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# 2019 Young Researchers Awards

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Finalists' Abstracts



## Table of contents

Ernstjan de Boer, <i>Future Scenarios for Repurposing Existing Natural Gas Transmission Pipelines for Hydrogen in Europe</i> .....	3
Marco Cavana, <i>Gas Network Modelling for a Multi-Gas System</i> .....	4
Michał Grzybowski, <i>Can hydrogen replace natural gas? – comparison of LNG and LH<sub>2</sub> value chains</i> .....	5
Perla Haddad, <i>RINGS - Research on the Injection of New Gases in Storages: The case of oxygen during biomethane storage</i> .....	7
Martin Kientz, <i>Renewable methane production by catalytic reduction of CO<sub>2</sub> using sunlight</i> .....	8
Aurore Lecharlier, <i>Characterization of biogas and biomethane: analysis and speciation of trace compounds</i> .....	9
Chirayu Thakur, <i>Biogas Cleaning for Catalytic Processes</i> .....	11
Jinrui Zhang, <i>Life cycle assessment and cost analysis of LNG supply chain with cold energy utilization</i> .....	12

# Future Scenarios for Repurposing Existing Natural Gas Transmission Pipelines for Hydrogen in Europe

*Ernstjan De Boer  
Hanze University of Applied Sciences  
Forschungszentrum Jülich*

With a very extended operational natural gas transmission grid in Europe and the current awareness of the energy transition, opportunities lie for combining both for a sustainable future. Research is done to the suitability of the European natural gas grid for transporting hydrogen gas. The question *if* the transmission network can be used for hydrogen transport has been answered in other research also. A more important question is *how* the European natural gas transmission network can be used in the future to help the energy transition.

This is done by creating a database of the European natural gas network, this database contains detailed information about the pipeline network like diameters, pressures, locations, and material types. Then, future scenarios for the natural gas and hydrogen demand are created, with higher and lower natural gas demand for 2030 and 2050 respectively. Hydrogen demand shows an increase in 2030 and an even bigger one in 2050. The demand of both gasses is divided over Europe using NUTS-2 regions. The supply of hydrogen comes from water electrolysis using surplus electricity and import at specific locations. This data is used as an input for the “FINE” – Framework for Integrated Energy System Assessment developed by Forschungszentrum Jülich. Using this Python-based framework, optimizations on the natural gas and hydrogen distribution through the transmission network are done for the different scenarios.

The model distributes hydrogen and natural gas separately, and gives energy flows for each pipeline in the database. If necessary, the model shows locations of new-built pipelines. Using the different simulated scenarios, seen is that starting in 2030, around 25% of the existing pipelines can be used for hydrogen transport in a hybrid network, and over 30% in 2050. The results are also plotted on a map of Europe to give an overview of the convertible pipelines.

# Gas Network Modelling for a Multi-Gas System

Marco Cavana,  
PhD Student, Department of Energy – Politecnico di Torino  
[marco.cavana@polito.it](mailto:marco.cavana@polito.it)

The latest years have known an increasing interest in the future role of the natural gas sector within the energy system. Belonging to the class of “fossil resources”, natural gas employment as an energy commodity has been questioned in the framework of the sustainability of the decarbonized energy system of the future. On the other hand, natural gas is widely recognized as the key enabler of energy transition. Within this dilemma, a stream of innovation has literally invested the gas system thanks to the concepts of “greening” the natural gas sector by means of renewable gases such as bio-methane, hydrogen and synthetic natural gas.

In 2018 only, four studies have been published with the common result that, in 2050, renewable gases injection will be more economically convenient than 100% electrification, with annual savings ranging between 8 and 138 billion € per year [1],[2],[3],[4] . On a more technical basis, the white paper by the Sustainable Gas Institute (2017) [5] presents a comprehensive study on the various options for a greener gas network.

Allowing renewable gases within the gas system would mean to decarbonize the natural gas value-chain, taking advantage of the already widespread pipeline infrastructure and justifying the today’s investment in its expansion. However, it forces the natural gas sector to face new issues and challenges because of its transition towards a multi-gas system. In this framework, suitable gas network modeling tools are necessary to evaluate the impacts and the opportunities of practices such as bio-methane injection and/or hydrogen blending at distribution or transmission level.

