Kaunas University of Technology

Faculty of Chemical Technology

Evaluation of Technologies for the Production of Renewable Methane

Master’s Final Degree Project

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Summary

The urge to use renewable fuels has become fundamental across the globe to diminish the utilization of fossil fuels in today's generation. One of the emerging resources such as renewable methane which is also called biomethane capable to be utilized in automobiles, injecting in natural gas grid heating and cooking purposes. It is a profitable asset as it conserves resources, provides utmost flexibility in usage and production, reduces carbon dioxide by creating a smaller carbon footprint, can be generated locally which makes it value-added biofuel and also competitive along with meeting the legal requirements of the EU. Three technological routes were analyzed to produce $1kWh_{thermal}$ biomethane. A reference scenario such as anaerobic digestion and membrane separation, 1st integrated process, such as gasification and methanation combined to the reference process, 2nd integrated process as the incorporation of the air plasma aided gasifier and methanation to the reference process. Therefore, mass and energy flows were analyzed to make the inventory data and to interpret the behaviour of the producing $1kWh_{thermal}$ biomethane. Thus, the goal of this thesis is propose sustainable methods to produce renewable methane via thermal technologies and methanation processes. The outcome revealed that 2nd integrated scenario leads to the higher efficiency of methane production, although there is an additional energy consumption during this process. A life cycle assessment was evaluated to determine the environmental impact of the reference scenario, 1st scenario and 2nd integrated scenario, where four main categories were analyzed specifically human health, climate change, resources as well as ecosystems based on IMPACT 2002+ for environmental impact evaluation. It was concluded that the 2nd integrated process requires 1.34 times a lesser number of resources and emits lesser pollutants by 1.25 times than the 1 st integrated process. Another way to produce renewable methane along with eliminating carbon dioxide can be via carbon dioxide methanation. A lab-scale experimental process was set up introducing gases such as hydrogen and carbon dioxide to produce methane and water. Temperature and gas composition was analyzed based on the molar ratio of CO_2 and H_2. The desired temperature for achieving the highest CO_2 conversion was ranging between 200-500℃. The gas compositions achieved for CH_4, CO, CO_2, H_2 was 50% - 70%, 0%, 0% - 2%, 20% to 65% respectively. The CO_2 conversion rate was also determined which ranged around 85% to 100%.

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Santrauka

Vienas iš būdų sumažinti iškastinio kuro naudojimą yra naudoti atsinaujinančius degalus. Tam tikslui galima naudoti atsinaujinantį metaną, kuris taip pat vadinamas biometanu, gali būti naudojamas kaip kuro rūšis, įpurškiant gamtinių dujų tinklą šildymui ir maisto ruošimui. Jo naudojimas mažina anglies dioksido emisijas, sukurdamas mažesnį anglies pėdsaką, gali būti sukurtas vietoje, todėl jis sukuria pridėtinės vertės biokurą ir taip pat yra konkurencingasbei atitinka teisinius Europos Sąjungos reikalavimus. Šiame darbe išanalizuoti trys technologiniai metodai (etaloninis scenarijus, t.y. anaerobinis skaidymas, 1-asis integruotas procesas, t.y. į etaloninį scenarijų integruojant dujinimą ir metaninimą bei 2-asis integruotas scenarijus, t.y. į etaloninį procesą įtraukiant oro plazmos dujofikatorių ir metaninimą. ąkWh terminio biometano gamybai. Buvo atliekami masės ir energijos balanso skaičiavimai bei rezultatai parodė, kad antrasis integruotas procesas lemia didesnį metano gamybos efektyvumą, nors šio proceso metu papildomai sunaudojama energija. Būvio ciklo vertinimas buvo atliktas siekiant nustatyti procesų poveikį aplinkai, naudojant IMPACT 2002+ metodą, SimaPro 9.1 programoje. Išanalizavus keturias pagrindines poveikio kategorijas, ty žmogaus sveikatą, išteklius, klimato kaitą ir ekosistemas, ,buvo padaryta išvada, kad 2-ajam integruotam procesui reikia 1,34 karto mažiau išteklių ir 1,25 karto išmetama mažiau teršalų nei pirmajam integruotam procesui. Kitas būdas gaminti atsinaujinantį metaną kartu su anglies dioksido pašalinimu gali būti anglies dioksido metanacija. Laboratorinis eksperimentas buvo atliktas naudojant dujas, tokias kaip vandenilis ir anglies dioksidas, metano gamybai. Temperatūra ir dujų sudėtis buvo analizuojama remiantis vandenilio ir anglies dioksido santykiu. CH_4, CO, CO_2, H_2 dujų sudėtis buvo atitinkamai 50% - 70%, 0%, 0% - 2%, 20% - 65%. Apskaičiuotas anglies dioksido konversijos laipsnis svyravo nuo 85% iki 100%.

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Abbreviations:

GHGs - Greenhouse gases

LHV – Lower heating value

GWP - Global Warming Potential

SS - Sewage sludge

AD – Anaerobic digestion

LCA – Life Cycle Assessment

Introduction

With the expansion of industries in the 21st century, greenhouse gases (GHGs) have escalated to ginormous amounts which have led all the countries to find greener and sustainable alternatives for energy production worldwide. The GHGs originating from natural and anthropogenic sources have some contrasting environmental problems such as smog formation, drought, heat-trapping which may further lead to human health issues such as lung cancer [1]. The two most potent GHGs present in the atmosphere are methane (CH_4) and carbon dioxide (CO_2). Although methane is practically lower in the atmosphere compared to carbon dioxide, it consumes adequately more thermal infrared radiation. Methane has higher global warming potential (GWP) i.e. 28 times for a 100-year time horizon than CO_2 [2]. Therefore, the emphasis on traditional energy must change with the use of renewable energy to diminish global warming.

The new modification of the Renewable Energy Directive (Directive (EU) 2018/2001) has set a modern goal for the European Union to use 32% of renewable energy by 2030 [3]. The Directive (EU) 2009/28/EC has given a great rise to the usage of biomethane in various countries. The year 2020 has marked a new beginning as the EU has overtaken the usage the fossil fuel by utilizing more renewable resources in the electricity mix sector by generating 38% from it whereas fossil fuel contributed only 37% [4]. Therefore, the need for focusing on sustainable energy has been important than ever before. Thus, this thesis will present the renewable production of methane via biomass and thermal technology, and experiments with methanation to see the possibility of utilizing the CO_2 amounts as well. The renewable methane produced via biomass is termed biomethane. Methane can also be produced by using waste CO_2 via carbon dioxide methanation. Carbon dioxide can be reduced in three main ways: reduce its emissions, CO_2 storage and lastly usage of CO_2. With the availability of robust CO_2 utilization technologies, the transformation of CO_2 to distinctive fuels as well as useful chemicals is attainable.

This fuel aids to decarbonize in heating and cooling of residential buildings can be utilized for cooking motives and substituted for natural gas, injected in gas grids and to achieve environmental-friendly transportation services. Biomethane promotes a circular economy by transforming the bio wastes such as sludge or digestate into greener and cleaner energy resources.

As per EU regulations, sludge utilization on agricultural grounds comes with meticulous restrictions as a result of the presence of heavy metals and micropollutants. On that account, effortless and effective disposal of sludge can be carried out by thermo-chemical treatment. Sewage sludge (SS) discharged from anaerobic digestion (AD) can be utilized as an energy source for thermal treatment. There are two integrated processes developed in this study. In the first integrated process, SS obtained from AD undergoes gasification and conditioning of syngas to produce pure biomethane. The second integrated process adds the SS to the gasifier aided with plasma and further facilitates syngas conditioning to produce biomethane. Accordingly, a reference scenario will be considered for generating biomethane from AD via biogas conditioning. Environmental assessments such as Life Cycle Assessment (LCA) will be carried out to identify an enhanced feasible technological method for 1 $kWh_{thermal}$ biomethane for the energy sector. In the thesis, the emphasis has also been on the utilization of CO_2 via the methanation process to produce methane.

Aim of the Project:

The project aims to propose renewable technologies for methane production and to address the utilization of carbon dioxide via experiments with methanation.

The main objectives are as follows:

1. To research the various technologies of renewable methane production technologies and methane conversion of carbon dioxide.
2. To propose two optimal thermal-based technological methods combining a biological method for renewable methane (biomethane) production.
3. To conduct mass and energy balances to produce $1kWh_{thermal}$ biomethane for performing the life cycle inventory analysis.
4. To perform the environmental assessment for different renewable methane technologies via life cycle analysis.
5. To conduct and investigate the experiments based on methanation to produce sustainable methane.

1. Literature Review

1.1. Greenhouse gases

The ginormous emissions of greenhouse gases (GHG) in the European Union (EU) have accelerated the usage of renewable energy. To reduce the GHGs, the council of the EU proposes the utilization of energy from sustainable sources which would be beneficial for heating, cooling, electricity and transportation purposes [5]. The GHG has been affecting human health and ecosystems in numerous ways such as lung cancer due to air pollution and the formation of smog, climate change by heat-trapping.

1.1.1. Methane

Methane, a colourless and odourless substance that is highly flammable and exceedingly abundant in the environment. It is formed by naturally occurring processes such as geological and biological mechanisms, the largest accumulation of methane is beneath the seafloor. It is mainly originated from the underground reservoir deposits of fossil fuels, livestock, waste management, biomass burning and rice cultivation [6]. Methane is the principal factor of natural gas.

Methane emissions can be reduced in the agricultural sector, fossil fuel usage and waste management. With the alarming rise of CH_4 levels, it is important to find greener ways to inhibit the increase of harmful CH_4 levels in the troposphere zone. There are estimations made that the major methane emitter industries such as oil and gas have released around 70 Mt of CH_4 in the atmosphere and the satellites detected a depletion of 5.5 Mt of CH_4 emissions globally in the year 2020 [7]. The scientists suggest that the inhibition of CH_4 emissions or generating new methods of production will benefit the reduction of climate change.

CH_4 confines the heat in the trospoheric region thus proves to be dangerous to the environment and adds to climate change. The dominant GHGs such as CH_4 and CO_2 cause adverse difficulties regarding the environment and human health. Elevated levels of methane consumed can cause health issues such as vision problems, vomiting, nausea, headaches and memory loss. Serious cases include breathing difficulties, heart rate and numbness cases.

Thus, the focus on conventional energy sources must be altered with the usage of renewable energy sources which will aid the occurring destruction. The recent years have witnessed a new trend of utilizing a distinctive sustainable source of energy namely biomethane. The new amendment in the Renewable Energy Directive (Directive (EU) 2018/2001) establishes a contemporary objective for the EU to utilize 32 % of renewable energy by the year 2030 [8]. The countries producing biomethane have been multiplying immensely given the directive (Directive (EU) 2009/28/EC).

Renewable methane is becoming a more prominent method for reaching climate targets among European Union governments and stakeholders. Methane is frequently touted as an automotive industry decarbonization option. In the recast Renewable Energy Directive for 2030 (RED II), renewable methane from waste is qualified for a 3.5 percent sub-target for advanced biofuel consumption, and it is highly promoted by Italy's "Biomethane Decree." Methane has a substantial environmental advantage since it releases substantially lower CO_2 and various pollutants that adds to smog. Methane also produces a higher amount of heat and light efficiency compared to any other hydrocarbon. This implies so the more natural gas is used to produce electricity rather than coal, or to fuel automobiles, trucks, and buses rather than gasoline, the fewer greenhouse gases and smog-related pollutants are created.

1.1.2. Carbon dioxide

Carbon dioxide gas is one of the major promoters of man-made GHGs, thus it causes one of the biggest impacts on climate change. The recent developments in the industrial economy have accelerated fossil fuel consumption, which leads to an increase of CO_2 in the tropospheric region. The amount of CO_2 present in the atmosphere in May 2020 is 417 ppm [9]. In 2018, the amount of total GHGs release accumulated in the atmosphere was up to 55.6 $GtCO_2$ [10]. CO_2 is classified as odourless, moderately dangerous and uncoloured gas which is followed by a pungent and sour taste. The main polluters are coal combustion, oil, and natural gas [10]. With the rising worldwide increase of CO_2 emissions, there has been a couple of problems that need to be addressed such as melting of glaciers at the planet's poles, level of ocean rise along with asymmetrical precipitation. As a result, it is vital to examine an appealing and efficient alternative towards Conversion of CO_2 and application.

The sectors that emit these harmful emissions are electricity generation and heating, fuel combustion, road transportation, manufacturing and construction and non-road transportation. Carbon dioxide's rising percentage in the atmosphere is significant due to its heat-absorbing characteristics. Heat is absorbed and emitted by the planet's landmass and marine waters, and this heat is stored in carbon dioxide molecules. This gas confines the radiation at the surface level of the earth which in turn forms ground-level ozone. The seas are warmed as the barometrical layer avoids cooling of eath at night time. It is well known that atmospheric CO_2 can be absorbed by the oceans but this ability can be hindered if the temperature of the waters is larger. CO_2 in the air content leads to another ecological impact on the environment such as air contamination which in turn causes climate change. Another environmental burden it causes is the downpour of acid rain. The precipitation is released with a higher acid content from the emissions of fossil fuel energy plants. The harmful effects are not just related to environmental concerns but also human health. There could be a degradation in the quality of well-being if exposed to these toxic gases on a higher amount regularly. If exposed to more than 10% CO_2, it will put the person at a higher risk of coma, seizures, or even death. It may include dizziness, troubled breathing, nervousness, tingling sensation or as a needle pricking, excessive sweating, feeling exhausted and tired, elevated heart rate, coma, convulsions, raised blood pressure, and asphyxia.

Every year, around 230 million tonnes (Mt) of CO_2 are utilized [11]. The fertilizer industry is the greatest customer, using roughly 130 $MtCO_2$ per year in urea production, trailed mostly by the oil industry, which uses 70 to 80 $MtCO_2$ for increased oil recovery (EOR) [11]. CO_2 is also commonly utilized to boost plant growth in food and beverage manufacturing, metal manufacturing, cooling, fire suppression, and greenhouses. Fuels, chemical products, mineral-based and garbage based building products, and CO_2 utilization to improve biological process yields are the five dimensions of CO_2-derived goods and services. When an application is adaptable, uses low-carbon energy, and replaces an item with greater life-cycle emissions, CO_2 can help achieve climate goals. CO_2 might be a valuable raw source for carbon-based goods.

1.2. Carbon dioxide conversion technologies

Carbon dioxide's perception has completely shifted mostly during a span of decades on research, culture, and companies and industries. Carbon dioxide is therefore not seen as a contaminant, but rather as a useful chemical and a significant carbon supply. CO_2 capture and purification technology that is already in use or development can achieve maximum purity CO_2 sources for chemical and fuel generation. There are a variety of ways for capturing hazardous CO_2 from the environment, comprising electrochemical, thermal, biochemical, chemo-enzymatic, and photocatalytic techniques [12]. CO_2 has previously been utilized in carbonated drinks, extinguishers, the food industry, fertilizer industry, and ice cold. It may also be transformed into valuable products like fuels and chemicals through various chemical, physical, and biological processes [12].

There are many benefits of adopting CO_2 conversions and mechanism and they are given below:

i. The cost will be very low or even negative once the plant is running. The major investments would be at the establishment of the facility.

ii. Carbon utilization technology can help businesses project a favorable image and reputation because, as governmental and societal responsibility mounts to reduce CO_2 emissions, carbon dioxide will be used to make profitable products.

iii. It will minimize the monetary funds for transportation since CO_2 will be reprocessed or recycled instead of capturing and storing.

iv. The industrial companies will acquire brand new shares of the market with the generation of new fuels and chemicals.

v. This technology provides the companies a favourable chance to indulge in the production of green technologies.

Despite the numerous products that CO_2 may produce, there is a big discrepancy between CO_2 created and CO_2 transformed. As a result, a better answer to this problem is to limit the usage of fossil fuels as a source of power and to encourage forms of clean energy for instance wind, sun, hydrothermal, and geothermal energy [13]. It will be proved very beneficial if the sustainable technologies are combined with various utilization of carbon dioxide methods, which would reduce the risk to a greater extent unquestionably. CO_2 as feedstock can be transformed into vital chemicals and fuels. One of the main important factors is the percentage of purity of the CO_2 required for each process. This can be done by separating the CO_2 amidst the carbon capture proceeded with dehydration and confining or compressing the gas flow which is necessary for the transportation. The price of the CO_2 conversion process depends upon the technical specifications, geographical location, and system boundaries [14]. Interestingly, Chauvy et al. [15] highlighted in their work that using CO_2 as a feedstock doesn't mean CO_2 is avoided. During the process, there are still energy sources that emit GHGs and can impact the sustainability of the process. Although, it is undeniable that the carbon utilization technology is said to be promoting a circular economy particularly for Europe. CO_2 reduction is both a difficulty and a potential for the world's energy and environmental sustainability. CO_2 use should be emphasized in global CO_2 mitigation methods, such as the use of CO_2 in environmentally friendly processes, the synthesis of industrial-scale valuable compounds from CO_2, and CO_2 recycling paired with renewable energy to save carbon sources.

1.2.1. Comparison of CO_2 utilization methods

1.2.1.1. Mineral carbonation

CO_2 mineralization, which involves reacting CO_2 with oxides of alkali or alkaline-earth metals to generate carbonates, is a viable approach for CO_2 chemical sequestration [16]. The raw materials that could be used for mineral carbonation are coal fly ash, steel slag, blast furnace slag, and phosphogypsum [16]. When compared to other developing CO_2 usage methods, CO_2 use through the manufacture of carbonate-based building materials (binder compounds, mineral aggregates, and cement) looks to be the most commercially viable. The acceptability of a specific CO_2 waste stream for a certain mineral carbonation route is influenced by the pureness, pressure, and temperatures of CO_2 resources.

The mineral carbonation provides an appealing pathway for meeting the utilization of CO_2 in the following ways:

i. solid carbonates, the relevant factors of mineral carbonation reactions, are often used in building products economies

ii. the science involved in producing carbonates based on calcium (Ca) and magnesium (Mg) is very well recognized, mineral carbonation

iii. By chemically linking CO_2 into durable, long-lived mineral carbonates, carbonation may utilize large amounts of CO_2.

iv. Because the reaction of CO_2 with alkaline substances is thermodynamically stable, it demands little, whether any, external energy.

Carbonation is a geographical occurrence in which calcium (calcium) or magnesium (magnesium)-containing minerals interact with carbon dioxide (CO_2) to create calcium or magnesium carbonate ($CaCO_3$ or $MgCO_3$), often recognized as limestone or dolomite, amongst the most prevalent geological formations created. Some distinct mechanisms are available for carbonation such as ex-situ, surficial, and in situ. Ex-situ procedure blends with the alkaline resource are delivered to the location and crushed into tiny particles and mixed with CO_2 in a selected reaction vessel for pressure with elevated temperature [17]. Surficial is when on-site at the surface, dilute or concentrated CO_2 reacts with the alkalinity source (e.g., mine tailings, smelter slag) [17]. In-situ methods the fluids containing CO_2 inside them circulate via underground porosity within the geological arrangement [17]. Various factors affect the pricing of the carbon mineralization such as CO_2 saturated in concentration, alkalinity in solution, and ideal reaction conditions.

CO_2 mineralization processes comprise of mainly 3 parts:

Carbonation: CO_2 becomes a substantial carbonate mineral when it interacts with calcium (Ca) or magnesium (Mg) oxide. To trap flue gas, the system is often installed onto existing industrial/power facilities. Building supplies engineered fill, and specialty building material can all benefit from these carbonated goods.

Concrete Curing: A technique related to carbonation useful for concrete or precast cement, but concentrating on the manufacture of high calcium carbonate ($CaCO_3$) instead of the energy-intensive steam concrete curing processes, resulting in improved toughness.

Novel Cement: CO_2 can be utilized as a prerequisite material that is needed for the cement. Binding the mineralized carbon dioxide inside the cement.

The environmental implications and potential benefits of CO_2 mineralization are very important to analyze its impacts on the environment. Throughout the last 10 years, alkaline waste materials have quickly grown and are now regarded as one of the most effective alternatives for stabilizing solid wastes while preventing global warming. CO_2 mineralization and use were revealed to be capable of simultaneously resolving and indirectly eliminating a substantial fraction of CO_2 (i.e., 4.02 Gt per year), resulting in a 12.5% decrease in worldwide human CO_2 emissions [18].

1.2.1.2. Biological conversion

Several beneficial products can be transformed from the biowastes like bio alcohols, charcoal, biogas, syngas, electricity, biodiesel as well as heat energy [19]. There are mainly two major processes that can convert to use products from bioconversion called physicochemical as well as biological methods [19]. The biological procedure included an AD, fermentation, microbial fuel cell, microbial enzymatic, and composting [19]. The usage of AD leads to the production of methane along with other hydrogen gases. The physicochemical methods include processes such as pyrolysis, gasification, incineration, hydrothermal carbonization, and landfill, etc [19]. With the usage of pyrolysis methods, biochar is generated; with biorefinery waste's hydrothermal carbonization, carbon and charcoal are formed; with gasification technique, syngas, methane, and hydrogen gases are formed, etc [19]. Other products such as bio-plastics are also formed. The sources of feedstock for biological conversion for CO_2 utilization can be obtained from the sectors of agriculture, domestic, animal husbandry and fruit and vegetables.

CO_2 conversion of the enzymatic process is the highest prevailing technique for its transformation to organic materials. It is known that the enzymatic bioconversion process is eco-beneficial and efficient because of its profound selectivity and specificity. In any biological conversion, water, sunlight, energy, and carbon dioxide are particularly used to produce any biofuel. Utilizing CO_2 to generate biofuel usually involves a photosynthetic process and a non-photosynthetic "electro fuel" method with the help of algae, cyanobacteria, and raslstonia eutropha.

1.2.1.3. Thermochemical conversion

Thermal chemical conversion includes the hydrogenation of carbon dioxide at low temperature to generate fuels like carbon monoxide, methane and CH_3OH [20]. It is a well known fact that the molecules of carbon dioxide are chemcially and thermodyna,ically stable, therefore, large quantity of energy is needed when carbon dioixe is utilized as a single reactant. It owuld be easier if other products involves have higher Gibbs free energy [20].

Cheng et al. [21] explored oxygen-deficient $NiFe_2O_4$ nanoparticles towards thermo - chemical CO_2 to CH_4 transformation. At a low temperature, this examination demonstrates the concurrent thermochemical reaction of H_2O and CO_2 using oxygen defects $NiFe_2O_{4-\delta}$ to attain good CO_2 conversion effectiveness. Through the use of oxygen vacancies to investigate such datasets revealed how active oxygen vacancies were responsible for the activation of CO_2 to CH_4 [21]. The higher concentration of oxygen voids in $NiFe_2O_{4-\delta}$, the more successful the splitting of H_2O and CO_2 is, and the greater the yield of CO_2 to CH_4 conversion [21]. Among the utmost techniques for the production of carbon-neutral fuel and solar energy storage, solar-directed two gradations thermochemical splitting of CO_2 is implied. The resulting redox reaction supplied carbon monoxide, which is the main precursor for liquid hydrocarbon fuels, and therefore, it results in the recycling and valorization of the CO_2 GHGs.

1.2.1.4. Photochemical conversion

An interesting approach in the conversion of CO_2 has been via photochemical conversion where solar light is being utilized. There are three paramount categories in this approach which are listed below [21]:

i. Uniform photoreduction with a molecular catalyst

ii. Photoelectrochemical transformation through a photocathode (which is semiconducting)

iii. Electrochemical conversion through an electrolyzer is energized with marketable photovoltaic gadgets.

