Container-Sized CO$_2$ to Methane: Design, Construction and Catalytic Tests Using Raw Biogas to Biomethane

Rohit Gaikwad 1,2,*, Sebastian N. B. Villadsen 3, Jan Pihl Rasmussen 2, Flemming Bjerg Grumsen 1, Lars Pleth Nielsen 4, Gary Gildert 5, Per Møller 1 and Philip Lødrup Fosbol 3,*

1 Department of Mechanical Engineering, Technical University of Denmark, 2800 Kongens Lyngby, Denmark; fbgr@mek.dtu.dk (F.B.G.); pm@epc-info.dk (P.M.)
2 Elplatek A/S, Meteorvej 10, 8700 Horsens, Denmark; jpr@elplatek.dk
3 Department of Chemical and Biochemical Engineering, Technical University of Denmark, 2800 Kongens Lyngby, Denmark; snbvi@kt.dtu.dk
4 Tribology Centre, Danish Technological Institute, Kongsvang Alle 29, 8000 Aarhus, Denmark; lpn@teknologisk.dk
5 Unicat Catalyst Technologies, Inc., Alvin, TX 77512-1516, USA; ggildert@unicatcatalyst.com
* Correspondence: rvg@elplatek.dk (R.G.); plf@kt.dtu.dk (P.L.F.); Tel.: +45-4525-2868 (P.L.F.)

Received: 2 November 2020; Accepted: 4 December 2020; Published: 7 December 2020

Abstract: Direct catalytic methanation of CO$_2$ (from CO$_2$/CH$_4$ biogas mixture) to produce biomethane was conducted in a pilot demonstration plant. In the demonstration project (MeGa-StoRE), a biogas desulfurization process and thermochemical methanation of biogas using hydrogen produced by water electrolysis were carried out at a fully operational biogas plant in Denmark. The main objective of this part of the project was to design and develop a reactor system for catalytic conversion of CO$_2$ in biogas to methane and feed biomethane directly to the existing natural gas grid. A process was developed in a portable container with a 10 Nm$^3$/h of biogas conversion capacity. A test campaign was run at a biogas plant for more than 6 months, and long-time operation revealed a stable steady-state conversion of more than 90% CO$_2$ conversion to methane. A detailed catalytic study was performed to investigate the high activity and stability of the applied catalyst.

Keywords: biogas; biomethane; CO$_2$ methanation; demonstration pilot plant; adiabatic reactors; movable container

1. Introduction

The biogas market is growing in Europe [1]. As the European gas network is trying to limit their dependency on fossil fuels and external suppliers, biogas is growing in its importance. By 2040, biogas may be the largest gas contributor to the grid in both the UK and the Netherlands [2]. However, as the natural gas consumption in the EU in 2015 was 416 billion Nm$^3$, and the potential biogas production was estimated to cover only 18.7% of this, there is an energy gap to be closed if biogas should replace natural gas in Europe [3,4].

Biogas consists of 48 to 65% methane (CH$_4$) and 36 to 41% carbon dioxide (CO$_2$) with N$_2$, O$_2$, and other different trace elements [5]. As CO$_2$ reduces the burning value by diluting the CH$_4$, biogas is considered a low-quality gas. Hence, many impurities must be removed before the biogas can be injected into the natural gas grid [6,7]. The process of purifying the CH$_4$ from the biogas is referred to as a first-generation biogas upgrading [8]. The amount of first-generation upgrading plants throughout Europe is growing with 540 plants in 2017 [1].
In first-generation biogas upgrading, CO\(_2\) is the main impurity and is removed by conventional carbon capture technologies, such as membrane, pressure swing absorption (PSA), amine/water scrubbing, or cryogenic technologies [9,10]. The CO\(_2\)-separated purified methane, also known as biomethane, is generally injected into the natural gas grid [11].

The storage or emission of the separated CO\(_2\) results in a large amount of wasted carbon source. In principle, this is a source of C-building blocks for chemicals and fuels. The emission of CO\(_2\) into the atmosphere increases the CO\(_2\) concentration in the air, which causes global warming and climate changes. In the second-generation biogas upgrading, the biogas is considered a carbon source where the biogas’ CO\(_2\) content is upgraded without separation [8]. Direct CO\(_2\) conversion to methanol or higher alcohols is not a viable option, as the CH\(_4\) from biogas must be converted to syngas before alcohol synthesis [12]. Additionally, if the CH\(_4\) is converted into syngas, the CH\(_4\) will add valuable H\(_2\) to the system during the reforming process. Alternatively, the CO\(_2\) hydrogenation to methane allows utilization of CO\(_2\) in biogas without further separation.

The availability of highly selective and efficient methanation catalysts allows CO\(_2\) conversion to CH\(_4\) [13]. This methanation process is known as the Sabatier process, which follows the exothermic reaction in Equation (1) [14].

\[
\text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta H_{298K} = -165 \text{ kJ/mol} \quad (1)
\]

This process requires large amounts of hydrogen (H\(_2\)) and has therefore, been proposed to store renewable energy through electrolysis [15]. In Denmark, wind turbines provide excess energy, which can be used for hydrogen production [16]. Methanation provides an excellent route to store renewable energy in the form of methane, which can be stored in a natural gas storage facility and transported using the gas grid on-demand to balance total power consumption. A nickel-based catalyst is typically used for the Sabatier process as it is known to have high selectivity and conversion [17]. Given these properties, converting a CH\(_4\)/CO\(_2\) gas mixture to pure CH\(_4\) is possible [18].

