

TKI-GAS POWER-TO-GAS PROJECT

Integration of Power-to-Gas and biogas supply chain

TKI Gas – TKI 01015

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Objective:

The objective of this study is to demonstrate by desk study to what extent methanation technology is or could be made suitable for biogas upgrading.

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EXECUTIVE SUMMARY

In the future our energy system will see a transition to a system that is based on sustainable and renewable energy sources of an intermittent nature. When more intermittent sustainable sources are introduced, the imbalance between supply and demand is no longer easy to absorb. In order to facilitate sustainable energy production and electricity production in particular in the best possible way, we are looking for opportunities to use and/or store the excess of sustainable energy production. As an alternative to conventional storage methods such as batteries or pump accumulation stations, Power-to-Gas (P2G) can play a role by converting electricity into gas - hydrogen. P2G uses electrolysis - a method to decompose water molecules into hydrogen and oxygen by means of electricity. In the Dutch methane economy it could be even more effective to convert hydrogen together with carbon dioxide into methane. This methane can serve as a natural-gas substitute and could have a partly green origin.

A natural-gas substitute can also be obtained from biomass by means of the anaerobic breakdown of organic matter. This 'green gas' production method is applied widely and has its own characteristics in the biogas production chain. The production chain of Power-to-Gas systems is completely different and contains significantly different technologies. Based on desk research DNV GL studied whether the production chains of biogas production and Power-to-Gas could be integrated from a technical point of view. Integration of these systems is expected to achieve synergies in terms of chain efficiency, carbon dioxide recycling and costs. More specifically, this report elaborated on the question to what extent methanation technology is suitable for performing biogas upgrading.

The use of methanation technology to upgrade biogas to natural-gas quality could make conventional biogas upgrading technology superfluous, depending on the technology that is used. There are specific differences between the chemical catalysis process and the biological catalysis process.

DNV GL found that the use of nickel catalyst (chemical methanation) is not applicable for untreated biogas because of the concentrations of H₂S and oxygen that may occur in raw biogas. Both components have a strong deactivating effect on reactive nickel. The oxygen tolerance of nickel catalysts is lower than the oxygen tolerance according to the gas grid injection specifications. In general it can be stated that the purity of the carbon dioxide supply gas, serving as the carbon source for chemical methanation, is an important condition for the process.

Biological methanation appears to be a viable technology in terms of tolerance for components that may be present in untreated biogas (and possibly in a number of types of flue gases). This would make biological methanation capable of using untreated biogas as the carbon source for the methanation process (Power-to-Gas). However, at the moment there is insufficient information available to be specific about the effects of trace elements in biogas on the effectiveness and efficiency of methanogenic archaea as biological catalyst for Power-to-Gas purposes.

Furthermore, there is very little practical experience with biological methanation in the Power-to-Gas chain, let alone the application of this technology for integrated upgrading of biogas. In order to make qualified statements about the applicability of biological methanation and the possibilities of using untreated biogas as the carbon source for the methanation process, fundamental research to the effects of specific components on catalyst material and practical studies must be carried out. Also practical validation of these technological integrations in operational environments is required.

LIST OF ABBREVIATIONS

Abbreviation	Description
BTX	Benzene, Toluene, Xylene
CH ₄	Methane
CO	Carbon monoxide
Co	Cobalt
CO ₂	Carbon dioxide
D4, D5	Siloxanes
Fe	Iron
GC	Gas chromatograph
HCN	Hydrocyanic acid
H ₂	Hydrogen
H ₂ O	Water
H ₂ S	Hydrogen sulphide
Ir	Iridium
CAT	Catalyst
kJ	KiloJoule
N ₂	Nitrogen
Ni	Nickel
NH ₃	Ammonia
O ₂	Oxygen
P2G	Power-to-Gas
Pd	Palladium
Pt	Platinum
R-F	Fluorine compounds
R-Cl	Chlorine compounds
Rh	Rhodium
Ru	Ruthenium
THT	Tetrahydrothiophene, an odorous substance that is added to natural gas for odour recognition
ΔH	Heat of generation or enthalpy

1 INTRODUCTION

In the future our energy system will see a transition to a system that is based on sustainable and renewable energy sources. Renewable energy sources are different from conventional fossil energy sources because of their low life-cycle carbon emissions and their intermittent nature.

When more intermittent sustainable sources are introduced, the imbalance between supply and demand is no longer easy to be absorbed by the energy system. In order to facilitate sustainable energy production and electricity production in particular in the best possible way, we are looking for opportunities to use and/or store the excess of sustainable energy production. As an alternative to conventional storage methods such as batteries or pump accumulation stations, Power-to-Gas (P2G) can play a role by converting electricity into gas - hydrogen. P2G uses electrolysis - a method to split water molecules into hydrogen and oxygen by means of electricity. However, the hydrogen that is released during electrolysis can be used in various ways. In function of the gas quality of the grid and the type of users that are supplied by the grid, the maximum amount of hydrogen is limited. Partly because the existing gas infrastructure is designed for using methane, which is the main component of current natural gas in the Netherlands, it is not possible to use hydrogen directly. Therefore it may be more effective to convert hydrogen together with carbon dioxide into methane. The methane that is produced during this methanation process can serve as a natural-gas substitute. A natural-gas substitute can also be obtained from biomass by means of the anaerobic breakdown (digesting) of organic matter. The produced biogas contains too much carbon dioxide to be able to use it directly as a natural-gas substitute. With a subsequent upgrading method, the surplus of carbon dioxide is removed from the biogas and the resulting gas, 'green gas', can be used as a natural-gas substitute. This 'green gas' production method is applied widely and has its own characteristics in the biogas production chain.

