

ENVIRONMENTAL IMPACTS OF BIOGAS UTILIZATION PATHWAYS

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Biogas is a clean and environmental friendly fuel that is generated typically from anaerobic degradation of biomass. Biogas, consisting mainly of CO₂ and CH₄, is an attractive renewable carbon source and its exploitation would be advantageous from both a financial and an environmental point of view. For syngas production the CO₂ reforming of CH₄ or Dry reforming of methane (DRM) reaction has been proposed as the most promising one. DRM has attracted considerable scientific interest in the past years, as it offers the possibility of simultaneous removal of two inexpensive and abundant carbon containing sources, which are also greenhouse gasses, and their transformation into useful chemical products. Moreover, the utilization of CO₂ as a feedstock for producing chemicals is tempting not only because it can contribute to the mitigation of greenhouse gas emissions, but also because it is an interesting challenge in exploring new concepts and new opportunities for catalysis and the chemical industry. In view of the production of useful chemicals and synthetic fuels, the dry reforming reaction of biogas catalyzed by nickel on alumina catalysts seems an appropriate way to produce syngas which is suitable for methanol or Fischer–Tropsch synthesis reactions which require H₂/CO ratio of 1 to 2.

Keywords: anaerobic digestion, biogas, catalytic conversion, environmental impact, reforming, waste

1 INTRODUCTION

Energy security concerns and the need for the mitigation of environmental impacts associated with energy generation from fossil fuels (e.g., greenhouse gas emissions), has accelerated the deployment of renewable fuels such as biogas. Arguably, the end use of biogas has a major impact on the overall environmental performance. Therefore, an integrated assessment of the environmental impacts of biogas deployment through a viable conversion pathway is necessary for the evaluation of the system processes, specifically to locate where overall environmental sustainability could be further enhanced. This could help inform decision-makers of the integrated performances of the alternatives, including the monitoring of impact on the social environment. A sustainable energy system, balances energy production and consumption with minimal negative impact on the environment. This should be coupled with inherent opportunities for implementation of social and economic activities.

The Greenhouse Gas (GHG) emissions, global warming and depletion of world fossil resources have become worldwide topics. Governments and energy industries are opting for cleaner, sustainable and renewable energy sources to generate power. Biogas is one of the most promising renewable fuels, as it is produced mainly through the anaerobic degradation of organic materials. Biogas contains about 55–65% methane (CH₄), 30–45% carbon dioxide (CO₂), and it can be utilized as a renewable energy source in combined heat and power plants, as a vehicle fuel, or as a substitute for natural gas.

However, during the past decades, the process of biogas reforming or carbon dioxide reforming of methane has received attention, and efforts have focused on development of catalysts which show high activity towards synthesis gas formation, and are also resistant to coking, thus displaying stable long-term operation. Since both CH₄ and CO₂ are considered as the main GHG, reforming of biogas not only reduces the amount of GHG

emissions, but in fact it recycles and increases the usability of these GHG by producing hydrogen or syngas. Hydrogen can be used in fuel cells as a power source and syngas may be further converted into hydrocarbons via the Fisher – Tropsch synthesis [1-3].

Catalytic processes being able to convert natural gas (methane) into hydrogen or synthesis gas have been extensively studied. Catalysts play a crucial role in the reactivity toward complete conversion of methane. However, each one of them induces different reaction pathways. Thus, the selection of the most appropriate catalyst plays a vital role in the dry reforming reaction for hydrogen or syngas production. Suitable active catalysts should additionally have the ability to maximize hydrogen yield, inhibiting coke deposition and CO production, as well. Catalysts based on noble metals are reported to be less sensitive to coking than are nickel-based catalysts. However, considering the aspects of high cost and limited availability of noble metals, it is more desirable, from the industrial point of view, to develop nickel-based catalysts which are resistant to carbon deposition and exhibit stable operation for extended periods of time. Ni-based catalysts have been investigated mostly for dry reforming reaction and have the potential to be used industrially in the future.

The present study provides an extensive review of biogas utilization pathways, as well as their environmental impacts, focusing on the biogas reforming reaction. Moreover, the reforming of a clean model biogas, which consists mainly of 60% methane (CH₄) and 40% carbon dioxide (CO₂), for synthesis gas production over Ni supported alumina catalysts, was experimentally investigated at atmospheric pressure in a fixed bed catalytic reactor.

2 BIOGAS PRODUCTION

Anaerobic digestion is a microbial conversion method that occurs in an aqueous environment, meaning that biomass sources containing high water levels (even

containing less than 40% dry matter) can be processed without any pre-treatment [4]. This is not the case for most other conversion technologies. Combustion, for example, only offers a net positive energy balance if the water content of the biomass or waste is below 60% and even then, most of the energy stored in the biomass is used for the evaporation of the contained water. Also, the energetic efficiency of pyrolysis and gasification decreases considerably with high water content, and the presence of water in the produced bio-oil is undesirable [5]. Thus, the use of these technologies necessitates an energy consuming pre-drying step for wet types of biomass and waste.

The valorization of the produced biogas (consisting of ca. 65% CH₄, 35% CO₂ and trace gases such as H₂S, H₂ and N₂) is energy efficient and environmentally friendly because of the low emission of hazardous pollutants. In most cases, biogas is valorized energetically in a CHP (combined heat and power) installation for the simultaneous generation of heat and electricity. These installations typically offer an electrical efficiency of 33% and a thermal efficiency of 45%. As pointed out by various studies [6], the emissions of volatile organic compounds (VOCs) are very limited since 99% of the volatile compounds are completely oxidized during combustion. This is in contrast to incinerators that suffer from the emission of hazardous compounds like dioxins, and hence require extensive flue gas purification. Alternatively, the biogas can be upgraded to natural gas purity and injected in the natural gas grid [7]. The produced slurry (digestate) is nitrogen rich and can, in most cases (depending on the nature of the biomass), be utilized in agriculture as a nutrient fertilizer and/or organic amendment [8]. A more novel application is to transform the digestate into biochar, which can be further employed as soil enhancer or an adsorbent for purification of wastewater or flue gas [9].