For biogas utilization, the Sabatier process has several advantages. Firstly, the usual operating conditions of a Sabatier reactor are close to ambient (350–400 °C and down to atmospheric pressure) [16], and secondly, only a single process is required for the upgrading. For comparison, methanol production from biogas requires two processes (reforming and methanol synthesis) with usual operating conditions of up to 830–910 °C and 50–100 bar [19]. Although process conditions are advantageous, there are significant cost and process constraints associated with the Sabatier process before its industrial-scale implementation. The reaction produces a significant amount of heat, raising reactor design constraints, and efficient heat removal systems are required to avoid catalyst deactivation and formation of local hotspots in the fixed bed reactor. Given this, many reactor design concepts were developed, such as multiple fixed bed reactors and heat exchangers in series [20], large recycling loops [21], feed and catalyst dilution [22,23], to mention some of the complexities with the Sabatier process.

Nickel catalysts are known to deactivate due to sulfur impurity in the biogas feed, which needs to be removed to parts per billion (ppb) levels before the feed gas is passed over the catalyst bed [24,25]. The main sulfur impurity in biogas is H\(_2\)S, with concentrations up to 10,000 parts per million (ppm) [26]. Today’s biogas applications, i.e., heat and power generation or first-generation upgrading, require the H\(_2\)S content of the desulfurized biogas to be <500 ppm and <4 ppm, respectively [27]. However, for second-generation utilization of biogas with a nickel catalyst, the H\(_2\)S content of biogas is required to reduce to 10–100 ppb [28]. If the H\(_2\)S is not removed from the biogas, it will react with nickel, blocking active sites and causing deactivation of the nickel catalyst according to the deactivation reaction (Equation (2)) below [20]:

\[
\text{H}_2\text{S} + \text{NiO} \leftrightarrow \text{NiS} + \text{H}_2\text{O} \quad \Delta G_{300K} = -48.5 \text{ kJ/mol} \quad (2)
\]

Thus, for second-generation utilization of biogas, further reduction of the H\(_2\)S content is required compared with today’s technologies.
This paper presents the results from thermocatalytic biogas upgradation to methane from the Methane Gas for Storage of Renewable Energy (MeGa-StoRE) demonstration project. In Figure 1, the project is schematically presented, where the desulfurization section purifies the raw biogas from the storage tank before entering the catalytic methanation, upgrading CO\textsubscript{2} using H\textsubscript{2}. In this case, the H\textsubscript{2} is produced by water electrolysis to produce biomethane, which is directly fed into the natural gas grid.

![Figure 1. Schematic presentation of the MeGa-StoRE project, including the methanation container and Green Hydrogen container.](image)

The overall project goal was to demonstrate second-generation biogas upgrading through the Sabatier process. Part of the project goal was to develop a new desulfurization process to meet the nickel catalyst requirements used in the thermochemical upgrading process. The MeGa-StoRE demonstration unit is shown in Figure 2. It included a larger 2-container-sized demonstration pilot plant. Hydrogen is produced in one container (not shown), and methanation of CO\textsubscript{2} (from biogas) is performed in the second container (shown). The present article mainly focuses on the methanation process. The desulphurization and hydrogen production processes are not discussed in the present work.

![Figure 2. The MeGa-StoRE project container situated at the NGF Nature Energy biogas plant, Midtfyn. In the container, a pilot plant desulfurization and methanation systems are present.](image)

This project provides a localized solution for small-scale biogas producers or farmers to convert their CO\textsubscript{2} in biogas into methane using green electricity, enabling energy storage. The container-sized process solution is a new simple approach for complex chemical processes, which until now is only working at a large scale at remote locations. This plug and produce approach for chemical processes will provide a new platform for many chemical processes.

Additionally, in this MeGa-StoRE project, we are trying to provide solutions to reduce global warming, provide alternate energy storage solutions, and promote renewable energy use. The project
is linked directly to the Danish Government's ambitious plan to be independent of fossil fuel by 2050 and cut the greenhouse gas emission by 70% by 2030.

2. Results and Discussion

2.1. Thermodynamic Calculations

CO₂ methanation reaction is exothermic in nature, where 4 moles of H₂ reacts with one mole of CO₂ to form one mole of CH₄ and 2 moles of H₂O as shown in the main reaction (Equation (1)).

Additionally, this main reaction is also followed by an exothermic reversed water gas shift (RWGS) reaction and endothermic CO methanation, as shown in Equations (3) and (4), respectively.

\[ \text{H}_2 + \text{CO}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O} \quad \Delta H_{298 \, K} = 41 \, \text{kJ/mol}. \]  

\[ \text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H_{298 \, K} = -206 \, \text{kJ/mol} \]  

The overall CO₂ methanation reaction (Equation (1)) is associated with a decrease in the overall number of gas molecules and releasing heat. Hence, according to Le Chatelier’s principle, the CO₂ methanation process should favor high pressure and low process temperature for high methane yield [29]. Thermodynamic equilibrium calculations were performed using Aspen Hysys V11 by the Gibbs free energy minimization method to identify the reaction conditions with maximum CO₂ conversion and methane selectivity. Figure 3 shows the effect of temperature and pressure versus CO₂ conversion.

![Figure 3](image-url)

**Figure 3.** Thermodynamic equilibrium curve of (a) CO₂ conversion (X_{CO₂}) and methane selectivity (S_{CH₄}) at 8 bar, 200–600 °C, (b) CO₂ conversion (X_{CO₂}) at 1, 4, 8, and 16 bar pressure at 200–600 °C using CO₂:H₂, 1:4 ratio.