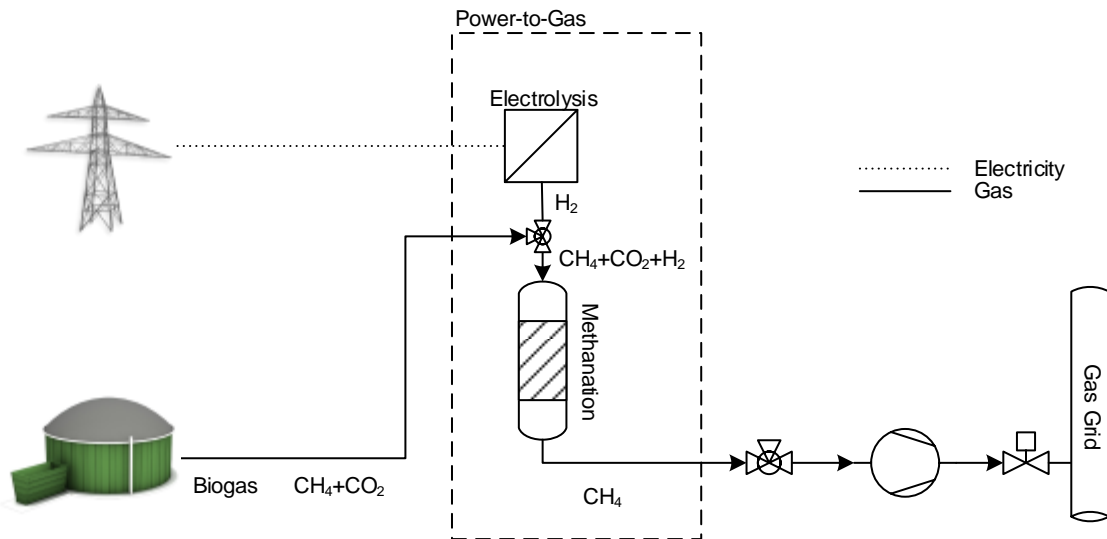



Figure 1: System configuration of the hypothesis

There is now a hypothesis that the Power-to-Gas and the digesting process could be integrated by using the surplus of carbon dioxide from biogas for the methanation process, see Figure 1.



This would make conventional biogas upgrading surplus to requirements and would make optimum use of the energy and mass flows in both processes and as many cycles as possible would be closed. Energy flows primarily include the production of hydrogen from solar and wind energy, the production of methane from biomass and reusing heat from the methanation process in the digesting process. For mass flows this situation mainly considers the reuse of carbon dioxide and water.

With the current investment costs for electrolysis a positive business case currently seems unrealistic, but the development prospects and market perspective of the technology offer significant cost reduction. The final report of the TKI project “Exploring the role of Power-to-Gas in the future Dutch energy system” [1] also shows that Power-to-Gas would have a strong role in a future energy system with far-reaching emission reduction targets.

Most studies support the technical potential of Power-to-Gas and support the need for follow-up studies of the system integration of Power-to-Gas systems with related sustainable energy systems in order to achieve synergies.

1.1 Objective

The objective of this study is to demonstrate by desk research to what extent methanation technology is or could be made suitable for biogas upgrading. This knowledge is relevant to optimising existing biogas upgrading systems and to defining the preconditions for system integration with Power-to-Gas to reduce the production costs in terms of financial and energetic parameters of sustainable natural-gas substitutes. The application of methanation for upgrading biogas has been studied, because the system integration of Power-to-Gas systems with existing biogas systems is expected to produce synergies in terms of chain efficiency, carbon dioxide recycling and possibly also in relation to the chain costs of biogas upgrading.

1.2 Scope, terms of reference and approach

This study determined the influence of the gaseous components in untreated biogas on the methanation process. It was assumed that the synthesis process of carbon dioxide and hydrogen into methane is achieved on the basis of a chemical catalysis process or on the basis of a biological catalysis process. The study investigated the effect of biogas components on chemical and biological catalysts and the issues in terms of integrating biogas production with methanation.

2 CONVENTIONAL BIOGAS CHAIN

The conventional biogas chain consists of biogas production, biogas purification, upgrading biogas to natural gas quality and injection into the gas grid or another form of application.

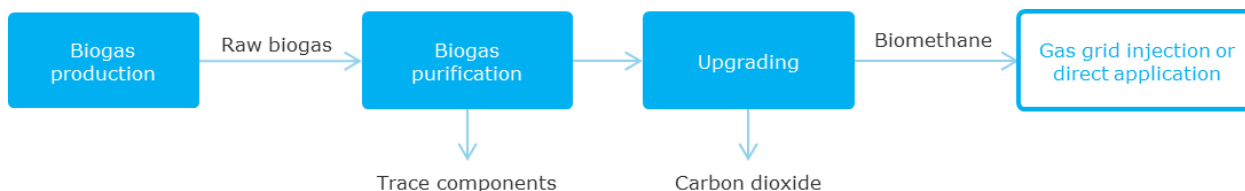


Figure 2: Conventional biogas chain

Each of these steps is considered in more detail in the following paragraphs.

2.1 Biogas production

Biogas is produced by the anaerobic degradation of organic material, also known as 'fermentation' or 'digesting process'. The composition of biogas is strongly dependent on the biomass that is fermented and can vary enormously as a result. Besides the main components methane and carbon dioxide, the gas mixture often consists of many other gaseous components, known as 'impurities', some of which may be corrosive or toxic or may have destructive effects on processing or end-user equipment. Table 1 provides the average composition of biogas, based on a large number of biogas measurements that were performed by DNV GL. Incidental extreme values have not been taken into consideration.

Table 1: Typical gas composition of raw biogas

	Components	Concentration range
Main components	Methane (CH₄)	50 - 60 mol%
	Carbon dioxide (CO₂)	40 - 50 mol%
	Nitrogen gas (N₂)	1 - 3 mol%
	Oxygen (O₂)	0.1 - 0.5 mol%
	Hydrogen (H₂)	0.1 - 1.5 mol%
	Water vapour (H₂O)	1 - 7 mol%
	Carbon monoxide (CO)	0 - 1 mol%
Trace components	Ammonia (NH₃)	0 - 308 ppm(mol)
	Hydrogen sulphide (H₂S)	20 - 850 ppm(mol)
	Terpenes	0 - 500 ppm(mol)
	Benzene, Toluene, Xylene (BTX)	0 - 7 ppm(mol)
	Hydrocyanic acid (HCN)	0 - 0.003 ppm(mol)
	Fluorine compounds (R-F, incl. HF)	0 - 1.3 ppm(mol)
	Chlorine compounds (R-Cl, incl. HCl)	0.1 - 5 ppm(mol)
	Siloxanes (D4 & D5)	0 - 3.4 ppm(mol)

2.2 Biogas purification

In the first step of conventional biogas chains, the most important impurities are removed from the biogas. This first purification step is essential to further upgrading of biogas, as the most common upgrading methods are affected adversely or unable to remove these impurities. In practice, biogas purification is carried out with separate processes, largely by using active carbon (adsorption) and/or cooling (phase separation). Hydrogen sulphide, ammonia, aromatic hydrocarbons, halogenated compounds, terpenes and silicon compounds are largely removed from raw biogas.