A new gas network model has been developed in order to simulate different portions of the gas infrastructure under possible future scenarios of distributed injection of renewable gases. The model is structured in such a way that it is easily adaptable to any network topology. It is based on transient fluiddynamic equations for the simulations of the pipelines and the gas is modeled as a mixture of 21 components by means of the GERG-2008 equation of state. The model is thus able to simulate transient behaviors of the gas network as well as to track the quality perturbations network-wide, in the framework of unconventional gas injection.

The model has been applied to a distribution gas network of a small rural municipality under different renewable gas injection scenarios:

- a) Biomethane injection: in order to show how to address the criticality of limited network capacity (taking advantage of the transient feature of the model);
- b) Hydrogen injection: in order to assess the impact of the gas quality perturbation as a consequence of distributed injection (taking advantage of the quality tracking feature of the model) as well as to evaluate the renewable energy storage potential of the whole network and its hourly trend, in the framework of power-to-gas employment.

The show-cases have both the purpose of showing the potentialities offered by the network modelling tool and to give illustrative results about the opportunities and the criticalities of practices related to the greening of the gas network and to the decarbonization of the natural gas sector.

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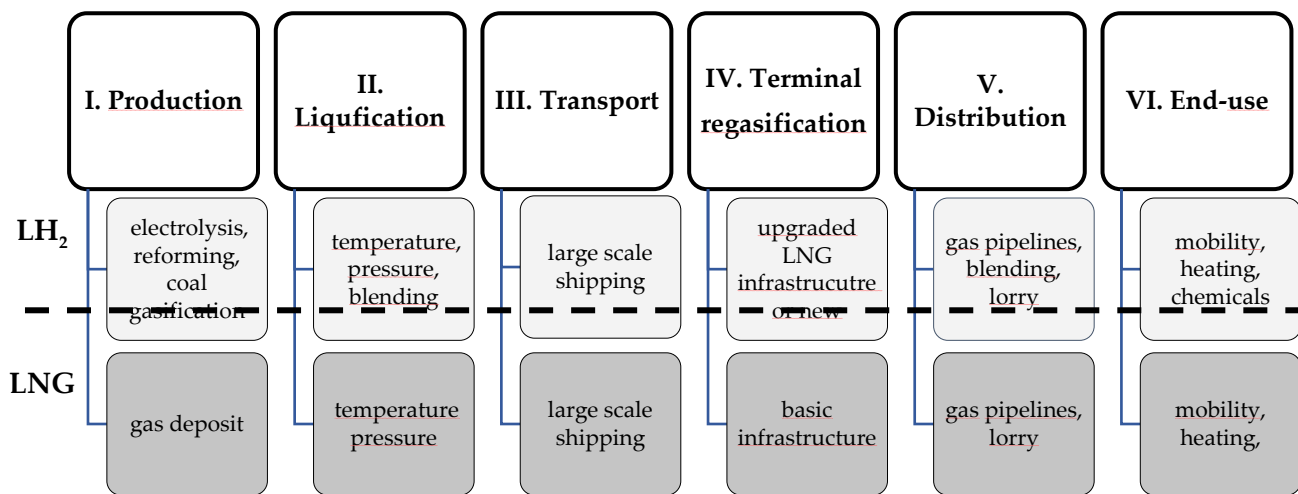
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# Can hydrogen replace natural gas? – comparison of LNG and LH<sub>2</sub> value chains

Michał Grzybowski, University of Warsaw

The hydrogen market, unlike LNG, is relatively young, however, both raw materials have many similarities, in particular, it can be seen when analyzing value chains. The LNG and hydrogen value chains have significant similarities in many aspects. Using the experience of the LNG market to create an environment for hydrogen seems to be very promising, especially since hydrogen is a great energy carrier that does not generate a significant carbon footprint. However, there are also some challenges which should be considered and evaluated like materials working in lower temperature and pressure.



The purpose of the article is to show similarities in the LNG and hydrogen chains that can be used to create a new market, as well as differences that will require additional infrastructure and logistics investments (CAPEX):