Anaerobic digestion is not only feasible in large-scale industrial installations, but can also be applied on a small scale. This observation specifically provides opportunities for anaerobic digestion in developing countries and rural areas, where energy supply is limited or even not available at all. One example is the use of simple biomass and waste digesters in rural areas in India that operate on weed and agricultural residues to provide cooking gas for households [10].

According to Appelsa [11] anaerobic digestion is a robust process and its application for the treatment of organic waste has been emerging spectacularly with an annual growth rate of 25% during recent years. Its main beneficial properties include (i) its ability to treat high moisture containing biomass, (ii) a very easy conversion into biogas (it is a naturally occurring process), which can be incinerated with a very limited generation of pollutants, and (iii) its robustness and applicability on small scale. Various types of biomass and waste are suitable for anaerobic digestion, and a co-digestion leads in most cases to superior digestion efficiencies. Although frequently used, the digestion mechanism is not yet completely understood because of the high complexity of the process. Assessment of the microbial community composition and evolution during digestion will most probably further elucidate the working mechanisms of the process. A further development of mathematical models is also necessary for optimization of the digestion system. In order to achieve higher conversion ratios and to improve the biogas production, there is a general

consensus that pre-treatment methods will be of crucial importance. However, more research is needed to identify their specific effects on biomass structure that enhance gas production. Finally, upgrading of the produced biogas will further broaden its applicability.

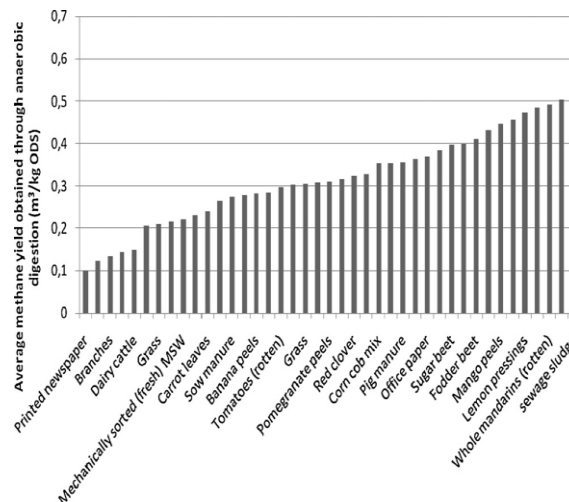


Figure 1: Overview of the average methane yield obtained through anaerobic digestion of the different waste streams.[11]

3 BIOGAS UTILIZATION

3.1 General

Biogas consists mainly of CH₄ (60–70%) and CO₂ (30–40%), but also water vapor and traces of nitrogen (N₂), hydrogen sulphide (H₂S) and ammonia (NH₃). These proportions, as well as the biogas yields, are largely determined by the raw materials digested and the digestion technology applied. For instance, the digestion of a raw material with a high fat content can provide a higher gas yield and a higher proportion of methane than the digestion of a raw material rich in carbohydrates. Since methane is the energy carrier in both biogas and natural gas, they can be used in the same applications. Methane is a potent greenhouse gas, and the emission of one kg of methane leads to the same global warming effect as the emission of 21 kg of carbon dioxide, calculated for a period of 100 years. The losses of methane from biogas systems should therefore be minimized. Much of the biogas is used at the same location as it is produced. However, biogas is usually produced continuously during the year whereas the demand can vary considerably. For example, the heat demand on farms can vary greatly due to variations in outdoor temperature, periodical need for drying of crops, etc [11-14].

Heat production is the most common and simple way of using biogas. It can be used in boilers developed for natural gas with minor adjustments of the boiler, and generally without more pre-treatment of the gas than the removal of water. Biogas can be used for district heating purposes when applicable, or for heating of buildings close to the biogas plant, for example, at farms. Access to a boiler for a district heating system can provide a means of reliable disposal of the gas throughout the year, whereas biogas production can exceed the heat demand in smaller systems, such as farms, during the summer.

Any excess gas should be flared off to reduce the emission of methane. Most digesters are heated by combustion of some of the biogas produced in the biogas plant. This usually corresponds to about 10% of the biogas produced in large-scale biogas plants and 30% in farm-scale plants. Biogas can also be used for combined heat and power production (CHP). There are many technologies available for CHP, for example, diesel engines, gas turbines and Stirling engines. The conversion efficiency is generally high, and may correspond to about 30–40% of electricity and 50% of heat, depending on plant size and conversion technology. The pre-treatment demands are often higher for CHP than when the gas is used for stand-alone heat production. In addition to the removal of water vapor, the pre-treatment should include removal of particles and corrosive components such as H₂S and chlorinated hydrocarbons. Biogas can be used in distribution systems and vehicles adapted for natural gas. Biogas intended for this application is upgraded to natural gas quality and pressurized. The gas is distributed to filling stations, either to public, quick-filling stations or slow filling stations mainly intended for heavy-duty vehicles.