Figure 3a shows the temperature effect on CO₂ conversion and CH₄ selectivity. The conversion kinetics are infeasible at low temperatures, while at high temperatures, the reaction is thermodynamically unfavorable. Almost complete CO₂ conversion and CH₄ selectivity are observed at a temperature of 200 °C, and further increases in the temperature cause the CO₂ conversion to decrease. At a stoichiometric H₂:CO₂ ratio of 4, the optimum temperature range for CO₂ methanation is 200 to 500 °C, where CO₂ conversion drops by only 20% and the CH₄ selectivity is 99%. With an increase in the temperature above 500 °C, the CO₂ conversion drops with CH₄ selectivity. CO and carbon formation is favored at a high-temperature, which reduces CH₄ selectivity drastically [30]. Figure 3b shows the effect of pressure on CO₂ conversion at different temperatures. The calculations reveal that an increase in the pressure favors the methanation reaction.
Additionally, according to Jurgensen et al., the elevated pressure increases the temperature at which carbon deposits occur \[31\]; hence, reaction at high pressure has dual advantages. However, the CO\(_2\) conversion is increased with increasing pressure up to a certain pressure, while further increase in the pressure does not significantly increase the CO\(_2\) conversion at high temperature. Hence, all reactions were performed at an optimum 8 bar pressure.

Reactor design plays an important role in exothermic CO\(_2\) methanation, especially using adiabatic reactors. The benefits of adiabatic reactors are that they are relatively simple in construction and maintenance, but it is not easy to manage the heat generated \[32\]. There is a risk of CO and/or carbon formation in case of too high reactor temperature. CO can be just a byproduct, but the catalyst surface’s carbon formation may completely deactivate the catalyst over time. Hence reaction heat management is of utmost importance to avoid carbon formation and catalytic deactivation. Generally, the heat is either managed by a specially tailored design reactor system, efficient cooling fluid surrounding the reactor, or diluting the feed gas with an inert gas to lower the heat generation per volume. Our state-of-the-art reactor design managed the heat generation per volume by adding total reactant feed in small portions at the inlet of all four reactors and circulating efficient cooling oil. This process resulted in stable temperature management within the optimal temperature range (<500 °C), and we achieved almost equilibrium conversion as expected by the above simulations (see also the discussion in Section 3).

Table 1. shows the expected temperature of the adiabatic reactor system, which was calculated by Aspen Hysys. The actual reactor temperature recorded by a thermocouple placed in the middle of the reactor showed that the reactor temperature was within the optimum range.

| Reactors | R1  | R2  | R3  | R4  |
|----------|-----|-----|-----|-----|
| Expected temperature (°C) | 471 | 488 | 421 | 348 |
| Actual reactor temperature (°C) | 485 | 485 | 475 | 358 |

2.2. Experimental Results

The pilot plant methanation system ran for approximately 6 months of operation hours, including the startup and shut down by varying reaction conditions to establish stable operating conditions. The methanation process ran continuously for 6 h at optimized reaction conditions using 8 Nm\(^3\)/h biogas and 16 Nm\(^3\)/h H\(_2\), and it was stable over the operation hours. Figure 4 shows the experimental data from the methanation reactor for CO\(_2\) conversion. The CO\(_2\) conversion was approximately 90% and remained almost steady over the test period. The methane selectivity was >99%. The catalyst was used for more than 500 h and did not show any sign of deactivation or activity loss over the entire period. Similar observations were also seen from catalyst characterization, where no significant carbon formation was observed by XRD, BET, TGA, which could suppress or inhibit the catalyst activity. Physically no carbon formation was observed on the catalyst surface at the inlet of the reactor, and no pressure drop change was observed across the reactors throughout the test campaign. This result indicated no significant carbon formation which could block the fixed bed reactors.
2.3. Catalyst Characterization

Figure 5 shows the X-ray diffraction (XRD) pattern of a fresh and used catalyst, respectively. The fresh catalyst shows broad XRD peaks corresponding to a small noncrystalline nature. The characteristic diffraction peaks at 37.2, 43.1, 62.9, and 75.2° corresponded to NiO (JCPDS = 47–1049), while the broad peak at 44° could be attributed to both NiO and Ni [33,34]. According to the database, the diffraction peaks at 44.5 and 51.9° were assigned to Ni (JCPDS = 87–0712). A small fraction of a catalyst sample after the reaction was taken from all four reactors inlet after a more than 6-month test campaign. The used catalyst diffraction pattern shows that the nickel crystallites have grown in size; according to the XRD database (JCPDS = 44–1418), most of the peaks are assigned to the Ni$_3$S$_2$ phase.

The Ni$_3$S$_2$ phase formation after the reaction indicated that feed biogas was contaminated with sulfur-containing compounds. This could be because of a sudden interruption of the desulfurization process during the test campaign. The backup carbon filter could not remove all the bulk sulfur from the biogas to ppb levels required by the Ni catalyst. A potential future improvement could be a sacrificial ZnO adsorbent before the active Ni catalyst, which can reduce the sulfur level to ppb in
case of such unforeseen conditions [35,36]. Still, it was surprising to see that the catalyst was active and showing more than 90% CO$_2$ conversion at all the time. This could be because the catalyst had better sulfur tolerance capability, or there was a possibility that only the top layer of the catalyst was poisoned as it was first to expose to biogas. Moreover, later, part of the catalyst was still active, which provides an active surface for the methanation reaction. According to Hepola et al., sulfur’s catalyst poisoning decreased along the catalyst bed [37]. Furthermore, before the reactor’s daily startup, hydrogen treatment might have reactivated some of the nickel sites [38]. A complete mechanistic study of sulfur poisoning was not a part of this pilot plant test campaign. The diffraction peak at 26.2° in both diffraction patterns are from the graphite base (JCPDS = 75-2078) used to support the catalyst sample for XRD analysis.