## Main similarities:

- **III. Transport** - liquefied hydrogen may be transported in ships similar in construction to those carrying LNG, it would be required to increase the tank walls resistance to higher pressures, lower permeability and lower temperatures. A much larger insulation would be recommended. Construction projects are under way to create vessels capable of carrying LH<sub>2</sub> (Kawasaki LH<sub>2</sub> tanker project, Equinor and DNV-GL LH<sub>2</sub> bunker vessel)
- **IV. Terminal regasification** - the construction and infrastructure in the LNG terminal is similar to that which could handle liquefied hydrogen. The difference is once again that the infrastructure for LH<sub>2</sub> would have to withstand much lower temperatures, higher pressures and lower permeability. Current LNG infrastructure (pipes, joints, pumps etc.) would need to be replaced or improved (significant CAPEX costs). In some cases, the construction of a new terminal could be more beneficial. (HySter is a common project of Japan and Australia in LH<sub>2</sub> market and infrastructure development.)
- **V. Distribution** - both hydrogen and LNG after appropriate processing in the terminal can be further transmitted by pipeline, tank transport. Transmission of hydrogen through pipes would require the construction of dedicated lines (significant CAPEX) or mixing with natural gas (different allowable hydrogen concentrations in gas in the EU), it is also possible to transport road over

shorter distances, in particular using hydrogen carriers that neutralize its physical properties (LOHC, ammonia, toluene).

- **VI. End-use** - the use of LNG and LH2 after processing at the terminal is relatively similar. Both hydrogen and LNG can be used in urban mobility (buses, FCEV cars), in heating (stoves for natural gas, hydrogen or a mixture of two gases), hydrogen also plays a significant role in the chemical and fertilizer industry.

#### **Main differences:**

- **I. Production** - obtaining hydrogen and natural gas is very different. Hydrogen does not exist in the free state, ultimately the most ecological method of hydrogen production is electrolysis based on renewable energy sources, but currently the most profitable are gasification of coal and reforming methane with or without carbon dioxide capture. Natural gas is free in deposits. For now, the costs of producing hydrogen by eco methods are high and strongly differ from the prices of natural gas extraction. Cost of hydrogen production from gas reforming is now 4-5 \$/kg.
- **II. Liquefaction** - hydrogen to be liquefied must be cooled to a critical temperature - 243 C \* and compressed to a pressure of 13 bar - then the hydrogen decreases its volume about 800 times. This process is much more energy-intensive than liquefaction of natural gas, where the required temperature is about - 162 C \* and pressure 4-5 bar. Organic liquids, ammonia, toluene or other carriers with which hydrogen reacts to form much less invasive and difficult to control compounds can help in the liquefaction and further transport of hydrogen. When using the LOHC method, hydrogen is transported at room temperature and pressure, only increased temperature and pressure are required for the reverse reaction.

USE OF EXPERIENCES AND MECHANISMS FROM THE LNG SECTOR MAY BE A GREAT OPPORTUNITY FOR A HYDROGEN MARKET. The main challenge is to deal with the onerous physical properties of hydrogen, whether by mixing it with other compounds, or by developing an improved infrastructure and fleet. The undeniable advantage of hydrogen is that it is a great energy carrier that can be produced ecologically, and its possibilities in modern decarbonized energy are large (RES stabilization, transport, energy storage). To lead to the expansion of the hydrogen market, it is worth ensuring its far-reaching transport and logistics, which are similar to the already mature LNG market.

# RINGS - Research on the Injection of New Gases in Storages: The case of oxygen during biomethane storage

P. HADDAD<sup>1,2</sup>, F. CASTERAN<sup>1</sup>, A. RANCHOU-PEYRUSE<sup>2</sup>, M. GUIGNARD<sup>2</sup>, P. CEZAC<sup>1</sup>, D. DEQUIDT<sup>3</sup>, P. CHIQUET<sup>4</sup>, G. CAUMETTE<sup>4</sup>

<sup>1</sup> University of Pau and Pays de l'Adour, E2S UPPA, Laboratory of Thermal Engineering, Energy and Processes (LaTEP), IPRA EA1932, 64000, Pau, France

<sup>2</sup> University of Pau and Pays de l'Adour, E2S UPPA, Institute of Analytical Sciences and Physico-Chemistry for Environment and Materials (IPREM)-CNRS, UMR 5254, 64 000, Pau, France

<sup>3</sup>STORENGY, 12 rue Raoul Nordling – CS50014 - 92777 BOIS-COLOMBES cedex, France

<sup>4</sup>TEREGA, 40 avenue de l'Europe - CS 20522 - 64000 PAU, France

The quest for new energy resources has exponentially bloomed in the last few years. Multiple substitutes for fossil fuels have been suggested in order to reduce their notorious outcomes mainly greenhouse gases effects. Aside of being renewable gases, hydrogen and biomethane had recently emerged as potent alternatives to hydrocarbons; however, limited data is available regarding their storage. Thus, the objective of our study is to assess the bio-geo-chemical impact of those gases, when stored in underground storage reservoirs (UGS). The first part of our project studied the effect of oxygen during biomethane storage and is presented in this paper.