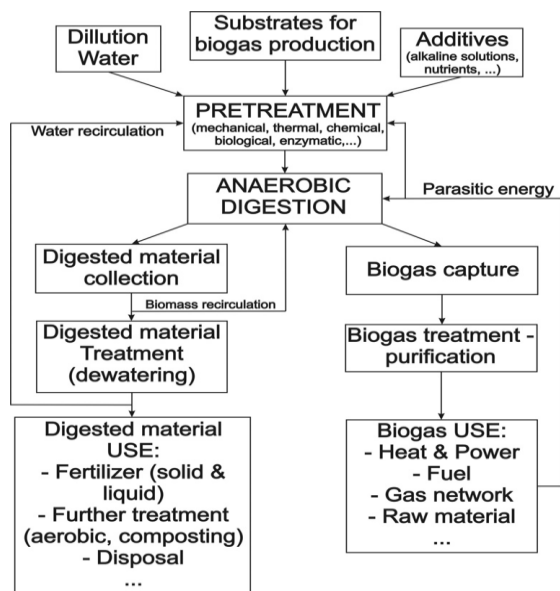


Figure 2: Block scheme of anaerobic digestion and biogas/digestate utilisation

3.2 Biogas as a fuel for combined heat and power applications

Burners and boilers used to produce heat and steam can be fueled by biogas. The direct substitution of biogas for natural gas or LPG, however, will not work for most standard commercially available burners. At given fuel gas feed pressures, gas must flow into combustion in the right stoichiometric ratio with air. Because of its high CO₂ content, if biogas flows through the burner orifice at the pressure intended for feeding methane or propane, the fuel-to-air ratio is insufficient to ensure flame stability. A relatively simple option is to provide the combustion equipment with a second “as is” biogas burner that operates in parallel with the first. In this case, regardless of the fuel used, air flow is kept constant. Burner orifices for the respective burners can be set such that each burner meters the proper amount of gas to meet combustion stoichiometry. This could require other

control measures such as (for simplest control) complete switchovers from pure biogas fuel to the fossil alternative, and modest (a few hours’ worth) backup biogas storage, but is otherwise straightforward.

Some operations that use landfill gas have adapted standard equipment to allow easy switchover from different fuel sources, whether landfill biogas, natural gas, or oil. Conversion of a boiler system to operate on biogas typically involves the enlargement of the fuel orifice and a restriction of the air intake. Important considerations include the capability of the combustor to handle the increased volumetric throughput of the lower-Btu biogas, flame stability, and the corrosive impact of raw biogas on the burner equipment. To prevent corrosion from H₂S and water vapor, operating temperatures should be maintained above the dew point temperature (250° F) to prevent condensation. It may also be advisable to use propane or natural gas for start up and shut down of the system, since higher operating temperatures cannot be maintained at these times. If the biogas has energy content lower than 400 Btu/scf, the combustion system may be limited by the volumetric throughput of the fuel, which may result in de-rating of the equipment. In addition, the burner orifice should be enlarged to prevent a higher pressure drop across the burner orifice due to the decreased heating value and specific gravity of the biogas results. However, orifice enlargement will degrade the performance of the burner if it is ever operated on natural gas or propane. To resolve this problem, the propane or natural gas can be mixed with air to create an input fuel with an equivalent pressure drop and heat input as the biogas. It is also possible to achieve fuel flexibility by using a dual burner system, as mentioned above. This allows optimum performance of the burners since they maintain the pressure drop for each fuel independently [15].

3.3 Biogas as an engine fuel

Electricity generation using biogas is a commercially available, proven technology. Typical installations use spark-ignited natural gas or propane engines that have been modified to operate on biogas. Diesel or gasoline engines can be modified to use biogas. Potentially, the more efficient Stirling engines could also be operated on biogas. Although waste heat from engine operations is used frequently in CHP applications, it is probably not practical to recover the small amounts of heat generated by engines used directly for specific uses such as irrigation or refrigeration. Biogas can be burned in gas engines and be converted into mechanical and thermal energy. By using an electric generator the mechanical energy of the reciprocating gas engine is converted to electrical energy at efficiency of 29–38% being dependent on gross power. The heat produced during the operation of gas engines can be recovered in heat exchangers and supplied to thermal consumers. For large-scale biogas power plants (>60 kW_e) diesel engines are used most frequently. A diesel engine can be rebuilt into a dual fuel engine or a spark ignited gas engine. The biogas/diesel dual-fuel engine can operate successfully with biogas substitution rate at above 90% by mass with no operational problems in a long-term. Best biogas combustion results are achieved with lean burn gas engines. At air-fuel ratios of 1.5, NO_x and CO concentrations of less than 500 ppm can be achieved. Biogas pressure of 8–25 mbar is utilized and H₂S removal below 1000 ppm is needed. Further, micro gas

turbines are also utilized, which offer lower combustion temperatures and thus lower NOX emissions than encountered in large-scale gas turbines. For gas turbines deeper biogas purification is needed. Produced biogas enters a compressor, which is followed by removal of moisture and then the dry compressed biogas enters an expander connected to an electric generator. The exhaust gases leave the micro gas turbines typically at 275°C. Flue gas leaving micro turbine enters a heat exchanger to transfer its energy to the AD heating system [16].

3.4 Biogas as a vehicular fuel

Utilization of biogas in the transport sector is a technology with great potential and with important socio-economic benefits. Biogas is already used as vehicle fuel in countries like Sweden, Germany and Switzerland. While the text of the regulations specifically refers to CNG fuel specifications, it can be argued that biogas should meet the same specifications as CNG for use as a vehicle fuel. The purpose of having minimum CNG fuel specifications is to ensure the compatibility of engines designed to operate on natural gas. Beyond the regulatory impediments to using raw biogas as a vehicle fuel the low methane content of raw biogas (typically 55% to 70%) combined with its inherent trace contaminants (especially H₂S) can have significant negative impacts on engine performance, durability, and emissions. While the degree of impact depends on both engine control and vehicle technology (e.g., open loop vs. closed loop, heavy duty vs. light duty), raw biogas is generally considered technically unsuitable as a vehicle fuel. For these reasons, there are no known vehicle engine manufacturers planning to offer products rated to operate on raw biogas as a fuel.

