# Biomethane in the EDGaR program and at ECN

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## 1. Introduction

For decades, large natural gas supplies have made the Netherlands nearly self-sufficient in energy, with (net) export of natural gas balancing (net) import of other fossil fuels. Natural gas provides nearly half of the Dutch primary energy use and represents a significant contribution to the Dutch economy. Dwindling gas reserves force the country to consider its future energy provision and position in the global energy market.

The Energy Delta Gas Research (EDGaR) program aims to deliver scientific and technological input to the discussion and decision process. The program is a joint effort of the major Dutch companies which trade, transport and distribute natural gas, of three universities and three research institutes. It runs for a period of five years, from 2010 to 2014, and has a total research budget of 42 million Euros. More details on the EDGaR program, organization, participants and projects can be found on www.edgar-program.com.

The program motto is “the role of gas in the transition to a sustainable energy supply”. The motto reflects two basic ideas. On the one hand, biomethane will play a part in the sustainable energy supply [1]. On the other hand, gas from fossil origin will be needed for many more years to fill the gap between energy demand and supply, and to provide back-up capacity and thus enable the use of intermittent renewable energy sources.

The EDGaR program encourages multi-disciplinary research, covering technical, economic, social and legal aspects on three themes:

1. From monogas to multigas
2. Future energy systems
3. Changing gas markets.

In total, 30 projects have been granted. This article presents a short overview of biomethane related subjects covered within EDGaR projects. More detailed information will be given on projects which involve research on the production of bioSNG, i.e. SNG (= Substitute/Synthetic Natural Gas) produced by gasification of biomass followed by catalytic conversion of the producer gas to methane.

## 2. Biomethane related projects

In a strict sense, the word biomethane refers to pure methane ($CH_4$) extracted from gas produced from biomass or by living organisms. Here, the term is used also in a broader sense to include landfill gas, biogas from digestion, and bioSNG which may contain significant amounts of other gases such as carbon dioxide ($CO_2$), nitrogen ($N_2$) or hydrogen ($H_2$).

Most of the biomethane related EDGaR projects are not even limited to biomethane in the broad sense. They study the consequences of fuel gases with components or properties different from what Dutch companies and consumers are used to. Hence, they consider not only biomethane but also e.g. LNG, natural gas from unconventional sources or mixed with $H_2$.

One set of projects, executed by the KIWA research institute in co-operation with the gas transport and distributing companies Gasunie[1], Enexis, Liander and Stedin, studies the effects of a number of gas components on materials commonly used in the gas transport and distribution infrastructure. Among the components studied are sulphur, chloride and nitrogen compounds, aromatic hydrocarbons, $CO_2$, CO and $H_2$. Materials considered are PVC, PE, NBR, steel, copper, and aluminium. Long-term exposure tests are performed for combinations and conditions which are likely to occur but for which available information is inconclusive.

Another set of projects studies the effect of “gas quality” on the performance and safety of household appliances, industrial burners, and equipment such as gas engines. Here “gas quality” stands for heating value, content of higher hydro-carbons, $CO_2$ or $H_2$, or Wobbe value. These projects are executed by the same partners plus Groningen University. Both theoretical and experimental work is performed on flame stability, flame lift, flashback, engine knock, ignition behaviour, and emissions. A related project, which has already been completed, aimed at setting specifications for silicon compounds in biogas, i.e. mainly in landfill gas and waste water treatment gas.

A third set of projects involves gas measurement technology, for combustion management, billing purposes or detection of trace compounds, especially siloxanes. Partners involved in (some of) these projects are Delft University, the research institutes ECN and KIWA, and again the gas companies Gasunie, Enexis, Liander and Stedin.

A number of projects studies gas market dynamics, e.g. security of supply and the behaviour of market players with respect to investments in biogas infrastructure, legal aspects, risks and liability. One project specifically investigates options to store biogas. These projects are executed by Delft University, Groningen University, Hanze Technical University, ECN, and the gas companies. Several projects in the next section are not restricted to bioSNG but also include biogas.

## 3. BioSNG related projects

Within the EDGaR program there are three bioSNG projects and one related project. Apart from the project leader ECN, parties participating are Groningen University, Delft University, Hanze Technical University, and the gas companies Gasunie and GasTerra.

Two projects (AGATE 1 and 2) involve research and technology development for bioSNG production. ECN and Groningen University study the conversion of “dry” and “wet” biomass, respectively. DNV-GL (on behalf of Gasunie) studies gas quality and process economics. Research by ECN and DNV-GL is directed towards a 4 MW SNG demo to be built in Alkmaar. More details follow in the next section.

The conversion of “wet” biomass starts with gasification in supercritical water, using bespoke nano-size catalyst particles. Research focuses on catalyst performance, catalyst recovery and up-scaling from a batch set-up to a continuous process.