Oxygen is usually present in the biogas and in biomethane, along with other impurities. During storage, those components may potentially interfere. As described by many studies, UGS harbor an anaerobic microbial life whose activity is already accounted for during the development of the gas sector. Interactions with oxygen in those reduced systems can modify the biogeochemical conditions of the reservoir furthermore, which can cause serious problems as changes in microbial diversity, well clogging, reduction or acceleration of known biodegradation reactions.

In view of the unknown outcomes of these interactions and in view of the lack of available studies in this setting, we conducted an experimental program that consisted of rebuilding, in the lab, the *in situ* conditions of UGS. We specifically studied the impact of oxygen injection. Our in-lab simulated reservoir consists of a batch reactor. Three phases were considered: (i) anaerobic groundwater sampled from the underground with autochthonous microorganisms; (ii) rock samples from the geological reservoir placed in a macro-porous basket; and (iii) gas phase simulating the biogas composition with interfering components.

A temperature of 37°C and a pressure of 60 bar were kept constant in the reactor, identically to our reservoir conditions. In the beginning, the sandy and porous solid phase was completely submerged in aquifer's water. At the end of this incubation time, one third of the solid remained submerged, and then the gas was injected.

The reactor was equipped with thermometers and barometers in order to provide continuous measurements of the temperature and pressure. The gas and the liquid phase were analysed with TCD-gas and ionic chromatography respectively. The impact on the microbial life was repeatedly examined through regular sampling of the water and monitoring of the changes in the composition of microflora. The pressure drop of the water sample was carefully lengthen during 3 hours to avoid any effect on the microbial life. At the end of the experiment, the solid phase is analysed by tomography and mineralogical analysis. Those measurements help in the identification of biofilm formation between our reservoir sand particles, and in the detection of degradation of this mineral phase.

Our first observations revealed a surprising and very fast proliferation of the microbial life under the pressure of 60 bar associated with a remarkable variation of the system. Anaerobic biodegradation of the aromatic compounds present in our simulated aquifer may be the reason behind this microbial development.

Further advances in our experiment will allow for an overall understanding of the implications of gas storage in underground reservoirs. Furthermore, the detection of alterations affecting microorganisms and their potential interaction with surrounding oxygen in this setting will set the starting point for a better comprehension of the biological, chemical and geological aspects of new gas storage techniques.

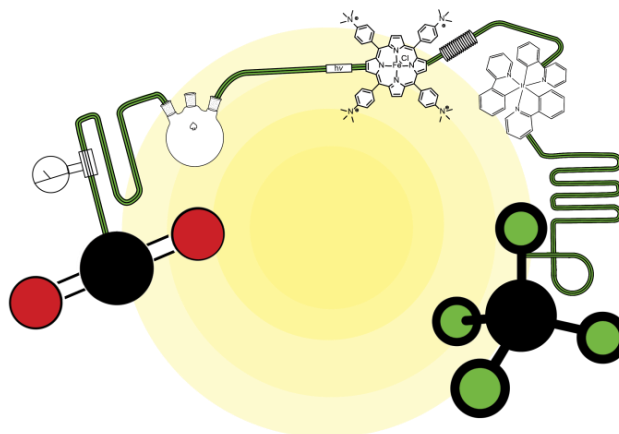
# Renewable methane production by catalytic reduction of CO<sub>2</sub> using sunlight

***Martin Kientz<sup>1,2</sup>, Julien Bonin<sup>1</sup>, Marc Robert<sup>1</sup>***

<sup>1</sup> Université de Paris, Laboratoire d'Electrochimie Moléculaire (LEM), UMR CNRS 7591, 15 rue Jean-Antoine de Baïf, 75205 Paris Cedex 13 France, <http://www.lemp7.cnrs.fr/>, [martin.kientz@univ-paris-diderot.fr](mailto:martin.kientz@univ-paris-diderot.fr)

<sup>2</sup> Gaz Réseau Distribution France (GRDF), 6 rue Condorcet, 75009 Paris, France, <http://www.grdf.fr>

Facing today's environmental and energy issues, the activation of small molecules such as nitrogen (N<sub>2</sub>) or carbon dioxide (CO<sub>2</sub>) represents a major challenge for both research and industry. In our recent studies, we have shown that it is possible to use solar energy in combination with appropriate molecular catalysts, consisting of abundant and non-toxic elements, to produce fuels, such as methane (CH<sub>4</sub>), from CO<sub>2</sub>. On a long-term perspective, this constitutes a strategic industrial target that would make possible to use CO<sub>2</sub> as a cheap and renewable raw material for the generation of energy-rich compounds and to bring it into a circular economy that would contribute to preserve the environment.



