)

CO_2 for biomethanation can be derived from biogas process. With biomethanation, the CO_2 in biogas will be reduced into methane. External H_2 is added to the process for the reaction to work (Voelklein et al., 2019). H_2 needed is derived from surplus renewable energy, like surplus wind or solar power. Since neither the supply of wind power nor solar power can be regulated, there are times when there is excess generation of energy. This happens when the energy supply is greater than its demand, for example at nighttime during very windy weather, and thus renewable power is being produced excessively. This extra energy can be used in electrolysis for making sustainable H_2, which can in turn be used in CH_4 production. This process of turning sustainably produced electricity into gas is called Power-to-Gas, or P2G. (Lecker et al., 2017; Liebetrau et al., 2017; Rusmanis et al., 2019; Tao et al., 2019) P2G can act as a solution to both intermittent renewable energy production and to energy storage problem, since biomethane can be stored and transported more easily that H_2 gas (Luo et al., 2012). H_2 is a very light gas and therefore difficult to handle, and it also has lower volumetric energy content in comparison to methane (10,88 MJ/m^3 and 36 MJ/m^3, respectively). This is why it is logical to use H_2 in CH_4 production, rather than using H_2 by itself. (Luo et al., 2012) Storing energy as methane is also more attractive option compared to traditional batteries, since there are many drawbacks to batteries, for example low storage capacity, costly production and need for corrosive and toxic materials (Angelidaki et al., 2018).

There are two main possibilities for P2G biomethanation: in-situ and ex-situ. In in-situ biomethanation, H_2 is directly injected into an existing (or new) biogas reactor, where it can react with biogas' CO_2 that is formed in the anaerobic digestion process. Ex-situ biomethanation uses an external reactor, into which both CO_2 and H_2 are directed, and where the Sabatier reaction then occurs. (Lecker et al., 2017; Rusmanis et al., 2019; Voelklein et al., 2019) More information about in-situ and ex-situ biomethanation is given in chapter 3.3.

3.2 Microbiology in biomethanation

Microbiology and the microbes present in biomethanation varies a bit, depending on whether in-situ or ex-situ method is used. In-situ biomethanation uses a biogas reactor with the complete anaerobic digestion process, and therefore the reactor usually contains necessary nutrients, diverse microbes and the process' intermediates, like VFAs (Angelidaki et al., 2018; Voelklein et al., 2019). Ex-situ biomethanation, however, uses an external reactor and therefore the two first phases of anaerobic digestion (hydrolysis and acidogenesis) do not occur, which makes the reactor microbiome simpler (Angelidaki et al., 2018; Voelklein et al., 2019).

3.2.1 Microbiological pathways in biomethanation

In biomethanation process, methane can be formed via two different pathways (Figure 2). Either hydrogenotrophic methanogens form methane directly from H_2 and CO_2, or aceticlastic methanogens form methane from acetate. (Angelidaki et al., 2018; Burkhardt and Busch, 2013) When external H_2 is added to methanogenesis, it strongly increases the amount of hydrogenotrophic methanogens and homoacetogens. At the same time, syntrophic acetate oxidation (SAO), which happens in the Wood-Ljungdahl pathway but to the opposite direction than homoacetogenesis, is suppressed. (Angelidaki et al., 2018)

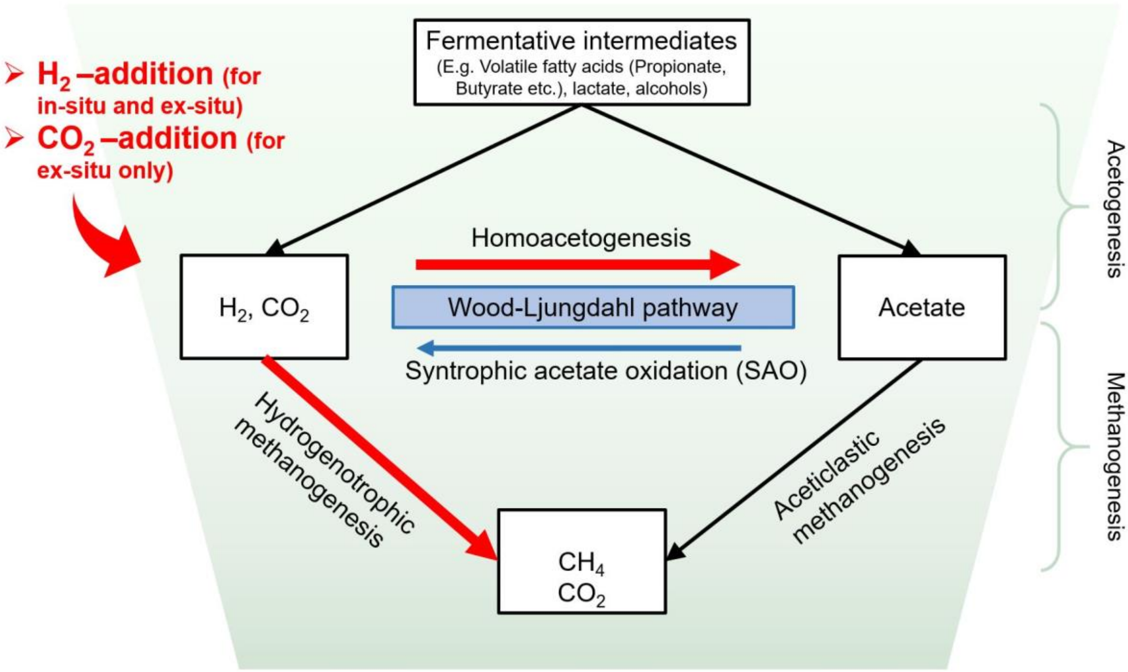


Figure 2 *Methanogenesis in biomethanation. H_2 addition causes increase in hydrogenotrophic methanogens and homoacetogens; these steps are displayed with red arrows. H_2 addition decreases SAO, and it is displayed with a blue arrow. Acetogenesis is displayed in the figure as the phase before methanation. Adapted from (Angelidaki et al., 2018)*

Methane formation by hydrogenotrophic methanogenic archaea happens through so called Wolfe cycle (Figure 3). Wolfe cycle presents the biochemical reactions in hydrogenotrophic methanogenesis pathway. (Thauer, 2012) During Wolfe cycle, hydrogenotrophic methanogenic archaea use H_2 as an electron donor, and through many biochemical reactions, CO_2 is reduced to CH_4 (Fu et al., 2021).

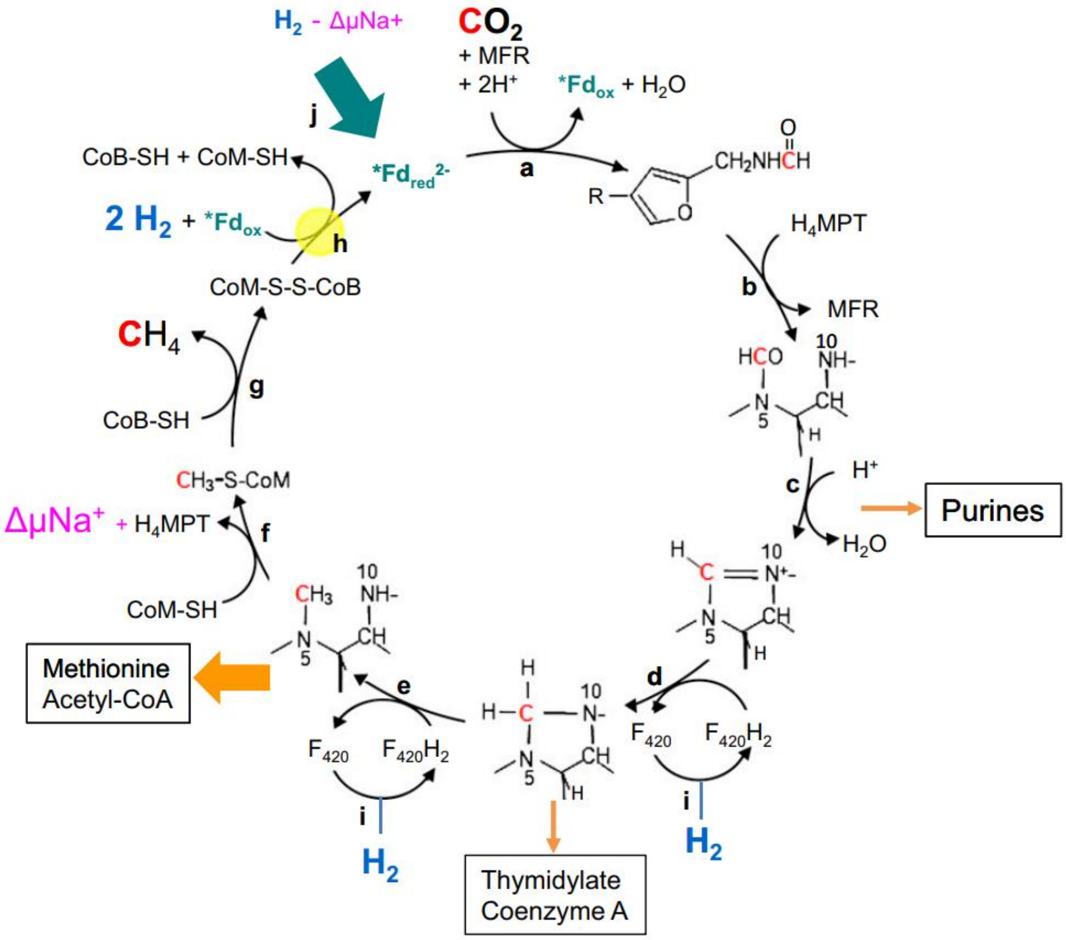


Figure 3 *Wolfe cycle. Picture is a screenshot from* (Thauer, 2012) *(Permission for usage granted)*

In aceticlastic pathway, acetogenic bacteria use Wood-Ljungdahl pathway to covert CO_2 into acetic acid (acetate) through homoacetogenesis (Equation 4). Subsequently, methane forming aceticlastic methanogenic archaea convert acetic acid into methane (Equation 5). (Angelidaki et al., 2018; Lecker et al., 2017)

$$4H_2 + 2CO_2 \rightarrow CH_3COOH + 2H_2O \tag{4}$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \tag{5}$$

Homoacetogenes compete for H_2 and CO_2 with hydrogenotrophic methanogenes (Lecker et al., 2017; Logroño et al., 2020). According to Sposob et al. (2021), when using trickle bed reactors (TBR) in biomethanation, homoacetogenesis is being seen as a process disturbance, because accumulation of acetate can decrease process pH and thus lower the methane production. Logroño (2020) also stated, that acetate acts as an undesirable sink of carbon and electrons, at methane production's expense.

3.2.2 Microbes in biomethanation

Microbiology of biomethanation is based on methanogenic archaea: hydrogenotrophic methanogens and aceticlastic methanogens (Angelidaki et al., 2018; Sposob et al., 2021; Voelklein et al., 2019). Methanogens are obligate anaerobes (Xu et al., 2020b), which means that their metabolism does not require oxygen, and some of their metabolic components are even destroyed by it (Coleman and Smith, 2007).

The most important microbes of biomethanation are hydrogenotrophic methanogens, which are able to directly form methane from H_2 and CO_2. (Angelidaki et al., 2018) Hydrogenotrophic methanogenic archaea have been proven to be predominant in ex-situ biomethanation (Sposob et al., 2021). It is desirable to manage the methanogenesis microbiota towards CH_4 production, rather than letting homoacetogens form acetate (Logroño et al., 2020). Therefore, different strategies can be used to increase hydrogenotrophic methanogens' abundance in the process: for example endogenously increasing hydrogenotrophic populations. (Angelidaki et al., 2018)

Hydrogenotrophic methanogens can function in both mesophilic and thermophilic temperatures. Luo and Angelidaki (2012) discovered, that under thermophilic conditions (55 °C), ex-situ biomethanation with H_2 and biogas injection caused higher methane production rate than under mesophilic conditions (37 °C). In the same study it was found out that the addition of H_2 and biogas to the process enriched selectively hydrogenotrophic methanogens. Bassani et al. (2015) also discovered, that even though mesophilic conditions produced biomethane with higher CH_4 content than thermophilic conditions (CH_4 contents of 89 % and 85 %, respectively), methane production rate from CO_2 was higher in thermophilic than in mesophilic conditions.

Hydrogenotrophic methanogens, and methanogens in general, can generally grow between pH 6.8 and 9.5, and have an optimal pH value for growth between pH 7.0 and 7.5 (O'Flaherty et al., 1998). Hydrogenotrophic methanogens have been found to be less sensitive to ammonia-rich environments than aceticlastic methanogens, which means that their abundance can increase in ammonia elevated conditions (Sposob et al., 2021). Hydrogenotrophic methanogens are also predominant methanogens in high nitrogen concentrations. The main hydrogenotrophic methanogen orders in ex-situ biomethanation have been found to be *Methanobacteriales, Methanomicrobiales and Methanococcales.* (Logroño et al., 2020) In addition to those three, other methanogenic orders capable of hydrogenotrophic methanogenesis are *Methanocellales*, *Methanomassiliicoccales* and *Methanopyrales* (Liebetrau et al., 2017). Luo and Angelidaki (2012) discovered, that in their ex-situ study, all of the microbial species found in both thermophilic and mesophilic-enriched cultures belonged to *Methanobacteriales* order.

Aceticlastic methanogens produce methane from acetate (Angelidaki et al., 2018). Their aceticlastic reaction splits acetate in a way that carboxyl-group is oxidized into CO_2 and methyl group is reduced to CH_4 (Liu and Whitman, 2008).

Only a few methanogens are capable of aceticlastic methanogenesis. Methanogens that perform aceticlastic methanogenesis include *Methanosarcina* and *Methanosaeta* from the order of *Methanosarcinales* and *Methanosaetaceae,* respectively. (Liebetrau et al., 2017) *Methanosarcina* utilizes methanol and methylamine in addition to acetate, whereas *Methanosaeta* only uses acetate (Liu and Whitman, 2008).

Aceticlastic methanogens generally only grow in temperatures under 65 °C (Liu and Whitman, 2008) and preferably in pH between 6.5 and 8.5 (Bassani et al., 2015). Aceticlastic methanogens are usually more sensitive to ammonia levels and pH in the process, than hydrogenotrophic methanogens (Bassani et al., 2015).

3.2.3 Nutrients required for microbes in biomethanation

Methanogenesis requires a sufficient level of different micro- and macronutrients for its key-enzymes and microorganisms. Essential macronutrients for methanogenesis include nitrogen (N), calcium (Ca), potassium (K), magnesium (Mg), phosphorus (P), sulphur (S) and sodium (Na). Essential micronutrients, also called trace elements, include elements such as iron (Fe), cobalt (Co), molybdenum (Mo), nickel (Ni), manganese (Mn), zink (Zn) and selenium (Se). Nutrients must be in soluble form for them to be accessible for methanogens, and they cannot be fixed in compounds that are precipitated, such as carbonates or sulphates, or absorbed. (Voelklein et al., 2017, 2016).