The Temperature Programmed Reduction of H$_2$ (H$_2$-TPR) is usually employed for estimating the reducibility of the catalyst. Figure 6 shows the H$_2$-TPR results for the fresh and used catalysts, respectively. The reduction patterns for a fresh catalyst showed two main reduction peaks; one at a lower temperature around 244 °C and another at a higher temperature above 550 °C. A sharp hydrogen consumption peak at 244 °C was attributed to reducing free NiO or weakly bonded NiO with Al$_2$O$_3$. At 579 °C, a broad peak corresponded to the reduction of a NiO, which is strongly bonded with Al$_2$O$_3$ [39]. A reduction at 400–600 °C generally corresponds to less reducible NiO species present in an aluminum oxide rich phase [40]. The H$_2$-TPR of used catalysts showed low-intensity peaks at 213, 252 °C indicating that very low reducible nickel species were present in the catalyst after the reaction.

![Figure 6. H$_2$-TPR of the catalyst before and after reaction at 8 bar, 350–500 °C.](image)

The BET surface area results for fresh and used catalysts are shown in Table 2. It is seen that the surface area of the used catalyst decreased by 75.6 m$^2$/g compared to the fresh catalyst. The catalyst reduction, carbon deposition on the catalyst surface leading to pore blockage, and crystalline phase transition leading to metal and support sintering are mainly responsible for the loss in the surface area [41–43].

| Catalyst       | $S_{BET}$ (m$^2$/g) |
|----------------|---------------------|
| Fresh catalyst | 170.7               |
| Used catalyst  | 95.1                |

In our case, XRD shows phase transition and increase in crystalline size due to the Ni$_3$S$_2$ phase, and this could be the reason for the loss in the surface area as the Ni$_3$S$_2$ phase can accelerate the
particle sintering and loss of surface area [44–46]. However, no significant catalytic activity loss was observed during the catalytic reaction, which shows that carbon species blocked no active species. Further detailed studies are needed to clarify this catalyst phase formation and its relationship with catalytic activity.

It is reported that the carbon deposition starts from the formation of graphitic carbon (150–250 °C) and amorphous carbon (250–500 °C) islands on the catalyst surface. The carbon species may encapsulate the active nickel sites, causing the catalyst’s deactivation, or the carbon may form filamentous carbon on the catalyst surface. The latter does not encapsulate active sites and will only reduce the catalytic activity [47]. Since we did not observe drastic changes in the catalytic activity over a 6-month test campaign, the latter type of carbon formations may very likely occur and thus be responsible for the loss in the overall surface area along with sulfur poisoning.

The fresh and used catalyst was tested for the decomposition of any species using thermo-gravimetric analysis (TGA). Figure 7a,b shows the TGA of a fresh and used catalyst, respectively. The results indicated that the total weight loss for fresh and used catalysts was ca. 8.2 and 9.6%, respectively. The fresh catalyst’s loss was due to water evaporation, decomposition of carbonates, and surface hydroxyl species. For the used catalyst, the change in weight loss was only 1.4%, which was negligible compared to the total time the catalyst was in operation. The small changes in the TGA graph of the used catalyst observed at 170 and 700 °C could be due to surface adsorbed species or carbon [48], but no major weight loss indicates that the carbon deposition was negligible on the catalyst. Furthermore, these observations were in good agreement with the decrease in the surface area and no major loss in catalytic activity.

![Figure 7](image_url)

**Figure 7.** Thermo-gravimetric analysis of fresh (a) and used (b) catalysts.

3. Materials and Methods

The methanization process was tested at a fully operating biogas plant (NGF Nature Energy, Midtfyn, Broby, Denmark). A pilot plant methanation reactor system was developed in a modular, movable container and a desulfurization plant, as shown in Figure 1. The pilot demonstration plant was constructed to work up to 10 Nm$^3$/h biogas conversion to methane at a temperature up to 600 °C and 15 bar pressure. A cylindrically shaped Ni-based methanation catalyst, MC-750R (supplied by Unicat), was used for the reaction. The catalyst consists of >65% nickel with support and binder. The catalytic tests were performed using biogas, which was directly supplied from the biogas digestion unit at the NGF Nature Energy biogas plant. Initially, the biogas was passed through an electro-catalytic scrubber, where almost all sulfur was removed. A backup carbon filter was installed to remove any traces of H$_2$S, which during testing was allowed to pass through the desulphurization plant. This carbon filter removes H$_2$S and other sulfur species to an undetectable range. Hydrogen was produced using a small-scale water electrolysis plant in a container. This container was running at all times during the campaign producing hydrogen at 16 Nm$^3$/h using a specially designed electrolyzer system developed and run by Green Hydrogen, Denmark.
3.1. Methanation Reactor

The methanization reactor system consisted of four reactors (R-1 to 4) placed in a series. Figure 8 illustrates the coupling of the feed gas, four reactors, and product separator. The reactors were made up in AISI304SS with an approximately 50 mm inner diameter and 8 L total volume, loaded with catalyst and support. The impact of conversion taking place on the reactor walls was assumed negligible. In an exothermic reaction, efficient heat management of the catalyst bed was required to avoid catalyst deactivation and maintain high activity. Hence, heat transfer oil of maximum bulk fluid operating temperature 370 °C (XCELTHEM SST) was used for the external heating and cooling of the reactant and product gases, respectively. The temperature of the oil was maintained using a 6 kW startup heater. The preheated oil was circulated using a specially designed spiral coiled tube around E-1 to preheat the feed gas. Moreover, to cool down the gas coming out reactor R-1 to R-4, the oil was circulated around the E-2 to E-5 heat exchangers through a coiled tube, respectively.