The Energy Transition Green Growth Act seeks to enhance France's energy autonomy, by cutting its greenhouse gas emissions and setting a target of 10% of renewable gas (about 30 TWh/year of renewable methane) in the total consumption by 2030. This objective is achievable on the condition that new sources of and processes for renewable gas have emerged, such as bio- and synthetic methane as proposed here.

To efficiently transform CO<sub>2</sub> using sunlight as the primary energy source, powerful, selective and robust catalysis is necessary, which requires a fine understanding of the mechanisms involved at the molecular level. In this presentation, I will give an overview of recent fundamental and applied studies performed at LEM in the use of molecular catalysts based on transition metals, focusing on iron porphyrins, to transform CO<sub>2</sub> into CH<sub>4</sub> using visible solar light as the energy input.[1-4] Our work first aims at understanding the key parameters of the chemical transformation reaction, in order to be able, in a second step, to optimize the catalytic cycle and to scale up the process for future industrial applications.

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# Characterization of biogas and biomethane: analysis and speciation of trace compounds

Lecharlier Aurore

[aurore.lecharlier@univ-pau.fr](mailto:aurore.lecharlier@univ-pau.fr)

*PhD student in Environmental Analytical Chemistry*

*IPREM & LFCR Laboratories, Université de Pau et des Pays de l'Adour, France*

*In collaboration with TERÉGA, France*

**Keywords:** energy transition, biomethane, trace compounds, preconcentration

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With the growing shortage of fossil fuels and the resulting urgency to lessen our dependency to those, the renewable energy sector and notably the biomass energy sector have undergone quite a boom. In particular, biomethanization plants upgrading organic wastes to biogas via anaerobic digestion are really taking off since a few years, contributing to the energy transition and to the circular economy. While this renewable biogas is mainly used *in situ* for heat and electricity production (co-generation), the biomethane produced by further purification of the biogas is the renewable substitute for natural gas and its injection in the natural gas transport and distribution grid is worldwide effective since the 1980's (1).

However, the biogas purification process aiming at reaching a gas quality equivalent to that of natural gas, is not 100% efficient and impurities coming from the digested wastes are found in the resulting biomethane at trace levels. Organic and anthropogenic waste sources used in digesters include agricultural, livestock, food-processing industry, paper industry, compost, wood and municipal wastes, and biogas can also be generated from landfills and waste water treatment sludge. Man-made molecules or molecules concentrated by humans in those wasted materials (silicones, polymers, oxygenated compounds, (halogenated) volatile organic compounds ((H)VOC), Nitrogen and Sulphur compounds, metal(loid)s, CO, CO<sub>2</sub>, NH<sub>3</sub>...), but also naturally occurring molecules (e.g. terpenes, volatile organometals...) volatilize during the anaerobic digestion and enter the gas phase, even in small amounts (traces, down to < ppb). The presence of these trace compounds, not present in natural gas, in biomethane can become problematic regarding its injection in the grid, its storage in underground gas storage facilities like aquifers or its utilization. Some trace contaminants may be corrosive (H<sub>2</sub>O, S-compounds, CO, CO<sub>2</sub> in the presence of humidity, O<sub>2</sub>, NH<sub>3</sub>, organometals, organohalogenated...) for gas transport, distribution and processing infrastructures, siloxanes can be abrasive and form deposits when combusting the gas in engines, terpenes can deteriorate polymeric or rubber materials like gaskets and can mask the THT odor added in the gas for safety gas detection purposes, and other compounds may cause sanitary or environmental damages during the storage or the final use phase.

In view of the complexity of biomethane matrixes, of the diversity of possible input wastes, of the variability of anaerobic digestion operational parameters, weather and geographical conditions, the comprehensive characterization of the trace compounds composition of biomethane is a hard task. The difficulty is that sampling and analysis of these compounds in gas is not routinely done by analytical labs, and needs more analytical development. Notwithstanding, most European gas grid operators already have quality standards for biomethane injection, specifying maximal allowed concentrations

of some trace compounds such as H<sub>2</sub>O, siloxanes, CO, CO<sub>2</sub>, NH<sub>3</sub>, some organohalogenated and some metals.