It is difficult to set an optimal concentration for nutrients needed in the biomethanation process, because the microbes involved in biomethanation differ from each other and have different nutrient requirements. Nutrient supplementation is also affected by many other things, such as feedstock trace metal concentrations, bioavailability and microbes' growth rate. It is, however, important to provide microbes with the nutrients that they need. (Voelklein et al., 2017) By adding important nutrients in the biomethanation process, microbial doubling time decreases and therefore microbe population increases. Nutrient supplementation is important especially in ex-situ biomethanation systems, since in addition to H_2 and CO_2 (or raw biogas), there are no other inputs to the biomethanation reactor, and thus external nutrient supply is needed. (Rusmanis et al., 2019) One trace element that has been proven to be important in biomethanation reactors, is tungsten (W). (Rusmanis et al., 2019) Also nickel (Ni) is important for methanogens, since Ni is needed in methane formation for the cell component cofactor F_{430} synthesis (Weiland, 2010).

3.3 In-situ and ex-situ biomethanation processes

The two main methods for performing P2G biomethanation are in-situ and ex-situ. In addition to in-situ and ex-situ, a third pathway for biomethanation has been recognized. This third pathway is called a hybrid process, and it mixes both in-situ and ex-situ methods. (Angelidaki et al., 2018) Hybrid process of biomethanation has not been studied as much as in-situ and ex-situ (Tao et al., 2019), but for example Tao et al. (2019) have done a study on novel hybrid combined in-situ/ex-situ system.

In-situ biomethanation (Figure 4) utilizes a waste- or wastewater-treating biogas plant as the biomethanation unit. Biogas reactor is fed with biomass as well as with H_2 from, e.g., electrolysis (Equation 6 (Ursúa et al., 2012)). Electrolysis requires water and electricity, which can be derived from i.e. renewable energy sources. By-product of electrolysis is oxygen. (Lecker et al., 2017; Rusmanis et al., 2019)

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

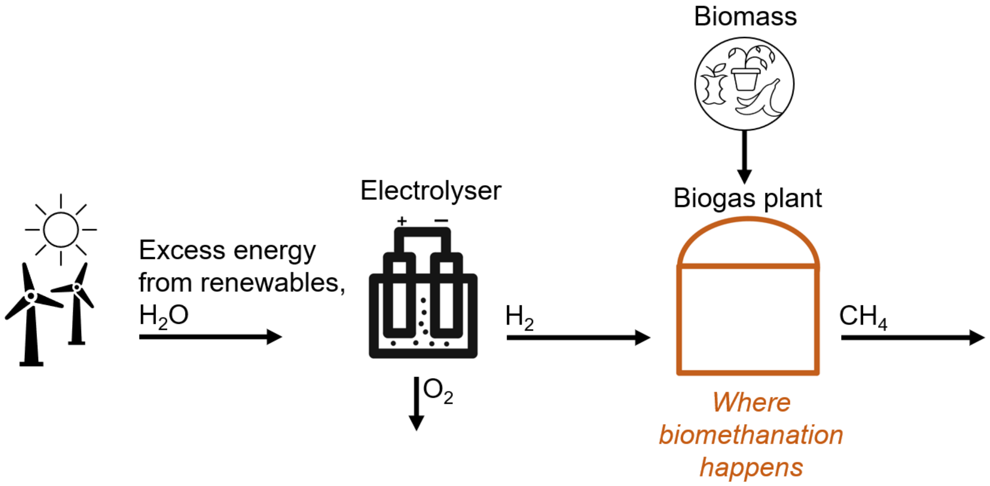


Figure 4 *In-situ biomethanation process. Excess renewable wind or solar power is utilized in H_2-producing electrolyser. H_2 is directed into biogas plant, which is fed with biomass. Biomethanation happens in the biogas reactor, with biomethane as the final product. Adapted from (Lecker et al., 2017; Rusmanis et al., 2019)*

Ex-situ biomethanation (Figure 5) utilizes an external biomethanation reactor, where CO_2 and H_2 are injected (Rusmanis et al., 2019). CO_2 can be derived from a biogas plant, but also from other sources.

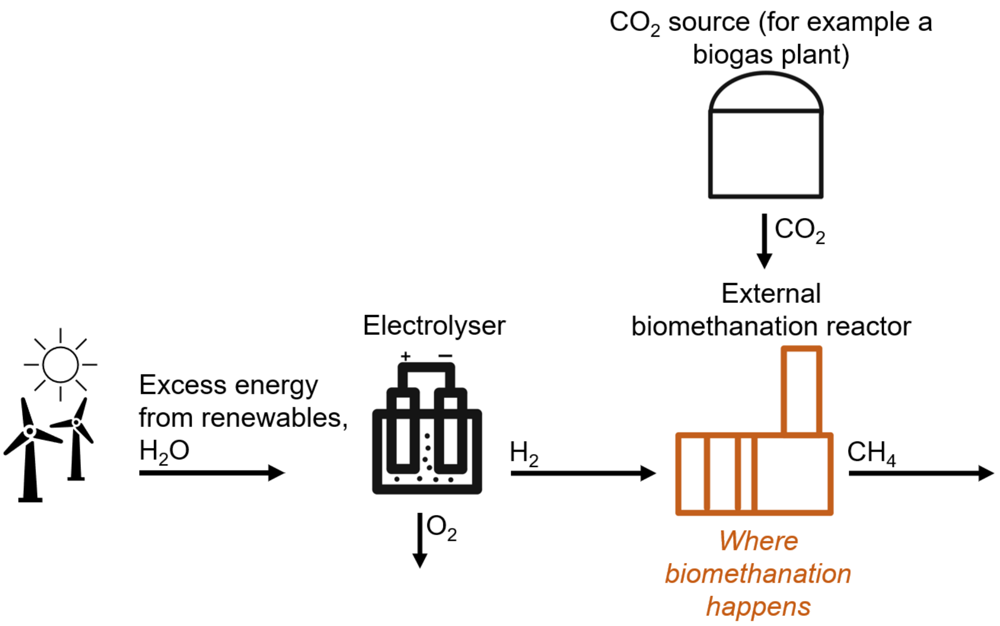


***Figure 5** Ex-situ biomethanation process. Excess renewable wind or solar power is utilized in H_2-producing electrolyser. H_2 is directed into external biomethanation reactor, which is fed with CO_2, e.g. from a biogas plant. Biomethane is the final product. Adapted from (Lecker et al., 2017; Rusmanis et al., 2019)*

The main advantage of in-situ biomethanation is its economic feasibility compared to more expensive ex-situ option, since biomethanation and biogas production can happen in the same reactor, and thus no new reactor is needed (Fu et al., 2021; Xu et al., 2020a) However, there are some considerable drawbacks in in-situ biomethanation.

In in-situ biomethanation, there is a risk of pH increase to levels higher than 8.5, which may lead to methanogenesis inhibition. The pH increase is due to bicarbonate removal from the process. (Angelidaki et al., 2018) When reactions occur in liquid phase, CO_2 is dissociated into H^+ and HCO_3^- (Equation 7), and when CO_2 is utilized due to methanogenesis, bicarbonate-alkalinity buffer capacity is reduced, H^+ concentration will decrease, and the reactor's pH will rise (Angelidaki et al., 2018; Angenent et al., 2018).

$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \tag{7}$$

Luo et al. (2012) investigated, that hydrogenotrophic methanogens consume bicarbonates, and this is what causes pH to increase. In the same study it was suggested, that in addition to external H_2, acidic organic wastes could be added to the reactor to keep pH low enough. Luo and Angelidaki (2013) later succeeded at keeping pH below 8 in in-situ biomethanation by co-digestion of acidic whey and manure, with addition of H_2.

In-situ method requires cost intensive automation and gas measurement equipment, because the amount of H_2 injected needs to be adapted to the amount of CO_2 produced in anaerobic digestion. Also, methane evolution rate (MER), also called methane production rate, is considerably lower in in-situ than in ex-situ biomethanation systems. (Lecker et al., 2017) MER is an important parameter, and it is used to calculate system performance. MER has a unit of $L/L_{VR}/d$, where L is the volume of methane, L_{VR} is the working volume of the reactor, and d is day. (Rusmanis et al., 2019) In-situ systems usually have low methane conversion efficiency, and in many cases it is necessary to apply post-treatment to in-situ process to reach higher methane concentrations (Angenent et al., 2018).

As mentioned in chapter 2.3, H_2 partial pressure needs to be kept at a very low level in anaerobic digestion's acetogenesis (Rusmanis et al., 2019). Injecting H_2 directly into biogas reactor can cause H_2 accumulation in the headspace of the in-situ reactor increasing H_2 partial pressure (Angenent et al., 2018), which in turn leads to reduced conversion rates of substrate. This can also inhibit methanogenesis. (Rachbauer et al., 2016) As for the increase in H_2 concentration in anaerobic digestion, it can inhibit the oxidation of VFAs in acetogenesis. This will lead to VFA accumulation in the process, which leads to acidification of the process. (Angelidaki et al., 2018; Fu et al., 2021; Mulat et al., 2017) Excess H_2 in acetogenesis also stimulates homoacetogenesis which happens in Wood-Ljungdahl pathway, which means that more acetate is being produced from H_2 and CO_2. This leads to increasing methane production through aceticlastic methanogenesis. (Liu et al., 2016; Mulat et al., 2017)

Ex-situ biomethanation has many advantages in comparison to in-situ biomethanation. Biogas process in anaerobic digestion unit is secured, since external H_2 is added into an external biomethanation reactor. Biochemical process in the biomethanation reactor is simpler, since it lacks the first phases of anaerobic digestion, hydrolysis and acidogenesis. Ex-situ biomethanation is also independent of biomass, and CO_2 can be derived from other origins than from biogas only (for example syngas), which makes the process more flexible. (Angelidaki et al., 2018) Also, in in-situ biomethanation, H_2 injection amount is strictly adapted to CO_2 produced in the reactor, which is not the case in ex-situ biomethanation. Ex-situ biomethanation process has no limitations in terms of substrate gas availability, and it is possible to inject larger amounts of substrate gases in the reactor. (Lecker et al., 2017)

However, ex-situ biomethanation also has its disadvantages. Ex-situ biomethanation requires an external reactor, so it might be economically not as feasible as in-situ biomethanation (Xu et al., 2020a) The biggest technical challenge in both in-situ and ex-situ biomethanations is a low gas-liquid mass transfer rate (Angelidaki et al., 2018; Voelklein et al., 2019). H_2 needs to be solubilized to be available for microbes in their metabolism.

Therefore, H_2 solubilization is considered to be the bottleneck of methanogenesis. Gas-liquid mass transfer rate for H_2 can be described by Equation 8. (Angelidaki et al., 2018; Lecker et al., 2017; Voelklein et al., 2019)

$$r_t = 22.4k_L a\left(H_{2g} - H_{2l}\right) \tag{8}$$

In Equation 8, r_t is the H_2 gas-liquid mass transfer rate, with a unit of $L/(L_{Reactor}d)$. The number 22.4 is the volume of 1 liter of H_2 per 1 mol of gas at standard conditions for temperature and pressure (STP), with a unit of L/mol. k_La is gas transfer coefficient with a unit of 1/d, H_{2g} is the gas phase concentration of H_2 (mol/L) and H_{2l} is the liquid phase H_2 concentration. (Angelidaki et al., 2018; Lecker et al., 2017)

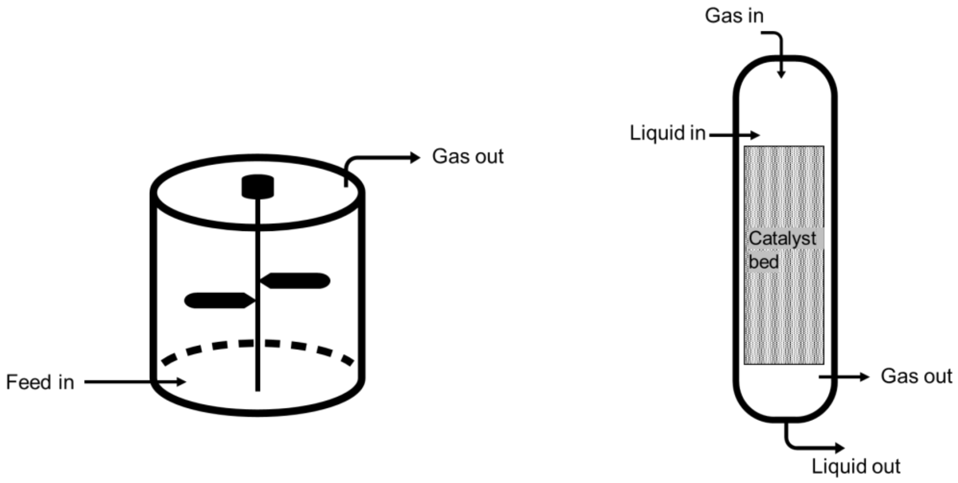
Some ex-situ biomethanation applications have overcome the obstacle of poor gas-liquid mass transfer rate by intense mixing and headspace pressure increase. However, these methods are difficult to achieve in in-situ biomethanation. (Angenent et al., 2018)

3.4 Case studies of biomethanation

Biomethanation has been the subject of many laboratory and some pilot-scale studies. Studies about biomethanation have been conducted with various reactor configurations and in in-situ, ex-situ and hybrid applications. In-situ biomethanation is the most studied application of the three (Sposob et al., 2021), but in the last couple of years, more studies have been done about ex-situ and hybrid applications. Ex-situ method has become more attractive because of its lack of in-situ method’s disadvantages (Sposob et al., 2021), which include increase in pH (Angelidaki et al., 2018), H_2 partial pressure increase and accumulation causing an inhibition of the process (Angenent et al., 2018; Rachbauer et al., 2016) and lower methane production rate (Lecker et al., 2017). Ex-situ biomethanation is also said to be more developed method, compared to in-situ, with many novel technologies and concepts tested in laboratory scale. (Rusmanis et al., 2019; Voelklein et al., 2019).

3.4.1 Reactors in biomethanation studies

The most common reactor designs in biomethanation studies include continuously stirred tank reactor (CSTR) and trickle bed reactor (TBR) (Figure 6) (Jensen et al., 2021b). CSTR is used in both in-situ and ex-situ applications, but TBR is used only in ex-situ applications (Angelidaki et al., 2018; Mads Bjørnkjær Jensen et al., 2021b; Lecker et al., 2017).



A) CSTR B) TBR

Figure 6 *Simple working principles of continuously stirred tank reactor (CSTR) (A) and trickle bed reactor (TBR) (B).*

CSTR is a traditional reactor type in anaerobic digestion (Rusmanis et al., 2019). It is a well-mixed reactor, which is semi continuously fed and mixed, while the product gas is removed simultaneously with feeding. Ideal CSTR has three assumptions: the reactor has a uniform temperature and concentration, output effluent has the same concentration as inside the tank and the tank is operating at steady state. (Foutch and Johannes, 2003) Stirring of the CSTR happens either via internal agitation or by recycling the contents internally or externally (Pereira and Tiberiu, 2019). In trickle bed reactors (TBR), reactant gas and liquid phases flow through a catalyst bed. Catalysts in TBRs are solid particles, on which a biofilm grows. The word “trickling” in the name comes from liquid trickling as a film over the catalyst. TBRs typically require cooling between operation stages. (Pereira and Tiberiu, 2019)

3.4.2 In-situ biomethanation studies

Comparison of some selected in-situ applications from research, their reactor types, substrates used, temperatures, pH, methane concentrations and methane production rates are displayed (Table 1). Only studies with continuous systems were included, since they are the most realistic to be scaled up in future applications. Only studies made during the last 10 years were collected. Most of the continuous in-situ studies have favored CSTR and thermophilic conditions. Their biomethane percentage from output gas has been 58–100 %.