![Figure 8. Reactor design of packed bed reactor (R-1, R-2, R-3, R-4), feed heater (E-1), and cooler (E-2, E-3, E-4, E-5) and product separator.](image)

The oil was pumped from the reservoir to circulate in reactor outlets through the spiral coil (E-2, E-3, E-4, E-5) at the desired flow to maintain individual reactor inlet gas temperature. Similarly, the feed, fraction of biogas, and hydrogen gas to the first reactor were passed through the preheater, where the temperature was maintained at 200 °C by circulating preheated oil. The flow of the oil was modulated to maintain the desired inlet gas temperature.

A detailed temperature profiling at each reactor inlet and outlet allowed us to monitor each reactor’s catalytic performance. The reaction temperature profile was monitored by placing the thermocouple at each reactor’s top, middle, and bottom positions. The biogas was split into four proportions, while all hydrogen was injected from the first reactor. An extensive process simulation has been performed to identify the exact feed concentration required for each reactor to maintain reactant stoichiometry. Accordingly, total H₂ in R-1 and biogas was added at each reactor inlet. All the gases were preheated by oil before entering the reactors. Subsequently, the produced gas was cooled down by circulating oil before injecting it back to the biogas system. In this test process, the produced gas was mainly biomethane with H₂ and unreacted CO₂. Given restrictive gas purity conditions for direct injection of biomethane into gas grids, the produced biomethane was injected back to the biogas tank.

Given safety concerns, the methane and hydrogen gas sensors were placed in the container to detect any minor gas leak. The leakage sensors were connected to an automatic control system that could perform an immediate shutdown of gas flowmeters in case of a major gas leak.

The gas analysis was performed using a portable high-resolution multi-component FTIR analyzer (atmosFIR, Protea Ltd. Cheshire, UK). The gas analyzer was placed at the gas exit after product separation, and gas analysis was performed after certain intervals to monitor the reaction progress. The gas analyzer consisted of a 4.2 m path length aluminum cell coated with nickel and pre-aligned coated mirrors. The optic consisted of a zinc selenide beam splitter. The frequency range was from
750 cm\(^{-1}\) to 5000 cm\(^{-1}\) with an average of 10 scans at a resolution of 4 cm\(^{-1}\). The analyzer was calibrated at 60 °C for biogas containing CH\(_4\), CO\(_2\), and H\(_2\)S up to 70%, 50%, and 5000 ppm, respectively.

3.2. Operational Procedure

The complete reactor setup was heat- and pressure-tested before placing the container at the biogas plant site. The modular container containing both the desulfurization and methanation reactor system was connected to the biogas storage tank after commissioning. Hydrogen production container was connected to the methanation reactor system.

As the CO\(_2\) methanation reaction is exothermic in nature, the excess heat was removed to avoid hotspots or overheating the catalyst bed and form carbon species on the catalyst surface. Additionally, the feed gases were carefully set to avoid cooling down the catalytic beds. Hence, the operating conditions were initially varied to find optimal reaction conditions for the continuous startup of all four reactors. To do this, the hydrogen feed flow rate and oil circulation to preheat the reactant gases were varied. Overall, the CO\(_2\) to H\(_2\) gas ratio was kept constant at all the time. However, the biogas flow at each reactor inlet was changed to avoid the fixed bed reactor’s cooling. The reactor pressure was kept around 8 bar at all the time. At the end of the test, the system was put into a “sleeping state” until the next day, i.e., the biogas feed flow was stopped, and the reactor was set to 200 °C under H\(_2\) flow until the next operation day.

3.3. Catalytic Tests

The catalyst was reduced in situ before the reaction at 300 °C and 0.5 bar pressure under a 50 mL/min hydrogen set flow. After catalyst reduction, the gas stream was switched to biogas and hydrogen feed. Typically, the feed gas composition was 38.5% biogas (60% CH\(_4\), 40% CO\(_2\)) and 61.5% hydrogen. The preheated gas at 200 °C was fed to the reactor; the catalyst bed temperature was varied from 300 to 550 °C. The produced gas exiting the pilot plant was analyzed immediately. Condensed water was drained and separated before the produced final gas was injected back to the biogas plant. The catalytic test ran for 6-8 h of continuous operation.

3.4. Catalyst Characterization

The catalyst was characterized by XRD, BET surface area, and H\(_2\) chemisorption before and after the reaction. After the reaction, catalyst samples were collected from the reactor inlet after the test campaign. The crystalline phases of fresh and after XRD determined reaction catalysts to identify phase change or loss in active phase due to long-time heat treatment and reaction. The XRD was performed using a Bruker D8 X-ray powder diffractometer (Karlsruhe, Germany) with Cu radiation in a parallel beam geometry. The XRD patterns were recorded with 2θ ranged from 25° to 85°.

N\(_2\) adsorption-desorption isotherms determined the BET analysis of the catalysts to find out whether there was any loss in the active surface area or pore blockage after the reaction. The BET analysis was performed using a micromeritics ASAP 2460 apparatus (Norcross, GA, USA). The samples were outgassed at 350 °C for 6 h before being subjected to N\(_2\) adsorption to ensure the data’s accuracy.