2.2.1 Active carbon

Purification with active carbon is based on adsorption. The components to be removed attach (adsorb) to the active surface of the carbon, which means it becomes less effective over time. Therefore carbon filters must be replaced periodically.

Active carbon is largely used to remove hydrogen sulphide and apolar compounds, such as terpenes and aromatic hydrocarbons. By impregnating active carbon with specific chemicals, such as potassium iodide or potassium permanganate, it is possible to strengthen the level of adsorption with chemisorption and to make it more suitable for removing a certain component.

In relation to the components that were identified in this study (Table 1), all trace components (ammonia, hydrogen sulphide, terpenes, aromatic hydrocarbons, halogenated compounds, terpenes and siloxanes) can be removed with impregnated active carbon. Oxygen can be removed from gases with chemisorption by means of impregnated active carbon. This process uses chemicals that convert oxygen into reactive chemical compounds and possibly water. It should be noted that impregnated active carbon is not proven to remove oxygen at an industrial scale. Industry uses catalytic oxidation specifically for oxygen removal. A metal, copper for example, binds the oxygen at high temperatures of up to approximately 200 °C. The disadvantage of this method is that other components in the biogas, such as methane and higher hydrocarbons, also oxidise and part of the product gas flow is lost.

2.2.2 Phase separation

Phase separation is based on physical properties of components, such as the boiling point, and makes targeted use of cooling. Cooling ensures that some gaseous components come below boiling point, which means that component can be captured in liquid form. The cooling temperature is decisive in terms of which components can be separated.

Theoretically speaking phase separation is able to remove all trace components. It should be noted that the purification system should be dimensioned to the evaporation temperatures of all the components that are to be removed. It should also be noted that phase-separation technology, such as cryogenic biogas upgrading systems, are not applied yet at a representative scale. However, increasing numbers of feasibility studies are carried out to include this method. Cryogenic technology is also used to increase the solubility of substances and to apply separation in that way.



2.3 Biogas upgrading

Upgrading biogas means that the energy value of the gas is increased by removing carbon dioxide from the gas flow. The biogas that enters the upgrading system contains methane and carbon dioxide, but often also low concentrations of nitrogen and oxygen. Carbon dioxide is separated from the gas flow and discharged separately. In practice, this carbon dioxide is vented or used for processes that use carbon dioxide.

Available processes include membrane upgrading, pressure swing adsorption, water absorption, chemical absorption and cryogenic upgrading. This report does not deal with the specific properties of the various upgrading processes.

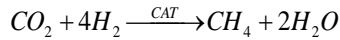
The upgrading methods that are applied at the moment are selective for removing carbon dioxide. The outgoing gas flow still contains the same amounts of nitrogen, oxygen, hydrogen and trace components as the raw biogas. However, the concentration of those components is higher than in the incoming gas flow, because part of the carbon dioxide is removed from the gas.

2.4 Injection

Before upgraded biogas (green gas) may be injected into the public grid, it must be verified that the gas complies with the injection specifications imposed by Appendix 2, Referred to in Articles 1 and 2, paragraph 2 of the Ministerial Scheme for Gas Quality, known as the Gas Quality Scheme), that was published in the Government Gazette on 21 July 2014[2]. This report does not deal with these injection specifications.

3 METHANATION

The conversion of hydrogen and carbon dioxide into methane is a reaction that takes place with a catalyst on the basis of the following general formula:



This may be a chemical catalysis process or a biological catalysis process. The following describes both processes.

3.1 Chemical catalysis process

Chemical methanation is based on the Sabatier reaction; an exothermal synthesis process whereby hydrogen and carbon dioxide react into methane at 300°C to 400°C over a catalyst. Chemical methanation is a reasonably developed technology that is available in the market commercially. However, the technology is only applied in various large-scale industrial applications.

The Sabatier reaction is a strong exothermal equilibrium reaction with the following equation:



According to the equation the products of the process are methane and water (vapour). Water must be removed from the process to prevent methane from being reconverted into carbon dioxide and hydrogen. The conversion into methane produces 165 kJ/mol of heat. The Sabatier reaction takes place by means of an interim reaction, the 'water-gas-shift' reaction [3]. This is a equilibrium reaction where carbon dioxide and hydrogen are converted into carbon monoxide and water.



It is assumed that the heterogeneous, catalytic reactions (a) to (c) take place in accordance with the Langmuir-Hinshelwood (HS) principle, where reactions take place between adsorbed active particles [4]. The reaction mechanism for this gas reaction is described in the reaction equations (d) to (h). The abbreviation 'CAT' in these formulas refer to the catalyst surface area.



Figure 3 is a schematic representation of reactions (d) to (h).