Table 1 *Summary of selected continuous in-situ biomethanation studies.*

Reactor type	Substrate	T [℃]	pH	Biomethane CH_4 [%]	Methane production rate [mL CH_4/(L_{VR}·d)]	Gas conversion efficiency [%]	H_2 loading [mL /(L_{VR}·d)]	Scale	Reference
CSTR	Whey and cattle manure	55	7.28–7.89	75	885	Almost 100 (H_2 conversion)	N.D.	Laboratory (Lab.)	(Luo and Angelidaki, 2013)
CSTR	Raw cattle manure	55	8.3	65	453.6	N.D.	686.4	Lab.	(Luo et al., 2012)
CSTR & batch	Grass silage	55	8.37	60.3	2520	72 (H_2 + CO_2 conversion)	5290	Lab.	(Voelklein et al., 2019)
CSTR	Sludge from a biogas plant	38	8.18	100	440	86 (H_2 + CO_2 conversion)	900 (pulse injections)	Lab.	(Agneessens et al., 2017)
CSTR	Liquid manure, straw, deep litter, grass and maize silage	52	7.5–7.8	63.6	N.D.	N.D.	443	Full-scale	(Jensen et al., 2018)
CSTR	Manure, deep litter, mixed agricultural material, grass and maize silage	52	7.7–7.8	maximum ca. 58–65	3600 (biogas production)	49 (H_2 conversion)	122 – 1796	Full-scale	(Jensen et al., 2021a)
UASB*	Potato starch wastewater	55	8,38	82	1145	94 (H_2 conversion)	1828	Lab.	(Bassani et al., 2016)

*UASB = up-flow anaerobic sludge blanket

N.D. = not determined

Agneessens et al. (2017) found out in their CSTR-type study that pulse H_2-injections are possible to conduct for in-situ biomethanation, but if the pulse's H_2:CO_2 ratio was increased to higher than 4:1, pH started to increase because of CO_2 depletion. Low CO_2 levels then again seemed to inhibit hydrogenotrophic methanogens. Also, accumulation of acetate was discovered during pulse H_2 injections. In the same study (Agneessens et al., 2017), it was discovered that the ratio 6:1 of H_2 and CO_2 was able to produce biogas with CH_4 content of 100 %, however, acetate started to greatly accumulate with this ratio, as well as with other ratios larger than 4:1. It has been common to add H_2 in a 4:1 relation to CO_2 to the process, because of the stoichiometric ratio of CH_4 process (Equation 3) (Burkhardt et al., 2015; Luo et al., 2012; Luo and Angelidaki, 2013, 2012; Voelklein et al., 2019).

There are not many full-scale studies about in-situ biomethanation. However, Jensen et al. (2018) conducted an in-situ study in full-scale (Table 1) in Denmark. They stated in their study, that laboratory scale in-situ studies have implemented various methods for easing H_2 gas-liquid mass transfer, but most of them would be too costly or difficult to operate in full-scale. In their study, they used venturi-type H_2 injection and headspace gas recirculation in order to ease H_2 gas-liquid mass transfer. It turned out that recirculation of H_2 is not the most sufficient way for H_2 mass transfer in full-scale in-situ, since H_2 was diluted with biogas by the recirculation and therefore the mass transfer driving force was reduced. Also, the study found that venturi-type injection should utilize smaller H_2 bubbles for better H_2 mass transfer. A Landia® GasMix system was used in the H_2 injection. (Jensen et al., 2018)

Bassani et al. (2016) found out in their in-situ experiment, that porous devices like ceramic sponge help H_2 mass transfer and therefore benefit H_2 uptake. They also stated that gas recirculation helps with the same issues. They managed to produce biomethane with CH_4 content being 82 % (Table 1).

3.4.3 Ex-situ biomethanation studies

Comparison of some selected ex-situ applications, their reactor types, substrates used, CO_2 sources, temperatures, pH, methane concentrations, gas conversion rates and methane production rates is shown (Table 2). Only studies with continuous operation were selected. Studies collected had to be 10 years old at the most. It was common to use pure CO_2 as the CO_2 source, biogas was used only in one study (Rachbauer et al., 2016). Biomethane percentages from output gas were 85–98 % in these studies.

Table 2 *Summary of selected continuous ex-situ biomethanation studies.*

Reactor type	Substrate	CO_2 source	T [℃]	pH	Biomethane CH_4 [%]	Methane production rate [mL $CH_4/(L_{VR}*d)$]	CO_2 conversion efficiency [%]	H_2 loading [mL $/(L_{VR}*d)$]	Scale	Reference
Continuous + ceramic diffuser	Grass silage	CO_2	55	8.2	85	850	53 (Gas conversion)	5400	Lab.	(Voelklein et al., 2019)
Continuous TBR	Mineral media, pig feed + sugar*	Biogas	37	6.8–7	96	ca. 3600**	> 96	5000	Lab.	(Rachbauer et al., 2016)
Continuous TBR	Sewage sludge as inoculum	CO_2	37	7.2–7.4	98	1490	> 95	6000	Lab.	(Burkhardt et al., 2015)
CSTR	Slightly adopted medium	CO_2	65	6.85	85	1 363 600	N.D.	N.D.	Lab.	(Seifert et al., 2014)
Biofilm plug flow reactor and TBR	Sewage sludge	CO_2	37	1	ca. 90	30 000	90 (gas conversion)	120 000	Lab.	(Savvas et al., 2017)

*Mineral media for TBR, pig feed and sugar for biogas plant

**3700 mL biogas /L_{VR}/d when biogas CH_4 content is >96 %

N.D. = not determined

Voelklein et al. (2019) discovered in their study (Table 2) about continuous ex-situ system, that a higher H_2 injection rate indicated also higher methane production rate, but at the same time lower conversion efficiency. They found out, that the higher the volumetric H_2 and CO_2 loading is, the lower the CH_4 content in the biogas would be. when H_2 loading was 5400 mL/L_{VR}/d, CH_4 content in biogas was 85 %, whereas when H_2 loading was 50 500 mL/L_{VR}/d, CH_4 content in biogas was only 23 %. The H_2:CO_2 ratio was kept at 4:1 the whole time. They then suggested a system of three ex-situ reactors in series for full-scale methanation unit, for increasing the CH_4 content in each reactor, up to 85 % CH_4 content and 3.6 L CH_4/(L_{VR}*d). They also suggested a hybrid process of combining in-situ and ex-situ, with the final specific CH_4 production of 96 % and methane production rate of 6434 m^3 CH_4/d. (Voelklein et al., 2019)

Rachbauer et al. (2016) had noticed the same as Voelklein et al. (2019): in their ex situ TBR experiments, biogas production rate was considerably lower when methane concentration in the output was higher. Biogas production rate was 6900 mL biogas/L_{VR}/d with biogas CH_4 content being ca. 60 %. When biogas CH_4 content was raised up to >96 %, biogas production rate dropped to 3700 mL biogas/L_{VR}/d (Table 2).

Generally, CSTRs produce higher methane production rates than packed bed reactors such as TBR (Muñoz et al., 2015). Thermophilic conditions have also produced higher methane production rates than mesophilic conditions (Rachbauer et al., 2016). CSTR’s can usually outperform other reactor configurations, since they are continuously mixed and therefore gas-liquid contact is higher; however, CSTR’s require a lot of energy. It is worth noticing, that these review articles used experiments which mainly used pure H_2/CO_2 mixtures and not real biogas as CO_2 source. (Rachbauer et al., 2016) It can be difficult to flawlessly compare different studies and their methane production rates or gas conversion efficiencies, since the studies themselves can differ a lot from each other, in terms of for example substrate, pH, temperature, reactor used, whether gas injection is continuous or done in pulses, and CO_2 source.

3.5 Biomethanation case examples in Europe

Biomethanation is still quite a novel method for producing methane, however, it has been investigated in some pilot scale studies (Lecker et al., 2017). There are plans for implementing biomethanation in industrial scale, for example in Tampere, Finland, where ex-situ biomethanation plant is being built to utilize waste incineration’s flue gases’ CO_2 (Palomaa, 2022). Some companies have already succeeded in realizing commercialized ex-situ biomethanation plants in Europe; below are some of them.

A German biomethanation company (Electrochaea) utilizes ex-situ P2G in commercial scale. It launched a couple biomethanation plants in Europe, including a commercial scale plant (Store&Go) in Solothurn Switzerland and a commercial scale project (BioCat) in Avedøre, Denmark. In Solothurn's plant, over 280 Nm^3 biomethane per day was injected into gas network over the course of more than 7 weeks of operation. H_2 producing electrolysis machinery was located next to the biomethanation plant, and CO_2 was derived from a near-by wastewater treatment plant. Biomethane's CH_4 content was 97 % and there was no purification needed. ("Electrochaea GmbH - Power-to-Gas Energy Storage | Technology," n.d.)

Another example of a commercialized P2G company is a Finnish company (Q-Power), which has made a couple pilot-scale biomethanation plants in Finland. In Vantaa, they collaborated with an energy company (St1) and generated biomethane from H_2 and bioethanol production's excess CO_2. Another pilot plant of theirs took place in Salo, where biomethanation was conducted for landfill gas. ("Ratkaisut - Q Power," n.d.)

Another Finnish P2G company (Ren-Gas) utilizes P2X (Power to X) in addition to P2G. In P2X, the final products are different biofuels, not only strictly methane, but also substances like methanol or ammonia ("Power-to-x (P2X) – Mitä se tarkoittaa ja miten se mullistaa energian- ja ruoantuotannon? - Uutiset - LUT," n.d.). The most recent projects of Ren-Gas include P2G biomethanation plants in Kotka and Tampere. They are both to be ex-situ plants, where CO_2 is derived from energy production's flue gases and H_2 from wind power plants. ("Etusivu - Ren-Gas Oy," n.d.).

4. MATERIALS AND METHODS

Calculations and literature reviews were conducted. In this chapter, process of the calculations is presented, as well as materials and methods related to the case study's and Finland's national biomethanation potential's investigations.

4.1 Process of the calculations

Calculations had three main parts (Figure 7): biomethanation potential calculations (i.e. how much methane can be produced from CO_2), H_2 production calculations and techno-economic analysis. These calculations were made for an individual biogas plant (referred as case study) and for Finland in the national level.

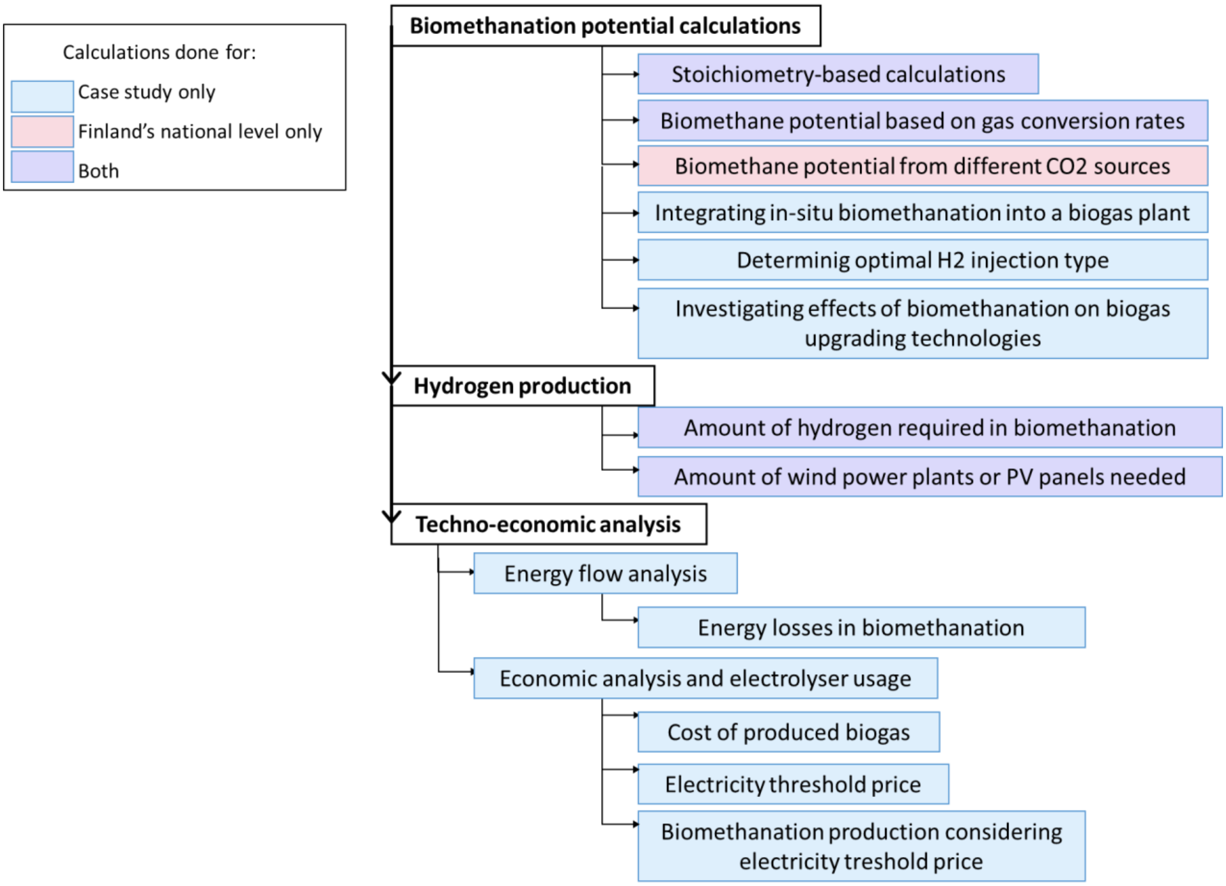


***Figure 7** Calculations process. Calculations were done in three parts: biomethanation potential calculations (i.e., how much methane can be produced from CO_2), H_2 production calculations and techno-economic analysis. Calculations were done for case study only (blue), Finland's national level only (red) or for both (purple).*

Investigation of different CO_2 sources included a calculation of biomethanation potential in Finnish bioethanol plants. Initial data considering the case study plant and Finnish bioethanol plants was received from the involved companies. The calculation methods are presented in the chapters below. Presentation of calculation methods focuses firstly on the case study, and then on the national potential.

4.2 Typical case study of a biogas plant

As a typical case study this thesis considered Gasum's Lohja biogas plant, which started its commercial operation in 2021 and uses biodegradable wastes (excluding sewage sludge) in its operation ("Lohjan biokaasulaitos | Gasum," n.d.). The biogas plant utilizes membrane technology in biogas upgrading before injecting biogas into the national gas grid.