The photocatalytic CO_2 conversion has a low dispersible quality of CO_2 in water, can make several products and the mechanism requires a lot of electrons and protons transfers [21]. To convert to hydrocarbon products, so far diverse catalysts have been developed such as graphene-based, pure TiO_2, doped, composite, ABO_3 perovskites structured [22] and germanium or gallium based photocatalysts. The widely used photocatalysts for CO_2 reduction are TiO_2 suspensions along with metals such as palladium, platinum, gold, copper or ruthenium, iron, silver, etc. The photocatalyst can also be paired with non-metals like sulfur, fluorine, and nitrogen.

The photochemical conversion reactor could be explained in 4 points:

i. The catalyst is activated by the UV or visible light derived from the sunlight or an illuminated light source [23].

ii. The electrons in the valence band (VB) leap into the conduction band (CB), simultaneously, the holes are left in the VB and form the negative- electron (e^-) and positive-hole (h^+) pairs, which respectively act as the reductants and oxidants for reducing and oxidizing the substances [23].

iii. The generated electron-hole pairs separate and transport to the surface of catalysts [23].

iv. CO_2 is reduced by the negative-electron and generates corresponding products such as CH_4, CH_3OH, and CO [23].

A study performed by Keffous et al. [24], investigated the microparticles SiC powder as a catalyst for CO_2 photoreduction into methanol under UV light. It was determined that the grain size and concentration have a great impact on the photochemical conversion of CO_2 to methanol [24]. The best yield of methanol was achieved when a concentration of 0.75 M of SiC powder of 17 µm grain size and exposure time to UV light of 2 h was assured [24]. The maximum molar concentration of methanol achieved was under UV irradiation of 365 nm. Therefore, the catalytic property of silicon carbide has proved its efficiency in the photochemical conversion of CO_2 into alcohol thus far under UV light [24].

Bonin et al. [25], experimented with the photochemical reduction of CO_2 using an iron porphyrin as a catalyst, an iridium complex $[Ir(ppy)_2bpy]^+$ as a sensitizer, and various amines as a sacrificial electron donor. Upon visible light irradiation, CO was the main product (178 TON in optimized conditions) and a substantial amount of CH_4 was also produced (32 TON, 10% catalytic selectivity) while H_2 was formed as a minor byproduct when acetonitrile was used as a solvent [25]. Among the various amines employed TEA appeared as the best choice to maximize CO_2 product formation [25].

1.2.1.5. Electrochemical conversion

The electrochemical process holds crucial for a liquescent form to maintain the renewable depository for energy from the sustainable energies within the arrangement of chemical energy which can be in chemicals and fuels. This method can create a variety of useful chemicals, including oxalic acid, CO, ethylene, ethanol, formic acid, methane, methanol, ethane, and other hydrocarbons and oxygenates. The major components that can cause a difference are temperature, pressure, electrode potential, renewable energy, effortlessness in operating the method, the support electrolytes, and the environmental prospect. The mechanism can be performed at room temperature and regular room pressure with handling the factors such as corrosiveness, release of material by accidental and defeat in components. The electrolytes are bound with higher efficiencies as even wastewater can be used to operate the anode mechanisms. The electrochemical mechanism is easy to operate, very sustainable as the electrolytes can be recycled, utilization of renewable energies are proved to be the usage of clean energy. This conversion is the most cost-effective and efficient as the electricity produced via sustainable sources [26]. The conversion via electrochemical is favourable as it is simple to prepare, greater efficiency, less overpotential, and quite a variety of reaction mechanisms available [26].

Although the significant hindrance takes place in discovering steady and cut-price catalysts. It is proved that greater catalytic action along with selectivity is found with sustainable biocatalysts [26]. The electrochemical reduction method is exceptionally governable, which makes it very practical for industries to use it in greater amounts. There are major two important aspects that make a huge difference such as biocatalyst and electrocatalysts for achieving the higher potential of electrochemical mechanisms. The biocatalyst requires an enzymatic mechanism for CO_2 conversion by an electrochemical pathway. This pathway possesses a steep reaction rate along with selectiveness but it should be noted that this process requires larger investments and transportation concerns. Electrocatalysts help in yield enrichment in the transition of carbon dioxide to useful products. There are various types of catalysts available such as complexed metal, nanostructure, transition metal, carbon metal, and carbon nanotubes [26]. The most common catalysts used for electrochemical reduction are metals along with their oxides and complexes. Several kinds of catalysts improve energy efficiency which is metal-based such as Cu, Zn, Pb, Pt, Fe, Ni, Au. Out of all, the most common and used to a greater extent is Cu, since Cu has greater capability to generate CO, HCOOH, CH_4, and C_2H_4. As a result, many such crucial aspects need to be considered when creating a catalyst for electrochemical conversions, such as constructing a low-cost catalyst, concentrating as much study on novel catalyst materials, and producing a high-efficacy, long-lasting catalyst that can be used in advanced manufacturing applications in the field. The catalysts can indeed be spilt into two categories: nanostructure catalysts and transition metal catalysts.

Nanostructure catalyst:

The improvement in lower overpotential would be improved by the energy efficiency is CO_2 electrochemical reduction [26]. Lim et al. [27] concluded that the usage of nanostructure catalyst on graphene would be able to provide good catalyst performance and along with lesser investment and maintenance fees.

Transition metal catalyst:

Certain catalysts with transition metals like phthalocyanine, porphyrins, bipyridines are utilized for the electrochemical reduction of CO_2 [26]. For the conversion of carbon monoxide, Kirk et al. [28] performed a theoretical study with palladium and nickel-doped graphene and concluded that this catalyst has greater performance, better selectivity, and efficiency.

There are various techniques in achieving the perfect reduction conversion which is given below [26]:

i. The biochemical conversion method utilizes bacteria as an energy source to produce methane.
ii. The bioelectrochemical technique operates with enzyme and methyl viologen along with carbon oxide and oxoglutaric acid to generate isocitric acid.
iii. The biophotoelectrochemical method utilizes enzyme and methyl viologen in the presence of light to form formic acid.
iv. The chemical mechanism with the presence of Na^-, Sn^{4-}, Mg^{2+} to generate carbon, carbon monoxide, and sodium oxalate.
v. Electrochemical mechanism approached in the presence of electricity for eg. Electrons and protons to form methane, formic acid and formaldehyde.
vi. Photochemical incorporated the factor of light to produce carbon monoxide, formic acid, and formaldehyde.
vii. Photoelectrochemical reaction induces electricity to inform of electricity and light to generate carbon monoxide.
viii. The radiochemical with the help of gamma radiation generate formic acid and formaldehyde.

This section describes the differences between various technological pathways as mentioned in previous' sections as shown in Table 1.

Table 1. Comparison of various technological routes for CO_2 utilization

Technology	Products	Advantages	Disadvantages/ Restrictions
Chemical Conversion			
Mineral Carbonation	1. Cement 2. Aggregates	• Indirect carbonation • Utilization of inorganic wastes	• Slow kinetics • High pressure and high-temperature operation • Expensive to implement
Electrochemical conversion	Chemicals Syngas	• Highly energy efficient • Highly controllable • Higher conversion efficiency • Convenient for industrial scale	• Chemical catalysis • O_2-substrates alternatives • Usage of stoichiometric additives that are not easily regenerated

		• Safe because toxic materials are not necessary	
Photochemical conversion	Chemicals (Methanol, Ethanol, CO, Formaldehyde, Formic acid)	• The direct use of solar energy • No excess energy is needed • There is no unfavourable environmental impact	• The resulting yield of the product is lower. • The selectivity of the product is quite low. More research to be done on the conduct of the metal oxides under the elevated-temperature circumstances.
Thermochemical conversion	Solar fuels Chemicals (Methane, CO, Syngas)	• Higher TRL • Existing infrastructure and techniques • The widest selection of goods available across conversion paths	• Overcoming • equilibrium conversion limitations • Process intensification • Improving product selectivity
Biological conversion			
Enzymatic conversion	Biofuels Bio-plastics Bio-alcohols Chemicals	• Does not require purified CO_2 streams • Can tolerate low CO_2 concentrations and impurities in the carbon sources	

1.2.2. Barriers for CO_2 utilization processes

The are mainly four critical obstacles in the development of the CO_2 utilization methods which are mentioned below:

1.2.2.1. The financial burden of CO_2 capture and transportation

Identifying the gaseous compounds of concentrated carbon dioxide which are prevailing near the sites of CO_2 utilization facility. Using improved separation technology can reduce the cost.

1.2.2.2. The energy demands in terms of carbon dioxide conversion

As a general rule, it is a prerequisite to operate CO_2 in terms of a co-reactant with additional compounds containing greater Gibbs free energies along with a catalyst that can provide a greater conversion at lessened temperatures. The formation of hydrogen should be taken into consideration as the main ways to generate it is via an energy-intensive process such as reforming of hydrocarbon.

1.2.2.3. Government incentives available for CO_2 conversion

The cost or share required for various applications of CO_2 processes will be different. It is advised to induce the policies and generate more money funding so as these technologies will be made more readily available for everyday use for the big companies.

1.2.2.4. Building community awareness in regards to CO_2 processes

The provision of many incentives could be the answer if society and the government see the importance and necessity of CO_2 utilization. It can be labeled in a different way such as carbon pricing for the product. This will bring awareness in terms of environmental concerns and more policies will be made in acknowledging its benefits.

1.2.3. Potential CO_2 utilization to produce renewable methane

This thesis presents two desirable techniques for renewable methane production, firstly via thermal added technologies using municipal organic waste and produced sewage sludge and secondly via CO_2 methanation using carbon dioxide and hydrogen gases in a series of lab-scale experiments. It is known that CO_2 is a dominant contributor to the uprise of temperature globally [29]. In recent years, the capture of carbon to store fuel and reduce major greenhouse gases was sought to be the ideal solution, but it was not made commercially available [29]. Carbon utilization has been the ideal focused these days where many companies sought to convert carbon dioxide to useable fuels and that can be incorporated into daily usage. CO_2 methanation is one particular method. The production of methane is beneficial as it absorbs the carbon from the atmosphere and also generates higher heat and energy than other hydrocarbons and can be utilized for heating, transportation, and cooking purposes. [30].

1.3. Renewable methane methods

To attain the climate change goals, the EU governments are centralizing towards the making of renewable methane and it is perceived as a means to be the decarbonization answer for the transportation sector [5]. The Renewable energy directive for 2021-2030 shows the target for the fair contribution of energy from sustainable origins in gross consumption of energy fro 2020, for eg. Lithuania's target is 23% and the highest target is set by Sweden and Latvia to 49% and 40% [31]. One of the preferences for meeting the Renewable Energy Directive (RED II directive) is utilizing qualifying feedstocks for the generation of renewable methane [32]. The new amendment in the RED (Directive (EU) 2018/2001) establishes a contemporary objective for the EU to utilize 32 % of renewable energy by the year 2030. Inexhaustible methane is interesting as the production of methane via a low-carbon substitute fuel route which can be produced by advanced and first-generation technology [5]. For EU decarbonization, the feasible methane can be generated from a broad range of feedstock and use second-generation technologies such as gasification and power to gas [5].

1.3.1. Applications and relevance

The feasible fuel biomethane can be originated from biomass generated from waste which is a non-polluting, clean and inexhaustible biofuel [33]. Biomethane can be used for transportation in heavy-duty and light-duty vehicles [34] [35], injecting in the natural gas grid, heating [36], and cooking purposes [37] [38]. It is a profitable asset as it conserves resources [39], provides utmost flexibility in usage and production, reduces the major GHG and carbon dioxide (CO_2) by creating a smaller carbon footprint [40], can be generated locally which makes it value-added biofuel and also competitive along with meeting the legal requirements of EU. It has been proved by various researchers that biomethane provides carbon utilization and better environmental performance compared to other fuels [40] [41] [42]. The quality requirements are mentioned in the standard ISO 16559:2014.

Methane consists of the lowest amount of carbon amount all hydrocarbons. The RE-methane can be in various types of methane as solar, biomethane, and wind. Biowaste material is seen as a source of interest as it clears the issues of waste management and also be a raw material for the generation of renewable methane. The RE-methane can be established as a main carrier for the energy processes, this would be termed as RE-methane economy. The technologies utilized earlier were mainly biological such as AD technology but in recent years thermal technologies were also analyzed such as thermal gasification of biowaste. It is a profitable asset as it conserves resources, provides utmost flexibility in usage and production, reduces the major GHG and carbon dioxides (CO_2) by creating a smaller carbon footprint, can be generated locally which makes it value-added biofuel and competitive along with meeting the legal requirements of EU. The countries producing biomethane have been multiplying immensely given the directive (Directive (EU) 2009/28/EC).

1.3.2. Utilization of municipal organic fraction and sewage sludge as feedstock

To diminish the environmental footprint and to use alternatives to fossil fuels with an additional source of income, the utilization of municipal organic waste and sewage sludge as second-generation feedstock by companies to produce renewable methane is advisable. These alternatives are a useful medium of green energy. The popular commercial route of using municipal organic waste is biogas production via anaerobic digestion (AD) and upgrading to biomethane. The AD route of biomethane production has been widely utilized with more than 17,000 biogas plants in the EU. Ardolino et al. [40] provides a technological route to produce biomethane via AD and then upgrading it to biomethane. Although AD provides organic waste utilization, fuel generation, reduction in GHGs it causes odour nuisance, and generated biogas is filled with impurities and higher CO_2 concentrations. Sewage sludge comprises biogenic elements and organic substances. Dehydrated sludge's volume makes up to >50% whereas the hydrated sludge ranges around 2.6% to11%. It is possible to use the SS as a fertilizer for soil due to its content but due to the heavy metal present inside, the legal standards are important to meet therefore, it is easier to utilize the SS as an energy feedstock for thermal processes.

The SS as an energy feedstock can be sent to the gasifier which creates syngas, and this can be upgraded to biomethane. Werle et al. [43] [44] proposed that the thermal treatment of SS is considered to be a promising substitute and that gasifier has many advantages compared to all thermal conversions. Calvo et al. [45] considered gasification as a waste to clean energy technology as it produces flammable gas from the SS. Seggiani et al. [46] concluded in their study that using SS and wood chips as a feedstock eliminates the hazardous release of chemical compounds to the atmosphere. Dogru et al. [47] conducted a lab-scale experiment utilizing SS to produce combustible clean gas at higher efficiency, they found that sewage sludge can be used to produce low-quality combustible gas with a thermal efficiency of 39% to 40%. An alternative technology that can provide higher methane content is gasification aided with plasma technology, which has been proven to be a highly attractive means for the waste to energy processing [48]. Morrin et al. [49] performed lab-scale experiments of two-phase gasification and air plasma to generate syngas (10-14 MJ/NM_3) from municipal waste (90 kt/yr). The production of syngas from gasification and air plasma technology has been identified as a positive impact on electrical efficiency, better environmental performance [50], greater gas production and carbon conversion efficiency [51], and minimum formation of toxins [52].

1.3.3. Utilization of carbon dioxide as feedstock via methanation

The unreacted gas CO_2 in some plants during various processes can be converted into a useful resource such as renewable, this can be via catalytic hydrogenation of CO_2 also known as CO_2 methanation [53]. The CO_2 methanation mechanism is given below:

$$CO_2 + 4H_2 \leftrightarrow CH_4 + H_2O \text{ ; } \Delta H_{298k} = -165.0 \text{ kJ mol}^{-1} \qquad \text{Eq. 1.3.3.1} \qquad [53]$$

This Eq. (1.3.3.1) signifies an important role during methanation due to its high equilibrium constants within their temperature variations of 200℃ - 500℃ [53].

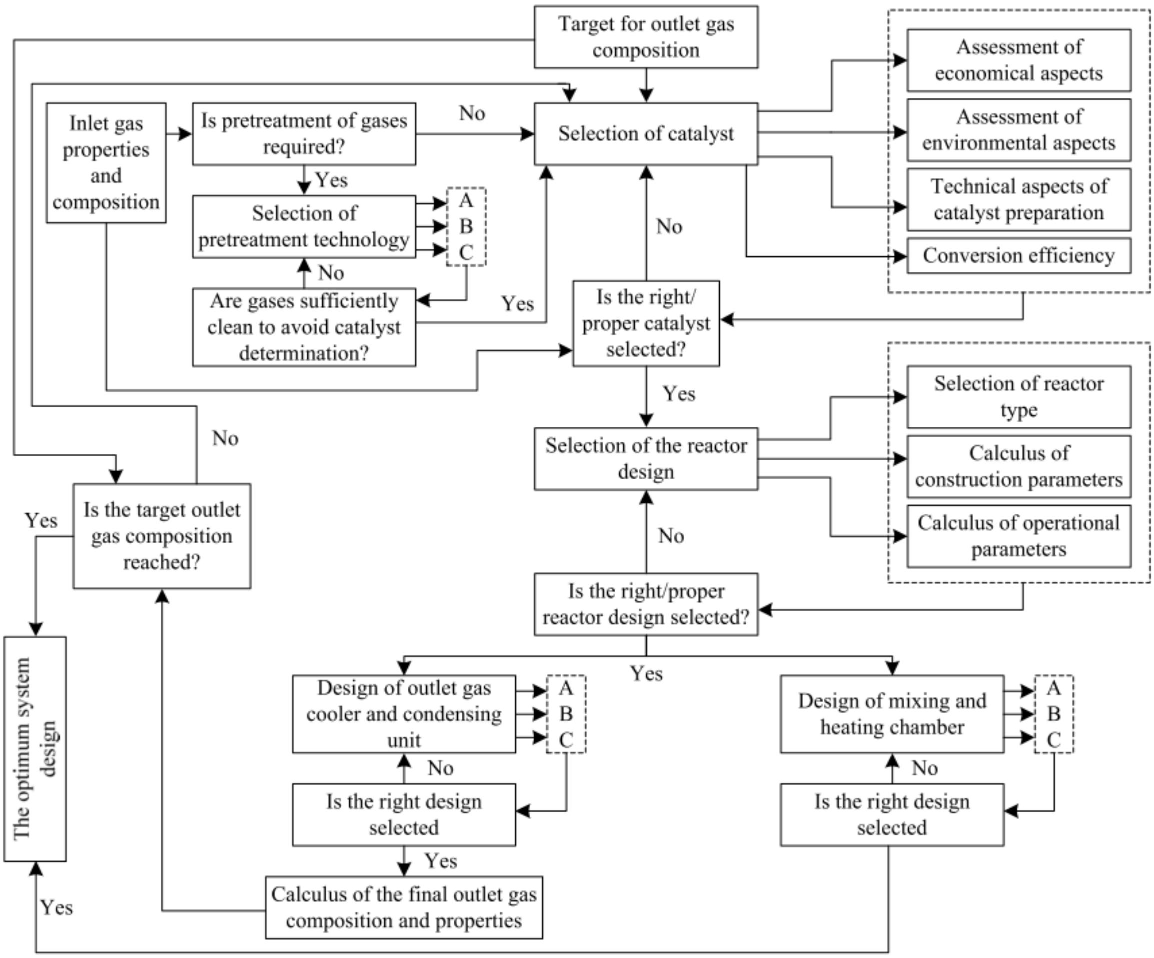

Figure 1. Flow chart about methanation operation [8]

CO_2 methanation is said to be environmentally friendly as it reduces CO_2 and also GHGs emissions and acts as an energy carrier [54] [55]. This process is an exothermic reaction, with elevated temperature the content of CH_4 will decrease and CO formation will be formed [53]. With increasing temperature and pressure, the CO_2 conversion will be reduced. The flow chart which shows about mechanism process is shown in **Figure 1**. The H_2:CO_2 ratio also plays a major role in CO_2 conversion, if the ratio is 2, then the CO_2 conversion is found to be only 50-70% [53]. If the ratio is equal to 4, then the carbon deposition is not formed, therefore, yielding a higher CO_2 conversion ratio [53].

1.3.4. Leakage concerns of renewable methane

While determining the efficiency of the GHGs of RE-methane, one of the most crucial factors is gas leakage. It is extremely high priced and tedious to measure the methane emissions from any RE-methane plant. Liebetrau et al. [56] concluded in their work that the leakage of methane primarily between 0.001% and 1.11% of the biomethane produced. It is advised to check regularly via gas cameras, handheld lasers, or measuring based on the gas concentrations based on gas samples [57]. When uncombusted gas such as methane is released into the atmosphere through exhaust from the gas engines of heat and power. There could be more leakage when combusting gases are utilized for heating or transportation purposes.

1.4. Summary of the literature review

With all the anthropogenic actions, methane and carbon dioxide are the major GHGs existing in the tropospheric region. Based on research conducted by Environmental Protection Agency (EPA) in 2019, 81% of GHGs were CO_2 [58]. Therefore, the literature review presents two short reviews. One part of it covers the production of renewable methane by the utilization of second-generation source material for instance municipal organic waste and sewage sludge. The popular commercial route of using municipal organic waste is biogas production via AD and upgrading to bio-CH_4. Another route that is gaining popularity is using the sewage sludge that is produced from anaerobic digestion. The sewage sludge is used as an energy feedstock for the gasification and air plasma and then further upgrading the syngas to biomethane. Another part covers a short review on how CO_2 can be utilized as a raw feedstock for converting it into useful chemicals and fuels. Carbon dioxide can be converted by thermochemical conversion, electrochemical conversion, photochemical conversion, biological enzymatic conversion and mineral carbonation. Therefore, to conduct CO_2 utilization, thermochemical conversion of CO_2 also recognized as CO_2 methanation was studied. CO_2 methanation is a Sabatier reaction that converts CO_2 and H_2 to CH_4 and H_2O. In the next sections, the performance of the technologies for producing renewable methane by combining biological and thermal methods are analyzed for a given functional unit. The second part is performing lab-scale experiments for carbon dioxide methanation to produce renewable methane and to check its conversion percentage.

2. Research Methodology

To inhibit fossil fuel usage and accelerate the acceptance of methane renewable fuels, thermal technologies and CO_2 methanation have been proposed.

2.1. Different principal schemes of methane generation

The goal is to generate 1 $kWh_{thermal}$ biomethane in the energy sector via three technologies (see **Figure 2**). The later sections review the main technological aspects taken into account during this study.

i. Reference scenario: Generation of biogas via AD and conditioning it to biomethane via membrane separation.

ii. 1st integrated scenario: Utilization of the sewage sludge originated from AD process and gasified to produce syngas and conditioned to biomethane via methanation.

iii. 2nd integrated scenario: The sewage sludge utilization that emerged from the AD mechanism and proceeds to air-plasma-aided gasification. The produced syngas is conditioned to biomethane via methanation.