3.5 Solid oxide fuel cells

Biogas fuel feeding presents an attractive option among emerging applications for fuel cells, especially for the high temperature ceramic type solid oxide fuel cells (SOFCs). Compared to natural gas (NG), it shows advantages of being indigenous and renewable, free of non-methane hydrocarbons (NMHC), with the exception of landfill gas and containing a large fraction of a methane-reforming agent (CO₂). Biogas fabrication inherently is a friendly and way to process waste streams of variable nature (sewage sludge, liquid organic industrial effluents, farm residues, landfill, municipal and industrial solid organic residues). If H₂S is removed, biogas is a valuable fuel for SOFCs. Since biogas is a CO₂-enriched fuel carbon deposition in a reforming process and in SOFCs must be carefully avoided by applying, e.g. an increased steam-to-carbon ratio such as above 0.5 on a molar basis [16, 17]. SOFCs could be an appropriate conversion technology for biogas, achieving reasonable efficiencies (30–40%) already in the smallest power range (5–20kW_e), being safe, silent and expected to be low in maintenance. It may probably be the only technology capable of directly converting low quality biogas from landfill. In laboratory tests, high electrical conversion was maintained down to very low methane levels (5%) [18], and performance drops of only 5% were registered when operating on mixtures of 30–70% CH₄-CO₂ compared to 70–30% CH₄-CO₂ [19].

3.6 Upgrading of biogas fuel to marketable gaseous fuels

Biogas fuel can also be upgraded to marketable gaseous fuels such as biomethane, compressed biogas, biohydrogen and syngas. This technological option

enables to accumulate energy which is very difficult with electrical energy [20, 21].

3.6.1. Biomethane

Biogas can be upgraded to biomethane (BM) and injected into natural gas grids. The treatment of biogas generally involves: (i) a cleaning process, in which the trace components harmful to the natural gas grid are removed and (ii) an upgrading process, in which CO₂ is removed to adjust the calorific value and relative density in order to meet natural gas specifications such as the Wobbe Index. After transformation, the final BM typically comprises 95–97% CH₄ and 1–3% CO₂. Main technologies for CO₂ removal include pressure swing adsorption (PSA), high-pressure water wash (HPWW), reactive absorption (RA), physical absorption (PA), membrane separation (MS) and cryogenic separation (CS) [16].

3.6.2. Compressed biogas

Compressed biogas (CB), much like natural gas, can be used to power motor vehicles such as city buses. Due to impurities biogas cleaning is usually required. Several innovative concepts and compression methods were generated and we have decided a piston cylinder system to be the most viable compression method. The best compression mechanism was determined to be a modified bicycle pump because it is inexpensive, easy to acquire, requires sensible effort, and can reach the desired pressure with a reasonable amount of time and effort. The ideal goal is to compress the equivalent of 6 hours of energy into a storage container that is portable, available, and uses standard fittings.[22]

3.6.3. Biohydrogen

Another alternative for biogas is a biogas-to-H₂ process for bio-hydrogen (BH) production via, e.g. water electrolysis. Budzianowski has proposed one another biogas-to-electricity cycle involving a H₂ step - decarbonized oxy reforming fuel cell (ORFC) cycle [16]. According to the ORFC cycle biogas undergoes catalytic oxy-reforming followed by shifting to a H₂/CO₂ mixture which is then separated. The produced hydrogen is consumed in a fuel cell, which supply a part of generated electricity to water electrolysis for oxygen production. Oxygen is conveniently consumed for biogas oxy-reforming thus eliminating nitrogen dilution problem in the system.

3.6.4. Syngas

Biogas can also be upgraded to bio-syngas (BS) via reforming [21-23]. Syngas is then well-suited for fuel cell applications. Moreover, during the past decades, the process of biogas reforming or carbon dioxide reforming of methane has received attention, and efforts have focused on development of catalysts which show high activity towards synthesis gas formation, and are also resistant to coking, thus displaying stable long-term operation. Since both CH₄ and CO₂ are considered as the main GHG, reforming of biogas not only reduces the amount of GHG emissions, but in fact it recycles and increases the usability of these GHG by producing hydrogen or syngas. Hydrogen can be used in fuel cells as a power source and syngas may be further converted into hydrocarbons via the Fisher – Tropsch synthesis.

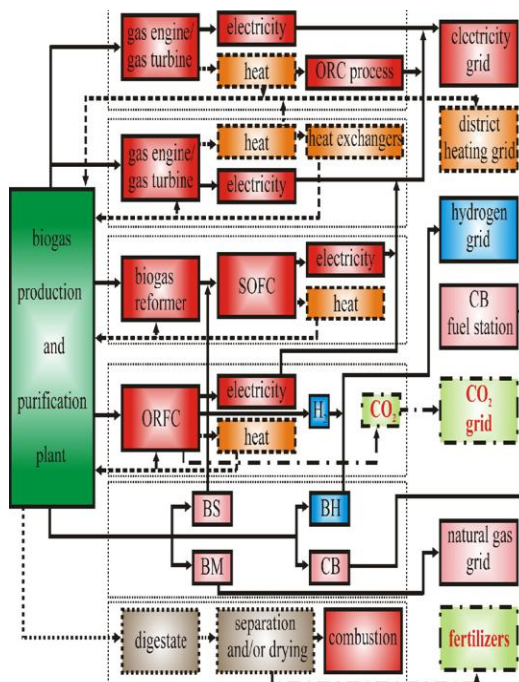


Figure 3: Summary of (i) Power technologies for biogas fuelled power plants and (ii) Biogas upgrading technologies to marketable gaseous fuels [16]