Biomethanation potential was studied mainly through in-situ biomethanation, since in-situ would likely have the lowest investment level for an existing biogas plant. This is because there is no need for an external reactor (Xu et al., 2018; Zhu et al., 2019). Calculations were performed based on actual data from one year's operation in the biogas plant, but it should be noted that as a new plant it was still partly in ramp-up phase.

4.2.1 Biomethanation potential in the case study

Biomethanation potential (the amount of biomethane derived from biomethanation) in the case study was determined. Stoichiometry-based calculations about biomethanation potential started with determining the total daily biogas production by multiplying daily biogas production per reactor working volume with the reactor's working volume. The daily CO_2 production was calculated by multiplying daily biogas production with biogas CO_2 content. H_2 requirement was calculated based on 4:1 H_2/CO_2 molar ratio, as this is the stoichiometric relation in the Sabatier reaction (Equation 3) and widely used in biomethanation studies (Burkhardt et al., 2015; Luo et al., 2012; Luo and Angelidaki, 2013, 2012; Voelklein et al., 2019).

Theoretical CH_4 production from biomethanation was calculated using Sabatier reaction and its stoichiometry assuming 100 % gas conversion. Theoretical masses of both CO_2 and H_2 required were calculated using Equation 9:

$$m = \rho V \tag{9}$$

where m [kg] is theoretical mass of the substance, ρ [kg/m^3] is gas density at NTP and V [m^3] is gas volume. Theoretical masses of both CO_2 and H_2 produced were calculated using their gas densities at NTP (1.97 kg/m^3 and 0.089 kg/m^3, respectively) ("Mekaniikka | Taulukot - Matematiikka, Fysiikka ja Kemia," n.d.).

Theoretical mass of formed CH_4 was calculated using Equation 10:

$$m(CH_4) = \frac{1}{4} * n(H_2) * M(CH_4) \tag{10}$$

where 1:4 is the stoichiometric relation of methane and hydrogen, $n(H_2)$ [mol] is the amount of substance for H_2 and $M(CH_4)$ [g/mol] is the molar mass of methane. Biomethane's energy content was calculated using the energy content of methane ("Biokaasun tuotanto maatilalla," n.d.).

Estimation of the gas conversion efficiency was determined for the in-situ CH_4 production. Case study uses a CSTR reactor, thus gas conversion efficiencies (49–100 %, Table 1) in previous in-situ CSTR studies were compared. Gas conversion efficiency of 85 % was used in this study. This was multiplied with the theoretical CH_4 production from biomethanation to get the actual CH_4 production.

Sensitivity analysis of biomethanation potential was calculated using biogas production rate of 10 % smaller or 10 % larger than original calculated value and gas conversion being 75 % or 95 % instead of the original 85 %.

Ex-situ biomethanation was examined as another biomethanation option for the case study. It was assumed that the new reactor that would have to be built, would be a TBR, because they have had very high gas conversion efficiencies (90–96 %) and biomethane's CH_4 percentages (90–98 %) in past studies (Burkhardt et al., 2015; Rachbauer et al., 2016; Savvas et al., 2017). Case study's ex-situ biomethanation's gas conversion efficiency was estimated to be 95 %. This gas conversion efficiency was multiplied with the theoretical CH_4 production. Comparison of in-situ and ex-situ biomethanation at the case study was made.

4.2.2 Integration of in-situ biomethanation into an existing biogas plant

The potential ways of technically integrating in-situ biomethanation into the existing case study's biogas plant were studied. In addition, based on the case study's operational parameters and literature, the effects of integration into an existing biogas plant were discussed. Considerations about H_2 injection type , possible recirculation of gases and stirring were done reflecting on other studies and biomethanation companies techniques (Agneessens et al., 2017; "Electrochaea GmbH - Power-to-Gas Energy Storage | Technology," n.d.; Jensen et al., 2018). Case study's operational parameters (i.e. reactor type and pH) were compared to other in-situ biomethanation studies with similar operational parameters and based on this, an estimation of the impacts on the integration was made. The studies that were compared to the case study were continuous in-situ biomethanation studies (Agneessens et al., 2017; Luo et al., 2012; Luo and Angelidaki, 2013; Voelklein et al., 2019; Zhu et al., 2019).

4.2.3 H_2 required in the case study

Energy required for H_2 production by current commercial water electrolyser with 83 % efficiency was determined based on Hodges et al. (2022). The electricity production of a regular wind power plant, wind power production and the number of wind power plants in Finland in 2021 were also determined (Suomen Hyötytuuli, n.d., Suomen Tuulivoimayhdistys, 2022). The power of the most powerful photovoltaic (PV) panels on sale in Finland is 500 Wp (Scanoffice, 2022).

With these initial values and the theoretical mass of H_2 needed for in-situ CH_4 production in the case study, the electricity required to produce the needed amount of H_2 was calculated. The mass of required H_2 was multiplied by 44 kWh (the energy required for producing 1 kg of H_2 via water electrolysis) and then with 0.83 (efficiency of typical state-of-the-art water electrolyser) (Hodges et al., 2022). The number of wind power plants or most powerful on-sale PV panels needed to produce this energy were determined, as well as the area required by needed PV panels (Tulituote, n.d.).

4.2.4 Effects of biomethanation on biogas upgrading technologies

Effects of biomethanation on membrane separation technology and on water scrubbing upgrading technology were investigated, because these biogas upgrading technologies are known to be in use in Finnish biogas plants. The case study utilizes membrane separation technology, and water scrubbing is the most widely used biogas upgrading technology (Nock et al., 2014).

This investigation was done as a literature review. Information about membrane separation technology (Awe et al., 2017; Brunetti et al., 2014; Chen et al., 2015; Deng and Hägg, 2010; Shin et al., 2019; Xu et al., 2018; Zhang et al., 2013) and water scrubbing technology (Nock et al., 2014; Wylock and Budzianowski, 2017) was collected. Results on the review are shown in chapter 5.

4.3 Finland’s national biomethanation potential

Finland’s national biomethanation potential was investigated focusing on existing and future biogas and biomethane producing plants and their CO_2 outputs (*Biokaasun tuotanto vuonna 2030*, 2022, “Suom. Biokierto ja Biokaasu ry,” n.d., “Tilastokeskus,” n.d.). Finnish wind power plants and PV panels were considered as the sustainable electricity source for H_2 production.

Bioethanol plants were investigated as another biogenic CO_2 source and compared with biogas plants' biomethanation potential. St1's Finnish bioethanol plants were used as an example, and information about them and their CO_2 production were used in the calculations.

4.3.1 Biomethanation potential calculations

Finland's national biomethanation potential was calculated for the present and for the future. For the present, data from year 2020 was used, because more recent and complete data from 2021 was lacking at the moment of writing this thesis. As for the future, specific calculations were performed for year 2030, since for that year there was predictive data available (Finnish Biocycle and Biogas Association). Landfill gas is a source of biogas which is decreasing over time, which is why it is not included in the calculations for the year 2030. It has been estimated that landfill biogas production would be 0.12 TWh in 2030 (*Biokaasun tuotanto vuonna 2030*, 2022), which is only 3 % of the entire biogas and CH_4 production of 2030 (altogether 4 TWh). However, landfill gas is included in the 2020 calculations, since in 2020 landfill gas as a biogas source was still relevant, 190 GWh out of 768 GWh ("Tilastokeskus," n.d.).

Two sources for CO_2 from biogas processes were determined. One was the CO_2 that is present in biogas formed during anaerobic digestion and the other one was the CO_2 retrieved from biogas upgrading (Figure 8).

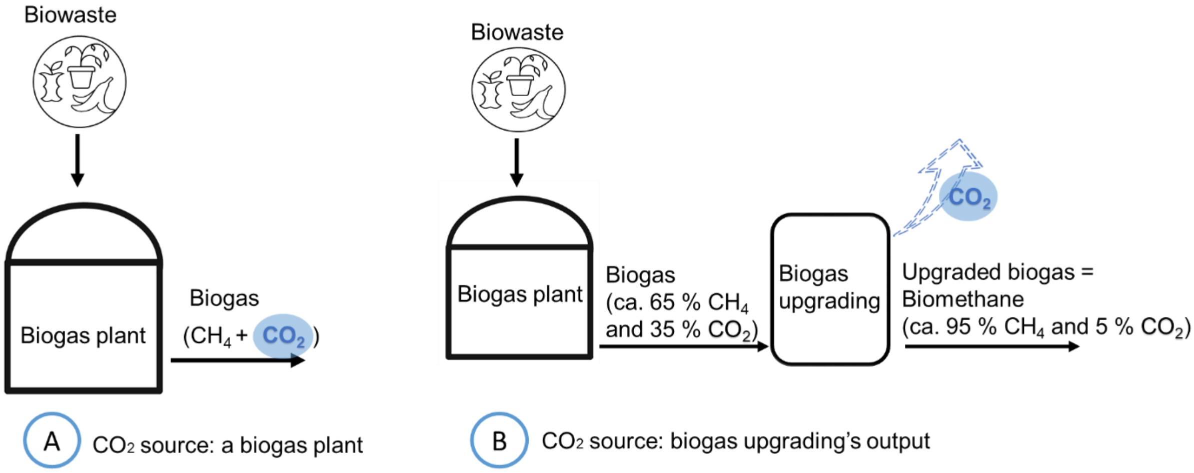
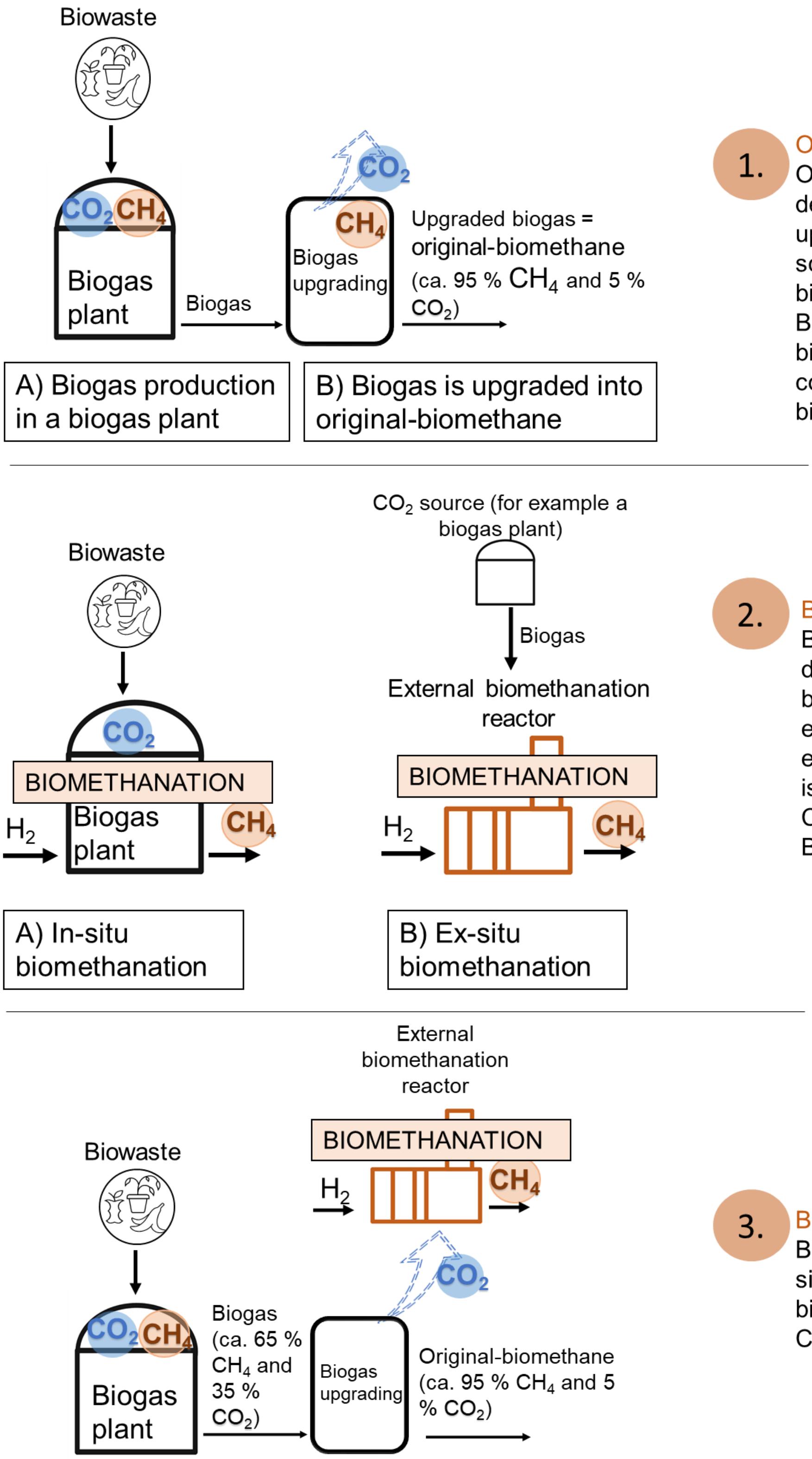


Figure 8 *CO_2 sources in Finland's national potential calculations. A = CO_2 present in biogas, B = CO_2 exiting biogas upgrading unit.*

It was assumed that there are three main biomethane types, based on how the biomethane is made (Figure 9). Original-biomethane represents biomethane derived from biogas upgrading process, with no biomethanation involved. Biogas-biomethane represents biomethane derived from either in-situ or ex-situ biomethanation, while using CO_2 from the biogas. Biogas-upgrading-biomethane represents biomethane derived from ex-situ biomethanation, with biogas upgrading output as the CO_2 source.



1. Original-biomethane
Original biomethane is derived from biogas upgrading (like water scrubbing), without biomethanation involved. Biogas is first produced in a biogas plant (A), and then converted into original-biomethane (output in B).

2. Biogas-biomethane
Biomethane derived from biomethanation, either in-situ (A) or ex-situ (B). Biogas is the source of CO2 in both A and B.

3. Biogas-upgrading-biomethane
Biomethane derived from ex-situ biomethanation, from biogas upgrading's output CO2.

Figure 9 *Three types of biomethane based on their origin. Original-biomethane is derived from biogas after the biogas upgrading unit, with no biomethanation involved (1). Biogas-biomethane is derived from either in-situ (A) or ex-situ (B) biomethanation of biogas (2). Biogas-upgrading-biomethane is derived from ex-situ biomethanation of* CO_2 *from biogas upgrading unit (3).*

Biomethane that is made by biomethanation (biogas-biomethane and biogas-upgrading biomethane, Figure 9) was in the key position while calculating biomethanation potential in Finland. Original-biomethane and biogas were included in the calculations when examining the total amount of biomethane produced in Finland.

4.3.2 Finland’s biomethanation potential in 2020

Finland’s biomethanation potential in calculations followed the pattern of calculating the case study’s biomethanation potential. Data about biogas production in Finland and the CO_2 amount produced by biogas plants was used in the calculations.

In 2020, 768 GWh of biogas and 110 GWh of biomethane was produced in Finland (Table 3) (“Tilastokeskus,” n.d.). This 110 GWh is biomethane produced by upgrading biogas.