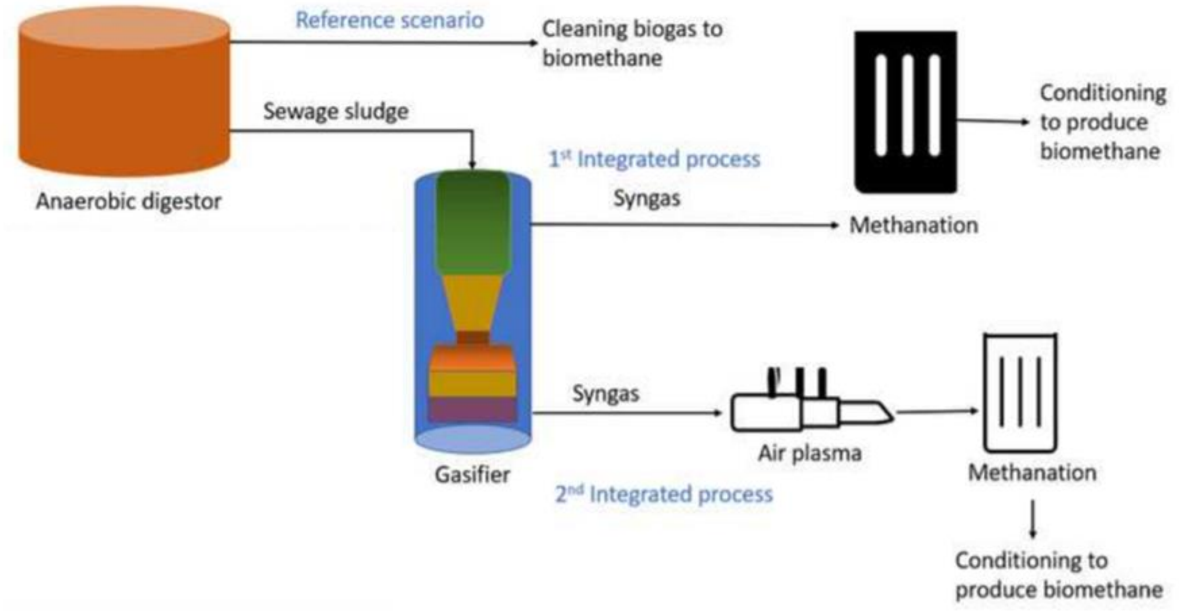

Figure 2. Usage of sewage sludge as feedstock to generate biomethane

2.1.1. Reference scheme

The reference scheme was obtained from the study performed by Ardolino et al. [40] which developed a sustainable production route of biomethane. This waste-to-energy route upgrades the produced biogas from AD to biomethane via membrane separation. The scheme consists of an AD reactor, biogas conditioning unit and upgrading unit called membrane separation as shown in **Figure 3**. This scenario utilizes the biological fragments of the municipal waste as an incoming raw feedstock. This infeed material undergoes mesophilic treatment in AD at 37-39℃ with some supplementary energy included. The AD operation consists of a 4 step biological mechanism to produce carbon dioxide and methane from organic carbon [59]. This process additionally develops some by-products called SS or digestate. The AD process generates wet biogas which undergoes the drying treatment via the biogas drying unit to diminish the liquid (condensed water) and generate dry biogas. It is pivotal to eliminate the condensed water from the biogas as it may deteriorate the quality of the pipe in the upgrading system by making it corrosive [38]. It is also essential to remove the water to produce 98% pure methane. In the membrane separation, 95-97% pure methane of high quality is produced along with some off-gases.

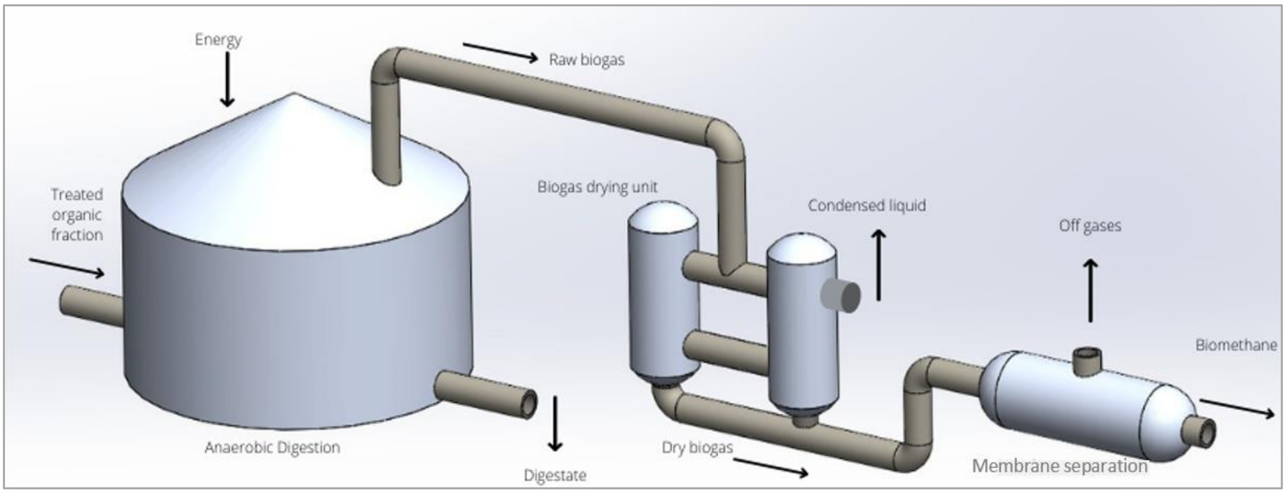

Figure 3. Reference case of organic municipal waste generating biomethane via anaerobic digestion and conditioning.

2.1.2. 1st integrated scheme

The 1st integrated scheme is a modified technological route with the addition of a gasifier unit and methanation to the reference scheme as mentioned in section 2.1.1. The inventory data for the reference scheme is taken from the same study as mentioned above in section 2.1.1. The data for gasification is attained from Striugas et al. [60]. In this integrated scheme, there are two methods of producing biomethane: through reference scheme and via gasification. The representation of the scheme is shown in **Figure 4**. The total production of biomethane via these two methods adds up to 1 $kWh_{thermal}$. The reference part follows the same procedure as mentioned in the section above. The secondary division consists of a dryer unit, gasifier, cyclone component, gas cooler and methanation. The process begins with the AD process generating biogas and SS. The SS is dried utilizing equipment called a dryer, thus the dried SS acts as an energy feedstock for the gasifier. In the dryer, additional air is required during the operation and supplementary woodchips are combined with SS to stabilize the drying process. The dried feedstock (woodchips and SS) consisting of a 50/50 ratio are sent to the gasifier equipment with an additional supply of air input. The SS is considered to be an energy feedstock and an alternative route for sustainable biomethane production the biomass of gasification is also deliberated to be a path to achieve circular economy and CO_2 neutral. The biomass undergoes gasification at 800℃ - 850℃ since it has been proved that increased temperature is a driving force to produce larger gaseous particulates such as syngas and some residues are acquired as a by-product. The produced syngas proceeds to the cyclone where the remaining char residues are eliminated. The hot syngas emerging out of the cyclone at 550 ℃ - 600 ℃ is sent to the gas cooler to cool down its temperature to 300℃. The gas cooler requires additional inpouring and outpouring of water. The syngas that exits the gas cooler enters the methanation reactor where high-quality biomethane is produced along with some non-reacted gases and water.

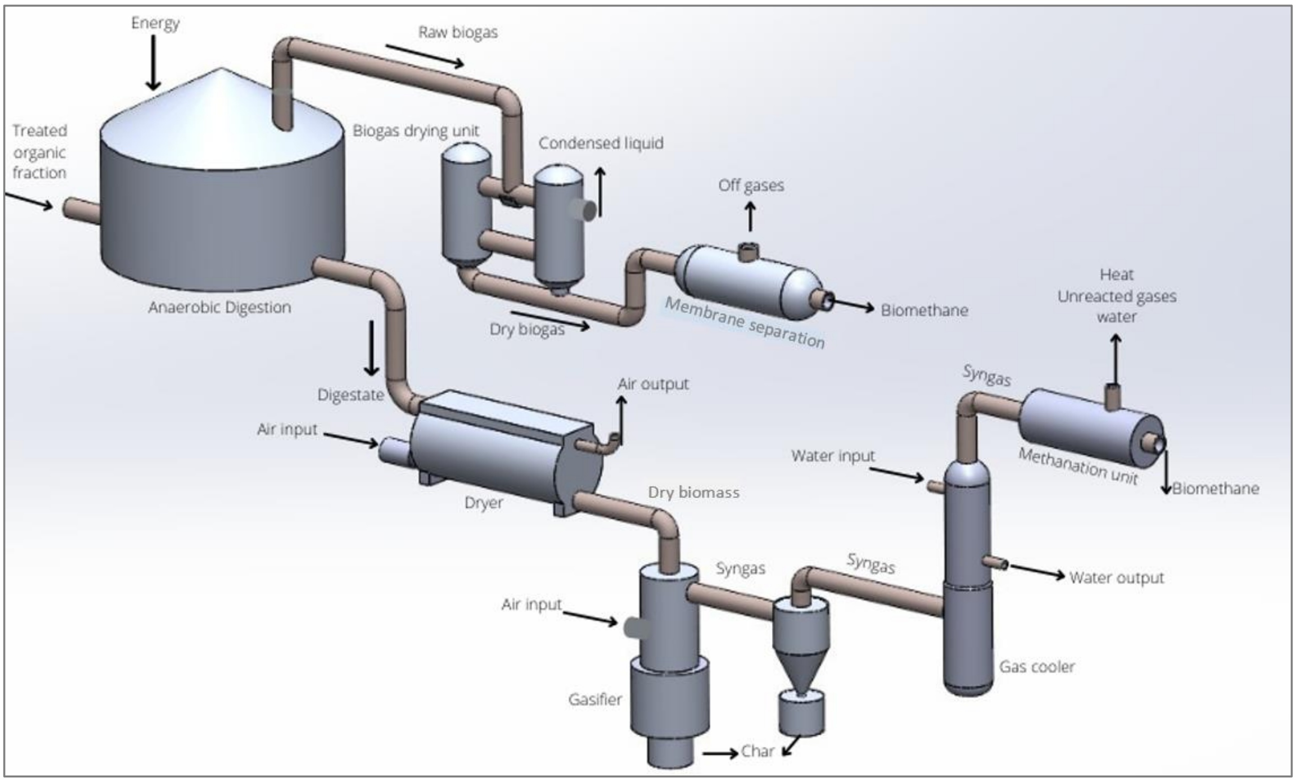

Figure 4. Flow scheme of 1st integrated case: process anaerobic digestion with gasifier and methanation.

2.1.3. 2nd integrated scheme

This integrated process follows the reference scheme as mentioned in section 2.1.1 using the same inventory data and the new incorporation of plasma-aided gasification and methanation. The inventory data of a new additional route is taken from the study performed by Striugas et al. 2017 [61]. The goal is to produce 1 $kWh_{thermal}$ biomethane with the combination of these two routes in this scheme. The secondary route consists of dryer equipment, gasifier unit, cyclone separator, air plasma, gas cooler and methanation. The schematic process is shown in **Figure 5**. The AD process produces SS which can be used as a renewable feedstock. The dryer equipment dries the feedstocks (SS and woodchips) added at a 50/50 ratio with supplementary air. The dried feedstock is further gasified to syngas and some char residues are released. The syngas is subject to eradicate the remaining char residues using a cyclone separator. Equipment called air plasma is introduced at this point to increase the purity and quality of the gas, it also produces a higher calorific value of the gas and to eliminates the excess unwanted gases into simpler compounds such as hydrogen and carbon monoxide. The hot syngas emerges from air plasma at 1100℃. The air plasma utilizes additional air, water and energy. The next step is to cool down the hot syngas to 300℃ via gas cooler equipment using water. The syngas is sent to a methanation reactor where high purified biomethane is produced along with some unreacted gases, water and heat.

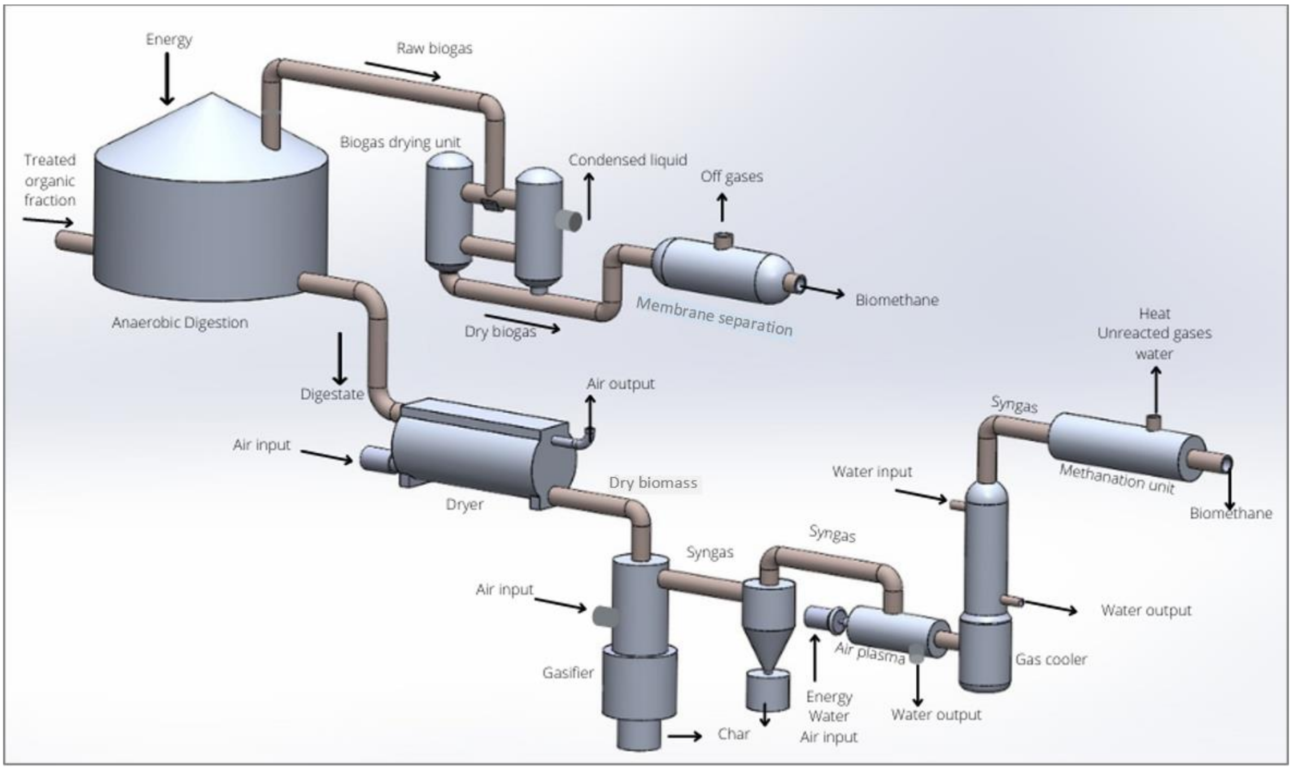

Figure 5. Flow scheme of 2nd integrated case: process anaerobic digestion with gasifier aided with gasifier and methanation.

2.2. Balances of material and energy

Material and energy flow is implied to be equivalent to the inflow and outflow along with any new product formed during the process.

$$\sum m = m_{in} - m_{out} \qquad \text{Eq. 2.2.1}$$

In equation 2,

$\sum m$ = the overall mass of the feedstock

m_{in} = feedstock's mass input

m_{out} = feedstock's mass output

$$\sum Q = Q_{in} - Q_{out} \qquad \text{Eq. 2.2.2}$$

In equation 3,

$\sum Q$ = the overall mass of the feedstock or fuel's energy

Q_{in} = energy input

Q_{out} = energy output

In equation 4,

$$Q_{physical} = m * c_p * \triangle T \qquad \text{Eq. 2.2.3}$$

$Q_{physical}$ = the overall mass of the feedstock or fuel's energy

m = mass of any feedstock or fuel

c_p = specific heat

$\triangle T$ = difference in temperature

$$Q = m * LHV \qquad \text{Eq. 2.2.4}$$

In equation 5,

m = mass of any feedstock or fuel

LHV = the feedstock or fuel's lower heating value

The lower heating value (LHV) means any amount of heat released in the course of the combustion process. To carry out a mass and energy balance, it is crucial to know the LHV of our feedstock or fuel, in our case, the LHV of woodchips and SS are 16300 kJ/kg and 8400 kJ/kg [60].

2.3. Life Cycle Assessment

In agreement with ISO 14040 [62] and ISO 14044 [63], there are four major phases of LCA, namely definition of goal and scope, inventory analysis, impact assessment and interpretation of results [64]. LCA is an evaluation tool also known as "cradle to grave" to assess the environmental performance focusing on the reduction of carbon emissions. It is important to perform LCA at the beginning of the process' design as it may benefit in gaining knowledge as to which equipment causes the highest impact in terms of energy or toxic emissions, thus it can be eradicated and improved. SimaPro 9.1 has been used for the comparison of biomethane technologies.

2.3.1. Life cycle analysis' goal and scope

The goal of this LCA study is to analyze the environmental impact caused by different renewable methane production technologies as mentioned in section 2.1. The functional unit was set as per the energy unit to understand the output fuel of these three processes, Therefore, the functional unit is taken to be 1kWh$_{thermal}$ of biomethane generation for the energy sector. The data obtained from the scientific papers are normalized in regards to generating 1kWh$_{thermal}$ of biomethane. The graphical representation of the system boundary of biomethane production is shown in **Figure 6**. It should be noted that there are some intermediates formed at different phases of the process which are not shown such as biogas, sewage sludge and syngas.

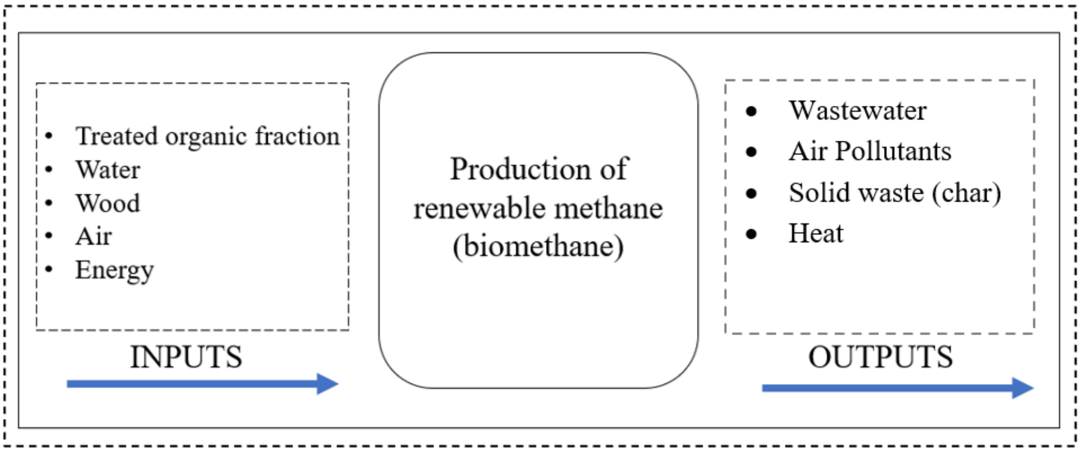

Figure 6. Illustrative representation of the system boundary for biomethane production

2.3.2. Investigation of inventory data

Inventory data is said to be the core of the LCA operation which involves determining the inputs such as feedstock, energy, water and outputs such as emissions to the environment. The impact categories describe environmental mechanisms which convert the outcomes of the LCI into environmental damages. Indicators can be derived from these mechanisms at intermediate levels (midpoints) or damages levels, (endpoints) after normalization. The reference numbers taken into account for LCA are derived from the mass and energy balance performed using the experimental data provided for reference scenario [40], 1st integrated process [60] and 2nd integrated process [61] respectively.

2.3.3. Evaluation and analysis of the impact

The results were analyzed by utilizing SimaPro 9.1 software, the applied method for the research was IMPACT 2002+. This method was developed by the Swiss Federal Institute of Technology which is combined modeling of midpoint and endpoint impact categories [65]. The normalization graphs were interpreted according to their endpoint impact categories. Normalization is evaluated by dividing the impact of a system under study by the impact of the reference system [66]. A bigger value means a higher difference and higher impact on the environment either positively or negatively. The impact categories evaluated were climate change, resource consumption, ecosystems and human health. Human health is illustrated by considering the human toxicity, respiratory effects and ozone layer depletion, the emission amounts along with their concentration and doses are an important factor in terms of human toxicity. The ecosystem quality is affected by land occupation, aquatic and terrestrial eutrophication which is the result of the land usage for the process, water released in the aquatic body and the chars released on the land. The climate change factor is highly dependent on global warming potential (GWP). The GWP is the warming caused by CO_2 as the pollutants contribute to this reaction by confining the earth's heat. The resources are based on the dependency of extraction or utilization of raw materials of any kind. The LCA impact assessment was carried out by the well-known software SimaPro 9.1. In this evaluation, only the endpoint categories were taken into consideration during the interpretation of the results. The results were presented in normalization graphs.

2.4. Methane production via CO_2 methanation experiments

The experimental study for the methanation process was carried out in a lab-scale pilot plant targeted to estimate the maximum operation situation as well as search the suitable commercial catalysts for the methanation of CO_2. 20 wt. % Ni-based catalyst such as Mg_2Ni with Al_2O_3 support was used to perform CO_2 methanation. There were two zones in the methanation reactor where the catalyst was situated as shown in **Figure 7**. The catalyst Mg_2Ni of 34% was mixed with the support material Al_2O_3 weighing 13.92g. Zone 2 consists of the support material Al_2O_3 of 66% (weight = 2.20g). The major components of the experiments were gas cylinders of CO_2 and H_2, a heater with ceramic walls, thermocouple, three pressure gauges, condenser, a reactor with silica gel, gas analyzer M-20L PN-0, a computer, pipes, a fume hood, oil container and recirculation vessel for oil as seen in **Figure 9**. The schematic diagram is displayed in **Figure 8**. The program used to see the temperature dependence, measure mass flow, analyze gas composition was Picolog recorder, Flow vision 1.33 model M-20NLPN-0-0 and Win data 3.

To begin the experiments, the main supply of electricity and ventilation system is turned on. The temperature sensor for setting the circulation oil temperature (thermal oil) is turned on. Thermal oil was set to 310°C, 320°C, 325°C, 330°C, 335°C, 340°C, 350°C and 359°C. The maximum limit for thermal oil is 360°C. The thermal oil input and output is measured by two temperature recorder at the entrance and the exit of the methanation reactor. The thermal oil is mainly utilized in the initial stage where it acts as a heating medium [67]. The pipes should connect the gas analyzer and the silica gel. The gas analyzer should be connected to the fume hood via pipes. For the oil chamber, argon gas is released before the experiment. The programs such as Picolog recorder, Win data 3, Flow vision should be opened and ready to note down the readings.

Once the experiments start, mass flow in l/min and the molar ratio is set, the gases CO_2 and H_2 are allowed to flow to the heater. The heater preheats the gases up to 250°C - 350°C. The preheated gases enter the methanation reactor where the Sabatier reaction takes place [68]. The thermal oil recirculates the whole time during the experiment. The gases after exiting the methanation reactor go to the silica gel. Silica gel is utilized as it provides excellent conversion rates regardless of owning a smaller surface area [29]. From the silica gel, it proceeds to the gas analyzer where the composition is noted and then the gases enter the fume hood. As the reaction forms methane and water, therefore, to condense the water created, the water-soaked with gaseous content is sent to the condenser [67]. Another opening from the methanation reactor is for a condenser where the remaining water is removed. Each test is run for about 30 mins to 60 mins.

At the end of the experiments, the volume and percentage of gas compositions for CO, CO_2, CH_4, H_2 are written down for each experiment. The temperature is noted for all the probes situated in the methanation reactor. The pressure gauges are recorded to be ranging from 10bar to – 11bar which was also similar to the study performed by Castellani et a. [68].