4 ENERGY EFFICIENCY AND LIFE CYCLE ASSESSMENT

4.1 Energy efficiency

Biogas is arguably a more versatile renewable energy source (cf. wind and solar energy), due to its determinate energy value and ease of storage, hence, potential utilization is significantly independent of factors such as geographical location and seasonality [24]. It can be used directly for heating and electricity generation, and as substitute for fossil fuel applications, e.g., transport fuel [25,26]. The potential utilization of the digestate [27] as fertilizer can also reduce dependence on energy intensive mineral fertilizers, to further mitigate GHG emissions [28]. Since the activation of the ban on landfilling of organic waste in Germany [29], the AD process provides a viable waste management option [30], but sustainable biogas utilization requires maintenance of a positive life-cycle energy balance. Analyses of energy balance in the life-cycle of biogas systems that have been reported to-date often lack bases for comparison due to varying accounting system and boundaries [31]. In particular, many studies on energy balance have focused on specific raw material [32-39], specific biogas systems [24,33-34,35,40-42], different waste management strategies [43-45], and on specific utilization options for biogas [46-49]. To the authors' knowledge, only the study by Berglund and Börjesson [31] has addressed the entire life-cycle of different biogas systems. However, Berglund and Börjesson [31] identified the main factors affecting the energy input/output ratio for biogas systems, but did not attempt to correlate these to the primary energy output. None of the analyses reviewed have coupled multiple feedstock scenarios to viable energy conversion pathways to assess: (i) impact of plant locations to minimise GHG emissions through reduced fossil fuel usage and elimination of existing technical and

policy obstacles; (ii) potential for integrated efficiency enhancement for reliability and to minimise cost; and (iii) overall system sustainability.

Results from the study of Pöschl [50] show that there could be significant variation in energy efficiency for biogas plants arising from feedstock resource and process adopted (single feedstock versus co-digestion), conversion technology applied, and digestate management technique. For single feedstock digestion, the Primary Energy Input to Output (PEIO) ratio ranged between 10.5% and 64.0%, depending on energy demand for feedstock supply logistics. For conditions analysed, the energy balances turned negative for transportation distances in excess of 22 km for cattle manure, 345 km for corn silage, and 425 km for MSW in single feedstock digestion scenarios, which could determine the most efficient sources of feedstock and subsequent disposal of digestate. For co-digestion of multiple feedstocks, the PEIO ranged between 45.6-48.6% and 34.1-55.0% for small and large-scale biogas systems, respectively, which suggests more stable processes in co-digestion. The recorded PEIO for small and large-scale biogas utilization pathways ranged between 4.1-45.6% and 1.3-34.1%, respectively, depending on efficiency of the respective energy conversion systems and potential substitution of different fossil fuels, which indicates the inherent potential for energy efficiency enhancement. For example, the most efficient utilization pathways for small and large-scale biogas plants was CHP generation with heat utilization at relatively short transmission distance (PEIO 6.2%) and upgrading of biogas specifically for gas grid injection, but using small-scale CHP to service process and biogas upgrading energy loads (PEIO 1.3%), respectively. Energy efficiency could be enhanced by up to 6.1% by recovery of residual biogas from enclosed digestate storage units. Energy performance of digestate management strategy depended on whether dewatering or drying was required to enhance transportation efficiency, but drying was sustainable only where surplus heat from energy conversion process was available.

4.2 Life cycle assessment

The number of Anaerobic Digestion (AD) plants treating biodegradable municipal, commercial and industrial wastes in the EU is set to increase rapidly in the next five years as central, regional and local governments implement strategies to meet the challenging targets for landfill diversion, CO₂ reduction and renewable energy generation. With such a large and rapid infrastructure development programme, decision makers must balance three key factors when deciding the nature and characteristics of the treatment infrastructure developed:

1. Economic – what solution provides the best economic value?
2. Technical – the solution must meet the technical requirements (i.e. effective waste treatment), and achieve high landfill diversion and recycling rates.
3. Environmental – ensure that the solution is environmentally sound and compares favourably with alternative options.

In the EU, anaerobic digestion is viewed as one of the most economic and technically appropriate method

for treating biodegradable municipal wastes such as source segregated food waste. The choice of whether to utilise biogas for electricity and heat generation, or upgrading the biogas to biomethane for transport fuel use or injection to the gas grid, is largely an economic decision or in many cases influenced by specific site restrictions. Increasingly, however, stakeholders are requesting guidance on the environmental costs and benefits of the various infrastructure options open to them.

Biogas production utilizes organic waste from renewable resources, and can be used in both small (<500 kWel) and large-scale (>500 kWel) energy generation plants and in decentralized energy generation. Therefore, if sustainably managed, biogas could make significant contribution to energy security and mitigation of the GHG emissions. The biogas is mainly used for electricity and heat generation and as substitute for natural gas after upgrading and purification to biomethane [51]. Applications of the spent feedstock or digestate from biogas production as fertilizer minimizes the use of energy intensive chemical fertilizers to further alleviate GHG emissions. The CO₂ neutral potential of fuels produced from renewable resources, hence, the minimal negative impacts to climate change, is often a strong argument in favour of renewable energies [52]. However, the impact mitigation may be reduced due to the energy and material consumed for cultivation (cf. Corn silage, grass silage, whole wheat plant silage) and the transport of feedstock. Additional emissions also arise from biogas plant operation, biogas utilization, and demand for transportation and disposal of the process residues and the digestate. All these factors have to be considered in quest for an environmental friendly and sustainable energy production from biogas [53]. A positive energy balance in biogas production and utilization pathways, including the application of AD process for waste management also enhances environmental sustainability of biogas as a renewable fuel [54].