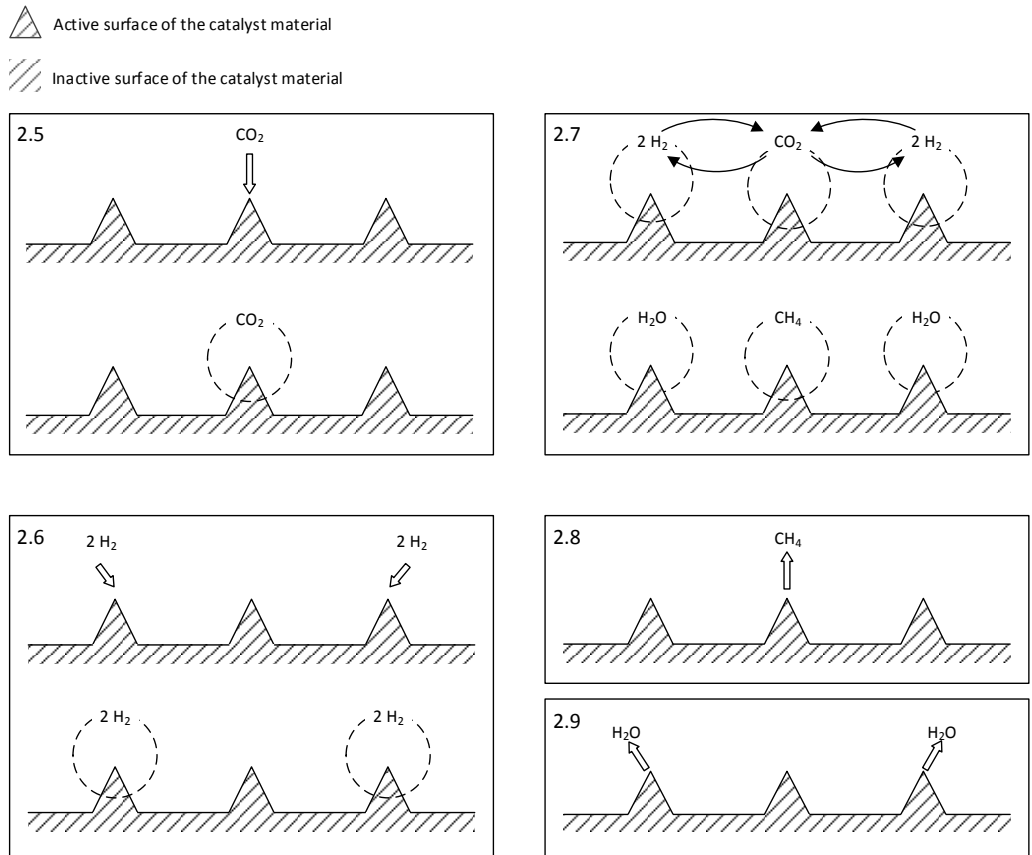


Figure 3: Schematic representation of the Langmuir-Hinshelwood principle [22]

The reactants carbon dioxide and hydrogen will adsorb to the catalyst surface (reactions (d) and (e)). This is where the reaction takes place between the adsorbed reactants, which means the reaction products methane and water are formed until equilibrium has been achieved (reaction f). The affinity of the formed reaction products to the catalyst material is less than that of the reactants, which means they will desorb; reactions (g) and (h) [5].

At the start the equilibrium reaction (a) will move from left to right due to the absence of methane and water, in other words the reactants carbon dioxide and hydrogen react to methane and water. As the concentrations of methane and water increase, the reverse reactions will also take place more and more, which means part of the formed methane and water will react back to hydrogen and carbon dioxide. This reverse reaction will take place until equilibrium has been achieved.

A certain amount of activation energy is required to start reaction (a). The activation energy is the smallest amount of energy that is required to activate atoms or molecules to a state where they can undergo a chemical reaction. During the chemical methanation process, a catalyst is used to increase the reaction speed and to reduce the activation energy. In order to start up the reaction a certain amount of energy is required. In the methanation process the activation energy is used to heat up the catalyst material.

In the case of an exothermal reaction, such as the Sabatier process, the reaction will continue after the reaction has been activated because this is more favourable from an energetic point of view and more energy is supplied than required for the reaction. An external heat source is no longer required.

3.1.1 Catalyst materials

The suitability and effectiveness of a catalyst is determined by the catalyst and the carrier material. The carrier material often consists of a metal oxide because of its large specific surface. A carrier with a large specific surface (m^2/kg) generally promotes the effectiveness of the catalyst as large amounts of catalyst material are present per volume-unit of material. The carrier material also determines the stability of the catalyst.

Nickel is mainly used for the methanation of carbon dioxide, carbon monoxide and hydrogen. It is also possible to use ruthenium (Ru), rhodium (Rh), platinum (Pt), iridium (Ir), cobalt (Co), iron (Fe) or palladium (Pd). On the basis of the information in literature, the following order of selection is used for the methanation of hydrogen and carbon dioxide, where the catalyst with the highest specific activity is listed first [7].

$\text{Ru} > \text{Fe} > \text{Ni} > \text{Co} > \text{Rh} > \text{Pd} > \text{Pt} > \text{Ir}$

However, literature study also demonstrates that the situation is slightly different for the methanation of carbon dioxide. It should be noted that different orders are given. The selectivity does not only depend on the catalyst material, but is also strongly affected by the carrier material. This may explain the discrepancies in the various literature sources. A recent literature review by Azelee e.a. [6] demonstrates that the highest methane production is expected from the following catalysts, from high to low:

$\text{Ru} > \text{Rh} > \text{Pt} > \text{Ir} \sim \text{Pd}$

Nickel must be mentioned separately, because the above overview is based on precious metals. Nickel is less selective for hydrogen/carbon dioxide than ruthenium or rhodium, but it is a lot cheaper. An adverse property of nickel is that at low temperatures ($< 250^\circ\text{C}$) carbon deposits occur sooner than with previous metals and that reduces the effective surface. Ruthenium causes carbon deposits to a lesser extent, but produces more higher hydrocarbons [7] that are not required in the end product (natural-gas substitute).

In summary it is possible to say that the listed precious metals are generally more effective than nickel, but weighing up the effectiveness and the costs generally means that nickel is the optimum catalyst. This project and many other commercial processes use nickel as a catalyst. This is in contrast to fundamental research where the emphasis is on maximising the conversion efficiency.

3.1.2 Catalyst degeneration

A decrease in the catalytic activity and selectivity over time is a process that is a continuous risk in catalytic processes. Therefore this risk should be taken into account during catalytic methanation. It is inevitable that catalysts lose their activity over time due to the loss of activated ions. However, for as long as this process occurs in a controlled manner degradation will take place slowly and engineering and investment decisions can be taken accordingly. Although normal degradation is inevitable, uncontrolled and immediate poisoning or deactivation must be avoided at all times. Table 2 represents the mechanisms for degeneration and deactivation.






Table 2: Degeneration and deactivation mechanisms of catalysts

Mechanisms	Type	Description
Poisoning	Chemical	Chemical adsorption of molecules to the catalyst which reduces the reaction surface of the catalyst.
Contamination	Mechanical	Deposit of reaction products on the reaction surface and the pores of the catalyst. This will result in a reduced effective surface area of the catalyst.
Thermal degradation	Thermal	Losing reaction surface, ion activity or impacting the support material to which the catalyst material is applied due to high temperatures.
Vapour formation	Chemical	The production of volatile components due to a reaction between catalyst material and gaseous components that causes a loss of active material.
Phase transition reactions	Chemical	Chemical reaction between gases or volatile components that are formed and catalyst or support material.
Grinding	Mechanical	Loss of catalytic activity due to the mechanical damage (grinding) of the catalyst and/or carrier material.









3.1.3 Effects of biogas components

This paragraph deals with the effects of components present in the biogas on nickel catalyst material.