The reducibility of the catalyst sample was determined by H\(_2\)-TPR. The measurements were carried out on a Micromeritics Autochem-II instrument (Norcross, GA, USA) with a reducing mixture of 5% H\(_2\) in N\(_2\) from 25 °C to 600 °C with a heating rate of 10 °C/min.

Methanation reaction on nickel catalyst generally forms carbon species on the catalyst surface. Hence, TGA (NETZSCH STA 449C, Selb, Germany) was performed on fresh and used catalysts to measure the carbon deposition after the catalytic tests. For accuracy, the used catalyst was ground to a powder before the measurement. After that, about 160 mg sample was loaded in a crucible, and the sample was heated to 950 °C at a ramping rate of 4 °C/min under argon flow (flow rate: 20 mL/min).
4. Conclusions

Direct methanation of CO$_2$ from an operating biogas plant was tested with varying reaction conditions. A four-stage fixed bed reactor system was developed to achieve maximum biomethane yield. The temperature profile shows that the reactor temperature could be maintained within the optimum range (<500 °C) according to simulation calculations. A stable operation of a few hours with almost 8 Nm$^3$/h biogas feed showed more than 90% CO$_2$ conversion with a small concentration of H$_2$ and CO in the upgraded biogas. The quality of the produced gas was enough to inject into the gas grid. However, an unrestrictive biomethane injection into the gas grid at the test site needs further cleaning by removing H$_2$, CO, and unreacted CO$_2$, which could easily be achieved by a gas separator system. The catalyst stability under harsh reaction conditions was supported by catalyst characterization after the reactions. Interestingly, Ni phase transformation to Ni$_2$S$_3$ was observed after reaction with loss in surface area, which needs further investigation using in-situ or operando characterization techniques. The catalyst does not show deactivation or loss in activity within the tested period and no major carbon deposits.

In summary, the demonstration of direct CO$_2$ methanation of real biogas using H$_2$ produced by water electrolysis was implemented successfully. The newly developed desulfurization unit worked well with almost complete sulfur removal and without any chemical waste production. A successful long-time stability test with 8 Nm$^3$/h biogas feed showed a Technical Readiness Level of 7. This result is an important and crucial step towards upscaling and industrial implementation of (desulfurization, H$_2$ production, and CO$_2$ methanation) state-of-the-art technology at the commercial level.

**Author Contributions:** P.M., L.P.N. conceptualization, funding acquisition; G.G. designed and build the pilot demonstration plant, J.P.R., G.G. methodology and designed the experiments; R.G. analyzed the experimental data, characterized the material, and performed thermodynamic calculations; F.B.G. catalyst characterization; R.G., S.N.B.V., P.L.F. prepared and wrote the original draft; R.G., P.M., L.P.N., G.G., F.B.G., P.L.F. involved in review and final editing. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was partially funded by the Danish funding program ForskEl, through the MeGa-StoRE project (journal number 12393).

**Acknowledgments:** The authors would like to thank the ForskEl program and project partners, DTU MEK, Elplatek A/S, Unicat Engineering and NGF Nature Energy for financial support. Furthermore, the authors acknowledged the personnel support at the NGF Nature Energy, Midtfyn Biogas Plant during pilot plant testing.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. European Biogas Association. *Annual Report 2018*; European Biogas Association: Brussels, Belgium, 2018.
2. Stern, J. *The Future of Gas in Decarbonising European Energy Markets: The Need for a New Approach*; The Oxford Institute for Energy Studies: Oxford, UK, 2017.
3. Scarlat, N.; Dallemand, J.-F.; Fahl, F. Biogas: Developments and perspectives in Europe. *Renew. Energy* 2018, 129, 457–472. [CrossRef]
4. Strauch, S.; Krassowski, J.; Singhal, A. Biomethane Guide for Decision Makers—Policy Guide on Biogas Injection into the Natural Gas Grid; Green Gas Grids; Deutsche Energie-Agentur (DENA): Berlin, Germany, 2013.
5. Rasi, S.; Veijanen, A.; Rintala, J. Trace compounds of biogas from different biogas production plants. *Energy* 2007, 32, 1375–1380. [CrossRef]
6. Walsh, J.L.; Ross, C.C.; Smith, M.S.; Harper, S.R. Utilization of biogas. *Biomass* 1989, 20, 277–290. [CrossRef]
7. Ryckebosch, E.; Drouillon, M.; Vervaeren, H. Techniques for transformation of biogas to biomethane. *Biomass Bioenergy* 2011, 35, 1633–1645. [CrossRef]
8. Villadsen, S.N.B.; Fosbøl, P.L.; Angelidaki, I.; Woodley, J.M.; Nielsen, L.P.; Møller, P. The Potential of Biogas; the Solution to Energy Storage. *ChemSusChem* 2019, 12, 2147–2153. [CrossRef] [PubMed]
9. IEA Bioenergy Task 37. *IEA Bioenergy Task 37—Country Reports Summary 2017, 2018*; IEA Bioenergy: Paris, France, 2018.
10. Yousef, A.M.; El-Maghlany, W.M.; Eldrainy, Y.A.; Attia, A. Upgrading biogas to biomethane and liquid CO$_2$: A novel cryogenic process. *Fuel* 2019, 251, 611–628. [CrossRef]
11. Friege, C.; Herbes, C. Some Basic Concepts for Marketing Renewable Energy. In *Marketing Renewable Energy*; Springer International Publishing: Cham, Switzerland, 2017. [CrossRef]