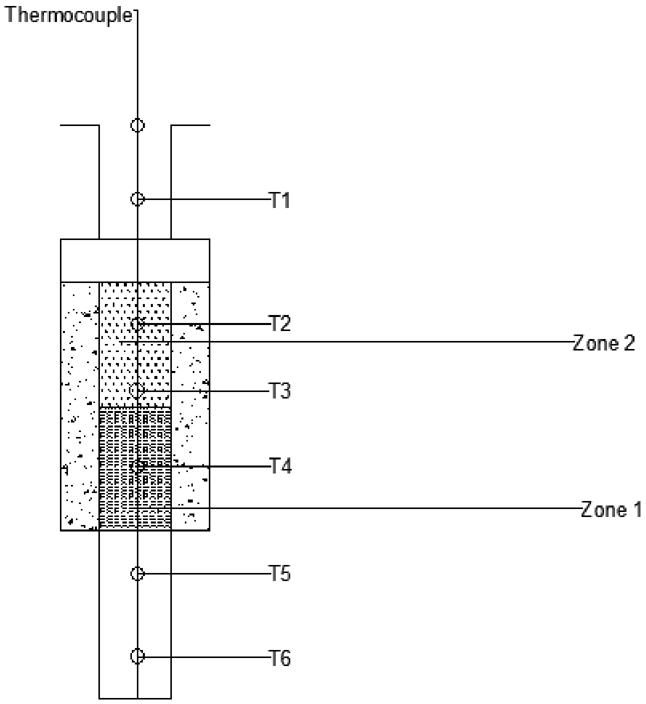

Figure 7. Methanation reactor with catalyst Mg_2Ni and support Al_2O_3

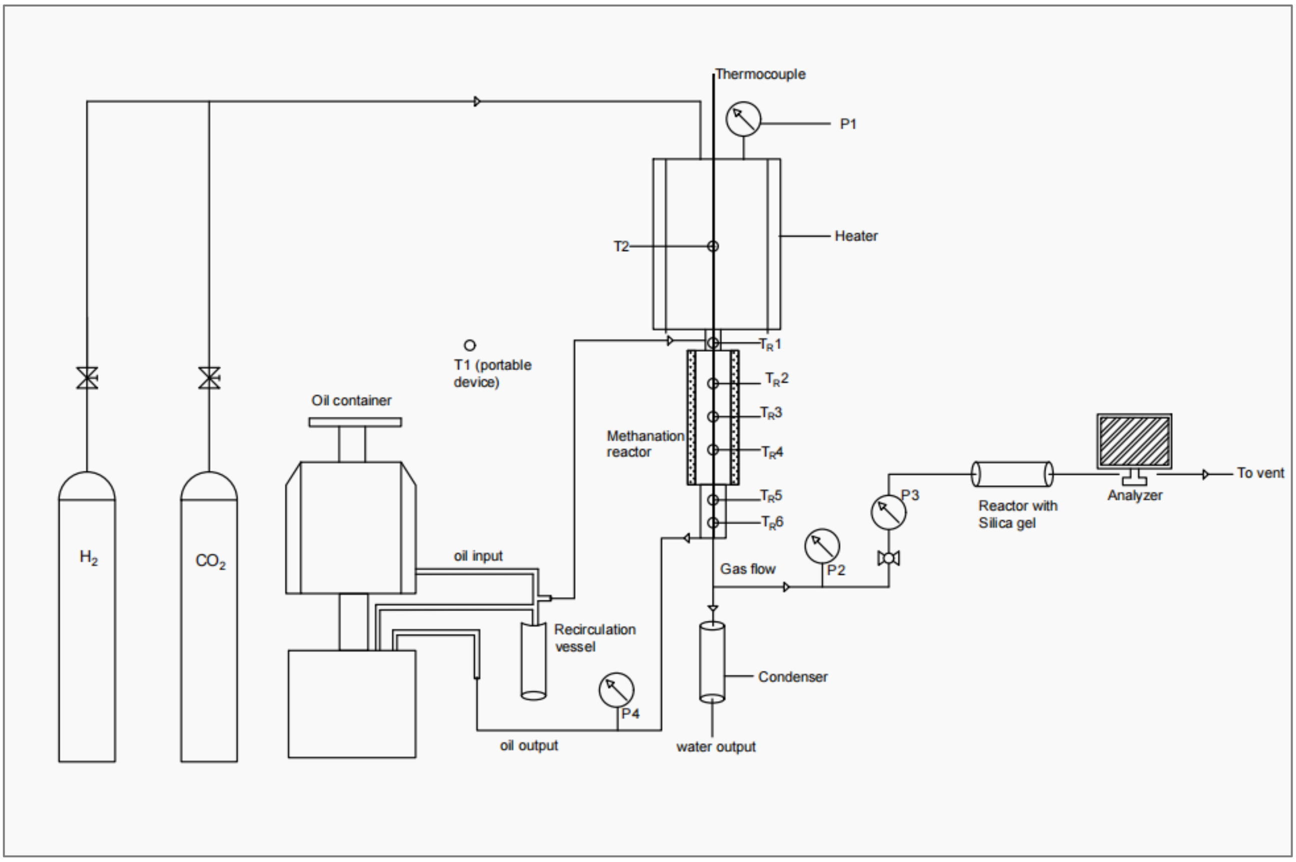

Figure 8. Diagram of the experimental flow process of methanation for producing methane from H_2 and CO_2

Figure 9. The laboratory experimental set up for CO_2 methanation

3. Research results and discussion

3.1. Review of mass and energy flow of methane production

The largest amount of sewage sludge (4.88kg) in the reference scenario was required to produce 1kWh$_{thermal}$ of biomethane in comparison to the 1st and 2nd integrated processes. The off-gases emitted in the scientific reference paper were 2.37 times more than the production of biomethane whereas in our case, the release off-gases were 2.24 times more than biomethane, which is slightly lower. The raw biogas produced (0.25kg) from an AD reactor contains about 55–65% methane (CH_4), 30–45% carbon dioxide (CO_2), traces of hydrogen sulfide (H_2S), and fractions of water vapour. The volume of the dry biogas reduces by 0.003 kg as the water content is removed and it further goes to membrane separation where the biogas containing 50% methane converts to biomethane, containing 95-97% methane concentration via permeate membranes as shown in **Figure 10** [69]. Biogas drying and membrane separation units are mainly operated around 26°C [70]. The methane losses generally occur between 0.1% to 5% depending on the type of treatment process [70] [40]. It should also be noted that the energy balance of the plant is directly proportional to the production of biomethane [71]. The main reduction of CO_2 emission profile comes from biogas production which leads to a negative emission release of CO_2 [71]. CO_2 can be saved increasingly when thermal energy recovery is considered. In this process, The CH_4 concentration in the retentate stream (the upgraded biogas) was raised to 92–95 mol% CH_4. The specific electrical energy consumption for biogas upgrading to be around 0.29 kWh/m^3. Therefore, this process produces 1kWh$_{thermal}$ of biomethane with a mass of 0.0763kg. Although the AD process is beneficial in several ways, the biogas produced contains big fractions of CO_2 [72]. Therefore, it is important to remove CO_2 to produce high-quality and pure biomethane [72]. With the addition of gasification and air plasma technological routes, we can see a better production of biomethane production.

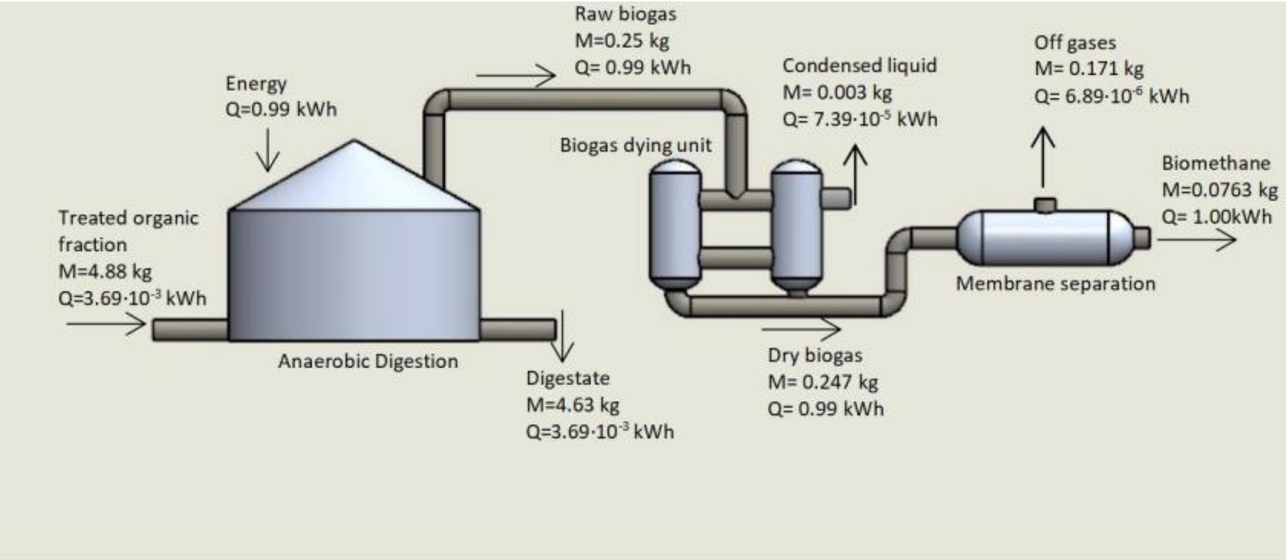

Figure 10. Mass and energy flow of 1kWh$_{thermal}$ production of biomethane with reference process

The digestate and wood chips were added to the dryer equipment as they are 100% energy resource, higher energy density, and space-saving. It should be noted that the increasing temperature of the dryer will reduce the drying time and increase throughput. It is observed that the digestate amount in process AD with gasifier is required higher than the process AD with gasifier and air plasma by

0.04kg to produce the required amount of biomethane. In the 1st integrated case, via Process AD, 0.29kWh biomethane is obtained using 1.38kg of the treated organic fraction as seen in **Figure 11**. In the same case, via gasification, 0.71kWh biomethane is obtained using the digestate amount and add wood chips. A higher amount of air input, wood chips, and energy input is needed for the gasifier reactor in 1st integrated case in comparison to the 2nd case. The dry biomass (1.99kg vs 0.76kg) acquired from the 1st integrated case contains higher heat amounts in comparison to the 2nd case with a difference of 2.55 kWh. The syngas obtained from the 1st integrated case is higher by 0.76kg from the 2nd integrated case. This can be explained due to the excess amount of feedstock provided in the 1st integrated case as the air blown in the 1st gasifier integrated case is 0.39 kWh times higher as compared to the 2nd integrated case. It is important that the pressure and temperature always must be maintained and shouldn't exceed the set threshold as the reactor chamber can get unstable.

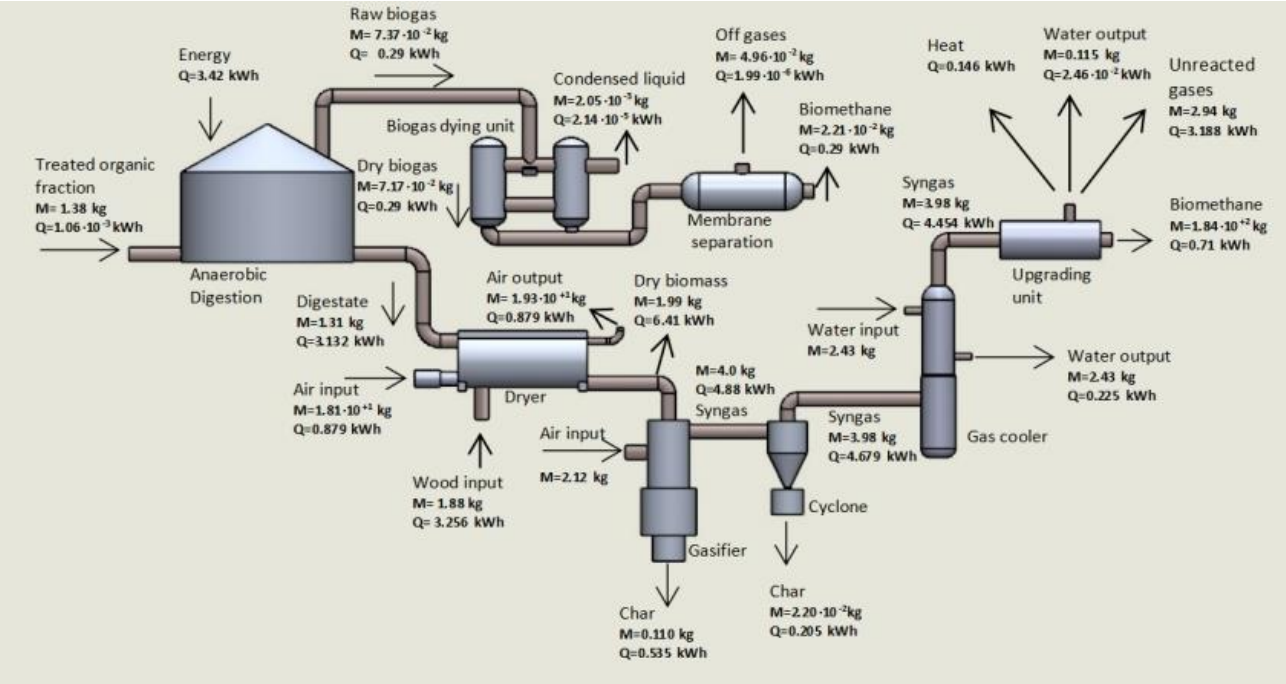

Figure 11. Mass and energy flow of 1kWh$_{\text{thermal}}$ production of biomethane with 1st integrated process

It is a well-known fact that the composition of syngas depends on the amount of oxygen in the air and the fuel composition. Biomass gasification can be affected by fuel properties such as fuel moisture, particle size, bulk density, heating value [73]. It is observed that in both cases, the gasifier produces higher amounts of char by-products in comparison to the cyclone. This is said to be as the increase in feedstock amount, the char production is higher due to the heat produced by the process of combustion. Huang et al. [74] suggested that the increase in equivalence ratio results in a higher temperature because more feedstock is being combusted to generate heat and to promote carbon conversion. The char generated from the gasifier in both cases have similar values in mass and energy. Whereas, in cyclone reactor, higher heat is produced in the 1stintegrated case in comparison to the 2nd integrated case with 0.13 kWh.

However, one of the major challenges in the gasification process is the contamination of the product syngas which causes major process and syngas end-user problems. Adding an air plasma unit, the concentration of the syngas changes, many hydrocarbons disappear, and this unit requires additional input of energy of 1.73 kW. Some part of electrical energy is converted to heat energy which is transferred to the syngas whereas the unconsumed amount is sent to the water-cooling part of the plasma reactor. The syngas sent to the air plasma unit in the 2nd integrated case has increased heat content due to the increased methane content. As it can be seen from **Figure 12** that the syngas exiting the plasma torch has an increased energy content of 4.55 kWh, this can be justified by the increase in sensible heat. The sensible heat is the amount of energy required to alternate the temperature with absolute to a minimum no changes in the substance. The sensible heat can be characterized by the increase in temperature from 600℃ to 1100℃. These results were also obtained by a few authors Materazzi et al. [51] Striugas et al. [61]. It should be noted the plasma field doesn't constraint the rate of reaction or its chemical mechanism. A study that analyzed the dual thermal stage for renewable methane production concerning waste treatment concluded that the dual thermal stage process is the best available technology to treat municipal solid waste as a result of the higher efficiency of methane production [75]. After the air plasma unit, the syngas is sent to the gas cooler vessel to cool down the temperature from 1100℃ to 300℃ to eliminate any leftover acid gas impurities and pollutants. The water that is released from the gas cooler contains a higher heat amount in the 2nd integrated case in comparison to the 1st integrated case with a difference of 0.37 kWh, this can be explained as the heat has emerged into the water. In the last step, i.e. methanation reactor, the biomethane produced via 2nd integrated case is 0.9 kWh and via AD is 0.1 kWh.

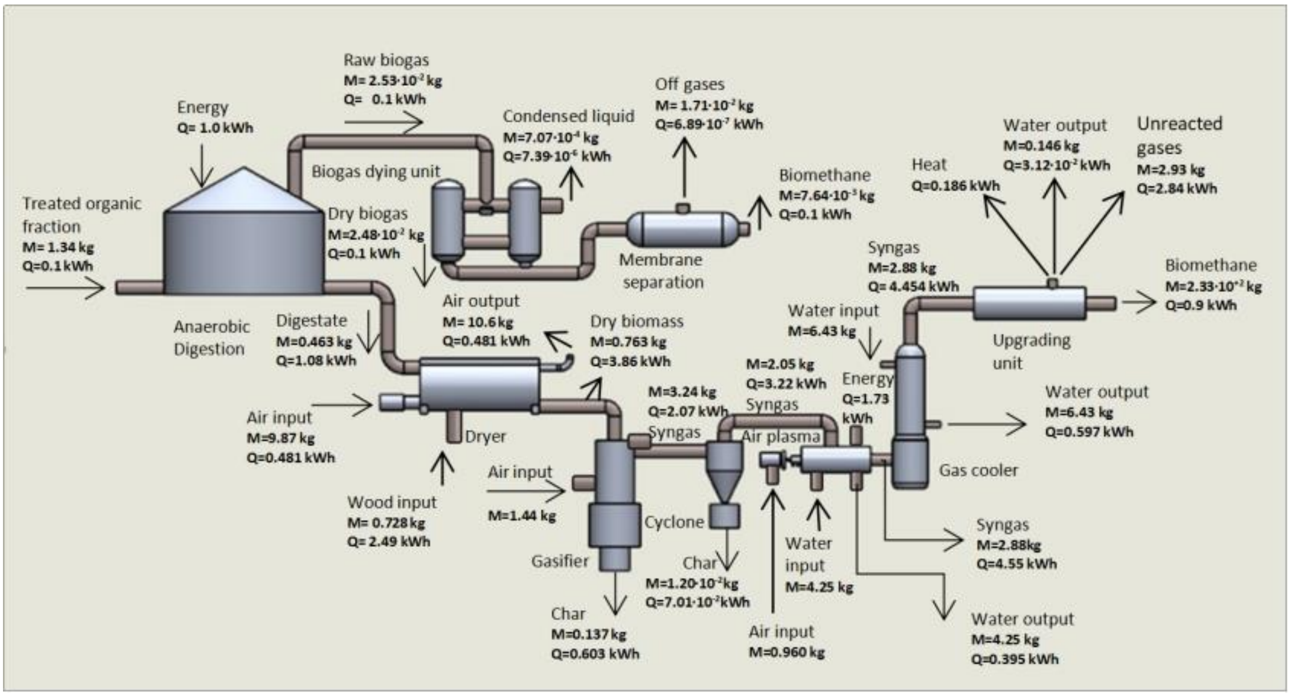

Figure 12. Mass and energy balances of 2nd integrated process with usage of anaerobic digestion, air plasma aided gasifier and methanation.

3.2. Calculated inventory data for Life Cycle Assessment

To determine the inventory data per the functional unit, the values are normalized by carrying out mass and energy balances.

Table 2. Computed inventory data for $1\text{kWh}_{\text{thermal}}$ biomethane production

Schemes	Mass (kg)	Energy (kWh)
Reference Scheme		
Inputs		
Treated Organic Fraction	$4.63\cdot10^{-3}$	$3.69\cdot10^{-3}$
Energy	0	1.00
Outputs		
Water	$7.07\cdot10^{-3}$	$7.39\cdot10^{-5}$
Off gases	$1.71.\ \cdot10^{-1}$	$6.89\cdot10^{-6}$
Sewage sludge	4.63	$3.69\cdot10^{-3}$
Biomethane	$7.64\cdot10^{-2}$	1.00
1st Integrated Scheme		
Inputs		
Treated organic fraction	1.34	$1.07\cdot10^{-3}$
Air	$2.00\cdot10^{+1}$	$8.80\cdot10^{-1}$
Water	3.10	0
Energy	0	3.42
Wood	1.33	3.26
Outputs		
Heat	0	$1.46\cdot10^{-1}$
Air	$1.93\cdot10^{+1}$	$8.80\cdot10^{-1}$
Water	2.54	$2.50\cdot10^{-1}$
Char	$1.62\cdot10^{-1}$	$7.41\cdot10^{-1}$
Non-reacted gases	2.99	3.19
Biomethane	$1.84\cdot10^{+2}$	1.00
2nd Integrated Scheme		
Inputs		
Treated organic fraction	$4.88\cdot10^{-1}$	$1.00\cdot10^{-1}$
Air	$1.23\cdot10^{+1}$	$4.81\cdot10^{-1}$
Water	$1.07\cdot10^{+1}$	0
Energy	0	2.81
Wood	1.02	2.49
Outputs		
Heat	0	$1.86\cdot10^{-1}$
Air	$1.06\cdot10^{+1}$	$4.81\cdot10^{-1}$
Water	$1.08\cdot10^{+1}$	1.02
Char	$1.49\cdot10^{-1}$	$6.73\cdot10^{-1}$
Non-reacted gases	2.95	2.84
Biomethane	$2.33\cdot10^{+2}$	1.00

3.3. Environmental analysis of proposed thermal methods

The major goal of the LCA analysis can be divided into two parts: firstly, to compare the three processes (reference scenario, 1st integrated process and 2nd integrated process) for the impact on the environment, resource consumption, and secondly, to identify the better-integrated process in terms of energy efficiency, carbon neutrality, and pollutants emitted to nature during this process.

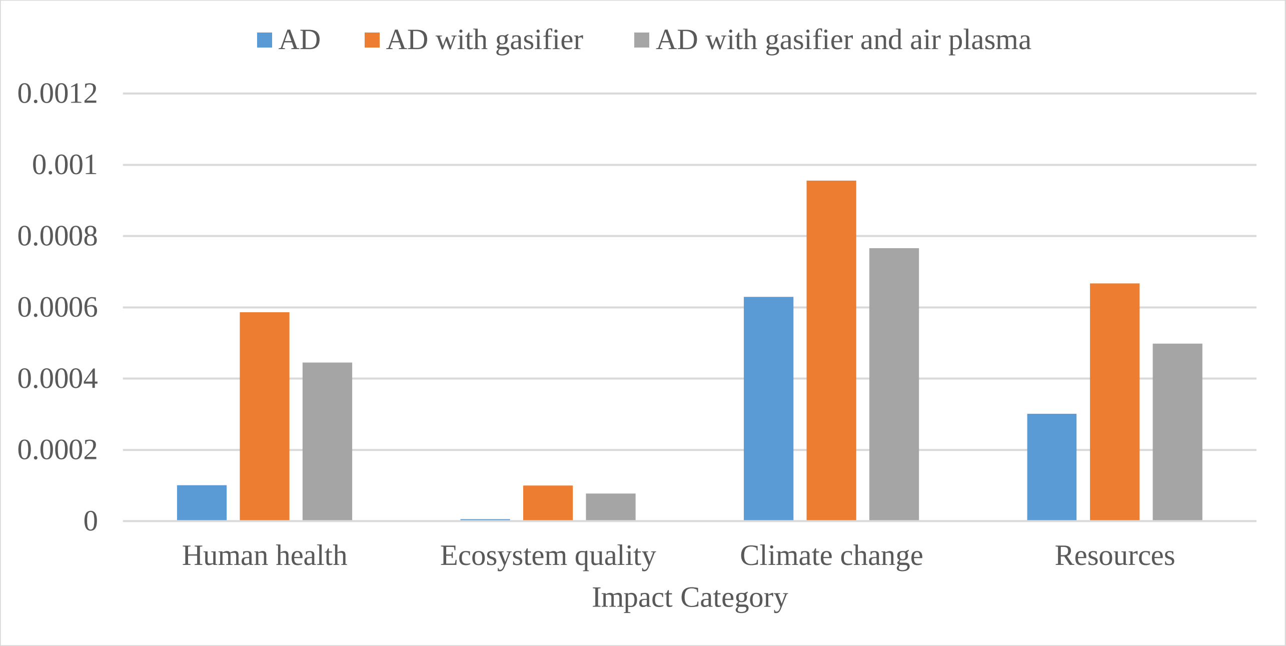

Figure 13. Interpretation of normalized data concerning damage category for three schemes to produce biomethane.