***Table 3** Biogas and biomethane production in Finland in 2020 and estimation for 2030, by plant type* ("Suom. Biokierto ja Biokaasu ry," n.d.) *Biogas/ biomethane production details are not specified for industrial plants which produce biogas or biomethane. Their production data is included in the data for co-digestion plants. This table does not include biomethane made by biomethanation. ("Suom. Biokierto ja Biokaasu ry," n.d., "Tilastokeskus," n.d.)*

	Number of biogas plants in Finland in 2021	**2020 biogas prodution (GWh)**	**2030 biogas production (GWh)**	**2020 CH_4 production (GWh)**	**2030 CH_4 production (GWh)**	**2020 total (GWh)**	**2030 total (GWh)**
Landfill gas plants	33	190	119	N.D.	N.D.	190	119
Farm scale plants	25	16	151	2	30	18	181
Industrial plants	9	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Biowaste + sludge co-digestion plants	26	323	156	108	500	431	656
Sludge anaerobic digestion plants	19	239	195	N.D.	100	239	295
Centralized agricultural biomass plants	N.D.	N.D.	N.D.	N.D.	1 300	N.D.	1 300
Middle-sized biogas plants	N.D.	N.D.	200	N.D.	165	N.D.	365
New technologies (in the future: P2G, bioethanol production's side streams, wood, etc.)	N.D.	N.D.	N.D.	N.D.	1 000	N.D.	1 000
Total	112	768	821	110	3095	877	3 916

N.D. = Not determined

The average CH_4 content of biogas, 65 %, was estimated based on literature (Angelidaki et al., 2018; Hilkiah Igoni et al., 2008; Liebetrau et al., 2017). The remaining of the biogas was assumed to be CO_2. The amount of H_2 required for biomethanation was calculated with 4:1 H_2/CO_2 ratio. The stoichiometric CH_4 production was calculated with Equation 9.

Simplifications and estimations were made when calculating the actual amounts of biogas-biomethane and biogas-upgrading-biomethane production potential. Approximation based on literature was used when determining average gas conversion efficiencies for different biomethanation systems. Gas conversion efficiencies were determined for in-situ CSTR, ex-situ CSTR and ex-situ TBR reactors, which are common in in-situ and ex-situ biomethanation processes (Jensen et al., 2021b). For biogas-biomethane potential in 2020, the options are either using existing biogas reactors for in-situ (in which case one of the most common existing reactor types is CSTR (Banerjee et al., 2021)) or building ex-situ reactors (in which case it would be sensible to build a reactor type that's already been tested in biomethanation studies, for example CSTR or TBR). All of the processes were determined to be continuous. It was estimated that the average gas conversion efficiencies were 90 % for CSTR ex-situ reactor, 95 % for TBR ex-situ reactor and 85 % for CSTR in-situ reactor (Voelklein et al., 2019; Zhao et al., 2021). These gas conversion rates were multiplied by the theoretical CH_4 production in biomethanation to get the annual CH_4 productions for each process. Finally, a mean value from the three CH_4 productions was obtained to get an estimation of a biomethanation reactor's annual average CH_4 production.

Biogas-upgrading-biomethane is made from the CO_2 removed in biogas upgrading process (z in Figure 10). The amount of CO_2 removed (z in Figure 10) from original-biomethane (y in Figure 10) was determined to find out, how much biogas-upgrading-biomethane would be possible to produce. Calculations were done based on assumptions made in Figure 10. The amount of removed CO_2 (z in Figure 10) was calculated by subtracting original-biomethane from initial, not yet upgraded biogas (x-y Figure 9), taking into account that the amount of CO_2 left in original-biomethane is assumed to be 5 %.

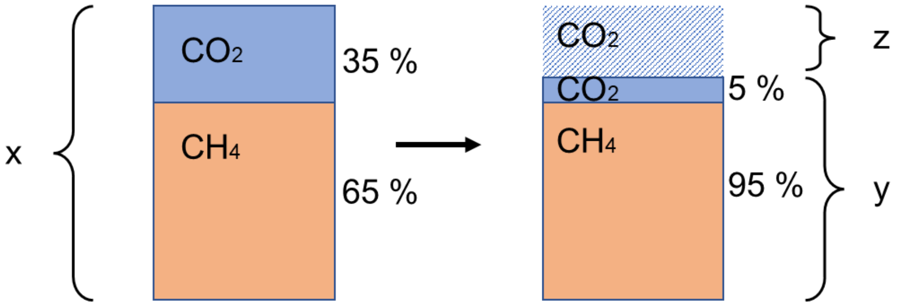


***Figure 10** Initial, to be upgraded biogas (x) and the upgraded biogas, called original-biomethane (y) with estimated CO_2 and CH_4 percentages. Z in original-biomethane represents the amount of CO_2 that can be used in biomethanation, when making biogas-upgrading-biomethane.*

Calculations of the amount of biogas-upgrading-biomethane were done almost the same way as in the case for biomethanation for biogas plants: first determining the theoretical CH_4 production and then the CH_4 production with appropriate gas conversion rate. In this case, only ex-situ biomethanation plants were considered in the biogas-upgrading-biomethane calculations.

4.3.3 Finland’s biomethanation potential in 2030

In 2021, the Finnish Government set a goal, according to which Finland’s combined biogas and CH_4 production should reach 4 TWh in 2030. Biogas production has been estimated to be around 1.2 TWh in 2030, thus increasing only 0.2 TWh from 2020. However, original-biomethane production has been estimated to grow to 2.8 TWh in 2030. (*Biokaasun tuotanto vuonna 2030*, 2022) Calculations on the 2030 biogas-biomethane potential were made like in the case of 2020.

Suomen Biokierto & Biokaasu ry (“Suom. Biokierto ja Biokaasu ry,” n.d.) has estimated that out of all the biogas-producing plant types, farm scale plants are the only ones which will increase their total biogas production (Table 3). In other plant types (except for landfills) original-biomethane production will strongly increase.

Calculations for determining the amounts of biogas-biomethane and biogas-upgrading-biomethane were done the same way as in the Finland’s national biomethanation potential in 2020 calculations.

Finland’s national biomethane production potential from 2020 was compared to Finland’s natural gas consumption of 20 718 GWh/a (Energian kokonaiskulutus energialähteittäin (kaikki luokat), n.d.), traffic energy consumption and road traffic energy consumption of 46 117 GWh/a and 42 423 GWh/a, respectively (Liikenteen energiankulutus 1990-2021, n.d.), heat production of 86 247 GWh/a (Työ- ja elinkeinoministeriö, 2020) and electricity consumption of 81 600 GWh/a (Tilastokeskus - Sähkön ja lämmön tuotanto 2020, 2021). These comparisons helped in understanding the significance of biomethanation and overall biogas and CH_4 production in Finland’s energy sector. H_2 required for biomethanation in Finland in 2020 and 2030 was calculated the same way as in the case for the case study.

4.3.4 Biomethanation potential in bioethanol plants

Bioethanol plants were also taken under observation as part of the Finland’s national biomethanation potential. Bioethanol production also produces CO_2, and bioethanol plant’s biomethanation potentials were compared to the case study’s biomethanation potential.

Data was from 2021 CO_2 production in all of St1’s bioethanol plants located in Finland. This data included five bioethanol plants, out of which four had CO_2 production in 2021. Biomethanation potential of these plants was calculated the same way as in the cases for 2020 and 2030 national biomethanation potential and the case study's biomethanation potential. However, in this case, only ex-situ biomethanation was considered while calculating biomethanation potential with appropriate gas conversion rate. This decision was made because in a bioethanol plant, there are two CO_2 sources: fermentation and a biogas plant (de Farias Silva and Bertucco, 2019; "St1 Etanolix food-waste-to-ethanol plant integrated into oil refinery in Gothenburg - Green Car Congress," n.d.). With two CO_2 sources, it was considered reasonable to transfer all produced CO_2 into an existing ex-situ reactor. The approximate gas conversion efficiency to CH_4 was decided to be 90 %.

4.4 Techno-economic analysis

Techno-economic analysis was performed for the case study using a study from Pääkkönen et al. (2018) as a model, though some changes to their original formulas were made. Techno-economic analysis included energy flow analysis and economic analysis. Economic analysis included only the energy of producing biomethane.

4.4.1 Energy flow analysis

Energy flow analysis was performed as part of the techno-economic analysis to find out how much energy derived from electrical power network (i.e. grid), could be stored as biomethane via biomethanation. To find out the energy flow through the biomethanation process, electricity grid, electrolysis and biomethanation process were considered. As for biomethanation process, energy required for H_2 injection or possible compressors or gas recirculation was not considered. The end use of biomethane after biomethanation reactor was also not considered.

The already calculated values for the H_2 amount required for biomethanation and the energy required for its production via electrolyser were used. Elctrolyser's energy consumption was calculated using different electrolyser efficiencies. Efficiencies were chosen as 83 %, because that is a typical efficiency for a state-of-the-art commercial water electrolysis (Hodges et al., 2022), and 70 % and 60 %, since these are common efficiencies for alkaline and PEM electrolysers (Gahleitner, 2013). The advantages of alkaline and PEM electrolyser are that they are commercially available and they can be switched off and on quickly (Gahleitner, 2013). It was assumed that the energy required for the electrolyser would be the initial energy (100 %) transferred from electricity grid, after which this amount of energy would decline after each stage. Percentages of energy left after each stage were obtained by comparing the energy needed for H_2 production and for biomethanation to the energy derived from grid.

4.4.2 Economic analysis of energy usage

Economic analysis was performed to find the economically feasible cost of producing CH_4 via biomethanation. The cost of biomethanation was calculated with Equation 11

$$P_{bioCH_4} = \frac{P_{el}}{E_{inproducedCH_4}} + P_{feedwater} - P_{avoidedCO_2} \tag{11}$$

where P_{bioCH4} is the cost of produced biomethane [€/MWh], P_{el} is the electricity price per hour [€/MWh], $E_{inproducedCH4}$ is the grid energy what is left on methane after its production from electrolysis and biomethanation [–], $P_{Feedwater}$ is the price of the water that is fed to electrolysis [€/MWh of CH_4 produced] and $P_{avoided\ CO2}$ is the price of avoided CO_2 emissions [€/MWh of CH_4 produced]. Equation 11 is adapted from Pääkkönen et al. (2018), where also a term for pressurizing CH_4 for grid was included. This term was deleted from Equation 11, because it was assumed that the biogas plants which utilize biomethanation, already have pressurizing units. This is the case especially if biogas upgrading and CH_4 transfer to gas grid already exist at a plant.

For Equation 11, values for required parameters were found online. Hourly electricity prices for P_{el} used in the Equation 11 were 33.32–46.53 €/MWh ("Sähkön tuntidata - Energiateollisuus," n.d.). Values for $E_{inproducedCH4}$ for different electrolysis efficiencies were already calculated in energy flow analysis. Price of water needed for electrolysis was calculated by multiplying the current price of water (3.42 €/m^3) ("Vesihuollon hinnasto ja palvelumaksuhinnasto 2022," n.d.) with the amount of water needed in electrolysis (9 L/kg H_2) (Webber, 2007) times H_2 required for electrolysis. Price of avoided CO_2 emissions were calculated by multiplying the amount of avoided CO_2 emissions (here: the amount of CO_2 that is used in biomethanation process and turned into methane) with the current price of CO_2 emission allowance in the EU (30 €/t) (Bua et al., 2021).

In this thesis, the first aim was to use only the excess electricity from renewables in H_2 production. However, there would not be enough electricity for biomethanation's needs if electrolysis would only use excess renewable electricity. Therefore, it would be necessary to use a different approach in determining the electricity usage for production of H_2. In their study, Pääkönen et al. (2018) determined a threshold price for producing CH_4, and whenever electricity price would be under that threshold, CH_4 production would be economically feasible. A threshold price was used in this study as well. CH_4 gas market price was determined to be 100 €/MWh (Karinen, 2022).

A threshold electricity price, with which biomethane production costs from Equation 11 would be lower than the gas market price, was iterated to be low enough for the cost of produced CH_4 to be lower than gas market price of 100 €/MWh. Threshold price for electricity was determined for case study considering the three electrolysers with different efficiencies, one at a time. Thus, three electricity threshold prices were interated. Only the threshold price corresponding to the highest electrolyser efficiency was used, to maximize the number of hours when biomethanation would be run.

Finnish daily electricity price data during the first four months of 2022 ("Market data | Nord Pool," n.d.) was examined and the average amount of hours per month, when electricity price is lower than the calculated threshold value, was calculated. The daily and hourly biomethanation energy productions were calculated. The hourly energy production was multiplied by the number of hours that biomethanation could be run with the electricity threshold prices, and finally the actual, economically feasible amount of biomethane produced in a year was calculated.

5. RESULTS AND DISCUSSION

This chapter presents the case study's calculations and Finland's national potential calculations.

5.1 Case study of a typical biogas plant

The biomethanation potential of a case study of a typical biogas plant was conducted. Case study calculations and sensitivity analysis were done based on in-situ biomethanation.

5.1.1 Biomethanation potential of the case study

Initial calculations included the daily biogas production of the case study's biogas plant, biogas plant's CH_4 production and CO_2 production (Table 4). H_2 required for biomethanation was calculated as 16 608 m^3/d. The annual CH_4 production from in-situ biomethanation was calculated as 1 249 700 m^3/a, and the total CH_4 production including CH_4 in the biogas and from biomethanation was calculated as 4 000 207 m^3/a (Table 4). This would equal 46.4 % rise in the case study's methane production per year. In-situ biomethanation's CH_4 production corresponds to 12.7 GWh/a of energy.

Table 4 *Results of the case study's biogas plant's initial calculations and its biomethanation potential calculations with in-situ biomethanation.*

Parameter	Value	Unit
Biogas production	11 700	m^3 biogas/d
Biogas CH_4 production	2 733 100	m^3 CH_4/a
Biogas CH_4 production	27	GWh/a
CO_2 production	4095	m^3/d
H_2 required for biomethanation	16 608	m^3/d
CH_4 production from in-situ biomethanation	1 267 100	m^3/a
Total CH_4 production including CH_4 in biogas and from biomethanation	4 000 207	m^3/a
Increase in CH_4 production	46.4	%

5.1.2 Sensitivity analysis of the case study's biomethanation potential

Sensitivity analysis based on changes in biogas production and gas conversion efficiency was made. If case study's biogas production would decrease by 10 %, CH_4 production by in-situ biomethanation with 85 % gas conversion would be 1 140 380 m^3/a (Figure 11) corresponding to 11.4 GWh/a. This means 10 % production reduction from the total CH_4 production (including biogas plant's biogas and CH_4 made by in-situ biomethanation). If case study's biogas production would increase by 10 %, CH_4 production in in-situ biomethanation with 85 % gas conversion would be 1 393 800 m^3/a and 13.9 GWh/a, which corresponds to total CH_4 production increase of 10 %.

If biogas production staying as it is, gas conversion efficiency of 75 % would cause CH_4 production in in-situ biomethanation to drop to 1 118 000 m^3/a and 11.2 GW/a, which equals 3.7 % drop in the original total CH_4 production with 85 % gas conversion rate. With 95 % gas conversion rate, the CH_4 production by in-situ biomethanation would be 1 416 200 m^3/a (Figure 11) corresponding to 14.2 GWh/a, which equals 3.7 % rise in the total CH_4 production.