12. Olah, G.A.; Goeppert, A.; Czaun, M.; Prakash, G.K.S. Bi-reforming of Methane from Any Source with Steam and Carbon Dioxide Exclusively to Metgas (CO-2H2) for Methanol and Hydrocarbon Synthesis. *J. Am. Chem. Soc.* **2013**, *135*, 648–650. [CrossRef]

13. Witte, J.; Calbry-Muzyka, A.; Wieseler, T.; Hottinger, P.; Biollaz, S.M.A.; Schildhauer, T.J. Demonstrating direct methanation of real biogas in a fluidised bed reactor. *Appl. Energy* **2019**, *240*, 359–371. [CrossRef]

14. Brooks, K.P.; Hu, J.; Zhu, H.; Kee, R.J. Methanation of carbon dioxide by hydrogen reduction using the Sabatier process in microchannel reactors. *Chem. Eng. Sci.* **2007**, *62*, 1161–1170. [CrossRef]

15. Castellani, B.; Gambelli, A.M.; Morini, E.; Nastasi, B.; Presciutti, A.; Filipponi, M.; Nicolini, A.; Rossi, F. Experimental Investigation on CO2 Methanation Process for Solar Energy Storage Compared to CO2-Based Methanol Synthesis. *Energies* **2017**, *10*, 855. [CrossRef]

16. Plechinger, M. Energy Watch. Available online: https://energywatchwatch.eu/EnergyRenewables/article12532617. (accessed on 2 December 2020).

17. Martinez, J.; Hernández, E.; Alfaro, S.; López Medina, R.; Valverde Aguilar, G.; Albiter, E.; Valenzuela, M.A. High Selectivity and Stability of Nickel Catalysts for CO2 Methanation: Support Effects. *Catalysts* **2019**, *9*, 24. [CrossRef]

18. Abelló, S.; Berrueco, C.; Montané, D. High-loaded nickel–alumina catalyst for direct CO2 hydrogenation into synthetic natural gas (SNG). *Fuel* **2013**, *113*, 598–609. [CrossRef]

19. Olah, G.A.; Goeppert, A.; Czaun, M.; Mathew, T.; May, R.B.; Prakash, G.K.S. Single Step Bi-Reforming and Oxidative Bi-Reforming of Methane (Natural Gas) with Steam and Carbon Dioxide to Metgas (CO-2H2) for Methanol Synthesis: Self-Sufficient Effective and Exclusive Oxidation of Methane to Methanol with Oxygen. *J. Am. Chem. Soc.* **2015**, *137*, 8720–8729. [CrossRef] [PubMed]

20. El Sibai, A.; Rihko Struckmann, L.K.; Sundmacher, K. Model-Based Optimal Sabatier Reactor Design for Power-to-Gas Applications. *Energy Technol.* **2017**, *5*, 911–921. [CrossRef]

21. Rönsch, S.; Schneider, J.; Matthischke, S.; Schlüter, M.; Götz, M.; Lefebvre, J.; Prabhakaran, P.; Bajohr, S. Review on methanation—From fundamentals to current projects. *Fuel* **2016**, *166*, 276–296. [CrossRef]

22. Matthischke, S. Unsteady-state methanation of carbon dioxide in a fixed-bed recycle reactor—Experimental results for transient flow rate ramps. *Fuel Process. Technol.* **2016**, *153*, 83–93. [CrossRef]

23. Fache, A.; Marias, F.; Guérre, V.; Palmade, S. Optimization of fixed-bed methanation reactors: Safe and efficient operation under transient and steady-state conditions. *Chem. Eng. Sci.* **2018**, *192*, 1124–1137. [CrossRef]

24. Bartholomew, C.H. Mechanisms of catalyst deactivation. *Appl. Catal. A Gen.* **2001**, *212*, 17–60. [CrossRef]

25. Abatzoglou, N.; Boivin, S. A review of biogas purification processes. *Biofuels Bioprod. Biorefin.* **2009**, *3*, 42–71. [CrossRef]

26. Persson, M.; Jönsson, O.; Wellinger, A. *Biogas Upgrading to Vehicle Fuel Standards and Grid Injection Biogas*: Upgrading I; IEA Bioenergy: Paris, France, 2006.

27. Albagaiue, L.B.; Hinge, J. *Biogas Upgrading Evaluation of Methods for H2S Removal*; Danish Technological Institute: Taastrup, Denmark, 2014; pp. 1–31.

28. Rabou, L.P.L.M.; Bos, L. High efficiency production of substitute natural gas from biomass. *Appl. Catal. B Environ.* **2012**, *111–112*, 456–460. [CrossRef]

29. Gao, J.; Wang, Y.; Ping, Y.; Hu, D.; Xu, G.; Gu, F.; Su, F. A thermodynamic analysis of methanation reactions of carbon oxides for the production of synthetic natural gas. *RSC Adv.* **2012**, *2*, 2358–2368. [CrossRef]

30. Stangeland, K.; Kalai, D.; Li, H.; Yu, Z. CO2 Methanation: The Effect of Catalysts and Reaction Conditions. *Energy Procedia* **2017**, *105*, 2022–2027. [CrossRef]

31. Jürgensen, L.; Ehimen, E.A.; Born, J.; Holm-Nielsen, J.B. Dynamic biogas upgrading based on the Sabatier process: Thermodynamic and dynamic process simulation. *Bioreour. Technol.* **2015**, *178*, 323–329. [CrossRef] [PubMed]