Research literature on the assessment of environmental impacts of biogas production systems have generally focused on: applications of renewable resources in the power sector in general [55,56]; the specific feedstock by geographical regions [57, 58]; case studies of biogas production plants [52, 59]; single biogas utilization pathways [60, 61], and; individual processes in biogas production chains [62]. Most have not benchmarked the potential impacts of technological variations to enable accurate assessment of sustainability. The study by Börjesson and Berglund [63] analyzed the process from feedstock sources to biogas utilization, including digestate handling in various scenarios, but they did not consider a range of innovative technologies that have become available for deployment of biogas, e.g., fuel cell technology, Stirling engine, Organic Rankine Cycle (ORC) and micro gas turbine. Most of the papers have also assigned the cumulative emission loads to impact categories created by a Life Cycle Assessment (LCA) in such a way that allocation of specific emissions is still obscure. Therefore, there is requirement for an integrated assessment of biogas technology options, based on multiple feedstock used for AD process combined with potential biogas utilization pathways and different digestate processing and handling methods.

The Life Cycle Inventory (LCI) of biogas production and utilization processes presented study by Poeschl et al

[64] has been used to locate unit processes that could provide opportunities to minimize emissions to the environment on the basis of feedstock supply logistics, biogas production processes, utilization pathways and digestate management strategies. Analyses have shown that the variations in emission level can be significant, with CO₂, fossil and CH₄, biogenic emissions as most significant in the biogas production and utilization processes. Life Cycle Assessment (LCA) [65] was conducted to compare different biogas systems to establish the basis for further improvement of environmental and public health impacts, hence, enhance environmental sustainability of biogas production and utilization pathways. Impacts of realistic case scenarios were analyzed by considering potential variations in; (i) feedstock type, (ii) biogas utilization options, and (iii) digestate processing and handling unit processes. The observed range of variations on the potential reduction of environmental impacts (established by LCA) and enhancement of energy conversion efficiency (established by energy balance) indicated a high inherent optimization potential based on judicious selection of biogas production and utilization pathways.

A life cycle assessment has recently been completed of potential biogas infrastructures on a regional scale [66]. Centralised and distributed infrastructures were considered along with biogas end uses of Combined Heat and Power (CHP) and injection to the gas grid for either transport fuel or domestic heating end uses. Damage orientated (endpoint) life cycle impact assessment method identified that CHP with 80% heat utilisation had the least environmental impact, followed by transport fuel use. Utilisation for domestic heating purposes via the gas grid was found to perform less well. A 32% difference in transportation requirement between the centralised and distributed infrastructures was found to have a relatively small effect on the overall environmental impact. Global warming impacts were significantly affected by changes in methane emissions at upgrading stage, highlighting the importance of minimising operational losses.

5 DRY REFORMING REACTION

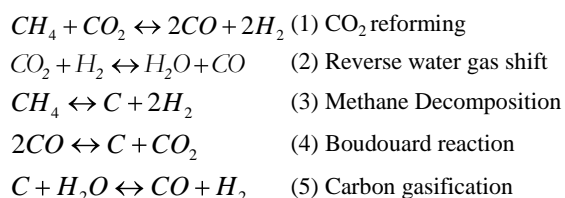
5.1 General aspects

As already mentioned, biogas is a clean and moreover an environmental friendly fuel, that is typically generated from anaerobic degradation of biomass (referring mainly to agricultural and/or industrial residues). Consisting mainly of CO₂ and CH₄, is an attractive renewable carbon source, making its exploitation being advantageous from both financial and environmental points of view [67]. Biogas composition varies depending on the source ranging from 55 to 65% for methane (CH₄) and 30 to 45% for carbon dioxide (CO₂) [68]. Catalytic processes that can be applied for biogas valorisation through hydrogen or syngas production are the same that are used for natural gas (methane) reforming: steam reforming, partial oxidation, dry and auto-thermal reforming [69]. The most promising one has been considered to be the CO₂ reforming of CH₄ or Dry Reforming of Methane (DRM) resulting to synthesis gas production.

Catalytic reforming of CH₄ with CO₂ (methane dry reforming) has attracted considerable scientific interest

for a long period of time over the past years, as it offers the possibility of simultaneous removal of two inexpensive and abundant carbon containing sources, which are also considered as mainly greenhouse gasses. Moreover, the utilization of CO₂ as a feedstock for producing chemicals is tempting not only because it can contribute to mitigation of greenhouse gas emissions, but also because it is an interesting challenge in exploring new concepts and new opportunities for catalysis and chemical industry. Dry reforming (DRM) process is considered to be more advantageous than the steam reforming or partial oxidation ones concerning syngas production since the H₂/CO ratio of its main product is near to one, suitable for Fischer–Tropsch and other synthesis reactions for the production of liquid hydrocarbons [70-72].

The network reactions in dry reforming may be summarised as follows:



5.2 Thermodynamic equilibrium analysis of CH₄–CO₂ mixture

In order to elucidate the biogas dry reforming reaction, theoretical values of product gas concentration for temperature values ranging from 300 to 1000°C were calculated. The software that has been used was the HSC Chemistry 5.11 and in order to calculate the conversion rates at the given operating reaction conditions the concept of minimizing the free energies has been applied. The calculations were performed at atmospheric pressure and stated temperature range. Fig. 4 depicts the thermodynamic equilibrium compositions of CH₄:CO₂=1.5 mixture at the temperature range of 300–1000°C and an atmospheric pressure.

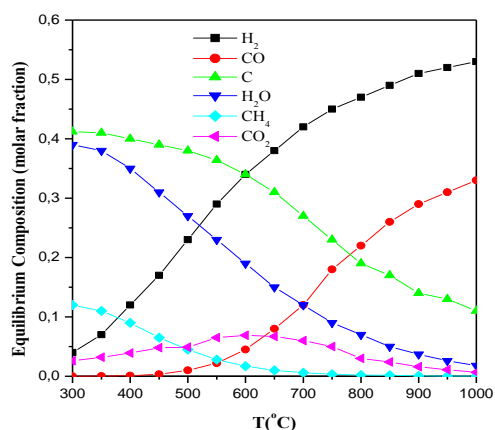


Figure 4: Thermodynamic equilibrium composition of CH₄:CO₂ =1.5 (molar) mixture as a function of temperature at P=1 atm.