Table 3: Effects of components in biogas on nickel catalyst

Component	Description of the effect(s)	Information availability	Showstopper for process? ¹
Methane (CH₄)	The heat capacity of methane is approximately 20% higher than that of the carbon dioxide/hydrogen mixture [16]. Therefore methane has a cooling effect in the reactor that reduces the reaction temperature. A lower reaction temperature produces a higher conversion rate. Adding methane at higher (>350°C) temperatures increases the chance of carbon deposits on the catalyst, which reduces the effectiveness.		No
Carbon dioxide (CO₂)	An excess of carbon dioxide in the reaction can cause excessive carbon monoxide production, by means of the water-gas-shift reaction, and that increases the chance of carbon deposits on the catalyst.		No
Nitrogen (N₂)	No adverse effects on the nickel catalyst. However, adding nitrogen does have an impact on the heat balance of the process, because of the heat absorption capacity; may be a positive or a negative effect.		No
Oxygen (O₂)	Oxygen causes deactivation of the nickel catalyst. Oxygen adsorbs easily to the catalyst surface, which reduces the effectiveness. On contact with oxygen, the active (positively charged) nickel is given a neutral charge (oxidation), which eliminates the reactive ability: $2Ni-CAT + O_2 \leftrightarrow 2Ni^{2+}O^{2-}$ (ionisation). In order to improve the effectiveness of the reaction, the adsorbed oxygen atoms (oxides) must be removed from the catalyst surface. This chemical reduction is carried out by flushing the catalyst with a low-oxygen gas, such as nitrogen or hydrogen. The tolerance of nickel as a catalyst material is lower than the injection specification for oxygen in the public gas grid (RTL and RNB grids; <0.5 mol% oxygen). Hydrogen is present at temperatures that are far above the flash point of hydrogen. Adding oxygen could lead to immediate combustion and possible explosion. Adding oxygen to the process must be avoided!		Yes
Hydrogen (H₂)	No adverse effects.		No

¹ This column notes whether addition of the relevant component is a showstopper for the process (immediately at exposure), whether there is insufficient knowledge available, or whether it does not have a critical impact.

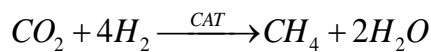
Water vapour (H₂O)	Water has no effect on the condition of the catalyst. However, the presence of water or water vapour does have a strong effect on the progress of the reaction. In the Sabatier reaction water is formed from the synthesis of hydrogen and carbon dioxide. However, because it is an equilibrium reaction, water, within the temperature range of the methanation process, may lead to the conversion of methane into hydrogen and carbon dioxide. This process would work on the basis of the water-gas-shift reaction. Water can also have a strong cooling effect, which means that the reaction temperature drops.		No
Carbon monoxide (CO)	Excessive presence of carbon monoxide in the process increases the chance of carbon deposits on the catalyst.		No
Ammonia (NH₃)	Nickel catalysts are able to decompose ammonia into hydrogen and nitrogen [9]. Adverse effects of adding small amounts of ammonia to the methanation reactor are not expected.		No
Sulphur compounds (e.g. H₂S, mercaptanes and THT).	Sulphur is rapidly adsorbed by nickel. In the temperature range of 250- 600°C, a sulphur concentration of 0.01 ppm in the ingoing gas leads to deactivation [10]. Deactivation of nickel following contact with sulphur occurs at a speed in function of the total catalyst surface and the sulphur load [11]: $\ln[(S_o/S) - 1] = k_d n_i t - (k_d n_i + k_d S_o)(x/V)$ $t = \text{time (h)}, n_i = \text{ingoing sulphur concentration (ppmw)}, S_o = \text{reaction surface at } t_o, s = \text{reaction surface at } t, V = \text{average flow speed (m}^3\text{h}^{-1}\text{)}, x = \text{height of catalyst bed (m)}; x/V = \text{LHSV}^{-1} \text{ or GHSV}^{-1}, k_d = \text{deactivation constant (h}^{-1}\text{ ppmw}^{-1}\text{)}.$ Addition of sulphur must be avoided!		Yes
Benzene, Toluene, Xylene (BTX) and Terpenes	Cyclic carbon chains may disrupt the balance between carbon and hydrogen atoms and bind to active nickel atoms. This may have a potentially adverse effect due to carbon deposits at high temperatures (>350°C). As yet the effects are not sufficiently known.		?
Fluorine compounds (R-F, incl. HF)	Insufficient information available.		?
Chlorine compounds (R-Cl, incl. HCl)	Insufficient information available.		?
D4-D5 siloxanes	Insufficient information available. However, the effects of siloxanes in combustion processes have extensively		No



	<p>been researched by DNV GL. From these experiments DNV GL obtained indications that siloxanes are capable of forming gum-like polymers in similar conditions as present in methanation. It seems likely that siloxanes are decomposed by the methanation catalyst. How the Si compounds exactly behave in the methanation process is at this moment insufficiently known.</p>		
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3.2 Biological catalyst

Biological methanation can be considered as an alternative to chemical methanation. In this process methanogenic archaea (the *Methanosarcina* species [23]) work in complex cooperation with co-enzymes as catalyst for the synthesis of hydrogen and carbon dioxide.



Methanogenesis is a process that occurs frequently in nature and in industry - wastewater treatment, digesting, rice paddies, morass areas and the formation of natural gas and oil. In oxygen-free conditions, the archaea culture uses carbon dioxide as oxidant and hydrogen as the electron donor to create methane [12]. The archaea work with mesophilic to thermophilic (45-70 °C) temperatures that are relatively low compared to the temperature range that is relevant to thermochemical methanation (200 – 600 °C).










Biological methanation is currently developed from the research phase, available in test reactors with up to 1,000 litres of reactor volume, to commercialisation [17][18]. Therefore there is only limited practical experience with the technology.

3.2.1 Effects of components in biogas on biological catalyst




As noted in Table 1, raw biogas may contain several components. Carbon dioxide in biogas provides the carbon source and the oxidant for the methanation process and is essential to the methanation process. Suppliers of biomethanation systems indicate that an important competitive property of the technology, and of biological catalysts, is that it is extremely robust in terms of tolerance of impurities. A practical example of this tolerance is the value of methanogenic archaea in soil remediation of higher hydrocarbons and BTX (Benzene, Toluene & Xylene) in polluted soils and aquifers, often used by the Environmental Microbiology discipline[12]. The methanogenic archaea work in symbiosis with other organisms on breaking down the pollution.