It should be noted that the 1st and 2nd integrated route depicts the biomethane production by treating the biowaste such as sewage sludge and thus shows the lower impact in comparison to the reference scenario due to their higher process efficiencies [40]. Following the above statement, impact categories such as human health, ecosystem quality, climate change, and resources were analyzed and are presented in **Figure 13**. The human health category illustrates the major pollutants emitted such as CO_2, CH_4, O_2, N_2 and H_2O and in comparison, with the reference scenario, 1st integrated process and 2nd integrated process are 5.81 and 4.41 times higher respectively (**Figure 13**). LCA study performed by Carnevale et al. [76] also concluded similar results that biomethane production via reference scenario shows a positive impact in terms of the greenhouse effect, ozone layer depletion but it caused higher methane losses and energy consumption. The ecosystem quality for the 1st integrated process and 2nd integrated process are 18 and 14 times higher than the reference scenario. It should be noted that only the major steps were considered for the reference process such as anaerobic digestion reactor, biogas drying and membrane separation which may be the reason for such differences. In a study conducted by Evangelisti et al. [50], it was found that the AD reactor is the most favorable route in terms of global warming potential (GWP) and acidification. In this study, we can see that the reference scenario of producing biomethane has also caused lower environmental impacts in terms of harmfulness and has a commercial TRL- technology readiness level [77]. It is seen that 1st integrated process is 1.5 higher whereas 2nd integrated process is 1.21 times higher than the reference scenario. Resource's category shows that 1st integrated process and 2nd integrated process require 2 and 1.5 times more than the reference scenario, this may be due to the additional requirements of resources such as water, wood, air and electricity at different amounts. The characterization impact results mainly in respect to global warming potential for 1st integrated process shows that it is 1.51 kg CO_2 eq higher than reference scenario whereas the 2nd integrated process is 1.21 kg CO_2 eq higher.

The LCA analysis by Ardolino et al. [40] shows that biomethane production via the only AD has an environmental behavior slightly worse than their presented worse case with the avoided impacts reduced by 2.41% for GWP. This means that the higher avoided impacts related to a larger biomethane production are partially balanced by direct and indirect impacts related to the internal energy consumption satisfied by external energy sources. Florio et al. [78] concluded that the electrical supply for AD and the wastewater treatment plant gives the main contributions with 50% or more while the biogas upgrading contributes with percentages higher than 20%, again due to its electricity consumption. Therefore, after the above-stated discussions, it is seen that the reference scenario can be implemented in a much better way integrating more technological routes in addition to eliminating the usage of raw materials and higher quantity and quality production of biomethane.

Further LCA was performed to compare two integrated processes mentioned in Section 2.1.2 and 2.1.3, concerning improving carbon neutrality. Therefore, with the addition of gasification and air plasma, we can see a better production of biomethane production. The impact categories such as human health, ecosystem quality, climate change, and resource consumption do not differ highly between these two processes, the 1st integrated process is higher by 1.3,1.3,1.25 and 1.34 times respectively as seen in **Figure 14**.

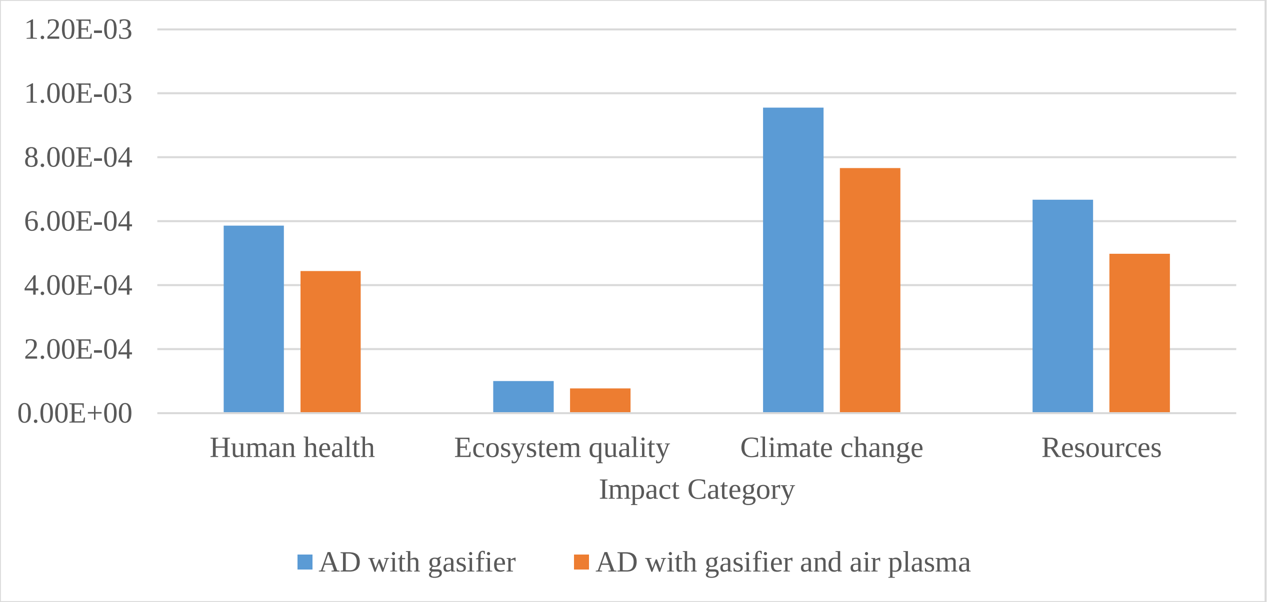

Figure 14. Comparative LCA analysis of two proposed integrated thermal processes to produce biomethane.

Biomass gasification is said to produce biomethane at a larger scale whereas AD requires a large amount of low-temperature heat which lowers its energy conversion efficiency. The process of adding sludge into the gasifier is an example of energy recovery from the AD that can prevent CO_2 emissions annually [79]. When the reference scenario is compared to 1st integrated process, the latter is found to have higher levels of carbon utilization and better environmental performance [40]. A study showed that although the energy produced from the digestion process is lesser than other processes such as gasification or pyrolysis or combustion, its pure net production is significantly higher due to the low energy consumption [40]. The 2nd integrated process is a two-stage thermal treatment system. The syngas produced from the gasifier along with other by-products such as ash, tars and liquid hydrocarbons is then treated in a high temperature 1100℃ air plasma converter. The plasma converter reforms a high-quality synthetic gas. The major contribution to CO_2 is the upgrading unit methanation [50].

3.4. Data interpretation of experiments with methanation

In this section, various factors were analyzed for the renewable production of methane such as performance of the Ni-based catalyst with Mg metal with Al_2O_3 support, temperature dependence on the H_2:CO_2 ratio, gas composition based on the H_2:CO_2 ratio and CO_2 conversion.

3.4.1. Catalyst material

The catalyst Mg_2Ni with Al_2O_3 support was utilized as it was found from studies performed by Karim et. al [80] as it was proved to be easily assessable and cheaper. A fixed reactor was used to maintain catalyst stability and also legitimate contact for the methanation mechanism to happen [29]. One of the important factors is the formation of catalyst poisoning with various chemical compounds [55]. The effectivity or efficiency of the used catalyst depends on CO_2 conversion. Nickel is one of the most selected catalysts as it comes with fewer expenses with high activity and it is widely used commercially for methanation projects industrially [81]. Rahmani et al. [82] performed some experiments with 20 wt% Ni/Al_2O_3 nanocatalyst and showed that it has higher activity and good stability for the methanation of CO_2. Therefore, the experiments performed in this thesis paper are Ni-based catalysts with non-hydrated intermetallic Mg metal [83] with Al_2O_3 support.

3.4.2. Temperature dependence vs H_2:CO_2 ratio

The temperature range is proved to be around 250°C - 400°C [55]. Chein et al. [84] concluded in their recent experimental study of CO_2 methanation that the ideal temperature is said to be within 400°C for achieving the highest CO_2 conversion and CH_4 yield at molar ratio H_2:CO_2 of 5. Since CO_2 methanation is exothermic in nature, Chein et al. [84] observed that a lesser temperature is desired for obtaining better CH_4 selectivity. The experiments conducted by Rahmani et al. [82] also concluded that with elevating temperature from 200°C - 350°C and increasing H_2:CO_2 molar ratio, the catalytic functioning improves. Therefore, it is seen that the temperature obtained from the temperature probes (T1-T6) from Table 3 with H_2:CO_2 molar ratio of 1:3.8, 1:4, 1:4.2, 1:4.5, 1:4.7 and 1:5; all range between 250°C - 500°C. T1 probe is on top of the methanation reactor where the gas enters from the heater, T2 and T3 probes are at the top part of the methanation reactor containing only the support material. T4 probe is where the catalyst and support material are situated. T5 and T6 probes are situated outside the methanation reactor thus, a decrease in temperature is noticed. At all measured mass flow (0.65 l/min, 0.9 l/min, 1.5 l/min, 2.0 l/min, 4.0 l/min and 5.5 l/min), same correlation is shown. Such that the temperature is highest at the T1 probe and the T6 probe has the lowest temperature. From these experiments, it can be said that to achieve a higher CO_2 conversion percentage, the T4 probe should be ranging between 300°C - 380°C. The overall temperature should be ranging from 200°C - 500°C (T1 to T6), as per the results presented in Table 3 and Figures 15, 16, 17, 18, 19 and 20, which is similar to the results obtained by the other researchers as mentioned above.

Table 3. Temperature differences in the methanation reactor at various molar ratios and mass flows.

Nr.	Mass Flow, l/min	CO_2: H_2	H_2: CO_2	H_2, l/min	CO_2, l/min	Catalyst reactor temperature (°C)					
						T1	T2	T3	T4	T5	T6
1	0.65	01:04.2	4.39	0.525	0.129	313.35	327.23	328.7	312.17	298.29	216.59

Nr.	Mass Flow, l/min	CO_2: H_2	H_2: CO_2	H_2, l/min	CO_2, l/min	Catalyst reactor temperature (°C)					
2	0.65	1:04	4.31	0.52	0.13	314.93	325.31	331.02	312.64	297.79	216.09
3	0.65	1:04	4.31	0.52	0.13	326.57	343.98	349.71	332.37	316.27	225.22
4	0.9	1:4,2	4.5	0.727	0.173	316.74	323.89	331.31	308.26	295.45	219.31
5	1.5	01:04.7	4.7	1.237	0.263	339.71	347.25	351.06	322.76	313.1	236.09
6	1.5	01:04.5	4.5	1.227	0.273	342.4	348.27	353.08	322.79	313.32	237.36
7	1.5	01:04.2	4.2	1.212	0.289	343.82	350.7	358.8	323.84	313.43	242.57
8	1.5	1:04	4	1.2	0.3	345.02	351.44	360.92	324.29	313.48	244.09
9	2	01:04.2	4.2	1.615	0.385	360.28	357.44	369.93	324.76	315.62	252.52
10	2	1:04	4	1.6	0.4	348.4	352.01	377.42	326.83	316.99	256.92
11	4	1:4,2	4.2	3.231	0.769	367.31	365.88	435.06	333.46	322.56	283.42
12	4	01:04.2	4.2	3.231	0.769	354.87	393.51	436.13	368.81	355.85	316.11
13	3	01:04.2	4.2	2.423	0.577	354.96	391.72	406.84	363.45	353.22	301.19
14	1.75	01:04.2	4.2	1.412	0.337	346.92	383.91	382.24	358.8	348.74	270.57
15	0.867	01:04.2	4.2	0.7	0.167	299.53	325.76	338.68	318.64	306.53	225.5

It should be noted that the remaining experiments are presented in the Appendix 2.

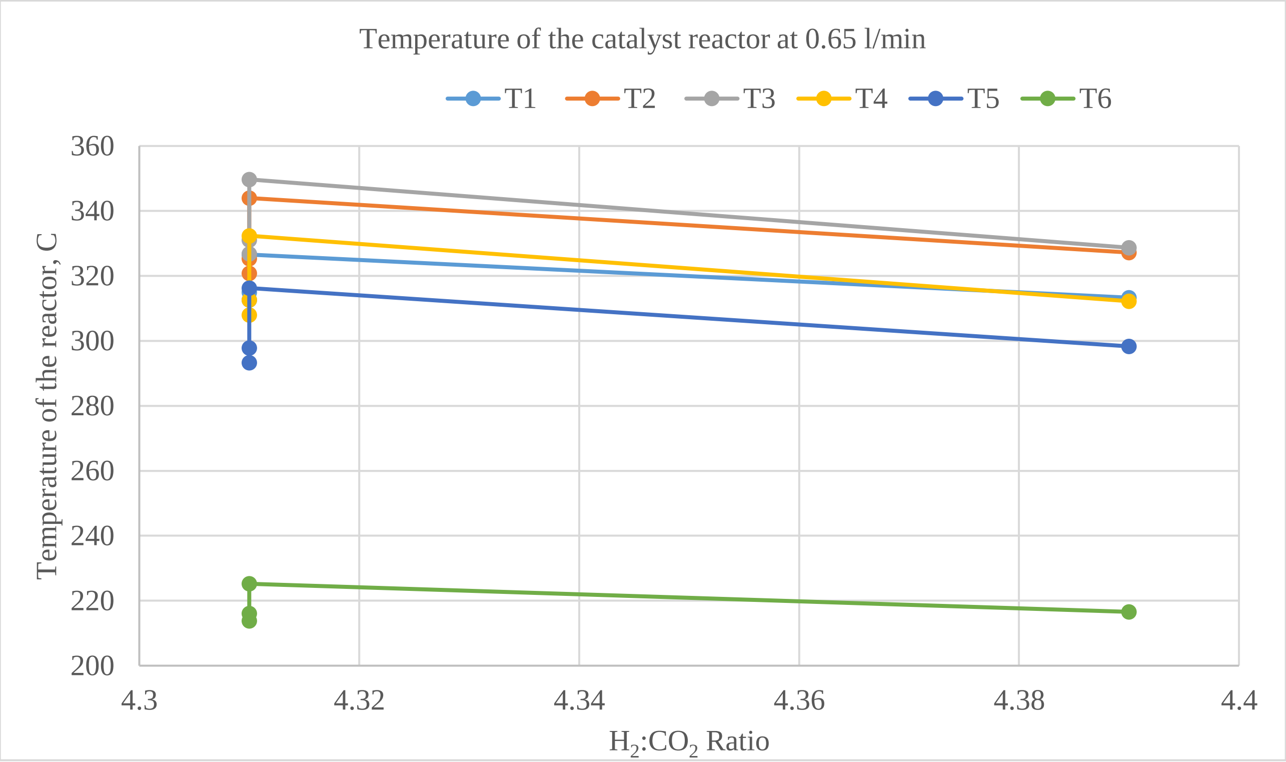

Figure 15. An illustrative graph of the temperature variation based on the molar ratio of H_2:CO_2 at mass flow 0.65 l/min

Experiments number 1-4 (see Table 3) were conducted with 0.65 l/min, the H_2:CO_2 molar ratios were set to be 1:4 for three experiments and 1:4.2 for the last. With all molar ratios, similar results are found concerning the temperature probes as shown in **Figure 15**. T1, T2, T3, T4, T5 and T6 ranging between 312°C - 327°C, 320°C - 343°C, 326°C - 349°C, 307°C - 332°C, 293°C - 316°C and 213°C to 225°C respectively.

The temperature probes have been analyzed concerning the H_2:CO_2 molar ratio at 0.9 l/min in **Figure 16**. Three experiments numbering 5-7 have been done with 0.9 l/min with a ratio of 1:4.2 for all. The temperature probes T1, T2, T3, T4, T5 and T6 varies between 316°C - 328°C, 323°C - 343°C, 331°C - 350°C, 308°C - 327°C, 295°C - 314°C and 219°C - 230°C respectively.

Experiments numbers 8-15 and 27 were done in accordance to 1.5 l/min with molar ratios 1:4, 1:4.2, 1:4.5, 1:4.7 and 1:5 for the experiments (some ratios were used repeatedly to confirm the data). As seen in **Figure 17**, T1 is around 336°C - 349°C, T2 ranges 345°C - 351°C, T3 varies around 351°C - 374°C, T4 circles around 322°C - 330°C, T5 results from 313°C - 318°C and T6 shows 236°C - 250°C respectively.

Temperature dependence on mass flow 2.0 l/min has been shown in **Figure 18**. The experiments number were performed with H_2:CO_2 molar ratios of 1:4.0, 1:4.2, 1:4.5, 1:4.7, 1:5. Temperature T1 ranges around 340°C - 360°C, T2 is said to be around 352°C - 357°C, T3 ranges between 357°C - 377°C, T4 results 323°C - 326°C, T5 observes 315°C to 316°C and T6 is around 246°C - 256°C.

The experiments shown in **Figure 19** show the temperature in correlation to the H_2:CO_2 molar ratio at 4.0 l/min. T1, T2, T3, T4, T5 and T6 temperature probes in the methanation reactor varies between 345°C - 367°C, 351°C - 367°C, 423°C - 455°C, 324°C - 347°C, 313°C - 336°C, 290°C - 296°C respectively. It can be seen that at 4.0 l/min, the temperature is higher for all temperature probes in comparison to the mass flows such as 0.65 l/min, 0.9 l/min and 1.5 l/min.

The experiment conducted with a mass flow of 5.5 l/min is presented in **Figure 20**. The temperatures are seen to exceed up to 500°C for the T3 probe and T6 probe tested 309°C, which is the highest of all T6 probes of other mass flows. Therefore, no further experiments were done with this mass flow.

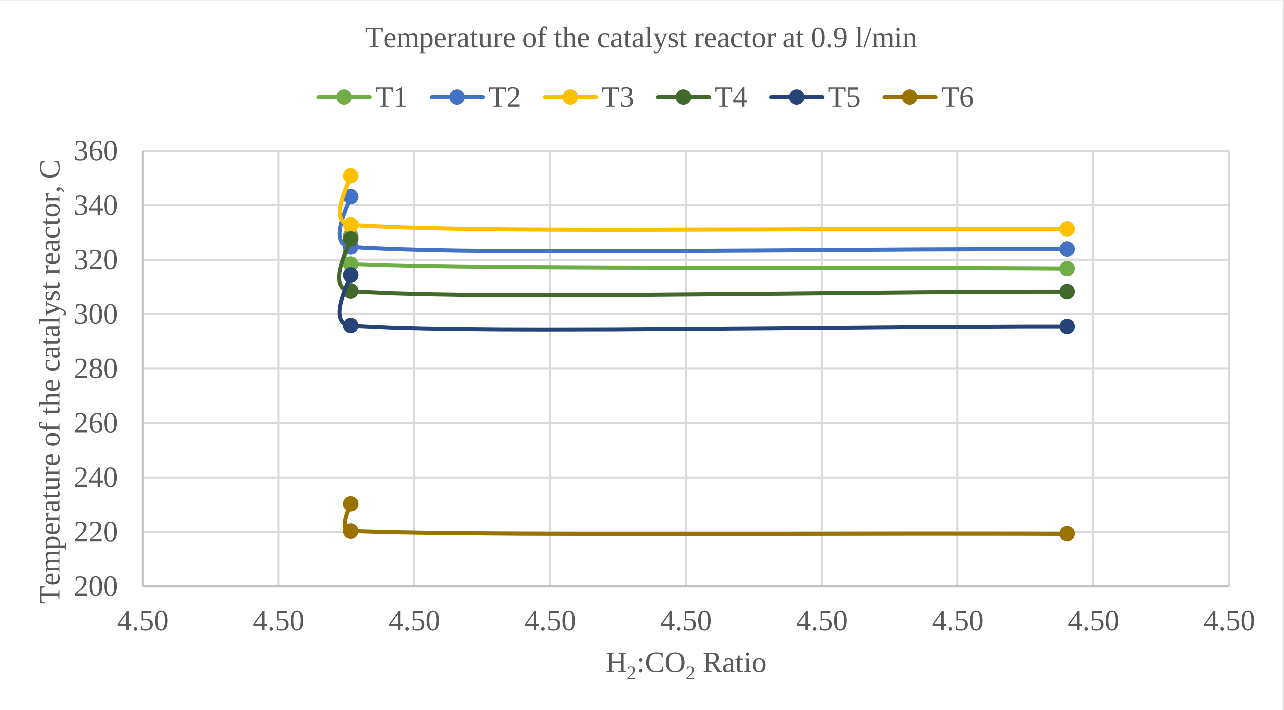

Figure 16. Effect of the ratio of H_2:CO_2 at 0.9 l/min on the temperature probes of the methanation reactor.