Biogas production rate dropping by 10 % has a larger effect on total CH_4 production than gas conversion efficiency dropping by 10 %. In a worst-case scenario where biogas production is 10 % smaller and gas conversion is 75 %, CH_4 production by in-situ biomethanation drops to 1 006 200 m^3/a corresponding to 1.0 GWh/a, which equals 13.3 % drop from the original total CH_4 production. Then again, in the best-case scenario (biogas production is 10 % larger and gas conversion is 95 %), the CH_4 production by in-situ biomethanation increases to 1 557 800 m^3/a and 15.6 GWh/a, equaling 14.1 % increase from the total CH_4 production. The largest impact is caused by the combination of increases in biogas production rate and gas conversion efficiency (Figure 11).

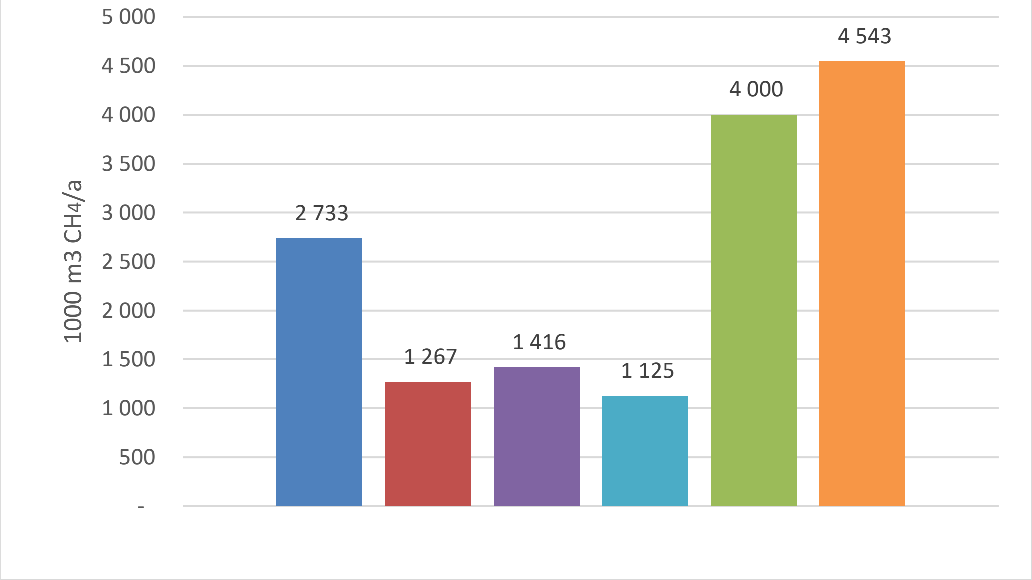


***Figure 11** CH_4 production in the case study: CH_4 production of biogas plant (blue), CH_4 production of in-situ biomethanation with 85 % (red) and 95 % (purple) gas conversions, CH_4 production with 85 % gas conversion and 10 % less biogas production (teal), the total CH_4 production including biogas and biomethanation with 85 % gas conversion rate (green), and the total CH_4 production (biomethanation and biogas involved) with 10 % increase in biogas production and 95 % gas conversion efficiency (orange).*

Case study's biomethanation potential in terms of ex-situ biomethanation was also investigated. Ex-situ option had gas conversion efficiency of 95 %. The CH_4 production for ex-situ option was 1 416 200 m^3/a, which corresponds to 14.2 GWh/a. This is 1.5 GWh/a more than with in-situ option. This amount would equal rise as large as 51.1 % in the case study's CH_4 production per year. It must be noted that both in-situ's and ex-situ's CH_4 productions were calculated with the assumption of biomethanation running unlimitedly, with no breaks in operation. This means that the H_2 production would also be continuous and not restricted by H_2 production price. This is hardly the case, since H_2 production from electrolysis is expensive in comparison to the price gotten from selling CH_4 (Pääkkönen et al., 2018). Therefore, biomethanation process might not be operated continuously at all times, thus the energy derived from biomethanation might be in fact lower than presented here.

5.1.3 Integration of in-situ biomethanation into an existing biogas plant

The effects of integrating in-situ biomethanation into the case study's biogas plant were investigated. The case study's reactor type, CSTR, is a common reactor type in biomethanation studies and has been used in many continuous in-situ applications (Agneessens et al., 2017; Jensen et al., 2018; Jensen et al., 2021a; Luo et al., 2012; Luo and Angelidaki, 2013). Therefore, it is assumed that having CSTR would suit well in the situation of adding in-situ biomethanation into the case study biogas plant. However, there has not been reports on a full-scale in-situ biomethanation reactor as big as the case study's reactor (total volume of single reactor 4100 m^3) to date. Jensen et al. (2018; 2021a) have come closest with their utilization of a 1200 m^3 biogas reactor. Large reactors are usually more heterogenous in terms of process conditions in comparison to lab-scale systems (Jensen et al., 2021a), which might pose problems with H_2 gas-liquid mass transfer.

Consideration about which H_2 injection type should be utilized in the case study, was done. Since poor H_2 gas-liquid mass transfer rate is usually the biggest issue in biomethanation (Angelidaki et al., 2018; Voelklein et al., 2019), it is important to choose an injection method which enhances the H_2 gas-liquid mass transfer rate as much as possible. If H_2 gas-liquid mass transfer and gas conversion are poor, H_2 will end up in the output gas with methane. This is a problem, since there should not be more than 1 % of H_2 blending in the Finnish gas grid (IEA, 2019).

Electrochaea has used H_2 injection into the bottom of the reactor tank in their Solothurn's ex-situ biomethanation plant. Their injected H_2 comes from electrolysis plant as pressurized gas, which makes it possible to inject it directly into the reactor. ("Electrochaea GmbH - Power-to-Gas Energy Storage | Technology," n.d.) Others have injected H_2 from the bottom of the tank as well (Jensen et al., 2018; Luo and Angelidaki, 2013). Jensen et al. (2018) found out in their study that their venturi-type bottom-fed injection system produced too large bubbles (10 mm diameter) and therefore H_2 gas-liquid mass transfer was not sufficient, since only 62 % of H_2 injected was consumed. After conducting a computational fluid dynamic model (CFD) they found out that H_2 gas should be injected as smaller bubbles of 2.5 mm diameter to enhance the gas-liquid mass transfer. (Jensen et al., 2018) Jensen et al.'s (2018) and Electrochaea's ("Electrochaea GmbH - Power-to-Gas Energy Storage | Technology," n.d.) studies were conducted in full-scale, which is why their solutions were considered as the most promising options for H_2 injection in our case study. Recirculation of the gas was not recommended, since Jensen et al. (2018) had problems with it in their full-scale in-situ: like explained in chapter 3.4.1, H_2 was diluted with biogas by the recirculation and therefore the mass transfer driving force was reduced (Jensen et al., 2018).

Case study uses continuous 3-blade stirring of 18 rpm. If in-situ biomethanation would be added to the case study's biogas plant, this stirring speed might prove to be too slow for efficient mixing. Continuous stirring has been linked to higher gas-liquid mass transfer in biomethanation (Luo and Angelidaki, 2013; Rachbauer et al., 2016), but high-speed stirring (at least 228 rpm, like found in Zhu et al. (2019)) could also interfere with methanogenesis in in-situ biomethanation operated in mesophilic conditions (Zhu et al., 2019). Wahid and Horn (2021) also found that too high stirring speed had negative effect on the microbiology and energy balance of the process, but that at 140 rpm the CH_4 production was at its highest. Based on this, the low stirring speed in case study would probably not have a drastic effect on in-situ biomethanation's methanogenesis, but to enhance the CH_4 production, the stirring speed would have to be increased. However, it is assumed that the stirring speed in use now is optimized for the biogas process, and it is not known, what kind of effects speeding up the stirring would have on anaerobic digestion at this plant. The downside of higher stirring is the increased costs that come with increased electricity usage, when stirring is sped up (Luo and Angelidaki, 2013).

The case study's pH is 8.5, which is already quite high for in-situ biomethanation. Like stated in chapter 3.2.2, hydrogenotrophic methanogens, which are the basis of biomethanation's microbiology, can live in pH between 6.8 and 9.5, and usually thrive best in pH of 7.0–7.5 (O'Flaherty et al., 1998). Since H_2 injection in in-situ biomethanation might increase the process pH (Angelidaki et al., 2018; Angenent et al., 2018; Luo et al., 2012), it is possible that case study's pH could increase too much: even pH above 8.5 has, in some cases, caused methanogenesis inhibition (Angelidaki et al., 2018). Therefore, it might be beneficial for the case study's biomethanation potential to decrease the reactor's pH closer to 7, if possible. This could be done with adding acidic organic wastes to feedstock (Luo et al., 2012). Then again, it has been found that hydrogenotrophic methanogens can thrive in higher pH's of 8.5–9 in ex-situ biomethanation, at least in thermophilic conditions (Chen et al., 2021), however, too high pH might affect the metabolism of other microbes in anaerobic digestion (Weiland, 2010; Xu et al., 2020b)

In-situ and ex-situ biomethanation options were compared for the studied case (Table 5). Different operational parameters, economic feasibility and risks were considered in the case on integrating either in-situ or ex-situ biomethanation into the case plant. Comparison was done considering only CSTR.

Table 5 *Comparison of in-situ and ex-situ biomethanation systems if either would be executed in the studied case*

	In-situ biomethanation's advantages and disadvantages	**Ex-situ biomethanation's advantages and disadvantages**
H_2 injection	Bottom-fed venturi-type injection system with 2.5 mm bubbles suggested (Jensen et al., 2018). Risk of poor H_2 gas-liquid mass transfer rate (Angelidaki et al., 2018; Voelklein et al., 2019).	Injection type should be chosen. Risk of poor H_2 gas-liquid mass transfer rate (Angelidaki et al., 2018; Voelklein et al., 2019).
Reactor type	Two 4100 m^3 CSTRs. Large reactor size might pose a risk for successful biomethanation because of its possible heterogenous process conditions (Jensen et al., 2021a).	Reactor type can be selected. Size is determined by CO_2 injection rate.
Stirring	18 rpm. Risk of stirring speed being too slow for efficient H_2 gas-liquid mass transfer (Zhu et al., 2019). However, stirring speed can be adjusted also with existing units.	Stirring speed could be selected as needed.
pH	8.5. Risk of increasing pH and causing process inhibition (Angelidaki et al., 2018; Angenent et al., 2018; Luo et al., 2012).	pH could be larger (8.5–9), especially in thermophilic conditions (Chen et al., 2021).
Temperature	40 °C. Likely not affecting biomethanation.	Temperature could be selected.
Investment needs	Electrolyser, H_2 injection, piping	Electrolyser, H_2 injection, piping, ex-situ biomethanation reactor

Ex-situ biomethanation option might be more flexible in terms of optimization of operational parameters and biomethanation's impacts on them (Table 5). Ex-situ option might also be more risk-free, in terms of successful biomethanation. However, in-situ biomethanation is usually cheaper and easier to install than ex-situ biomethanation (Fu et al., 2021; Xu et al., 2020a) as there is no need for an external reactor.

In-situ biomethanation option is quite uncertain and has faced many difficulties in other biomethanation studies with the effects that follow H_2 injection. These difficulties have included pH rise (Luo et al., 2012), poor H_2 gas-liquid mass transfer (Jensen et al., 2018), poor methane production rates (Jensen et al., 2021a; Luo et al., 2012) and accumulation of acetate (Agneessens et al., 2017). However, in-situ biomethanation seems very promising technology, considering its affordability and easy connectivity into a reactor, and it would be necessary to conduct more full-scale in-situ biomethanation studies to find out the optimal operational parameters for it.

5.1.4 H_2 required for the case study

Theoretical volume of H_2 required for the case study's continuous in-situ biomethanation was 6 062 100 m^3/a. Electricity required to produce this amount of H_2 was 29 GWh/a with the average state-of-the-art water electrolyser efficiency of 83 %.

A minimum of 4 average wind power plants are required to produce the electricity needed for electrolysis in the case study. Here an average wind power plant means a plant which produces 8 GWh of electricity a year ("Suomen Hyötytuuli – Tuulivoima," n.d.). The minimum number of the most powerful PV panels on sale in Finland would have to be 57 to cover the electricity need. These PV panels require altogether an area of 138 m^2. The PV energy production was calculated using the manufacturer's theoretical energy production potential; thus, the actual number of PV panels might be larger.

The feasibility of H_2 production for CH_4 depends on a couple of things. First, the renewable energy source (wind power plant or PVs) needs to be located so that biomethanation can easily access it without too large electricity losses. Secondly, electricity bought from the renewable energy sources must be cheap enough. And thirdly, if there are no renewable energy sources nearby, the costs of buying or building the required amount of wind power plants or PVs would have to be low enough. More research should be done to investigate the importance of the location and costs of renewable energy in biomethanation.

5.1.5 Effects of biomethanation on biogas upgrading technologies

Case study's membrane unit used for biogas upgrading might benefit from biomethanation, but there could also be drawbacks. In a study from Deng and Hägg (2010), biogas was lead to two-stage membrane upgrading unit and the effects of membrane input gas' CO_2 concentration were investigated. The designed CO_2 concentration was 35 % and the aim of the CH_4 purity in in output gas was 98 %. Their study showed that an input CO_2 concentration higher than the designed value can result in a lower CH_4 purity in the final output gas, although CH_4 recovery can increase. When the CO_2 concentration in membrane input gas was under the designed value, CH_4 purity still fulfilled the aim value but CH_4 recovery decreased. (Deng and Hägg, 2010) Based on this, input gas' CH_4 content plays a role in membrane technology: if the input gas has already a high CH_4 content, and if the CO_2:CH_4 selectivity of the membrane is good enough (a great selectivity value is $\alpha=500$ (Brunetti et al., 2014)), a membrane separation with less stages could be sufficient. However, it could be a trade-off between sufficient CH_4 purity and CH_4 recovery (Deng and Hägg, 2010). It is assumed that the case study has a certain optimized number of stages in its membrane unit. If the input gas' CH_4 content rises, the hypothesis is, that the amount of available membrane stages will provide cleaner CH_4, or that sufficient upgrading could be done even with fewer stages. Therefore, more input gas could likely be fed into the membrane unit, and the capacity of the unit would grow.

However, a couple studies (Awe et al., 2017; Brunetti et al., 2014; Shin et al., 2019) have shown that when CO_2 concentration in feed gas is lower, membrane's permeate gas' CO_2 percentage decreases, because of lack of driving force in pushing CO_2 through the membrane to the permeate side. So, the higher the CO_2 concentration in the input gas, the higher the CO_2-% in permeate. Also, if CO_2 content in the input gas is lower, there can be also be bigger levels of CH_4 in the permeate, since some of CH_4 is escaping through the membrane wall (Shin et al., 2019). This escaping of CH_4 is usually solved via recirculation of permeate gas. (Awe et al., 2017; Shin et al., 2019) There should be more investigations made to fully understand how biomethanation affects membrane upgrading.