Recent studies by Seifert et al. [13] have proven on the basis of laboratory tests that the biological methanation process on the basis of flue gases of impure biogas hardly differs from the process based on a pure hydrogen/carbon dioxide mixture. Unfortunately the study report does not contain insight into the exact composition of the used substrate gases. The relevant study does not confirm the position that biological methanation in terms of resistance to contamination in the gas phase is a viable technology for methanising hydrogen and carbon dioxide.

Table 4: Effects of components in biogas on biological catalyst material

Component	Description of the effect(s)	Information availability	Showstopper for process? ²
Methane (CH₄)	In the biological methanation process methane does not affect the effectiveness of the catalyst. Methanogenic archaea are selective for carbon dioxide and hydrogen as substrate.		No
Carbon dioxide (CO₂)	An excess of carbon dioxide in the reactor can cause acidification of the process (dissolving carbon dioxide reduces the pH), which means the biological processes can be inhibited.		No
Nitrogen (N₂)	Nitrogen can dissolve in gaseous form in water and in other forms, such as N ₂ O, NH ₃ , NH ₄ ⁺ , HNO ₂ , NO ₂ ⁻ or HNO ₃ . There is not enough known about its effects on the biological methanation process.		No
Oxygen (O₂)	Although the biological methanation process is anaerobic, the archaea strain that is being used as biocatalyst is a relatively oxygen-tolerant species. Tests have proven that low concentrations of oxygen (<0.8 mol%) in the biological process do not have any effect on the methane production [23]. In higher concentrations oxygen will have a toxic effect on the organisms.		Not at low concentrations
Hydrogen (H₂)	No effects		No
Water vapour (H₂O)	No effects		No
Carbon monoxide (CO)	Insufficient information available.		No
Ammonia (NH₃)	When ammonia dissolves in water you create ammonium hydroxide, a moderately strong alkaline compound. An excess of ammonia may raise the pH in the reactor and has the potential to cause a disruption of the biological process. Specific effects for the biological methanation process are as yet unknown.		No
Sulphur compounds	Hydrogen sulphide is a gas that is produced by sulphate reducing bacteria during the digesting		No

² This column notes whether addition of the relevant component is a showstopper for the process, whether there is insufficient knowledge available, or whether it does not have a critical impact.

(e.g. H₂S, mercaptanes and THT).	process. Methanogenic archaea do not experience direct problems from the presence of hydrogen sulphide and will not degrade it. However, hydrogen sulphide may lower the pH of the process water by forming sulphuric acid through dissolution in water and that has a negative impact on the habitat of the archaea culture. The concentrations at which hydrogen sulphide may occur in biogas produces little risk of a significant pH reduction.		
Benzene, Toluene, Xylene (BTX) and Terpenes	<p>Conventional soil remediation technology uses archaea cultures to degrade BTX compounds. However, it is not known whether the archaea culture that is used in biological methanation (<i>Methanosarcina</i>) is able to degrade BTX. The level of tolerance is not known either.</p> <p>However, in relation to terpenes it is known that the presence of d-limonene has a negative effect on biogas production [15]. However, the relevant study does not produce any insight into the part process of biodigesting (hydrolysis, acidogenesis, acetogenesis or methanogenesis) or the ambient conditions (temperature, pH, etc.) that are disrupted by d-limonene. The study did not make any specific statements about the possible effects of d-limonene on methanogenesis and therefore the study in question does not enable us to make any statements about the effects of d-limonene on biological methanation.</p>		Not expected at low concentrations
Fluorine compounds (R-F, incl. HF)	We know about fluorine and chlorine compounds that research into the effects of methyl fluoride (CH ₃ F) and methyl chloride (CH ₃ Cl) on methanogenesis has shown that biological methane production is inhibited significantly when a concentration of 0.01% CH ₃ Cl and CH ₃ F is added. The methanogenesis stops completely with concentrations that exceed 0.1% of halogenes [14]. However, this concentration is an order of magnitude higher than the concentration that is present in biogas. There is little cause to assume that halogenated hydrocarbons in the concentrations, as they are available in biogas, have a significant inhibiting effect on the methanation process.		Not expected at low concentrations
Chlorine compounds (R-Cl, incl. HCl)	The methanogenesis stops completely with concentrations that exceed 0.1% of halogenes [14]. However, this concentration is an order of magnitude higher than the concentration that is present in biogas. There is little cause to assume that halogenated hydrocarbons in the concentrations, as they are available in biogas, have a significant inhibiting effect on the methanation process.		Not expected at low concentrations
D4-D5 siloxanes	Study results of [8] suggest that there are no indications to assume that siloxanes have a toxic effect on the organisms. However, study results that are specific to siloxanes in biological methanation are not available.		No



Besides these trace components, biogas may also contain micro-organisms that come from the digesting process to the gas phase. Studies by DNV KEMA demonstrate that archaea, eukarya and bacteria may be present in raw biogas flows that are released on digesting organic and animal material [21]. These organisms may cause a disruption of the biological catalyst culture, which may lead to reduced effectiveness and efficiency of the process. Total process disruption of the methanogenic archaea in biological methanation, by disruption on the basis of micro-organisms that were carried along from the digestion process, is not expected.

This chapter noted already that little is known about using a biological catalyst to purify and upgrade untreated biogas. However, it is the case that biologically produced gases, particularly those of pure biological cultures, general do not contain bio-toxic components [13].

3.2.2 General application performances

An important benefit of biological methanation compared to chemical methanation is that the technology is capable of ramping up and down over its full capacity range within seconds and it is suitable for highly dynamic operation [18][13].

Electrochaea, supplier of biological methanation reactors, argues that small-scale systems are able to respond within a few seconds to an increase or decrease of substrate (capacity to scale up or down), for large-scale systems this would take a few minutes. Methanogenic archaea are also able to go into 'hibernate' mode when the process conditions allow, e.g. a decrease in substrate supply and lowering the temperature. This means the system can be put in stand-by mode for a few weeks or months and then the archaea culture can be activated rapidly when process conditions are optimised (increase of substrate supply and increase in the process temperature) [18]. Process efficiency is claimed to be 75% - 80% [18]. An anticipated disadvantage may be the energy requirement to maintain a constant temperature of 20-40°C or 45-60°C degrees. The same temperatures are maintained in anaerobic digesting of organic waste and require approximately 5% of the total energy capacity.