Another subject covered by Groningen University is the use of radiocarbon ($^{14}C$) analysis for certification of the biological origin of biomethane [2]. Radiocarbon analysis of $CO_2$ in flue gas is already used at power plants which fire biomass or co-fire biomass and fossil fuel, to determine

[1] Research on behalf of Gasunie is performed by DNV-GL, part of which used to be the Gasunie research department.

which proportion of the power output comes from biomass.

In case of bioSNG produced at ECN from a mixed biomass/fossil fuel it could be shown that the biomethane $^{14}C/^{12}C$ ratio, i.e. its “bio-origin fingerprint”, differed substantially from the one in the fuel. Further research is needed to allow development of a certification standard for biomethane based on $^{14}C$ analysis.

A third project (SNG Impact) studies subjects related to future large-scale bioSNG introduction, i.e. up-scaling of the technology, price and value, social and environmental implications.

The fourth project (Synthetic Methane) studies the production and use of $CH_4$ to provide power storage and back-up capacity which are needed to allow large contributions of intermittent renewable power sources. It is a version of the Power-to-Gas (P2G) concept which implies storage of excess (renewable) power in the form of $H_2$ produced by water electrolysis. The $H_2$ can be made to react with $CO_2$ to produce $CH_4$ according to the Sabatier reaction $CO_2+4H_2 \Leftrightarrow CH_4+2H_2O$. The required $CO_2$ can be a pure stream from $CO_2$ capture, or part of a mixed stream such as biogas or producer gas from a biomass gasifier. The additional process costs and energy penalty should be offset by the better match to the existing gas infrastructure.

## 4. BioSNG research at ECN

ECN intends to develop a bioSNG process consisting of MILENA indirect gasification, OLGA tar removal, adsorbents for gas cleaning, and commercial catalysts for conversion of cleaned producer gas into “raw” bioSNG, i.e. a mixture of mainly $CH_4$ and $CO_2$. Initially, amine scrubbing will be used to remove $CO_2$ from the raw bioSNG, but ECN is also developing a process for $CO_2$ removal by adsorbents which can be regenerated with steam [3].

MILENA indirect gasification and OLGA tar removal will be presented in another contribution to this conference [4]. Here, the remainder of the process will be described.

Downstream OLGA, the producer gas cleaning should remove all components which may harm the methanation catalysts. The main contaminant is sulphur, which is present mainly as hydrogen sulfide ($H_2S$), carbonyl sulfide (COS) and thiophene ($C_4H_4S$), and smaller amounts of methane- and ethane-thiol ($CH_3SH$ and $C_2H_5SH$), carbon disulfide ($CS_2$), and other more complex and heavier compounds.

Research at ECN focuses on conversion or removal of $C_4H_4S$. Active carbon is an appropriate adsorbent, but it is quickly saturated by benzene ($C_6H_6$) and toluene ($C_7H_8$) which are present in 1000 and 100 times higher concentrations. Active carbon can be regenerated with steam and the resulting aromatic mixture may be burned or sold [5]. Another option is conversion of $C_4H_4S$ into $H_2S$ by use of a hydrodesulfurization (HDS) catalyst. Tests at atmospheric pressure showed that nearly full conversion can be obtained at low gas velocity and high temperature. Performance increases with pressure, according to tests performed in a test rig built with EDGaR support (see Figure 1).

*Figure 1. Test rig with producer gas dryer, 6 bar compressor and HDS reactor.*

Simple sulphur compounds and other contaminants can be removed upstream and/or downstream the HDS reactor. To that end, the SNG test rig at ECN (see Figure 2), also built with EDGaR support, contains two reactors at atmospheric pressure and two reactors at higher pressure. The test rig contains three more reactors, intended for catalyst testing.

*Figure 2. SNG test rig containing reactors for adsorbents (left) and catalysts (right).*

The HDS catalyst also promotes the water gas shift (WGS) reaction and hydrogenation of unsaturated hydrocarbons. This reduces the risk of carbon deposition at the methanation catalyst. Aromatic compounds are not affected. They can be removed (e.g. as discussed above) or reformed by reaction with steam to carbon monoxide (CO) and $H_2$. The test rig shown in Figure 2 is used to determine the optimal operating conditions.

The test rig is also provided with bottle gas supply. This allows simulation of gas recycling, which is commonly used to limit the temperature rise in fixed-bed methanation reactors. It also allows to simulate of $H_2$ addition, relevant to P2G as discussed above.

In 2014, the complete test set-up from MILENA to HDS and SNG will be used for a test of several hundred hours, as final preparation for the detailed design of the Alkmaar SNG demo.

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