5.3 Supported catalysts for DRM reaction

During the past decades, the catalytic process of carbon dioxide (dry) reforming of methane has received attention; much effort has been focused on development of catalysts which exhibit high activity and high yield

towards synthesis gas production, while they are also quite resistant to coking, thus displaying stable long-term operation, as well. The catalysts based on noble metals are reported to be less sensitive to coking than are nickel-based catalysts [73-79]. A list of supported noble metal catalysts used for the methane dry reforming reaction is presented in Table 1.

On the other hand, extensive development of supported catalysts, based on non-noble metals, such as Fe, Co, Ni, is preferred from the industrial standpoint due to economical reasons. The main drawback of this kind of catalysts is that they usually exhibit high initial activity, which was almost completely lost within a couple of hours; most probably due to extensive carbon deposition on their surface, originating either from the methane decomposition or CO disproportionation. However, considering the aspects of high cost and limited availability of noble metals, it is more desirable, from the industrial point of view, to develop nickel-based catalysts which are resistant to carbon deposition and exhibit stable operation for extended period of time [80-83]. A list of supported non-noble metal catalysts for the methane dry reforming reaction is presented in Table 2.

Table 1: Catalytic performance of supported noble metal catalysts for the DRM reaction

Noble Metal Catalysts	Methane Conversion (%)	H ₂ /CO	Ref.
Rh(0.5wt%) on YSZ	90	-	22
Rh(0.5wt%) on Al ₂ O ₃	84.4	-	11
Pt(0.4at/nm ²) on nanofibrous Al ₂ O ₃	65.5	0.68	23
Ru (2wt%) on MgAlO _x	95	-	13
Ru (2wt%) on MgAlO _x	95	1.91	24
Rh(1wt%) on spinel	68	0.97	25

Table 2: Catalytic performance of supported non-noble metal catalysts for the DRM reaction

Nickel Catalysts	Methane Conversion (%)	H ₂ /CO	Ref.
Ni(17wt%) on La ₂ O ₃	70	-	8
Ni(5wt%) on CaO-Al ₂ O ₃	51.32	0.85	26
Ni(5wt%) on CaO-Al ₂ O ₃	73	-	18
Ni(2wt%) on α-Al ₂ O ₃	77.3	1.40	21
Ni(14wt%)-K(0.5wt%) on γ-Al ₂ O ₃	81.3	0.4	27
Ni(13.5wt%)/K(2wt%) on CeO ₂ -Al ₂ O ₃	89	-	28
Ni(xwt%) on ZrO ₂ -MgO	27	-	29
Ni(15wt%) on CeO ₂ -ZrO ₂	55	0.70	15
Ni(8wt%) on Ca/α-Al ₂ O ₃	84.6	0.966	28
Ni(15wt%) on γ-Al ₂ O ₃	87.25	1.40	This study

From literature surveys and analyses, [84-100] it can be seen that noble metals catalysts exhibit promising catalytic performance, in terms of methane conversion, as well as yield to synthesis gas. Among ruthenium, rhodium, and platinum catalysts, ruthenium revealed the most attractive catalytic performance toward DRM reaction. Nevertheless, transition metals such as Ni and Co are often preferred, because noble metals are more scarce and costly. Nickel catalysts have propensity to be deactivated due to surface coke formation and sintering of the nickel particles. Despite this, it would be more

desirable, from industrial point of view, to develop nickel-based catalysts which would be resistant to carbon deposition and exhibit stable operation for extended periods of time. Carbon is one of the major causes of catalyst deactivation and when the rate of carbon formation is greater than the rate of carbon gasification, carbon accumulates in the catalyst bed, causing catalyst deactivation and plant shutdown. Industrially, this problem is solved by addition of excess steam or oxygen, which increases the cost of syngas production. The use of suitable supports, such as CeO₂ and La₂O₃ can prevent the carbon deposition to some extent. The other way to improve the anti-coking property of catalyst is to introduce a second metal component to form a bimetallic catalyst system.

6 BIOGAS TO SYNGAS OVER NICKEL CATALYSTS

In order to evaluate the catalytic performance of nickel catalysts for the biogas reforming reaction, a series of nickel catalysts with different metal loadings (7wt% and 15wt%) were synthesized using the wet impregnation method and tested for syngas production.

Specifically, the biogas reforming reaction was carried out at atmospheric pressure in a fixed-bed continuous flow reactor. The catalytic reactor was made of quartz and was operated at temperatures ranging from 700 to 900°C, at atmospheric pressure (1 atm) and with a constant molar CH₄/CO₂ ratio of 1.5, simulating an ideal model biogas. The total flow rate was 200 ml min⁻¹, controlled by mass flow meters (MW Instruments, MFC) and consisting of a mixture of CH₄/CO₂ (100 ml min⁻¹) in He (100 ml min⁻¹) corresponding to a gas hourly space velocity (GHSV) of 1200 h⁻¹. The reaction temperature was controlled by a thermocouple placed in the middle of catalyst-bed. The amount of catalyst used during the catalytic runs was 10 cm³ and it was diluted with 10 cm³ γ-Al₂O₃ pellets calcined at 800°C. Product gases were analyzed by online gas chromatography (Agilent 7890 A) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Before catalytic measurements the catalyst was reduced in situ at 700°C for 2 h in flow of pure H₂ for activation.