The objective of this thesis is henceforth to select and test the most suitable techniques for the sampling and analysis of selected trace compounds in biomethane and thus to build a database of the trace compounds present in biomethane in function of the input waste types, of the anaerobic digestion process operational parameters and of the biogas upgrading process. To achieve this, analytic physico-chemical methods are developed to preconcentrate (while sampling), quantify and speciate the trace compounds.

For the analysis of trace compounds, preconcentration is of paramount importance to obtain analyte levels higher than the LOD of analytical instruments. In this project the preconcentration is done on the one side by sampling gas on site under high pressure (up to 100 bar) and on the other side by adsorption, absorption, amalgamation, cryotrapping or chemotrapping. Adsorption is executed on self-prepared adsorbent multibed cartridges (XAD-2/Coconut activated coal; Tenax TA/Carboxen 1000; Carbopack B/Carboxen 1000) designed to sorb analytes in a broad range of volatilities: (H)VOC, pesticides, oxygenated compounds, N-, S- and Si-compounds. The separation and quantification of adsorbed compounds is performed via thermal desorption and GC-(GC)-MS. The SIFT-MS technique will also be used to investigate the time stability of gas samples stored in different containers including the adsorbent cartridges.

Concerning the trapping of volatile metals, several techniques are employed: absorption in acid bubbling solutions (HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> for metals other than Hg; KMnO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> for Hg) followed by ICP-MS for the speciation and quantification, cryotrapping followed by GC-ICP-MS, specific Amasil<sup>®</sup> gold coated sand traps amalgamating Hg followed by CV-AFS, and specific AgNO<sub>3</sub> chemotrapping followed by AFS for As speciation and quantification. The speciation of metals is essential since it determines their reactivity, solubility, toxicity, bio-availability, corrosiveness...

All the analytical sampling-preconcentration techniques are developed to be high pressure resistant and ATEX certified to be able to sample gas on site directly from the pipelines, whatever the pressure (>100 bar), to avoid dilution of the trace compounds by depressurization, but also to avoid *in situ* contamination, sample transfer and sample transport.

# Biogas Cleaning for Catalytic Processes

*Chirayu Thakur*  
*Hanze University of Applied Sciences*

An adsorption based removal of trace sulfur compound, Dimethyl sulfide (DMS) using commercially available sorbent materials was tested under laboratory conditions using bench scale gas mixture. An extensive literature study was carried out to understand the various aspects of experimental conditions and sorbents tested in previous works. The literature from previous experimental works were categorically studied under different themes such as effect of moisture, effect of metal impregnations, effect of bed geometry, effect of space velocity and co-adsorption. The experimental setup was designed in manner by which the knowledge gained from the literature study could be applied to investigate and analyze the influence of important parameters which were previously less examined for desulfurization of biogas.

The aim of the experimental research was to make recommendation on the selectivity of commercially available sorbent materials that could be used for field demonstration based on their performance at different set of experimental conditions on the laboratory scale. The bench scale gas mixture was majorly composed of carbon dioxide, methane, water and their proportions resembling those in agricultural biogas. The water in the gas mixture was studied at three different stages: at dew point of 4°C, 20°C and 40°C. Limonene was added to the gas mixture in one of the stages to observe the effect of co-contaminants on the DMS removal performance. Analytical techniques such as mass spectrometry and micro-Gas chromatography were used for detection and quantification of gases. The sorbents were analyzed by performing temperature programmed oxidation (TPO) for the fresh and used samples and results were compared to have a preliminary understanding of the adsorption mechanism on the sorbent surfaces.

The results from the breakthrough experiments showed that the sorbent SulfaTrap™-R2, which is a zeolite, performed the best displaying high sorbent capacity for DMS adsorption at conditions with relatively less water content in the gas mixture. Norit RGM3, a copper oxide impregnated steam activated carbon, performed robustly and exhibited little influence of water content within a range of ~5000 to ~16000 ppm on the sorbent breakthrough performance. Overall, the performance of all the sorbents was evidently hampered in the conditions of high water content in the gas. Addition of limonene was seen to have a marginal impact on sorbent breakthrough performances as compared to conditions without any limonene addition. However, the nature of curves were steeper in conditions with limonene as co-contaminant indicating higher rate of increase in concentration of DMS in the outlet.