It should be noted that the technology for biological methanation is still in a developmental stage. At the moment the first MW scale projects are under preparation.

4 SIMULTANEITY OF OPERATION

The production of biogas is a stable base-load process. Depending on the level of the applied digesting processes, there may be fluctuations in the biogas quality. However, the fluctuations in the production quality are generally very small and are presumed negligible. Figure 4 illustrates the production pattern of wind energy on land (production profile of wind on land in June and July 2013) and of biogas, as carbon source for methanation. The figure provides a clear insight into the difference in production patterns - wind energy is produced with a fluctuating profile, whilst biogas is produced extremely constantly. With a flexible application of Power-to-Gas, and the availability of a base load of carbon dioxide in biogas, there is an imbalance in the hydrogen/carbon dioxide ratio.

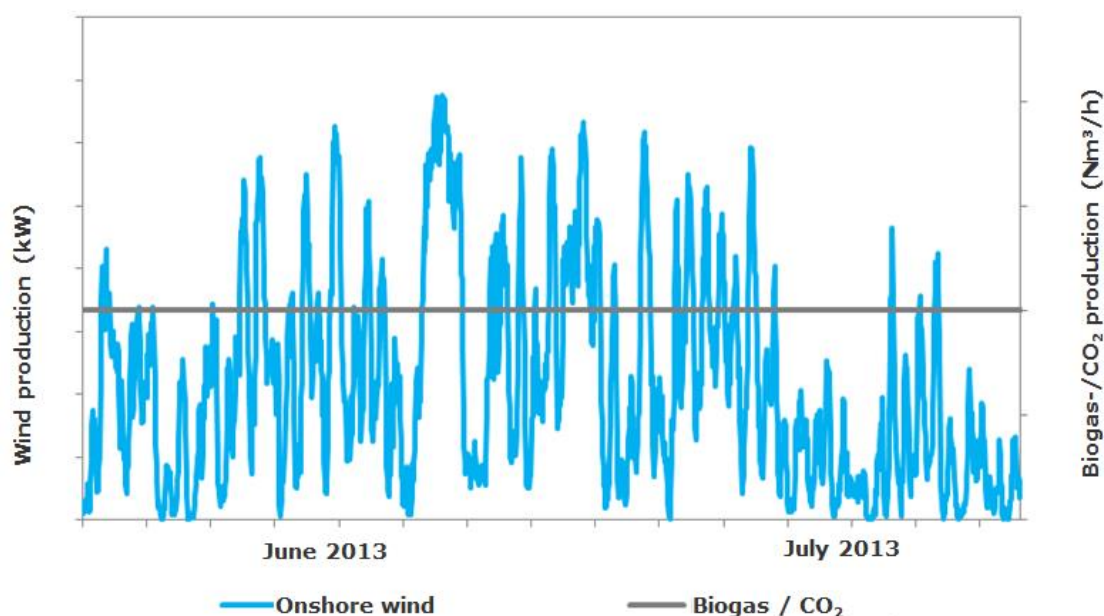


Figure 4: Illustration of the production profile of wind energy and biogas (as carbon source for methanation).


Chemical methanation

Chemical catalysts are sensitive to ratio differences because they change the temperature ratios in the reactors. On the other hand the effect on the conversion rate of the reactants to the products, which means the outgoing gas composition with an excess of carbon dioxide as reactant, will produce more carbon dioxide in the product gas. From a system perspective it is not desirable that the ratio between hydrogen and carbon dioxide changes constantly, because it has an impact on end user equipment and it is more difficult to guarantee that the injection requirements are met. The combination of biogas production (base-load) and Power-to-Gas (fluctuating) requires matching substrate or energy flows in order to avoid system disruption or energy loss.

Biological methanation

Manufacturers of biological methanation systems claim that biological methanation is a flexible technology in terms of capacity fluctuations and start-up/shut-down. The archaea culture seems to be able to adjust to the environmental conditions and substrate.

However, from a process-technological point of view it can be stated that the alkalinity in the biological reactor will change as the ratio of the substrate flows changes. An excess of carbon dioxide may cause acidification of the reactor, which changes the habitat of the archaea culture and possibly causes



disruption of the process. From a system point of view it does not appear desirable to have too many fluctuations in the substrate ratio between hydrogen and carbon dioxide. However, the level of tolerance of the biological catalyst to the fluctuations in the substrate flow (raw biogas) has not been studied sufficiently to make founded statements in this report. When biogas upgrading is integrated with biological Power-to-Gas systems, matching substrate or energy flows is required to avoid system disruption or energy loss.

In conclusion

The integration of Power-to-Gas with biogas production (Power-to-Gas as biogas upgrading system) requires matching of the substrate flows on the basis of the difference in the supply nature of biogas production and wind/solar. To achieve this, there are several possibilities:

- Temporary storage of biogas to ensure biogas is available when Power-to-Gas is required (biogas availability for upgrading follows the production profile of Power-to-Gas);
- Temporary storage of hydrogen to ensure the Power-to-Gas system can follow the production profile of biogas production (and peaks of hydrogen are stored temporarily)
- Use (purchase) electricity from the electricity grid at times when there is no wind/solar supply, to ensure Power-to-Gas can follow the production profile of biogas production.
- Install conventional biogas upgrading alongside Power-to-Gas to ensure that biogas upgrading and Power-to-Gas can operate independently of each other (when Power-to-Gas is required, carbon dioxide from the conventional upgrading system is used for methanation).
- Install a combined heat power unit near the Power-to-Gas unit to ensure that biogas applications and Power-to-Gas can operate independently (when Power-to-Gas is required, biogas is used for methanation and when Power-to-Gas is not required, biogas is turned into electricity in a combined heat power station).

Whichever of the above-mentioned technical options is most suitable depends largely on the financial health of the configurations in relation to the efficiency of the different configurations. A technical economic analysis of these configurations was not part of the scope of this study. DNV GL therefore recommends further study into the business cases of each of the configurations.

5 CONCLUSIONS

The use of methanation technology to upgrade biogas to natural-gas quality could make conventional biogas upgrading technology superfluous, provided and depending on the technology that is used, pre-switched biogas purification is used to remove specific gas components.

There are specific differences between the chemical catalysis process and the biological catalysis process.