According to the analysis and metering mentioned above, the conversion of CO₂ and CH₄ can be calculated as defined in Eqs. (6) and (7), while the yield of H₂ can be calculated as defined in Eqs. (8) respectively:

$$X_{CH_4} (\%) = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}} \times 100 \quad (6)$$

$$X_{CO_2} (\%) = \frac{F_{CO_2,in} - F_{CO_2,out}}{F_{CO_2,in}} \times 100 \quad (7)$$

$$Y_{H_2} (\%) = \frac{F_{H_2}}{2F_{CH_4,in}} \times 100 \quad (8)$$

The methane and carbon dioxide conversions for the catalysts tested in biogas reforming reaction, carried out at temperature values ranging between 700 to 900°C, are shown in Figure 5. It is seen that in the lower temperature range (700-820°C), Ni/Al₂O₃ with 7wt% nickel, gave slightly lower methane and CO₂ conversions. For both catalysts, the conversions increase with increasing

temperature, reaching high values above 820°C even for low metal loadings.

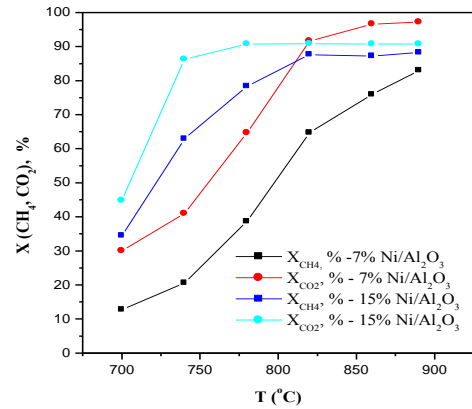


Figure 5: Effect of reaction temperature to methane and carbon dioxide conversion

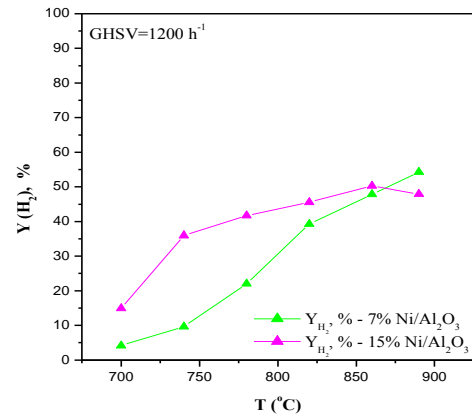


Figure 6: Effect of reaction temperature to hydrogen yield

The effect of reaction temperature on catalyst activity and hydrogen yield has been studied. Figure 6 presents the hydrogen yield variation with temperature for both catalysts. It can be depicted that hydrogen yield values increase with increasing nickel loading for reaction temperatures ranging between 700-850°C. Moreover, for temperature values higher of 850°C hydrogen yield reaches its maximum value for both catalysts.

Furthermore, as it can be depicted from Figure 7, the higher methane conversion values, at temperature range from 700 to 850°C for the catalyst with the higher metal loading, results in an increase to hydrogen production, and a further increase in the H₂/CO molar ratio to the product mixture.

The catalytic performance results of the nickel supported on alumina catalysts for the biogas reforming reaction at a temperature value of 860°C is depicted in Table 3. It can be seen that increasing the nickel loading from 7 to 15 wt%, methane conversion and hydrogen yield increase significantly, which can be attributed mainly to the methane decomposition reaction, leading to higher carbon deposition on catalyst surface. The results (Table 3) also reveal that that H₂/CO ratio increases significantly, whereas there are slight differences in CO₂ conversion values for both catalysts.

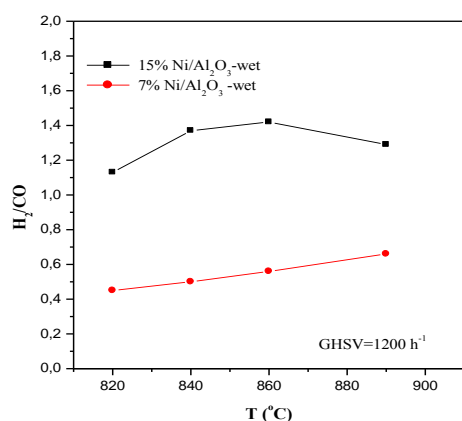


Figure 7: Effect of reaction temperature to H₂/CO molar ratio

Table 3: Catalytic performance of nickel supported on alumina catalysts for the biogas reforming reaction at 860°C

Catalyst	X _{CH₄} %	X _{CO₂} %	Y _{H₂} %	H ₂ /C O	Carbon (mgC/ mg cat)
7Ni/Al ₂ O ₃	71.5	95.0	48.5	0.55	0.180
15Ni/Al ₂ O ₃	87.3	91.0	50.3	1.40	0.330

7 CONCLUSIONS

The biogas produced by anaerobic digestion is a clean and environmentally friendly fuel, although it contains only about 55–65% of CH₄. Other constituents include 30–40% of CO₂, fractions of water vapour, traces of H₂S and H₂, and possibly other contaminants (e.g. siloxanes). In most circumstances, it can be introduced in power gas engines (preferably in a combined heat and power (CHP) installation) without further purification. However, upgrading is needed for more novel applications like vehicle fuel and fuel cells. If properly upgraded, the biogas can also be introduced in the natural gas grid. The latter applications obviously provide a higher added value to the biogas.

Recent research is focused on the conversion of biogas to organic (high value added chemicals). This is mostly achieved by converting the methane into syngas (mixture of H₂ and CO), and using this gas as a feedstock in organic industry. Therefore, the reforming reaction of a clean model biogas, which consists mainly of 60% methane (CH₄) and 40% carbon dioxide (CO₂), for synthesis gas production over Ni supported alumina catalysts, was experimentally investigated. It can be concluded that the DMR process seems to be very promising producing syngas with an elevated H₂/CO ratio about to 1-1.5, which is considered to be the most appropriate for Fischer–Tropsch and other synthesis reactions for liquid hydrocarbons production.

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