# Life cycle assessment and cost analysis of LNG supply chain with cold energy utilization

Jinrui Zhang,  
University of Groningen

As the trade of LNG is increasing rapidly, it is essential to find the best way to supply and use LNG from an economic and environmental point of view. Liquefaction of NG consumes a substantial amount of energy, which equivalent to up to 10% of supplied NG. LNG is then kept at the temperature of -162 °C and slightly higher than atmospheric pressure. LNG has not only high chemical energy (combustion energy) but also high physical exergy (cold energy). However, the cold energy is usually wasted and transferred to seawater or air at the regasification terminal. Furthermore, the cold energy could damage the nearby environment because of the extreme cold. Therefore, there is a need to recover LNG cold energy for both saving costs and protecting the environment. The LNG cold energy utilization technology includes cryogenic carbon dioxide capture and storage (CCCS), cryogenic power generation (CP), air separation (ASU), cryogenic seawater desalination (CSD), local cryogenic warehouse and food processing (CWF). The potential location of cold energy utilization is shown in Figure 1. This project aims to use life cycle assessment combined with a cost analysis to identify a win-win situation and trade-offs in the life cycle of the LNG supply chain with cold energy utilization.

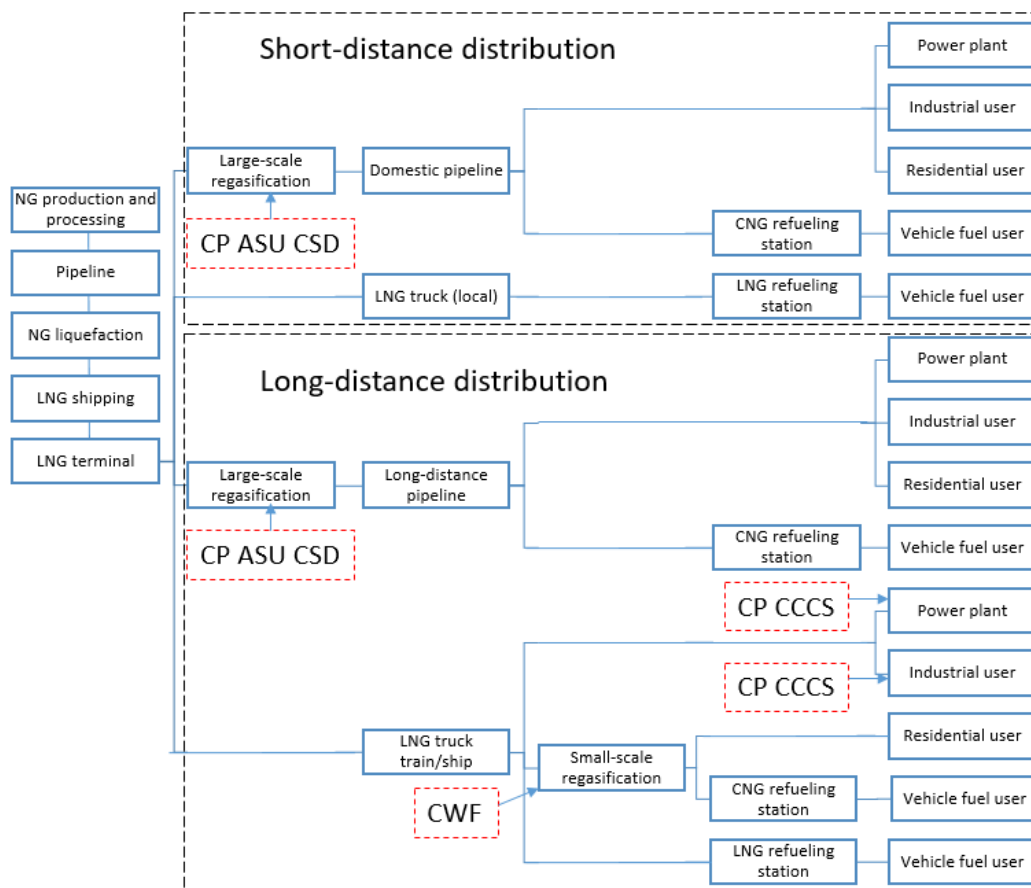


Figure 1: LNG supply chain with cold utilization