Water scrubbing technology is another biogas upgrading technology, which might benefit from lower CO_2 concentration in the input gas. Wylock et al. (2017) found that a lower CO_2 content in the input gas resulted in more efficient water scrubbing and output gas with higher CH_4 content. However, this also led to higher methane losses. When CO_2 content in the input gas increased, CH_4 content in the output gas decreased. (Wylock and Budzianowski, 2017) Therefore, it can be assumed that water scrubbing technology in biogas upgrading would produce output gas with higher methane concentration, if biomethanation would precede it. However, the possible methane slips and how much of the methane slips is tolerable at the expense of more efficient water scrubbing should be considered.

5.1.6 Techno-economic analysis of the case study

Energy flow analysis showed that the electrolyser's energy consumption increased as the electrolyser's efficiency decreased (Table 6). With 83 % electrolyser efficiency, electrolyser's energy consumption was 0.077 GWh/d.

Table 6 *Energy flow analysis results for the case study*

Energy flow analysis	Unit	Case study
H_2 required	kg/d	1458
Energy needed for H_2 production	kWh/d	64 144
CH_4 production by in-situ biomethanation	kWh/d	34 237
Electrolyser energy consumption		
83 % electrolyser efficiency	kWh/d	77 000
70 % electrolyser efficiency	kWh/d	92 000
60 % electrolyser efficiency	kWh/d	107 000

The amount of energy left after biomethanation was 47 %, 40 % and 34 % when using electrolyser efficiencies of 83 %, 70 % and 60 %, respectively (Table 7). This means that up to 47 % of the grid energy fed into the system could be stored as biomethane.

Table 7 *Energy flow after each stage (grid, electrolyser and biomethanation).*

	Case study		
Electrolyser efficiency	83 %	70 %	60 %
Amount of energy left after each stage			
Grid	100 %	100 %	100 %
Electrolyser	83 %	70 %	60 %
Biomethanation	47 %	40 %	34 %

Energy flow analysis shows that the higher the electrolyser efficiency is, the bigger the significance of biomethanation on energy losses will be. The highest amount of grid energy was left after biomethanation (47 %), when electrolyser with the highest efficiency was used. In the study from Pääkkönen et al. (2018), a maximum of 70 % of the initial grid electricity was left after biomethanation. However, they did not take gas conversion efficiency into account, and they used a higher maximum electrolyser efficiency of 90 %. They also used a higher biogas CO_2 content of 45 % (vs. 35 % used in this study), which leads to larger CH_4 production (Pääkkönen et al., 2018). When biogas CO_2 content is larger, more H_2 is needed in biomethanation, which increases the energy required for H_2 production.

For the economic analysis, values for parameters in Equation 10 were discovered. Price of water needed for electrolysis ($P_{Feedwater}$) was calculated as 16 600 €/a and 1.31 €/MWh of produced CH_4. The price of avoided CO_2 in emission allowance ($P_{avoided\ CO2}$) was calculated as 79 500 €/a and 6.27 €/MWh of produced CH_4. With 83 % electrolyser efficiency, the price for electricity (P_{el}) should be maximum of 46.50 €/MWh = 4.65 c/kWh, for the biomethanation’s costs to be lower than the gas market price of 100 €/MWh. With electrolyser efficiency of 70 %, the threshold price for electricity is 38.88 €/MWh (3.89 c/kWh), and with electolyser efficiency of 60 % the threshold price is 33.32 €/MWh (3.33 c/kWh). The average amount of hours when electricity price was under 46.50 €/MWh in the first four months of 2022, was 212.4 h/m. This makes total of 2549 h/a. If biomethanation would run only during these hours, which is 29.1 % of the whole year, the total CH_4 production would be 3.7 GWh/a. One needs to notice, that these calculations do not include investment costs of biomethanation or electrolyser. These will further increase the biomethanation production costs.

Biomethanation’s production costs with 83 % and 70 % electrolyser efficiencies were compared to the electricity threshold prices of 46.50 €/MWh (83 % electrolyser efficiency) and 38.88 €/MWh (70 % electrolyser efficiency) and to 132.66 €/MWh, which was Finland’s average electricity market price in May 2022 (“Market data | Nord Pool,” n.d.) (Figure 12). With the current gas market price of 100 €/MWh, biomethanation could be run very limitedly. Electricity prices in Finland are rising because of the current geo-political situation with Russia’s war in Ukraine and the price increase in natural gas (Parviala, 2022). Because of that, it will be difficult to run biomethanation economically, if the price obtained from selling biomethane does not increase. On the other hand, biogas and biomethane are starting to act as an attractive replacement option of natural gas, because of these price increases (Sallinen, 2022). Increasing their production would also improve Finnish regional economy and the security of supply (Virolainen-Hynnä, 2020).

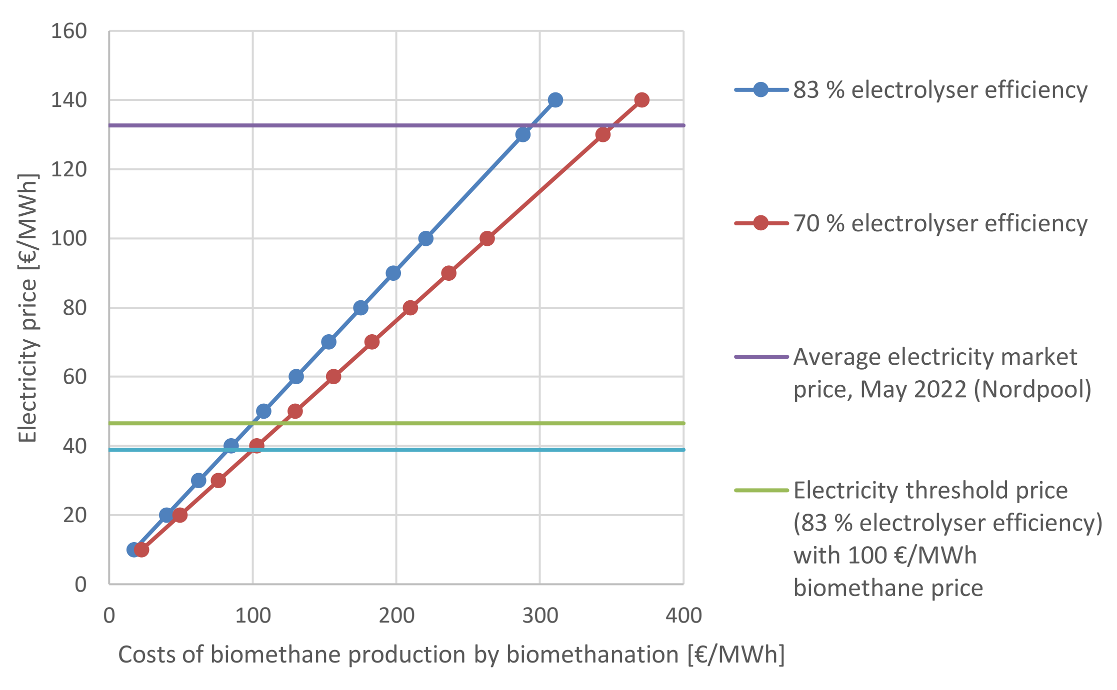


Figure 12 *Comparison of biomethanation costs, electricity threshold price when gas market price is 100 €/MWh, and the average electricity market price in Finland in May 2022*

If the gas market price would double to 200 €/MWh, the electricity threshold price would be 90.76 €/MWh, with 83 % electrolyser efficiency. In the first four months of 2022, electricity price was under this threshold for an average of 416 h/m, which would make 4992 h/a. This is 57 % of the whole year, and if biomethanation would run during this time, it would produce 7.1 GWh/a, almost twice as much as with 100 €/MWh market price. However, with electricity prices currently increasing in Finland (Parviala, 2022), the actual amount of economically feasible biomethanation hours might be lower in the future.

The fluctuation of electricity usage poses a problem in biomethanation. Wahid et al. (2019) found out in their study, that H_2:CO_2 molar ratio should be kept as close to 4:1 as possible at all times, because divergence from this ratio will cause in-situ biomethanation process instability. This means that if CO_2 flow is somewhat constant, H_2 flow should also be kept at a constant. This will not happen if electrolysis is not continuous. To solve this problem, H_2 storages should be built near biomethanation plants; however, this increases the investment costs of biomethanation. Another option could be to store biogas or CO_2 and to inject them into an ex-situ biomethanation reactor, once H_2 prices would be low enough.

While start-ups and shutdowns of biomethanation process might be problematic in terms of H_2:CO_2 molar ratio, they might not be such a problem for the biomethanation's microbes. Resent biomethanation studies with start-ups and shutdowns were investigated. In one study, a bubble column ex-situ biomethanation reactor was run for a total of 405 days, with two long shut-down periods (both H_2 and CO_2 additions were stopped), lasting for 34 and 23 days (Laguillaumie et al., 2022). During the shut-down, the relative composition of microbes in the reactor changed, but the methanogenic activity was restored in 8 days after the start-up. Hydrogenotrophic methanogens in the reactor suspended their growth during shut-down but reactivated quickly when H_2 and CO_2 additions started again. (Laguillaumie et al., 2022) An in-situ study investigating microbes during fluctuating H_2 supply was not found, however, and the results of Laguillaumie et al.'s (2022) study cannot be compared directly to the case study.

Instead of using electricity threshold prices, excess electricity could be used for electrolysis. However, like stated in chapter 4.4.2, there is not enough negative priced electricity in Finland. Electricity price in Finland has been negative only a handful of times. It turned negative for the first time ever on 10th of February 2020 (Parviala, 2020). Since then, the same happened 2 times during 2020 (Harjumaa and Kokkonen, 2021; Koskinen, 2020; Manninen, 2020) and once in 2021 ("Market data | Nord Pool," n.d.). In 2020, electricity price in Finland was negative for a total of 9 hours (Harjumaa and Kokkonen, 2021). If excess electricity would be the only source of electricity for electrolysis, H_2 would be produced only a couple times a year, each time lasting for some hours only. For example, on 5.4.2021, electricity price was negative between 01 and 06 o'clock in the morning in Finland (Kyytsönen, 2021). During that time, electricity was produced 42 300 MWh in total ("Sähkön tuntidata - Energiateollisuus," n.d.). This would not have been enough electricity to provide for the whole Finland's biomethanations' electrolysis, which would require 731 500 MWh/a (as introduced in 5.2.2) to produce enough H_2.

It is assumed, that phenomenon of electricity price turning negative will continue happening in the future. (Manninen, 2020) In Germany and Denmark, it is much more common for the electricity price to dip to below 0, since these countries use a lot of wind power (Harjumaa and Kokkonen, 2021). In Denmark, electricity price turned negative a total of 21 times in 2021, with the price being as low as -36 €/MWh at the lowest ("Market data | Nord Pool," n.d.). Finland's wind power production is growing rapidly (Mainio, 2022), which could indicate more negative-priced electricity in the future.

5.2 Finland’s biomethanation potential

Finland’s national biomethanation potentials and total CH_4 productions were investigated. In the following subchapters, the total CH_4 production includes CH_4 productions in biogas (the main product of biogas plants), original-biomethane (derived from biogas after the biogas upgrading unit, with no biomethanation involved), biogas-biomethane (derived from either in-situ or ex-situ biomethanation of biogas) and biogas-upgrading-biomethane (derived from ex-situ biomethanation of CO_2 from biogas upgrading unit) (Figure 9). Total biomethanation potential includes all biomethane production by biomethanation.

5.2.1 Finland’s biomethanation potential in 2020 and 2030

Theoretical volume of H_2 required was calculated for both years 2020 and 2030 (Table 8). The total biomethanation potential was 42 049 400 m^3/a corresponding to 420 GWh/a in 2020, and 154 736 300 m^3/a, corresponding to 1 547 GWh/a in 2030 (Table 8). Including biogas production, the total CH_4 production corresponded to 1 300 GWh/a in 2020 and 5 430 GWh/a in 2030 (Table 8, Figure 13). The biogas-biomethane production with the gas-conversion efficiencies considered, was calculated as 37 119 300 m^3 CH_4/a for 2020 and 30 804 500 m^3/a for 2030 (Table 8, Figure 13 and Figure 14). Biomethanation potential from biogas-biomethane will therefore actually be smaller in 2030 than in 2020.

Table 8 *Calculation results for Finland's national biomethanation potential, total* CH_4 *production, theoretical volume of* H_2 *required in biomethanation, and biomethane productions by type (biogas-biomethane and biogas-upgrading-biomethane) in 2020 and 2030.*

Parameter	Unit	2020	2030
Theoretical volume of H_2 required for biomethanation	m^3/a	189 397 100	684 421 600
Biogas-biomethane production	m^3/a	37 119 300	30 804 500
Biogas-upgrading-biomethane production	m^3/a	4 930 100	120 788 500
Total biomethanation potential	m^3/a	42 049 400	154 736 300
	GWh/a	420	1 547
Total CH_4 production	m^3/a	129 849 400	542 874 600
	GWh/a	1 300	5 430

Biogas is the biggest CH_4 production source in 2020. By converting the CO_2 in biogas to CH_4, biogas-biomethane would equal almost a third (28 %) of the total CH_4 production. Original-biogas's share of the total CH_4 production in 2020 is 9 %, and the share of biogas-upgrading-biomethane is only 4 %. (Figure 13) Biogas-upgrading-biomethane's share of the total CH_4 production in 2030 increases to 23 %, because the share of original-biomethane increases greatly, from 110 GWh/a in 2020 to 3100 GWh/a in 2030 (*Biokaasun tuotanto vuonna 2030*, 2022) (Figure 14). Therefore original-biomethane production would correspond to 58 % of the total CH_4 production in 2030 (Figure 13).