32. Jekaterina, P.; Gatis, B.; Darja, M. Modeling of the Adiabatic and Isothermal Methanation Process. *Environ. Clim. Technol.* **2011**, *6*, 79–84. [CrossRef]

33. Moon, D.H.; Lee, S.M.; Ahn, J.Y.; Nguyen, D.D.; Kim, S.S.; Chang, S.W. New Ni-based quaternary disk-shaped catalysts for low-temperature CO2 methanation: Fabrication, characterization, and performance. *J. Environ. Manag.* **2018**, *218*, 88–94. [CrossRef] [PubMed]
34. Wu, H.; Yin, K.; Qi, W.; Zhou, X.; He, J.; Li, J.; Liu, Y.; He, J.; Gong, S.; Li, Y. Rapid Fabrication of Ni/NiO@CoFe Layered Double Hydroxide Hierarchical Nanostructures by Femtosecond Laser Ablation and Electrodeposition for Efficient Overall Water Splitting. *ChemSusChem* 2019, 12, 2773–2779. [CrossRef]

35. Dannesboe, C.; Hansen, J.B.; Johannsen, I. Removal of sulfur contaminants from biogas to enable direct catalytic methanation. *Biomass Convers. Biorefin.* 2019. [CrossRef]

36. Frilund, C.; Simell, P.; Kaisalo, N.; Kurkela, E.; Koskinen-Soivi, M.-L. Desulfurization of Biomass Syngas Using ZnO-Based Adsorbents: Long-Term Hydrogen Sulfide Breakthrough Experiments. *Energy Fuels* 2020, 34, 3316–3325. [CrossRef]

37. Hepola, J.; Simell, P.; Kurkela, E.; Ståhlberg, P. Sulphur poisoning of nickel catalysts in catalytic hot gas cleaning conditions of biomass gasification. In *Studies in Surface Science and Catalysis*; Delmon, B., Froment, G.F., Eds.; Elsevier: Amsterdam, The Netherlands, 1994; Volume 88, pp. 499–506.

38. Gac, W.; Zawadzki, W.; Rotko, M.; Slowik, G.; Greul, M. CO₂ Methanation in the Presence of Ce-Promoted Alumina Supported Nickel Catalysts: H₂S Deactivation Studies. *Top. Catal.* 2019, 62, 524–534. [CrossRef]

39. Khzouz, M.; Gkanas, E.I. Experimental and Numerical Study of Low Temperature Methane Steam Reforming for Hydrogen Production. *Catalysts* 2017, 8, 5. [CrossRef]

40. He, Z.; Wang, X.; Liu, R.; Gao, S.; Xiao, T. Performances of different additives on NiO/γ-Al₂O₃ catalyst in CO methanation. *Appl. Petrochem. Res.* 2016, 6, 235–241. [CrossRef]

41. Gao, Y.; Meng, F.; Ji, K.; Song, Y.; Li, Z. Slurry phase methanation of carbon monoxide over nanosized Ni–Al₂O₃ catalysts prepared by microwave-assisted solution combustion. *Appl. Catal. A Gen.* 2016, 510, 74–83. [CrossRef]

42. Zhu, L.; Yin, S.; Wang, X.; Liu, Y.; Wang, S. The catalytic properties evolution of HZSM-5 in the conversion of methanol to gasoline. *RSC Adv.* 2016, 6, 82515–82522. [CrossRef]

43. Li, P.; Park, Y.H.; Moon, D.J.; Park, N.C.; Kim, Y.C. Carbon Deposition Onto Ni-Based Catalysts for Combined Steam/CO₂ Reforming of Methane. *J. Nanosci. Nanotechnol.* 2016, 16, 1562–1566. [CrossRef] [PubMed]

44. Dou, X.; Veksha, A.; Chan, W.P.; Oh, W.-D.; Liang, Y.N.; Teoh, F.; Mohamed, D.K.B.; Giannis, A.; Lisak, G.; Lim, T.-T. Poisoning effects of H₂S and HCl on the naphthalene steam reforming and water-gas shift activities of Ni and Fe catalysts. *Fuel* 2019, 241, 1008–1018. [CrossRef]

45. Méndez-Mateos, D.; Barrio, V.L.; Requies, J.M.; Cambra, J.F. A study of deactivation by H₂S and regeneration of a Ni catalyst supported on Al₂O₃, during methanation of CO₂. Effect of the promoters Co, Cr, Fe and Mo. *RSC Adv.* 2020, 10, 16551–16564. [CrossRef]

46. Albertazzi, S.; Basile, F.; Brandin, J.; Einvall, J.; Fornasari, G.; Hulteberg, C.; Sanati, M.; Trifirò, F.; Vaccari, A. Effect of fly ash and H₂S on a Ni-based catalyst for the upgrading of a biomass-generated gas. *Biomass Bioenergy* 2008, 32, 345–353. [CrossRef]

47. Luisetto, I.; Tuti, S.; Battocchio, C.; Lo Mastro, S.; Sodo, A. Ni/CeO₂–Al₂O₃ catalysts for the dry reforming of methane: The effect of CeAlO₃ content and nickel crystallite size on catalytic activity and coke resistance. *Appl. Catal. A Gen.* 2015, 500, 12–22. [CrossRef]

48. Awad, A.; Salam, A.; Abdullah, B. Thermocatalytic decomposition of methane/methanol mixture for hydrogen production: Effect of nickel loadings on alumina support. *AIP Conf. Proc.* 2017, 1891, 020330. [CrossRef]