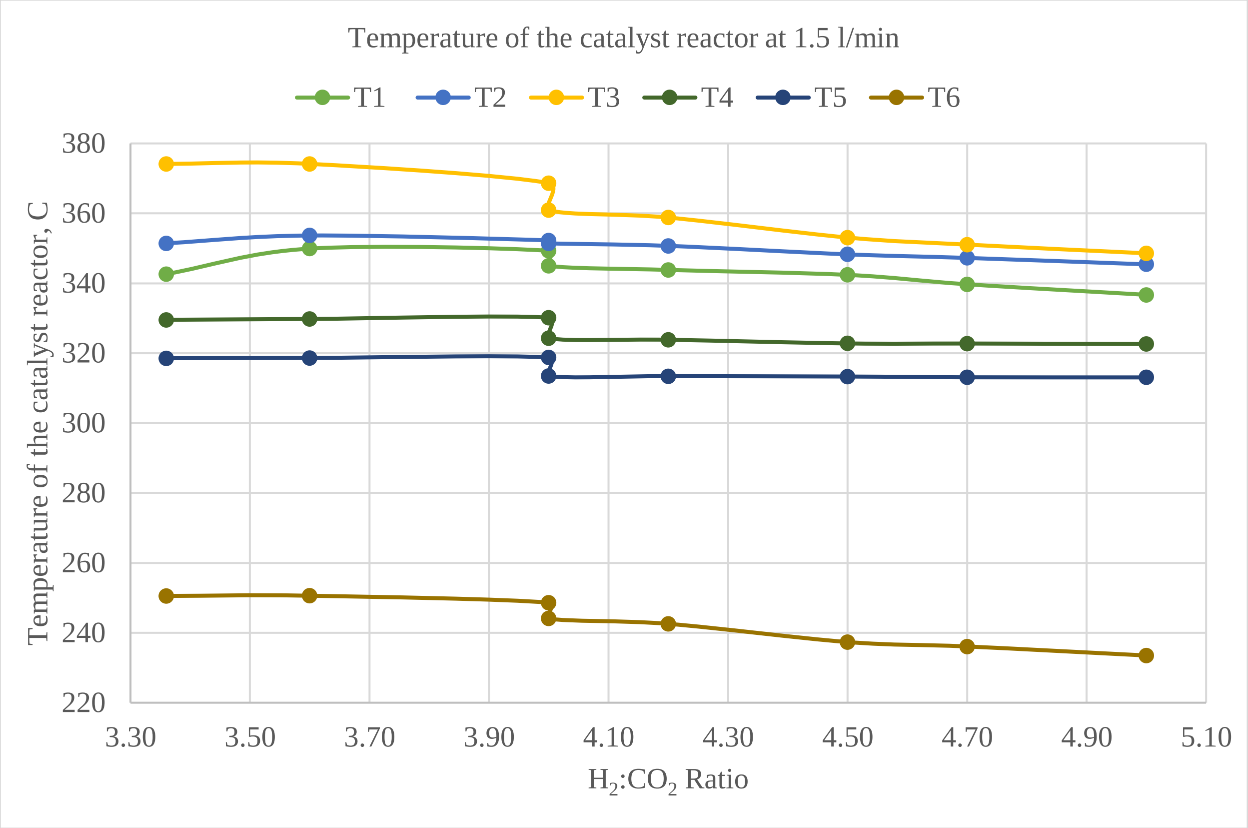

Figure 17. A demonstration of the temperature variation based on the ratio of H_2:CO_2 at 1.5 l/min

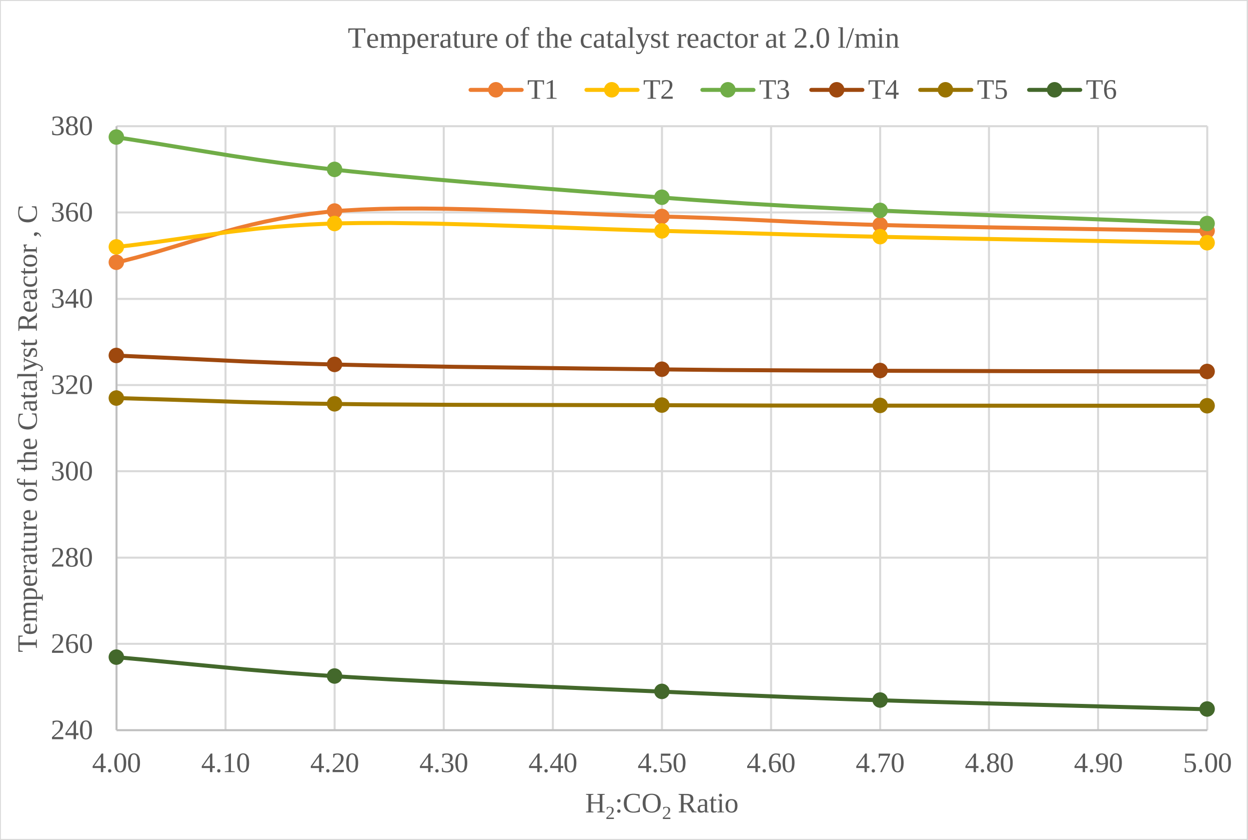

Figure 18. A representative graph of the temperature variation based on the ratio of H_2:CO_2 at 2.0 l/min

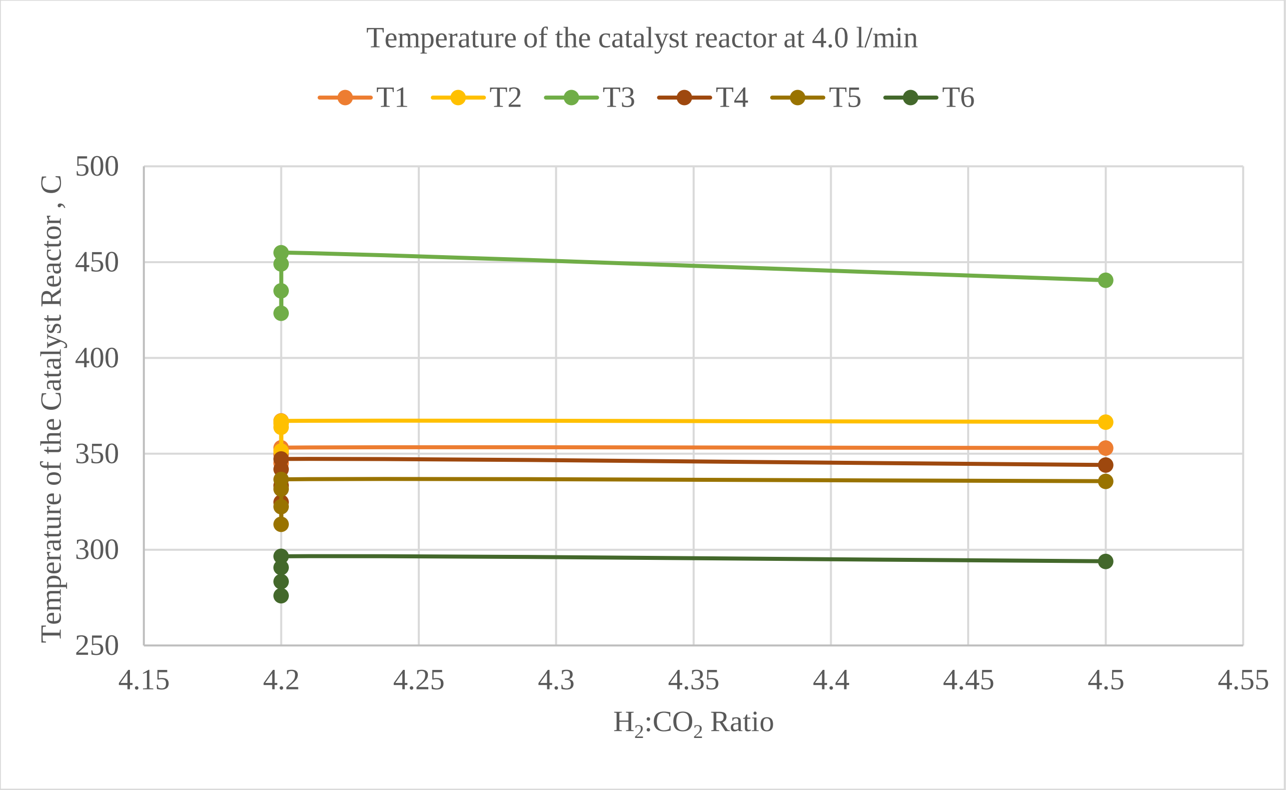

Figure 19. A representation graph of the temperature variation based on the ratio of H_2:CO_2 at 4.0 l/min

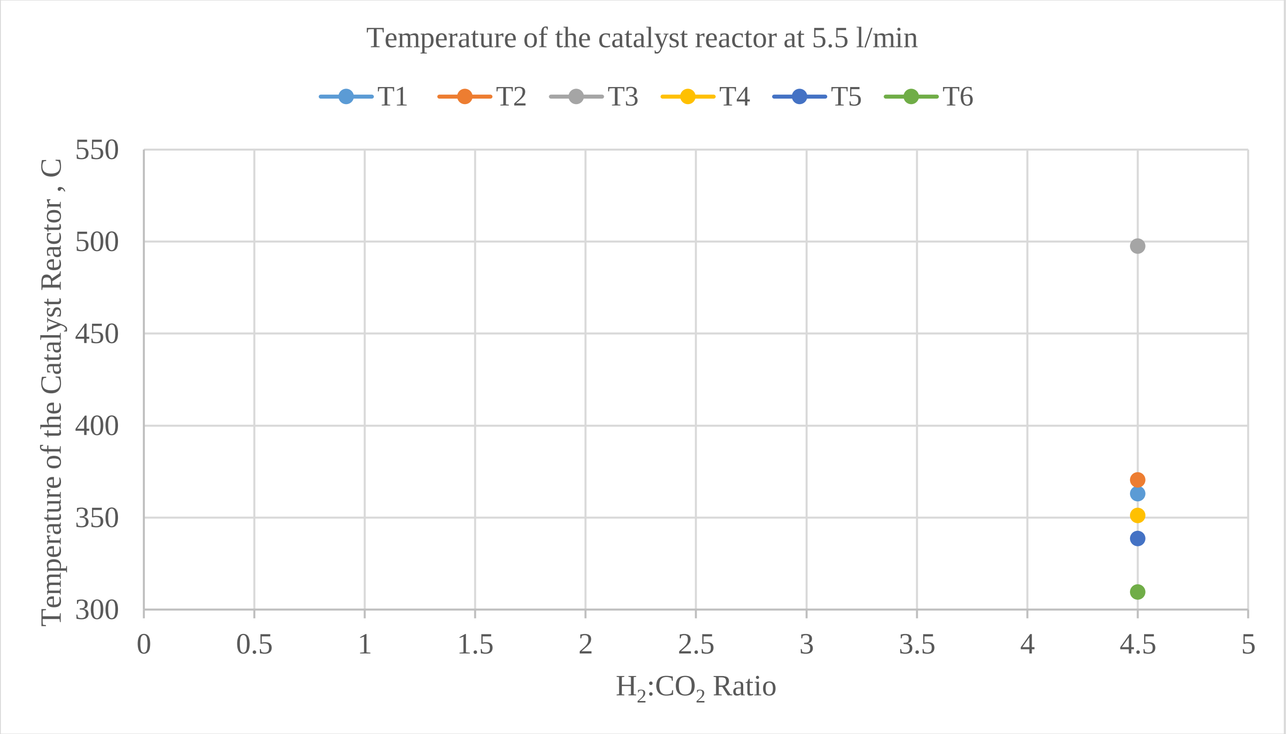

Figure 20. The maximum ratio of H_2:CO_2 (5.5 l/min) analyzed for the temperature of the catalyst reactor

3.4.3. Gas composition vs H_2:CO_2 ratio

This section describes the gas compositions formed after the experiments which were further analyzed by the gas analyzer. The results are presented in Table 4, Table 6 (see in Appendices) and **Figures**

21, 22, 23, 24, 25, 26 and 27. It is observed that when the molar ratio increased from 4.0 to 5.0, the gas composition of CH_4 decreases, therefore, it is concluded that the best molar ratio for H_2:CO_2 would be centered around 4. Since there was no formation of CO, it can be said that the catalyst functioned well for CO_2 methanation at various molar ratios and mass flows.

Figure 21 represents the obtained gas composition after the experiments at 0.65 l/min mass flow with molar ratios H_2:CO_2 of 1:4 and 1:4.2 mostly. There was no formation of CO, 54% - 63% was the composition of CH_4, H_2 between 12% to 23%, O_2 was formed in very low amounts ranging between 3.6% to 4%, CO_2 was formed next to negligible 0% - 0.17% which is one of the main criteria seen is the experiment see Table 4.

Figure 22 shows the achieved gas composition at 0.9 l/min alongside molar ratios H_2:CO_2 of 1:4.2. The gas composition shows good results as there was no CO formed, O_2 was formed around 2% to 2.2%, CH_4 ranged between 61% - 63%, hydrogen ranging between 20% - 21%, CO_2 reached around 0.01% - 0.11%.

Figure 23 also depicts the gas compositions achieved from the gas analyzer with molar ratios H_2:CO_2 of 1:4, 1:4.2, 1:4.5, 1:4.7 and 1:5. The gas compositions of CO, CH_4, CO_2, H_2 are as follows: 0%, 38% to 74%, 0% to 11%, 5% to 46% respectively. Two experiments formed higher CO_2 percentages ranging 8% and 11% at molar ratio 1:4.2, therefore more experiments were performed with the same molar ratio to check if it is a continuous pattern, but it didn't follow the same pattern. Therefore, it may be some sought of experimental error.

Figure 24 portrays the compositions of gases formed after CO_2 methanation at 2.0 l/min mass flow. The molar ratios analyzed were: 1:4, 1:4.2, 1:4.5, 1:4.7 and 1:5. The gas compositions for H_2, CH_4, CO_2, CO are 17% to 49%, 37% to 71%, 0% to 1% and 0% respectively.

Figure 25 illustrates the compositions of gas output analyzed in the gas analyzer at mass flow 4.0 l/min. Most experiments were performed at 1:4.2 and 1:4.5 molar ratios of H_2:CO_2. The gas composition of H_2, CO_2, CO, CH_4 are as follows: 2.3% to 3%, 0.7% to 1.3%, 0%, 12% to 71% respectively.The gas composition of 12% for CH_4 was considered very low, therefore many other experiments were performed with the same molar mass and mass flow, thus the remaining experiments ranged between 50-71% of CH_4.

Figure 26 displays the gas composition for molar mass of H_2 and CO_2 at 1:4.5 at 5.5 l/min. The formation of CO was 0%, CO_2 was 0.2%, CH_4 was 50% but further experiments were not conducted as section 3.4.2 describes the exceeding temperature which was not advantageous for CO_2 methanation.

Figure 27 illustrates a graph with all experiments which shows the gas compositions of CH_4, CO_2, CO, H_2 which are recalculated by removing the air. Table 6 shows the gas compositions of all experiments without air. As it can be seen from **Figure 27**, 50% - 70% CH_4 was formed, CO formation was none, CO_2 was next to negligible and hydrogen was 20% - 65%.

Table 4. The resulting gas compositions of the sabateri reaction with certain molar ratios and mass flows.

Nr.	Mass Flow, l/min	CO_2: H_2	H_2: CO_2	H_2, l/min	CO_2, l/min	Gas composition, %					
						CO	O_2	N_2	CH_4	CO_2	H_2
1	0.65	1:4.2,0	4.39	0.525	0.129	0	3.6	13.54	54.46	0	23.12
2	0.65	1:4,0	4.31	0.52	0.13	0	4.1	15.42	61.91	0.11	12.51
3	0.952	1:4,2	4.5	0.769	0.183	0	2	7.52	62.7	0.01	20.82
4	1.5	1:4,2	3.36	1.212	0.288	0	1.1	4.14	74	11.21	5.56
5	2	1:4.2,0	4.2	1.615	0.385	0	1.1	4.14	60.31	0.11	27.77
16	3	1:4.2,0	4.2	2.423	0.577	0	2.3	8.65	60.52	0.73	27.1
18	0.867	1:4.2,0	4.2	0.7	0.167	0	1.4	5.27	66.03	0.1	27.29
8	4	1:4,2	4.2	3.231	0.769	0	0.8	3.01	58.04	1.77	31.26
9	4	1:4,5	4.5	3.273	0.727	0	0.9	3.39	12.74	47.91	180.25
10	5.5	1:4,5	4.5	4.5	1	0	1	3.76	50.91	0.28	38.4
11	1.5	1:5,0	5	1.25	1.667	0	0.9	3.39	46.67	0.02	41.81
12	2	1:5,0	5	1.636	0.364	0	1	3.76	41.86	0.05	46.2
13	2	1:4.5,0	4.5	1.636	0.364	0	1.4	5.27	52.78	0.43	35.69
14	2	1:4.5,0	4.5	1.636	0.364	0	1.5	5.64	52.8	0.11	35.74
15	4	1:4.2,0	4.2	3.231	0.769	0	2.3	8.65	60.53	1.34	26.64

It should be known that the remaining experiments are presented in the Appendix 1 (gas compositions calculated without oxygen) and 3 (gas compositons with oxygen).

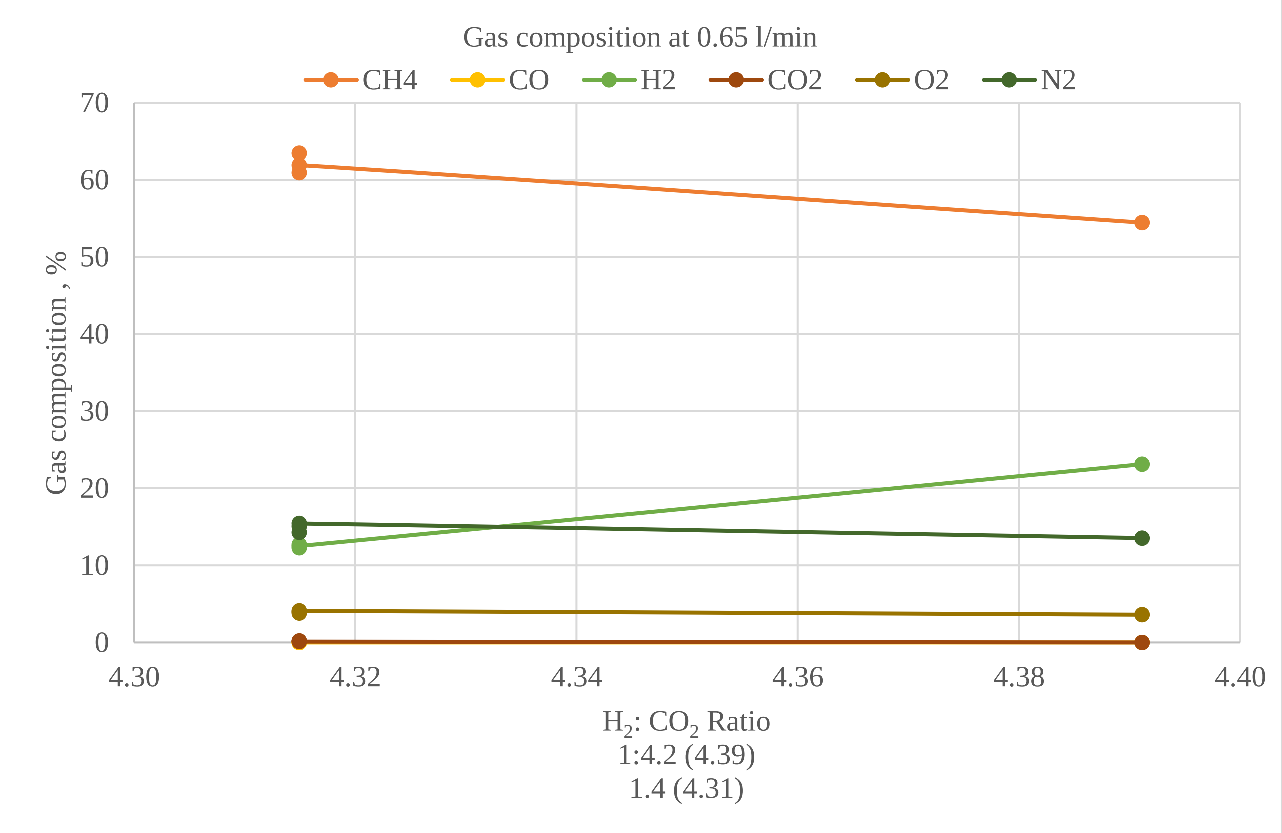

Figure 21. Effect of gas composition at 0.65 l/min on the conducted experiments at molar ratios of H_2:CO_2

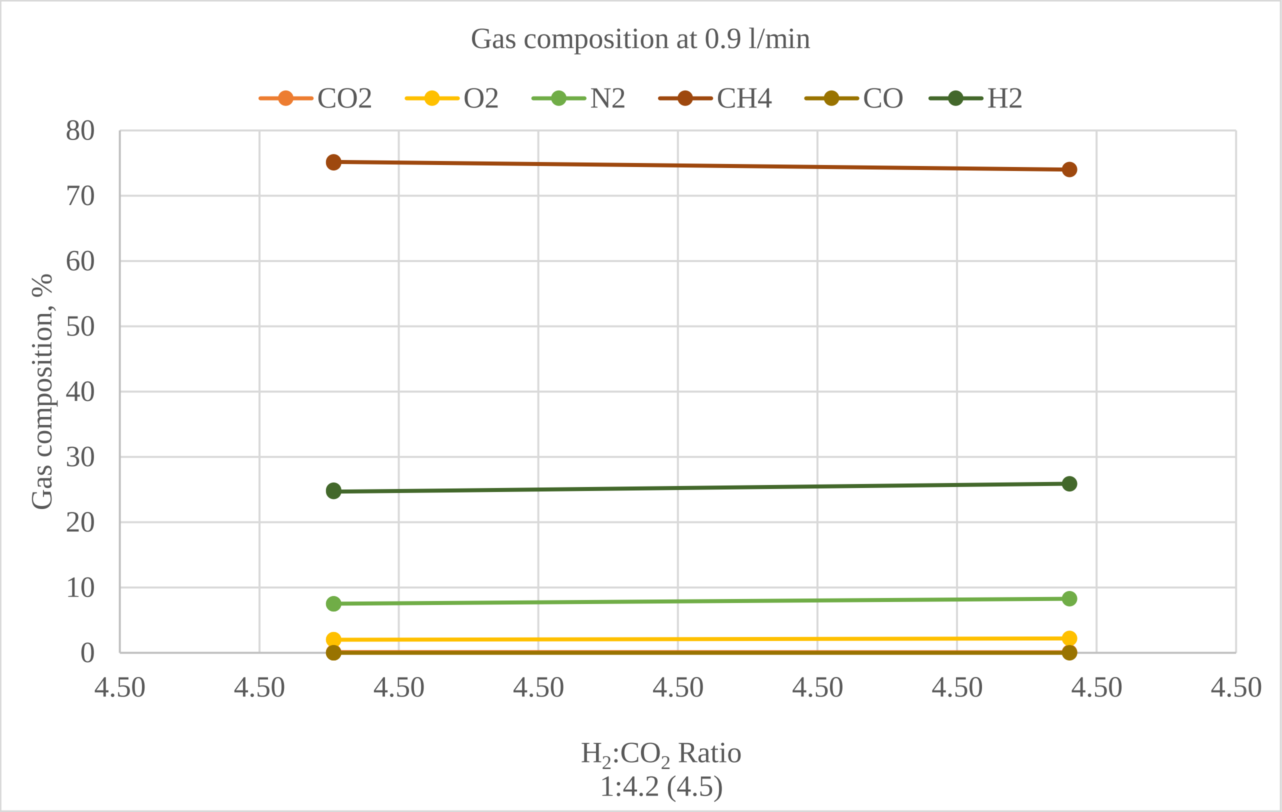

Figure 22. Resulting gas composition at 0.9 l/min at various molar ratio of H_2:CO_2