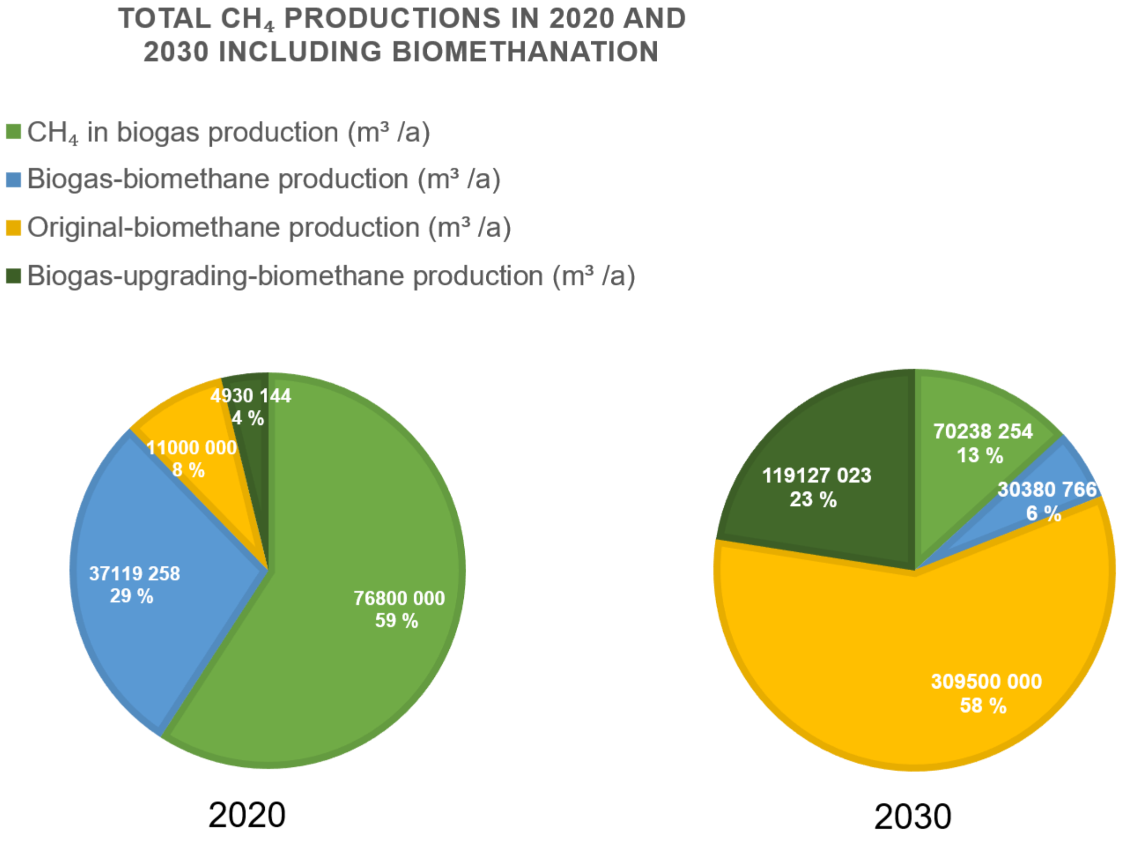


Figure 13 *The shares of each CH_4 production type (biogas, original-biomethane, biogas-biomethane and biogas-upgrading-biomethane (Figure 9)) out of the total potential CH_4 production in 2020 and 2030.*

The total CH_4 production of 1 300 GWh/a in 2020 and 5 430 GWh/a in 2030 (Table 8) would equal 47.23 % rise in the biogas energy production in 2020, and 39.32 % rise in the biogas energy production in 2030. It must be noted that the biomethanation potentials were calculated with the assumption of biomethanation running unlimitedly, with no breaks in operation.

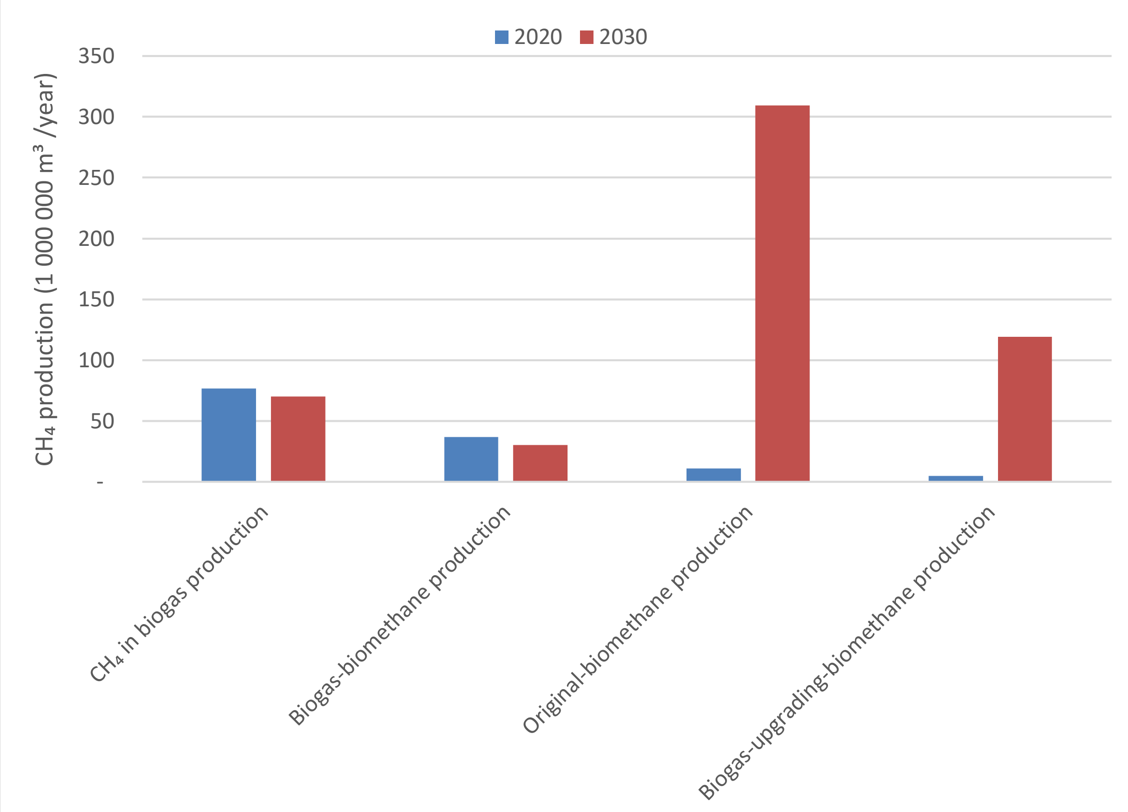


Figure 14 *Annual CH_4 productions by type (biogas, original-biomethane, biogas-biomethane and biogas-upgrading-biomethane (Figure 9)) in 2020 and 2030*

In addition to gas conversion efficiency, other factors that influence the national biomethanation potential in Finland, are the operational parameters which also affect the microbiology of the process. CH_4 production was calculated using gas conversion efficiency estimates for different reactor types. In terms of methane production rates, ex-situ biomethanation reactors are generally better than in-situ reactors (Lecker et al., 2017). However, calculations on biomethanation potential could not be done without considering in-situ reactors as well, since they are the more economically feasible option of the two (Fu et al., 2021; Xu et al., 2020a) and therefore more likely to be implemented in existing biogas reactors. In the calculations, it was not specified, whether biomethanation reactors would be mesophilic or thermophilic. If all biomethanation reactors would be made thermophilic, their methane production rate could be larger than in mesophilic reactors (Bassani et al., 2015; Luo and Angelidaki, 2012). Feedstock has also an important role in the CO_2 and CH_4 production rates in biogas plants, and thus influences biomethanation potential as well. A general percentage of the CO_2 content in the national biomethanation potential calculations was estimated, however, this CO_2 content in the output gas largely depends on feedstock characteristics. Different feedstocks produce different amounts of CO_2 (Riihimäki et al., 2014), therefore, biogas plants' biomethanation potential will vary. It must also be noticed, that the national biomethanation potential calculations considered all biogas plant types listed in Table 3, when in fact the smallest farm scale plants might not be able to utilize biomethanation, because of its low profitability compared to the high investment costs (Winquist et al., 2018).

Results from total CH_4 production in 2020 were compared to some parameters from Finland's energy sector: natural gas consumption, traffic energy consumption and road traffic energy consumption, heat production and electricity consumption in Finland (Table 9). With biomethanation, the year 2020's total CH_4 production would correspond to 2.8 % of the energy required for 2020 traffic energy consumption, 3.1 % of the energy required for 2020 road traffic energy consumption or 6.3 % of the 2020 natural gas consumption in Finland (Table 7). If results from 2030 biomethanation potential were considered as well, the calculated total CH_4 production would correspond to more than a fourth of Finland's 2020 natural gas consumption. Since there would be so much more original-biomethane production than just biogas production in 2030, biogas-upgrading-biomethane's share of the whole Finland's national biomethanation potential in 2030 is large. However, Finland's energy sector's values for 2030 are not known yet.

***Table 9** Finland's national biogas and CH_4 production with or without biomethanation in 2020 compared to the Finnish energy sector's chosen parameters*

	Production (GWh)	**Percentage of traffic energy consumption (2020)**	**Percentage of road traffic energy consumption (2020)**	**Percentage of heat production (2020)**	**Percentage of electricity consumption (2020)**	**Percentage of natural gas consumption (2020)**
Combined biogas and original-biomethane production (no biomethanation included)						
2020	878	1,9 %	2,1 %	1,0 %	1,1 %	4,2 %
Combined biogas and CH_4 production, including biomethanation						
2020	1298	2,8 %	3,1 %	1,5 %	1,6 %	6,3 %

Finland's national biomethanation potential in 2020 turned out to be quite insignificant when comparing it to the natural gas consumption, traffic energy consumption, road traffic energy consumption and heat production and electricity consumption in Finland in 2020 (Table 7). The share of biogas and CH_4 production in the whole electricity consumption in Finland is low (1.6 % in 2020) compared to Germany, where biogas and CH_4 production comprises 5.1 % of gross electricity generation in 2018 (*Bioenergy in*

Germany Facts and Figures 2020, 2020). However, it is safe to say, that if Finnish Biocycle and Biogas Association are right with their prediction of 4 TWh combined biogas and CH_4 production in 2030 (*Biokaasun tuotanto vuonna 2030*, 2022), and if natural gas consumption and road traffic energy consumption do not increase much from 2020, biogas and CH_4 will be significant factors in the future when replacing natural gas in Finland. The high prices of natural gas resulting from Russia's war with Ukraine will increase the competitiveness of biogas and CH_4, and natural gas consumption might decrease over time (Sallinen, 2022).

5.2.2 Biomethanation potential in bioethanol plants

Calculations showed that the CH_4 production obtained from the four Finnish bioethanol plants included in this study ranged from 147 400 m^3 CH_4/a (CH_4 production in the smallest bioethanol plant) to 498 800 m^3 CH_4/a (CH_4 production in the largest bioethanol plant).

Bioethanol plants' and this thesis' case study's biomethanation potentials were compared to one another. When comparing different CO_2 sources' effects on biomethanation, the amount of produced CH_4 depends mostly on the amount of available CO_2 at the source. With continuous operation, bioethanol plants' ex-situ biomethanation systems would produce 1.47–5.06 GWh of extra energy per year from the four bioethanol plants. This is 8.7–11.3 GWh less than what this thesis' case study would produce with in-situ biomethanation in its biogas plant. Based on this comparison, an industrial-size biogas plant is able to produce more CH_4 by biomethanation than an industrial-size bioethanol plant. However, there was no additional information about bioethanol plants' feedstock types or flowrates, so a more accurate comparison could not be executed. When comparing the bioethanol plants' biomethanation potential to the whole Finland's biomethanation potential in 2020 (calculated in chapter 5.2.1), bioethanol plant's potential is 0.35–1.20 % of the national biomethanation potential.

Based on the calculations, it can be stated, that while bioethanol plants are a promising source of biogenic CO_2, their biomethanation potential is rather insignificant. Also, since bioethanol plants should utilize ex-situ biomethanation plants instead of in-situ, the costs of building an external biomethanation reactor might be quite large, especially when comparing it to the small amount of biomethane it could produce.

5.2.3 H_2 required for national biomethanation

The theoretical volume of H_2 required for continuous biomethanation production was calculated as 189 397 100 m^3/a for 2020 and 684 421 600 m^3/a for 2030. The amount of electricity required for this H_2 production was calculated to be 742 GWh/a for 2020 and

2680 GWh/a for 2030. The number of average wind power plants needed to produce this energy is 112 for 2020, and 404 for 2030. The number of 500 Wp PV panels needed would be 1787 for 2020 and 6458 for 2030. These PV panels would take up area sized 4307 m^2 in 2020 and 15 565 m^2 in 2030. However, one must notice, that the values calculated for electricity requirements are valid only if the process of producing H_2 has an efficiency of 100 %. Therefore, these are the minimum values for electricity requirements and the number of wind power plants and PV panels. The actual number of PV panels needed might be higher, because the PV energy production was calculated using the manufacturer’s theoretical energy production potential.

The number of wind power plants in Finland in 2021 was 962 (“Tuulivoima Suomessa 2021,” 2022), so to produce all required H_2, there would have to be 42 % more wind power plants in 2030 than there were in 2021. This number might be achievable, since it is estimated that the number of wind power plants will triple in Finland by 2025 (Mainio, 2022).

6. CONCLUSIONS

Continuous in-situ biomethanation potential in the case study was calculated as corresponding to 46 % increase in the case study's annual CH_4 production. While 46 % is a very noticeable increase, most likely the actual in-situ biomethanation would not produce quite as much biomethane. The calculations were done based on stoichiometry, and gas conversion efficiency was considered as the only parameter that has a potential of lowering the full biomethanation production potential. However, there are also other factors that might cause smaller biomethanation potential in the case study, because the case study's operational parameters were not ideal for optimal in-situ biomethanation. There have also been multiple studies stating the difficulty of H_2 gas-liquid mass transfer in biomethanation, and problems related to H_2 gas-liquid mass transfer might occur in the case study as well. Ex-situ biomethanation (with biomethanation potential corresponding to 52 % increase in the case study's annual CH_4 production) was estimated to be a more flexible option in terms of biogas plant's operational parameters and biomethanation's impacts on them. However, ex-situ biomethanation plant's investment costs would most likely be a lot higher than those of in-situ biomethanation's. This is the result of ex-situ technology requiring an external biomethanation reactor.

Techno-economic investigation of the case study showed that with the current gas market price, the threshold electricity price with which in-situ biomethanation in the case study would be economically feasible, would be 4.65 c/kWh. The 4.65c/kWh is fairly low price of electricity, especially at the time of writing this thesis, with electricity prices increasing. Considering the electricity prices during the beginning of the year 2022, this threshold price would result in biomethanation operating at only 29 % of the full biomethanation capacity. Economical biomethanation's operation hours would increase with the increase of gas market price. Techno-economic analysis did not include the investment costs of biomethanation and electrolyser, and biomethanation's actual costs are estimated to be higher.

Finland's national biomethanation potential turned out to be quite significant in terms of the potential increase in CH_4 production, especially in the year 2030. In 2020, utilizing continuous biomethanation equals 48 % increase in energy production if compared to the realized biogas and biomethane production of 878 GWh/a in 2020. In 2030, continuous biomethanation utilization equals 40 % increase in energy production if compared to the predicted biogas and biomethane production of 3.88 TWh/a in 2030. National biomethanation potential compared to Finland's energy sector's requirements is low in

2020, but in 2030 the relevance of biomethanation will be much bigger, resulting to a total CH_4 production of 5.4 TWh/a. With the 2020 production of biogas and biomethane (including the biomethanation calculations made in this thesis), it would be possible to replace 6.3 % of Finland’s natural gas consumption. Bioethanol plants as part of national biomethanation potential are quite trivial, because of their small CO_2 production. Lots of estimations and simplifications were done in the Finnish national biomethanation potential calculations, and the biomethanation potential would most likely be different using more detailed initial values.

As for increase in energy production, biomethanation’s importance to a company can be significant, as long as the production price of CH_4 via biomethanation is not too high, and it is possible to utilize biomethanation continuously. Nationally, the impact of biomethanation is not very large when compared to the Finnish energy sector’s energy requirements. However, ex-situ biomethanation technology is already in developing phase in Finland. Developing a working in-situ full-scale rector would be interesting because of its cheaper investment costs. Well operated biomethanation reactor can, in the best-case scenario, be a great and effective way of boosting biogas plant’s methane production. In 2030, if the prediction of 4 TWh/a combined biogas and CH_4 production will come true, biomethanation’s significance in the Finnish energy sector will grow. The current geo-political situation affects energy prices and can also have an influence on biomethanation’s cost-effectiveness and attractiveness.

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