Chemical methanation on the basis of a nickel catalyst is a process that converts carbon dioxide and hydrogen into methane extremely effectively under controlled and stable process conditions. The process has been applied for decades in industrial processes for methanation of hydrogen and carbon dioxide. However, the use of a nickel catalyst for upgrading untreated biogas is excluded due to the concentrations of hydrogen sulphide and oxygen that may occur in raw biogas. The oxygen tolerance of nickel catalysts is even lower than the oxygen specification for injection into the gas grid.

In general it can be stated that the purity of the carbon dioxide that serves as the carbon source for chemical methanation is an important condition for the process. A constant hydrogen/carbon dioxide ratio appears essential to safeguarding an effective and efficient process. The process technological options for dynamic operation must be studied further.

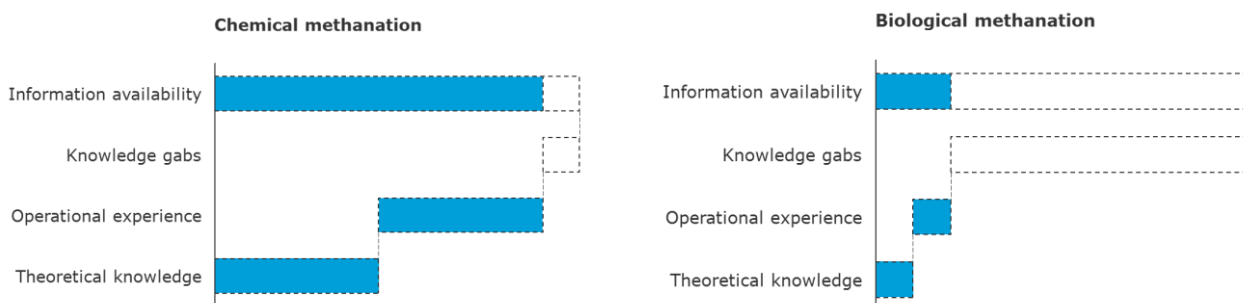
Biological methanation appears to be a viable technology in terms of tolerance for components that may be present in untreated biogas (and possibly for a number of types of flue gases). This would make biological methanation capable of using untreated biogas as the carbon source for the methanation process (Power-to-Gas).

However, at the moment there is insufficient information available to be able to be specific (in quantitative terms) about the effects of trace elements in biogas on the effectiveness and efficiency of methanogenic archaea as biological catalyst for Power-to-Gas purposes. Although theoretical considerations appear to demonstrate indications that confirm the applicability of methanogenic archaea as biological catalyst, more research and validation are required to ascertain a viable role for this technology. The same applies to further verification of the options of biological methanation for dynamic process control (fluctuating supply of substrate flows). Furthermore, currently there is very little practical experience with biological methanation in the Power-to-Gas chain, let alone the application of this technology for integrated upgrading of biogas.

Besides the effects of biogas components on the biological catalyst, the fact that the product gas of biological methanation may contain components that ensure that the product gas may not comply with the injection conditions for the gas grid must be taken into account.

6 POTENTIAL FOLLOW-UP STUDIES

On the basis of this study, the following figure provides a qualitative indication of the knowledge and experience available for the two methanation methods. In summary it can be stated that little is known about biological methanation (in general).



On the basis of the above insights, DNV GL determines that there is a need for more details on the following topics:

Component specific effects

DNV GL found that there are quite a lot of knowledge gaps regarding the effect of specific components on chemical or biological methanation catalysts. In particular for the BTX components, fluorine components, chlorine components and siloxanes it is unknown how they might affect the methanation process, if at all (both for biological and chemical catalysts). It is therefore advised to further investigate the effects of these components on different catalyst materials and in different typical process conditions (temperature, flow, etc).

Practical validation biological methanation

As stated in the conclusion of this report, biological methanation in particular seems a potentially valuable technology in terms of robustness and integration options with the biogas chain. At the moment this technology is in a transition phase from R&D to commercialisation. In order to make founded statements about the applicability of biological methanation and the possibilities of using untreated biogas as the carbon source for the methanation process, practical studies must be carried out and practical validation is required. For biological methanation in particular, there is no operational experience of monitoring trace components in biogas and the effect on the methanation process. This applies to the components terpenes, halogenated hydrocarbons, hydrocyanic acid and siloxanes whose effects are not currently known on the methanation process.

Dynamic operation of chemical methanation is important to system integration

The challenge for chemical methanation is in the purity of the CO₂ flow that is offered to the process and in the need for dynamic operation of the process. The Power-to-Gas demonstration project in Rozenburg (TKI 01015) has proven that the process works well in stable operational conditions. However, when substrate (hydrogen and carbon dioxide) supplies fluctuate this will have an impact on the effectiveness and efficiency of the process. What those exact effects are and to what extent the process is influenced quantitatively is not known as of yet. It is recommended to carry out further studies into the options for chemical methanation in a dynamic environment (fluctuating substrate flows).



Economic feasibility study into different configurations


This study determined that matching substrate flows is required to control the methanation process. However, the way in which matching substrate flows is achieved from a technical point of view - storing biogas, hydrogen or purchasing electricity at times when there is no wind or solar energy supply - depends on economic considerations. As research into the economic feasibility of the various configurations did not form part of the scope of this study, DNV GL recommends to have further research carried out.

Integrate hydrogen production into the existing biogas chain

This report provides insight into the options to move the biogas upgrading function to methanation in the Power-to-Gas chain. As stated in the conclusion, the proposed system integration produces a few new research questions. Another way to integrate the two chains is by integrating hydrogen production into the existing biogas production (digesting). At the times when electricity consumption is required to balance the electricity grid and/or the electricity market, electrolysis can be used to produce hydrogen that can be supplied directly to a biodigester. The conventional biodigesting process produces hydrogen as an interim product in the acidogenesis/fermentation step, following which it is converted into methane by means of acetogenesis and methanogenesis. Adding hydrogen from electrolysis to the digesting process is likely to improve methane production in the digester. Biogas is then conditioned to become a natural-gas substitute by means of existing purification and upgrading methods. At the moment it is not yet known to what extent hydrogen can be added to biogas reactors without causing process disruption. Practically, it is recommended to study and verify what the maximum permissible hydrogen fraction is for biogas reactors and the maximum carbon dioxide conversion rate of the system in view of quantifying the possible energetic and economic synergies of this system integration.

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