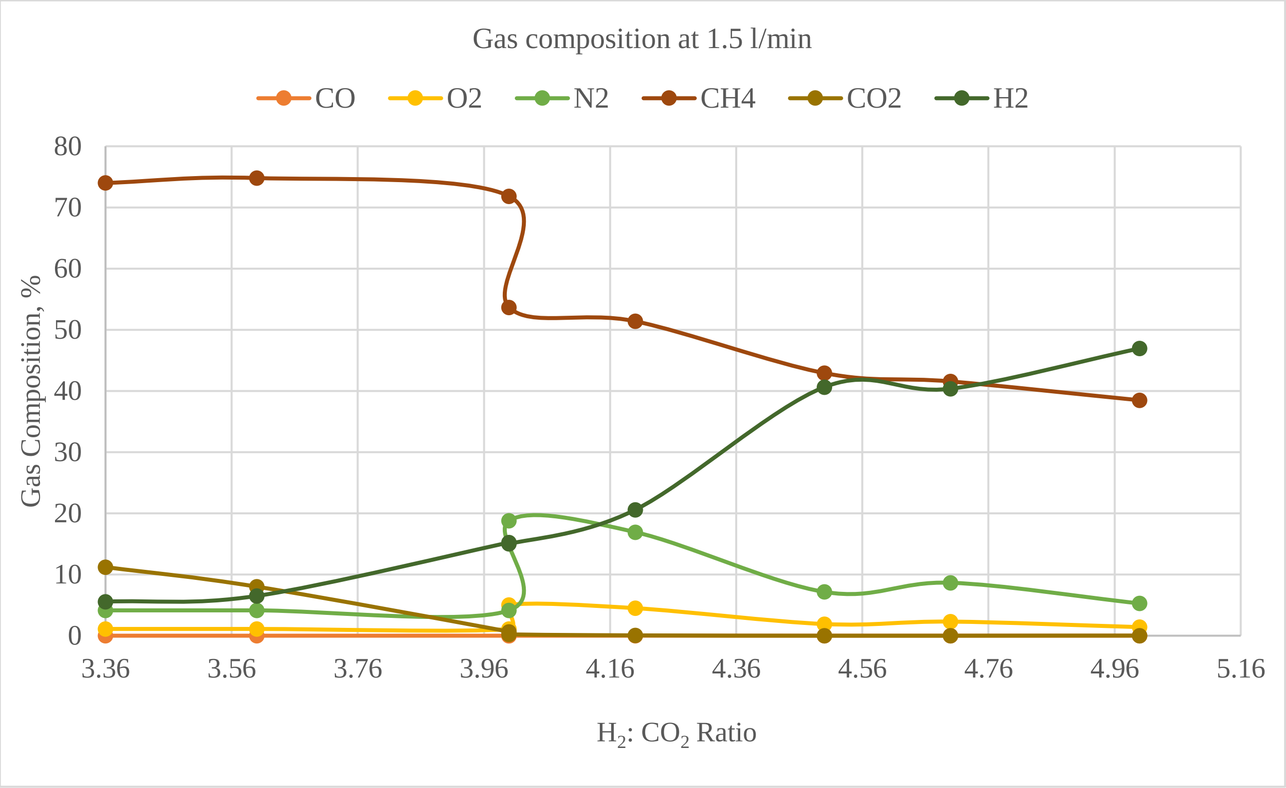

Figure 23. Performance of gas composition at 1.5 l/min at increasing molar ratio of H_2:CO_2

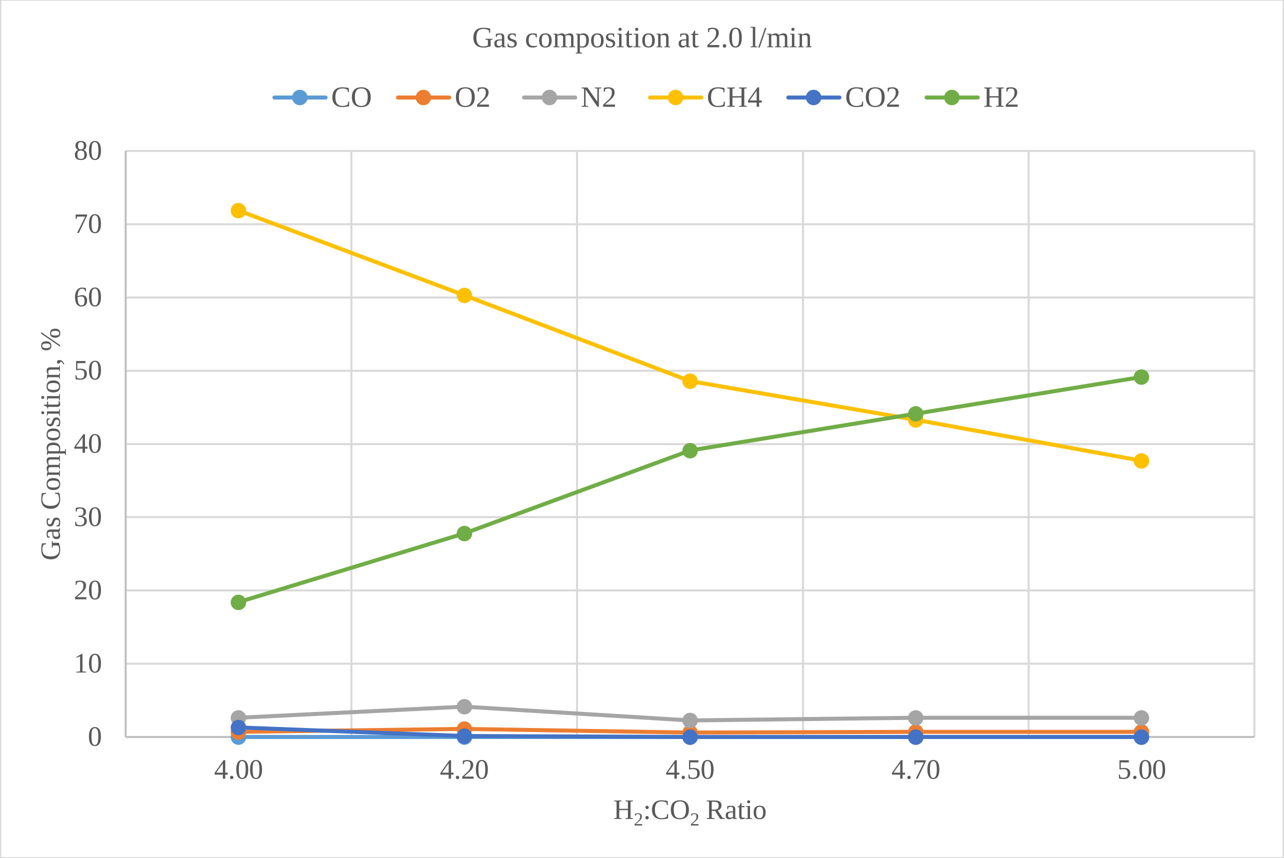

Figure 25. Gas composition at 2.0 l/min at different molar ratio of H_2:CO_2

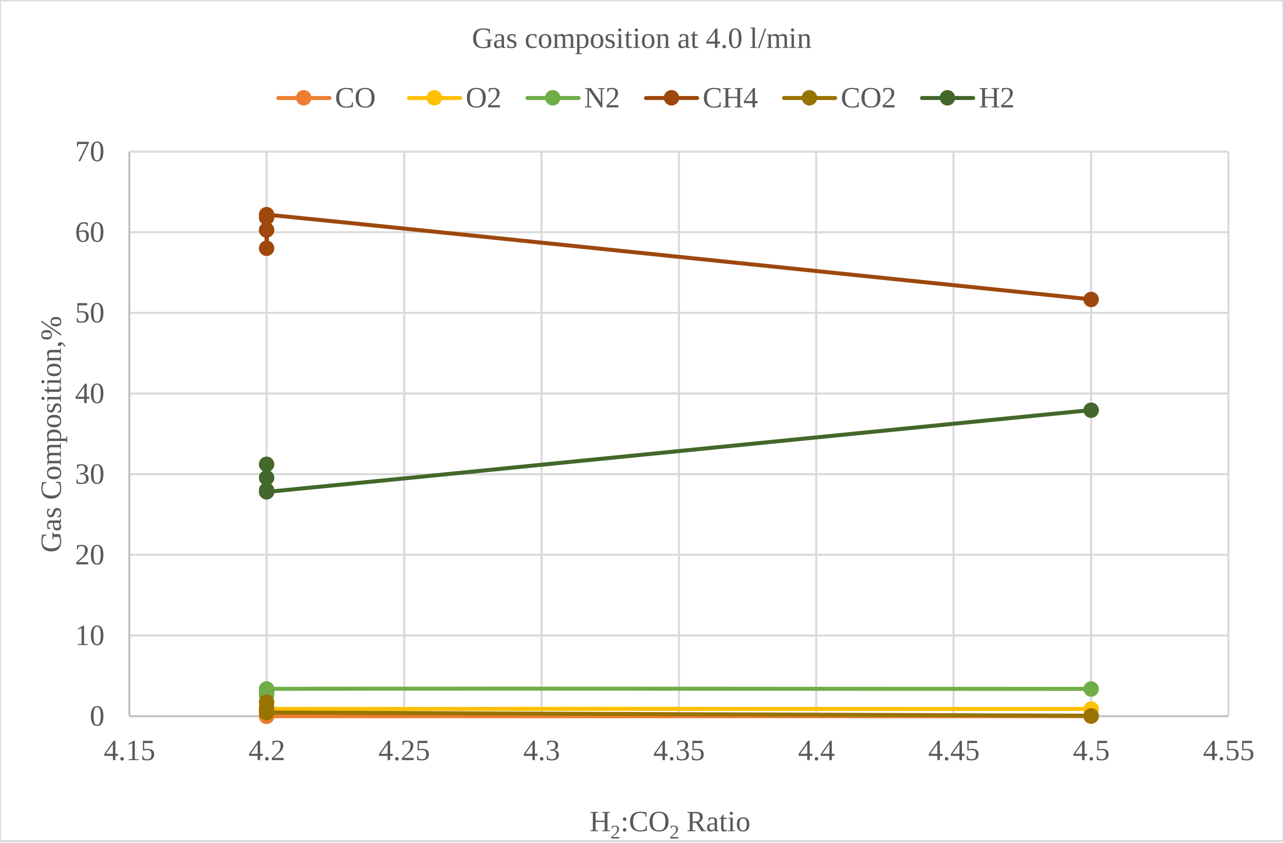

Figure 24. Effect of gas composition at 4.0 l/min on the performed experiments at molar ratios of H_2:CO_2

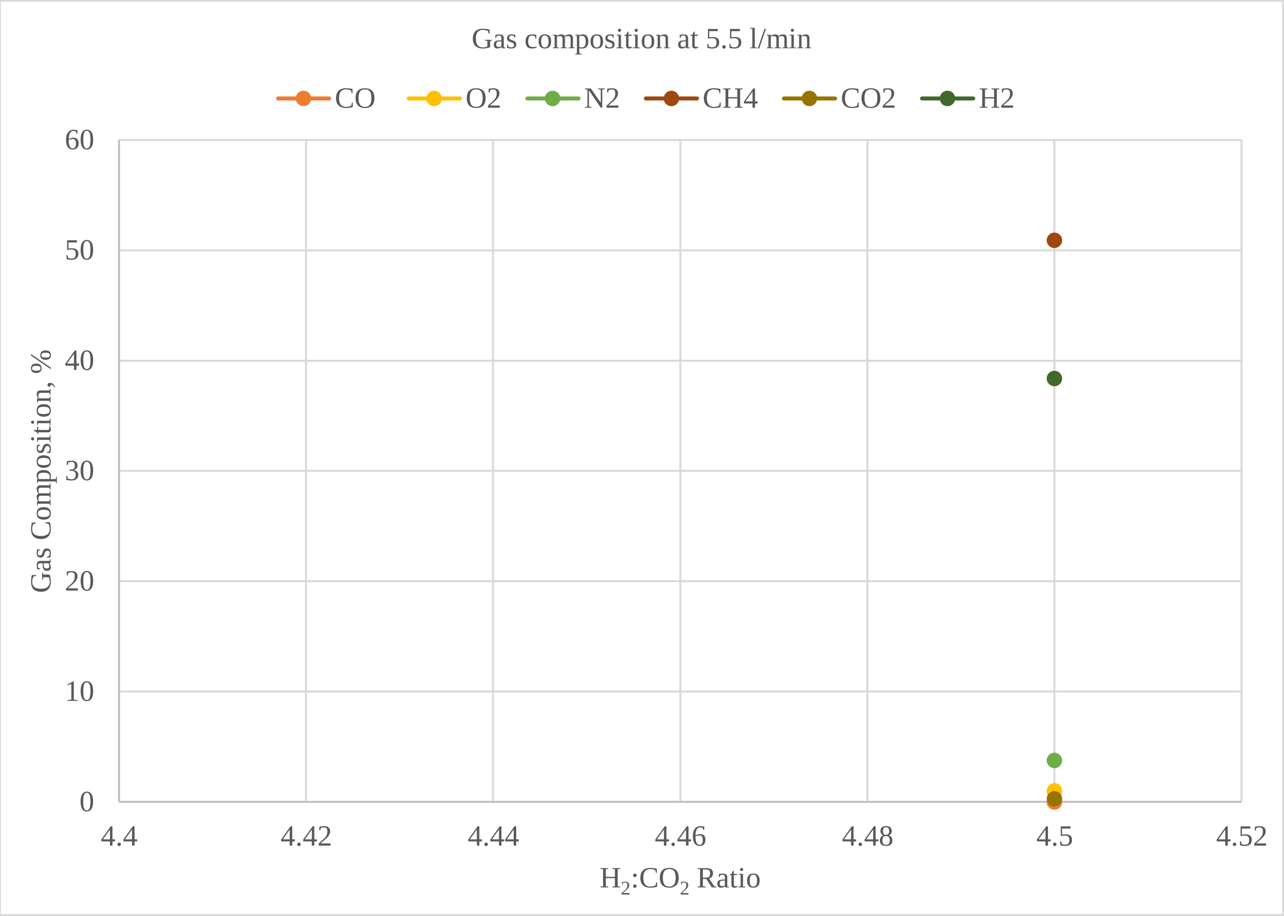

Figure 27. Gas composition at 5.5 l/min at various molar ratio of H_2:CO_2

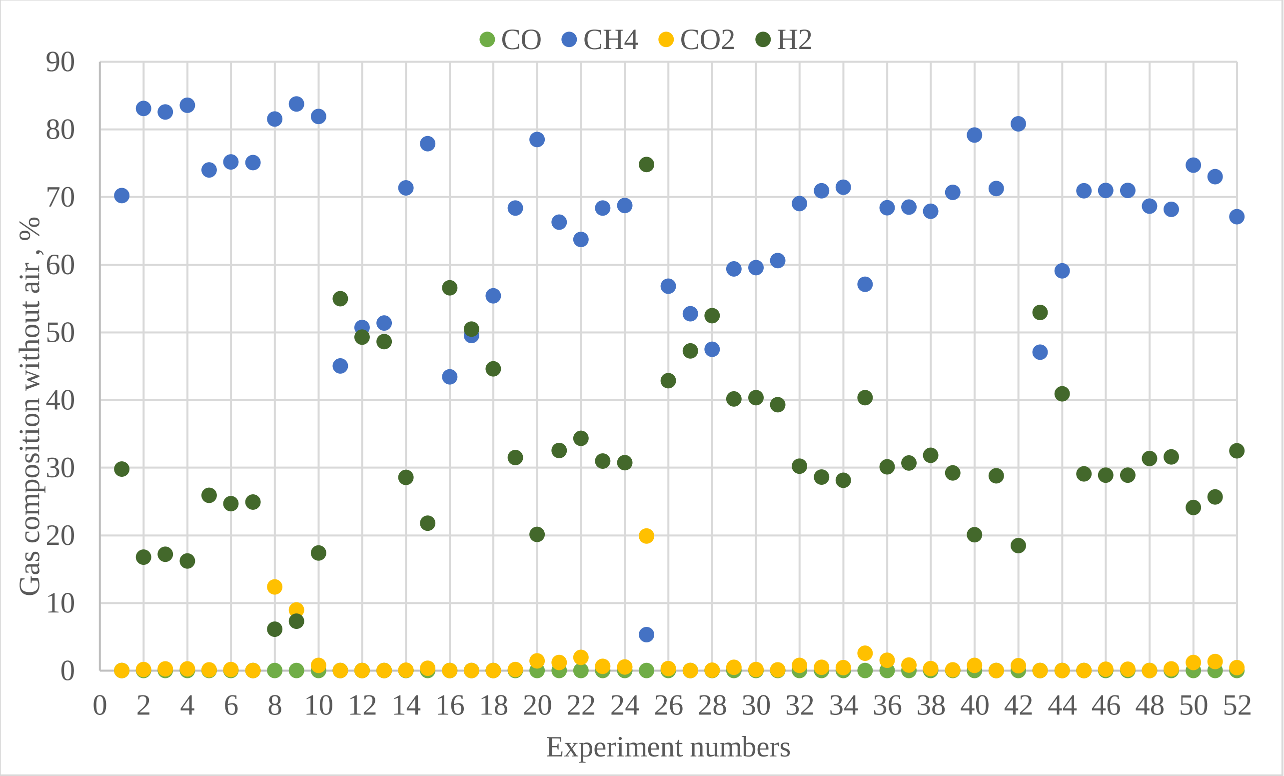

Figure 26. The calculated gas composition values excluding oxygen with respect to H_2:CO_2 molar ratio

3.4.4. CO_2 utilization and methanation

Carbon dioxide methanation has been recognized due to its ability to replace conventional fuels such as fossil fuels [29]. The power to gas hypothesis has also been utilized to understand and modify the methanation processes. Two main factors were analyzed namely CO_2 conversion (X_{CO2}) in this lab scale experiments from the following equations:

$$X_{CO2} = \frac{n_{CO2(in)} - n_{CO2(out)}}{n_{CO2(in)}} * 100 \qquad \text{Eq. (6)} \qquad [85]$$

Where

n = mole streams

The topmost conversion of CO_2 is accomplished at 300°C - 400°C temperature variation [55].

Table 5. Conversion of carbon dioixde values at different ratios and mass flows.

Experiment Number	**Mass Flow**	**CO_2: H_2**	**Recalculated gas composition without air:**				**Gas volume after reaction (recalculated according to gas composition), l / min**
			CO	CH_4	CO_2	H_2	
1	0.65	1:4.2,0	0	70.2	0	29.8	100
2	0.9	1:4,2	0	74.01	0.1	25.9	100
3	0.952	1:4,2	0	75.18	0.13	24.69	100
4	1.5	1:4,2	0	83.76	8.97	7.28	100
5	1.5	1:5,0	0	81.89	0.74	17.36	100
6	1.5	1:4.7,0	0	50.73	0	49.27	100
7	1.5	1:4.5,0	0	51.36	0	48.64	100
8	1.5	1:4.2,0	0	71.36	0.07	28.57	100
9	1.5	1:4,0	0	77.9	0.33	21.77	100
10	2	1:4.5,0	0	55.39	0.01	44.6	100
11	2	1:4.2,0	0	68.39	0.12	31.49	100
12	2	1:4,0	0	78.48	1.42	20.1	100
13	1.75	1:4.2,0	0	67.89	0.27	31.84	100
14	0.867	1:4.2,0	0	70.68	0.11	29.21	100
15	0.835	1:4.0,0	0	79.17	0.74	20.08	100

It should noted the the rest of the experiments are listed in the Appendiix 4.

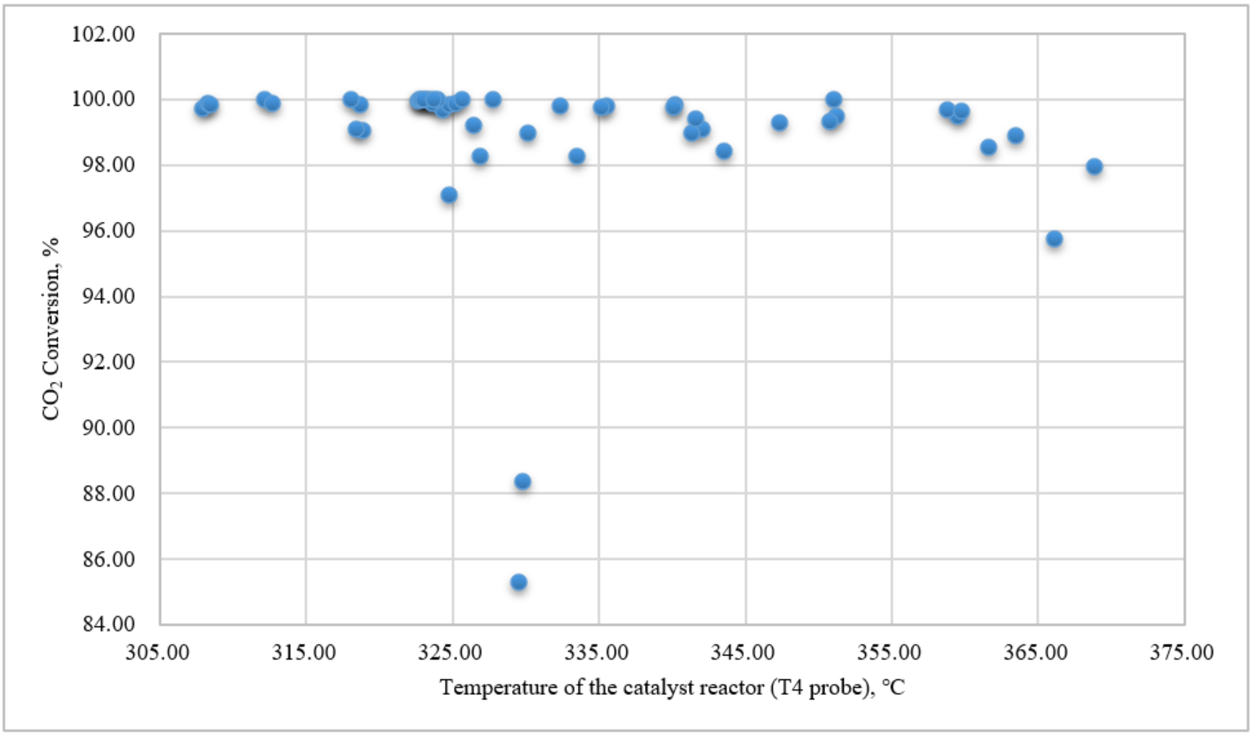

Figure 28. CO_2 conversion performance over a Mg_2Ni/Al_2O_3 catalyst concerning the temperature of the catalyst reactor.

Figure 28 shows the CO_2 conversion based on the temperature (T4) probe where the catalyst is situated. All experiments (1-52) as seen from Table 5 are included in this graph. The conversion is mainly ranging between 85% to 100%. Out of all 52 experiments, only two experiments (no. 8 and 9) showed the lowest efficiency 85% and 88%, this is because the obtained gas composition of CO_2 is the highest (11% and 8%). The remaining experiments observed the CO_2 conversion percentage ranging between 95% to 100%. A similar study was performed with the gases obtained from biogas and the optimum temperature was said to be up to 400°C to avoid the production of CO in the reaction [86]. The study was conducted with a similar catalyst and the $H_2:CO_2$ molar ratio has resulted in 4 [86]. The calculated CO_2 conversion was up to 75% which is slightly lower than the results obtained in this thesis. Guilera et al. [87] found similar results with $H_2:CO_2$ molar ratio at 4, the resulting temperature ranging between 300°C - 350°C achieved CO_2 conversion from 80% to 100%.

Conclusions

1. The ginormous emissions of greenhouse gases in the European Union have accelerated the usage of renewable energy. Since methane and carbon dioxide are the major greenhouse gases, the techniques to make them useful have been the center of the literature review. It was found that methane can be generated using municipal organic waste via biological and thermal methods. The renewable methane can also be produced with carbon dioxide with CO_2 methanation, this way the unreacted CO_2 gas can be utilized and turned around to be a source of energy.

2. The thesis presented two integrated conceptual designs in correspondence to renewable methane production where combined technological routes via anaerobic digestion and thermal technologies were analyzed to produce biomethane in terms of energy production, resource consumption, environmental impacts.

3. The material and energy balances showed that to generate $1kWh_{thermal}$ of biomethane, the reference scenario requires 4.88 kg of feedstock whereas the 1st integrated process and the 2nd integrated process require 1.38 kg and 1.34 kg of the municipal treated organic fraction. This shows that it requires lesser feedstock to produce $1kWh_{thermal}$ of biomethane, thus, the integrated processes can be said to be more environmentally friendly than other routes and promotes a circular economy.

4. The environmental impact was assessed for reference scenario, 1st integrated scenario and 2nd integrated process using life cycle analysis. Environmental impact categories such as climate change, ecosystems, resource consumption and human health were analyzed. It was found that the 2nd integrated processes show 1.3 times the high-quality environmental performance with lower methane losses and better carbon utilization in comparison to the 1st integrated process.

5. The carbon dioxide can be utilized from existing plants via methanation in converting to methane. In the performed lab-scale experiments, the CO_2 methanation was carried out using a 20% Ni catalyst namely Mg_2Ni and supported material Al_2O_3 of 13.92 g and 8.83g. The desirable temperature for the highest CO_2 conversion was to be around 200℃-500℃ around molar ratios of 4. The gas compositions achieved for CH_4, CO, CO_2, H_2 was 50% - 70%, 0%, 0% - 2%, 20% to 65% respectively. It is observed that when the molar ratio increased from 4.0 to 5.0, the gas composition of CH_4 decreases, therefore, it is concluded that the best molar ratio for H_2:CO_2 would be centered around 4. The CO_2 conversion was achieved at 85% to 100%.

6. The main goal of the thesis was to find technologies to produce renewable methane. Therefore, it was accomplished in two parts. 1st part was achieved as two integrated processes were proposed with biological – thermal processes which showed better environmental performance and used lesser resources to produce $1kWh_{thermal}$ biomethane. The second part was the utilization of carbon dioxide by performing methanation to produce methane and water from carbon dioxide and hydrogen.

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Appendices

Appendix 1 Gas composition (without O_2) vs H_2: CO_2 molar ratio

Table 6 The calculated gas composition without oxygen

Experiment Number	Mass Flow	CO_2: H_2	Recalculated gas composition without air:				Gas volume after reaction (recalculated according to gas composition), l / min
			CO	CH_4	CO_2	H_2	
1	0.65	1:4.2,0	0	70.20	0.00	29.80	100
2	0.65	1:4,0	0	83.07	0.15	16.79	100
3	0.65	1:4,0	0	82.58	0.23	17.19	100
4	0.65	1:4,0	0	83.54	0.26	16.19	100
5	0.9	1:4,2	0	74.01	0.10	25.90	100
6	0.952	1:4,2	0	75.18	0.13	24.69	100
7	0.952	1:4,2	0	75.06	0.01	24.93	100
8	1.5	1:4,2	0	81.52	12.35	6.13	100
9	1.5	1:4,2	0	83.76	8.97	7.28	100
10	1.5	1:5,0	0	81.89	0.74	17.36	100
11	1.5	1:5,0	0	45.03	0.02	54.95	100
12	1.5	1:4.7,0	0	50.73	0.00	49.27	100
13	1.5	1:4.5,0	0	51.36	0.00	48.64	100
14	1.5	1:4.2,0	0	71.36	0.07	28.57	100
15	1.5	1:4,0	0	77.90	0.33	21.77	100
16	2	1:5,0	0	43.42	0.00	56.58	100
17	2	1:4.7,0	0	49.51	0.00	50.49	100
18	2	1:4.5,0	0	55.39	0.01	44.60	100
19	2	1:4.2,0	0	68.39	0.12	31.49	100
20	2	1:4,0	0	78.48	1.42	20.10	100
21	4	1:4,2	0	66.28	1.19	32.53	100
22	4	1:4,2	0	63.73	1.94	34.33	100
23	4	1:4,2	0	68.37	0.64	30.99	100
24	4	1:4,2	0	68.75	0.51	30.74	100
25	4	1:4,5	0	5.29	19.89	74.82	100
26	5.5	1:4,5	0	56.83	0.31	42.86	100
27	1.5	1:5,0	0	52.73	0.02	47.24	100
28	2	1:5,0	0	47.51	0.06	52.43	100
29	2.0	1:4.5,0	0	59.37	0.48	40.15	100
30	2	1:4.5,0	0	59.56	0.12	40.32	100
31	2	1:4.5,0	0	60.59	0.10	39.31	100
32	2	1:4.2,0	0	69.03	0.77	30.21	100
33	2	1:4.2,0	0	70.92	0.50	28.58	100
34	2	1:4.2,0	0	71.45	0.41	28.14	100
35	4	1:4.5,0	0	57.10	2.56	40.33	100
36	4	1:4.2,0	0	68.39	1.51	30.10	100
37	3	1:4.2,0	0	68.50	0.83	30.67	100
38	1.75	1:4.2,0	0	67.89	0.27	31.84	100
39	0.867	1:4.2,0	0	70.68	0.11	29.21	100
40	0.835	1:4.0,0	0	79.17	0.74	20.08	100

41	0.835	1:4.0,0	0	71.23	0.00	28.77	100
42	0.802	1:3.8,0	0	80.81	0.73	18.46	100
43	2	1:5,0	0	47.07	0.00	52.93	100
44	2	1:4.5,0	0	59.09	0.00	40.91	100
45	2	1:4.2,0	0	70.92	0.00	29.08	100
46	2	1:4.2,0	0	70.96	0.19	28.86	100
47	2	1:4.2,0	0	70.96	0.18	28.86	100
48	2	1:4.2,0	0	68.65	0.00	31.35	100
49	2	1:4.2,0	0	68.17	0.26	31.57	100
50	2	1:4.0,0	0	74.72	1.18	24.10	100
51	2	1:4.0,0	0	73.01	1.31	25.68	100
52	2	1:4.2,0	0	67.09	0.42	32.49	100

Appendix 2 Temperature of the catalyst reactor vs H_2: CO_2 molar ratio

Table 7 Temperature (T1-T6) probes from the methanation catalyst reactor

Nr.	Mass Flow, l/min	CO_2: H_2	H_2: CO_2	H_2, l/min	CO_2, l/min	Catalyst reactor temperature (℃)					
						T1	T2	T3	T4	T5	T6
1	0.65	1:4.2	4.39	0.525	0.129	313.35	327.23	328.7	312.17	298.29	216.59
2	0.65	1:4	4.31	0.52	0.13	314.93	325.31	331.02	312.64	297.79	216.09
3	0.65	1:4	4.31	0.52	0.13	326.57	343.98	349.71	332.37	316.27	225.22
4	0.65	1:4	4.31	0.52	0.13	312.6	320.76	326.85	307.93	293.24	213.86
5	0.9	1:4,2	4.50	0.727	0.173	316.74	323.89	331.31	308.26	295.45	219.31
6	0.952	1:4,2	4.50	0.769	0.183	318.45	324.75	332.83	308.47	295.80	220.36
7	0.952	1:4,2	4.50	0.769	0.183	328.9	343.27	350.8	327.74	314.44	230.27
8	1.5	1:4,2	3.36	1.212	0.288	342.64	351.44	374.17	329.55	318.55	250.55
9	1.5	1:4,2	3.60	1.227	0.273	349.91	353.66	374.15	329.79	318.64	250.61
10	1.5	1:5	4.00	1.250	0.250	349.29	352.27	368.65	330.14	318.75	248.61
11	1.5	1:5	5.00	1.25	0.25	336.7	345.41	348.57	322.63	313.07	233.51
12	1.5	1:4.7	4.70	1.237	0.263	339.71	347.25	351.06	322.76	313.10	236.09
13	1.5	1:4.5	4.50	1.227	0.273	342.4	348.27	353.08	322.79	313.32	237.36
14	1.5	1:4.2	4.20	1.212	0.289	343.82	350.7	358.8	323.84	313.43	242.57
15	1.5	1:4	4.00	1.200	0.300	345.02	351.44	360.92	324.29	313.48	244.09
16	2	1:5	5.00	1.667	0.333	355.67	352.92	357.43	323.14	315.20	244.85
17	2	1:4.7	4.70	1.649	0.351	357.1	354.36	360.45	323.31	315.23	246.94
18	2	1:4.5	4.50	1.636	0.364	359.06	355.73	363.46	323.63	315.32	248.94
19	2	1:4.2	4.20	1.615	0.385	360.28	357.44	369.93	324.76	315.62	252.52
20	2	1:4	4.00	1.6	0.4	348.4	352.01	377.42	326.83	316.99	256.92
21	4	1:4,2	4.2	3.231	0.769	367.31	365.88	435.06	333.46	322.56	283.42
22	4	1:4,2	4.2	3.231	0.769	345.25	351.58	423.42	324.79	313.3	276.02
23	4	1:4,2	4.2	3.231	0.769	349.66	363.93	449.11	342.01	331.69	290.73
24	4	1:4,2	4.2	3.231	0.769	353.22	367.16	455.03	347.31	336.68	296.52
25	4	1:4,5	4.5	3.273	0.727	353.03	366.67	440.55	344.19	335.73	293.95

26	5.5	1:4,5	4.5	4.5	1	362.99	370.6	497.5	351.21	338.74	309.62
27	1.5	1:5	5	1.25	1.667	311.81	343.84	341.52	324	314.93	341.13
28	2	1:5	5	1.636	0.364	323.48	349.16	346.53	325.2	316.85	251.29
29	2.0	1:4.5	4.5	1.636	0.364	326.47	352.27	351.6	326.39	317.01	254.25
30	2	1:4.5	4.5	1.636	0.364	330.71	360.59	359.87	335.48	326.44	260.25
31	2	1:4.5	4.5	1.636	0.364	333.48	365.14	364.52	340.2	331.2	263.56
32	2	1:4.2	4.2	1.615	0.385	366.29	368.28	341.29	341.29	331.45	265.57
33	2	1:4.2	4.2	1.615	0.385	339.19	374.65	377.66	350.79	340.99	272.05
34	2	1:4.2	4.2	1.615	0.385	342.44	381.99	386.05	359.53	349.71	277.66
35	4	1:4.5	4.5	3.273	0.727	351.83	391.03	423.26	366.08	355.16	313.06
36	4	1:4.2	4.2	3.231	0.769	354.87	393.51	436.13	368.81	355.85	316.11
37	3	1:4.2	4.2	2.423	0.577	354.96	391.72	406.84	363.45	353.22	301.19
38	1.75	1:4.2	4.2	1.412	0.337	346.92	383.91	382.24	358.8	348.74	270.57
39	0.867	1:4.2	4.2	0.700	0.167	299.53	325.76	338.68	318.64	306.53	225.50
40	0.835	1:4	4	0.668	0.167	300.81	326.42	339.8	318.84	306.23	226.6
41	0.835	1:4	4	0.668	0.167	301.01	326.33	334.99	318.06	307.01	229.88
42	0.802	1:3.8	3.8	0.634	0.167	301.5	326.92	336.5	318.36	318.36	306.79
43	2	1:5	5	1.667	0.333	347.13	381.12	324.51	323.02	305.32	215.56
44	2	1:4.5	4.5	1.636	0.364	351.69	392	324.98	323.71	305.85	220.52
45	2	1:4.2	4.2	1.615	0.385	356.6	401.01	325.52	325.62	306.58	224.51
46	2	1:4.2	4.2	1.615	0.385	369.39	410.39	335.52	335.17	315.58	229.08
47	2	1:4.2	4.2	1.615	0.385	364.82	414.94	340.55	340.07	320.15	231.34
48	2	1:4.2	4.2	1.615	0.385	368.46	422.5	350.63	351.04	328.87	232.47
49	2	1:4.2	4.2	1.615	0.385	372.31	430.06	359.62	359.77	337.08	236.72
50	2	1:4	4	1.6	0.4	373.2	433.46	359.98	361.62	337.6	239.2
51	2	1:4	4	1.6	0.4	366.01	416.32	340.92	343.5	320.37	230.37
52	2	1:4.2	4.2	1.615	0.385	365.09	412.54	340.63	341.63	319.92	228.60

Appendix 3 Gas compositions of the methanation reaction vs H_2: CO_2 molar ratio

Table 8 Representation of the gas composition percentage based on different mass flows of hydrogen and carbon dioxide

Nr.	Mass Flow, l/min	CO_2: H_2	H_2: CO_2	H_2, l/min	CO_2, l/min	Gas composition, %					
						CO	O_2	N_2	CH_4	CO_2	H_2
1	0.65	1:4.2,0	4.39	0.525	0.129	0	3.6	13.54	54.46	0	23.12
2	0.65	1:4,0	4.31	0.52	0.13	0	4.1	15.42	61.91	0.11	12.51
3	0.65	1:4,0	4.31	0.52	0.13	0	4	15.05	60.95	0.17	12.69
4	0.65	1:4,0	4.31	0.52	0.13	0	3.8	14.30	63.45	0.2	12.3
5	0.9	1:4,2	4.50	0.727	0.173	0	2.2	8.28	61.9	0.08	21.66
6	0.952	1:4,2	4.50	0.769	0.183	0	2	7.52	63.65	0.11	20.9
7	0.952	1:4,2	4.50	0.769	0.183	0	2	7.52	62.7	0.01	20.82
8	1.5	1:4,2	3.36	1.212	0.288	0	1.1	4.14	74	11.21	5.56
9	1.5	1:4,2	3.60	1.227	0.273	0	1.1	4.14	74.81	8.01	6.5
10	1.5	1:5,0	4.00	1.250	0.250	0	1.1	4.14	71.83	0.65	15.23
11	1.5	1:5,0	5.00	1.25	0.25	0	1.4	5.27	38.48	0.02	46.96
12	1.5	1:4.7,0	4.70	1.237	0.263	0	2.3	8.65	41.56	0	40.37
13	1.5	1:4.5,0	4.50	1.227	0.273	0	1.9	7.15	42.92	0	40.64
14	1.5	1:4.2,0	4.20	1.212	0.289	0	4.5	16.93	51.4	0.05	20.58
15	1.5	1:4,0	4.00	1.200	0.300	0	5	18.81	53.67	0.23	15.00
16	2	1:5,0	5.00	1.667	0.333	0	0.7	2.63	37.71	0	49.14
17	2	1:4.7,0	4.70	1.649	0.351	0	0.7	2.63	43.28	0	44.14
18	2	1:4.5,0	4.50	1.636	0.364	0	0.6	2.26	48.58	0.01	39.12
19	2	1:4.2,0	4.20	1.615	0.385	0	1.1	4.14	60.31	0.11	27.77
20	2	1:4,0	4.00	1.6	0.4	0	0.7	2.63	71.87	1.3	18.41
21	4	1:4,2	4.2	3.231	0.769	0	0.7	2.63	60.28	1.08	29.59
22	4	1:4,2	4.2	3.231	0.769	0	0.8	3.01	58.04	1.77	31.26
23	4	1:4,2	4.2	3.231	0.769	0	0.8	3.01	61.85	0.58	28.03
24	4	1:4,2	4.2	3.231	0.769	0	0.9	3.39	62.2	0.46	27.81
25	4	1:4,5	4.5	3.273	0.727	0	0.9	3.39	12.74	47.91	180.25
26	5.5	1:4,5	4.5	4.5	1	0	1	3.76	50.91	0.28	38.4
27	1.5	1:5,0	5	1.25	1.667	0	0.9	3.39	46.67	0.02	41.81
28	2	1:5,0	5	1.636	0.364	0	1	3.76	41.86	0.05	46.2
29	2.0	1:4.5,0	4.5	1.636	0.364	0	1.4	5.27	52.78	0.43	35.69
30	2	1:4.5,0	4.5	1.636	0.364	0	1.5	5.64	52.8	0.11	35.74
31	2	1:4.5,0	4.5	1.636	0.364	0	1.6	6.02	53.71	0.09	34.85
32	2	1:4.2,0	4.2	1.615	0.385	0	2	7.52	61.26	0.68	26.81
33	2	1:4.2,0	4.2	1.615	0.385	0	2.2	8.28	62.74	0.44	25.28
34	2	1:4.2,0	4.2	1.615	0.385	0	2.3	8.65	63.03	0.36	24.82

35	4	1:4.5,0	4.5	3.273	0.727	0	2.3	8.65	51.25	2.3	36.2
36	4	1:4.2,0	4.2	3.231	0.769	0	2.3	8.65	60.53	1.34	26.64
37	3	1:4.2,0	4.2	2.423	0.577	0	2.3	8.65	60.52	0.73	27.1
38	1.75	1:4.2,0	4.2	1.412	0.337	0	5.3	19.94	50.49	0.2	23.68
39	0.867	1:4.2,0	4.2	0.700	0.167	0	1.4	5.27	66.03	0.1	27.29
40	0.835	1:4.0,0	4	0.668	0.167	0	1.5	5.64	73.33	0.69	18.6
41	0.835	1:4.0,0	4	0.668	0.167	0	1.6	6.02	66.18	0	26.73
42	0.802	1:3.8,0	3.8	0.634	0.167	0	2.1	7.90	75.06	0.68	17.15
43	2	1:5,0	5	1.667	0.333	0	1.5	5.64	42.65	0	47.96
44	2	1:4.5,0	4.5	1.636	0.364	0	1.5	5.64	54.01	0	37.4
45	2	1:4.2,0	4.2	1.615	0.385	0	1.6	6.02	64.76	0	26.55
46	2	1:4.2,0	4.2	1.615	0.385	0	1.7	6.40	64.86	0.17	26.38
47	2	1:4.2,0	4.2	1.615	0.385	0	1.9	7.15	64.76	0.16	26.34
48	2	1:4.2,0	4.2	1.615	0.385	0	2	7.52	62.3	0	28.45
49	2	1:4.2,0	4.2	1.615	0.385	0	2.1	7.90	61.89	0.24	28.66
50	2	1:4.0,0	4	1.6	0.4	0	2.1	7.90	68.04	1.07	21.95
51	2	1:4.0,0	4	1.6	0.4	0	3.1	11.66	62.75	1.13	22.07
52	2	1:4.2,0	4.2	1.615	0.385	0	2	7.52	60.66	0.38	29.38

Appendix 4 Computed carbon dioxide conversion values vs H_2: CO_2 molar ratio

Table 9 Methanation experimental data with calculated CO_2 conversion values

Nr.	Mass Flow, l/min	H_2: CO_2	H_2: CO_2	H_2, l/min	CO_2, l/min	Catalyst temperature rector (T4 probe), °C	CO_2 (Gas composition obtained, %)	Gas volume after reaction (recalculated according to gas composition), l / min	CO_2 Conversion %
1	0.65	1:4.2	4.39	0.525	0.129	312.17	0.00	0.191	100.00
2	0.65	1:4	4.31	0.520	0.130	312.64	0.11	0.158	99.87
3	0.65	1:4	4.31	0.520	0.130	332.37	0.17	0.166	99.78
4	0.65	1:4	4.31	0.520	0.130	307.93	0.20	0.172	99.73
5	0.90	1:4.2	4.50	0.727	0.173	308.26	0.08	0.264	99.88
6	0.95	1:4.2	4.50	0.769	0.183	308.47	0.11	0.275	99.83
7	0.95	1:4.2	4.50	0.769	0.183	327.74	0.01	0.253	99.99
8	1.50	1:4.2	3.36	1.212	0.288	329.55	11.21	0.379	85.28
9	1.50	1:4.2	3.60	1.227	0.273	329.79	8.01	0.397	88.35
10	1.50	1:5	4.00	1.250	0.250	330.14	0.65	0.397	98.97
11	1.50	1:5	5.00	1.250	0.250	322.63	0.02	0.639	99.95
12	1.50	1:4.7	4.70	1.237	0.263	322.76	0.00	0.590	100.00
13	1.50	1:4.5	4.50	1.227	0.273	322.79	0.00	0.524	100.00
14	1.50	1:4.2	4.20	1.212	0.289	323.84	0.05	0.425	99.93
15	1.50	1:4	4.00	1.200	0.300	324.29	0.23	0.394	99.70
16	2.00	1:5	5.00	1.667	0.333	323.14	0.00	0.862	100.00
17	2.00	1:4.7	4.70	1.649	0.351	323.31	0.00	2.634	100.00
18	2.00	1:4.5	4.50	1.636	0.364	323.63	0.01	4.361	99.88
19	2.00	1:4.2	4.20	1.615	0.385	324.76	0.11	0.584	99.83
20	2.00	1:4	4.00	1.600	0.400	326.83	1.30	0.533	98.27
21	4.00	1:4.2	4.20	3.231	0.769	333.46	1.08	1.227	98.28
22	4.00	1:4.2	4.20	3.231	0.769	324.79	1.77	1.267	97.08
23	4.00	1:4.2	4.20	3.231	0.769	342.01	0.58	1.198	99.10
24	4.00	1:4.2	4.20	3.231	0.769	347.31	0.46	1.214	99.27

26	5.50	1:4.5	4.50	4.500	1.000	351.21	0.28	1.880	99.47
27	1.50	1:5	5.00	1.250	1.667	324.00	0.02	0.567	99.99
28	2.00	1:5	5.00	1.636	0.364	325.20	0.05	0.797	99.89
29	2.00	1:4.5	4.50	1.636	0.364	326.39	0.43	0.656	99.22
30	2.00	1:4.5	4.50	1.636	0.364	335.48	0.11	0.682	99.79
31	2.00	1:4.5	4.50	1.636	0.364	340.20	0.09	0.644	99.84
32	2.00	1:4.2	4.20	1.615	0.385	341.29	0.68	0.584	98.97
33	2.00	1:4.2	4.20	1.615	0.385	350.79	0.44	0.583	99.33
34	2.00	1:4.2	4.20	1.615	0.385	359.53	0.36	0.562	99.47
35	4.00	1:4.5	4.50	3.273	0.727	366.08	2.30	1.339	95.76
36	4.00	1:4.2	4.20	3.231	0.769	368.81	1.34	1.179	97.95
37	3.00	1:4.2	4.20	2.423	0.577	363.45	0.73	0.886	98.88
38	1.75	1:4.2	4.20	1.412	0.337	358.80	0.20	0.526	99.69
39	0.87	1:4.2	4.20	0.700	0.167	318.64	0.10	0.271	99.84
40	0.84	1:4	4.00	0.668	0.167	318.84	0.69	0.230	99.05
41	0.84	1:4	4.00	0.668	0.167	318.06	0.00	0.250	100.00
42	0.80	1:3.8	3.80	0.634	0.167	318.36	0.68	0.223	99.09
43	2.00	1:5	5.00	1.667	0.333	323.02	0.00	0.816	100.00
44	2.00	1:4.5	4.50	1.636	0.364	323.71	0.00	0.680	100.00
45	2.00	1:4.2	4.20	1.615	0.385	325.62	0.00	0.583	100.00
46	2.00	1:4.2	4.20	1.615	0.385	335.17	0.17	0.580	99.74
47	2.00	1:4.2	4.20	1.615	0.385	340.07	0.16	0.575	99.76
48	2.00	1:4.2	4.20	1.615	0.385	351.04	0.00	0.608	100.00
49	2.00	1:4.2	4.20	1.615	0.385	359.77	0.24	0.606	99.62
50	2.00	1:4	4.00	1.600	0.400	361.62	1.07	0.549	98.53
51	2.00	1:4	4.00	1.600	0.400	343.50	1.13	0.564	98.41
52	2.00	1:4.2	4.20	1.615	0.385	341.63	0.38	0.61	99.40