

RESEARCH

DEVELOPMENT

ONGOING RESEARCH
SUPPORTED BY GAZNAT
(2016 – 2020)



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RESEARCH

DEVELOPMENT

MISSION AND COMMITMENT OF GAZNAT

Gaznat is committed to transporting and supplying natural gas to its customers and business partners right across the gas supply chain on the best possible conditions as regards safety and price.

Since natural gas is an essential element of the future energy mix for Switzerland and the world, Gaznat regards developing and promoting this commodity as an essential task which will enable this form of energy to take its rightful place and make a full contribution to security of supply for everyone.

Through its technical and commercial activities, as well as its research and development efforts, Gaznat is committed to the advancement of the gas industry, with the aim of helping it adapt to technological developments, especially the digitalisation of society.

GAZNAT, A FORWARD-THINKING COMPANY

As part of its commitment to funding research and development projects, Gaznat entered into an agreement with the Swiss Federal Institute of Technology in Lausanne (EPFL) to launch calls for projects at the laboratories and research institutes.

Six research projects have been selected. Of the projects chosen, three relate to the field of carbon chemistry, two investigate the capture and sequestration of CO₂, and the other examines the potential for micro-cogeneration.

Two new calls for projects will be launched in the next few years.

THE SIX PROJECTS CURRENTLY IN PROGRESS ARE:

1. CO₂ capture using high-performance graphene membranes
2. Electrochemical conversion of CO₂ to methane
3. Potential for and obstacles to the use of micro-cogeneration based on natural gas
4. Development of a new class of catalysts based on non-precious metal oxides
5. Development of cells that convert CO₂ into fuel using solar energy
6. Risk study of seismicity induced by geological sequestration of CO₂

RESEARCH CHAIRS SUPPORTED BY GAZNAT

CHAIR GAZ NATUREL – PETROSVIBRI

Prof. Lyess Laloui

The Chair Gaz Naturel – Petrosvibri at the Laboratory for Soil Mechanics (LMS) of the EPFL (Lausanne) develops research and knowledge in the field of the geological storage of carbon dioxide (CO₂). Carbon Capture Storage (CCS) is currently considered worldwide as one of the possible technologies to support the reduction of carbon dioxide concentration in the atmosphere.

The sequestration in deep underground formations represents the safest solution to store the captured CO₂ for thousands of years. Several engineering issues have to be faced to deploy this technology in safe conditions. Caprock integrity is one of the most fundamental aspects to be assessed. Overpressure generation due to the CO₂ injection, thermal effects, and generation of fractures are major factors that could affect the integrity of the caprock leading to CO₂ leakages. In addition, induced seismicity due to faults slipping represents an additional issue that cannot be neglected.

GAZNAT CHAIR FOR ADVANCED SEPARATIONS LAS

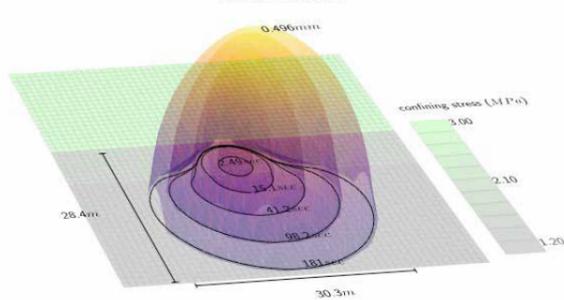
Prof. Kumar Varoon Agrawal

The Laboratory of Advanced Separations (LAS) is engaged in synthesizing ultimate membranes that significantly exceed performance limit of the polymeric membranes, making the separation processes for gases and vapors highly energy-efficient. Since the membrane separation process is usually diffusion-controlled, the synthesis of the ultimate membranes amounts to synthesizing the thinnest-possible molecular-selective barriers that are stable in the operating conditions.

GAZNAT CHAIR ON GEOENERGY

Prof. Brice Lecampion

Fracture evolution



Naturally, a two-dimensional (2d) film hosting molecular-selective pores is the ultimate membrane because the flux through the membrane is inversely proportional to the membrane thickness.

To realize these 2d membranes, LAS has established a multidisciplinary program in chemistry, material science and chemical engineering, focusing on the synthesis, processing, and characterization of inorganic, nanoporous 2d materials (single-layer graphene, nanosheets derived from layered nanoporous materials). LAS is studying several synthetic routes (chemical vapor deposition (CVD), molecular layer deposition (MLD), hydrothermal and solvothermal synthesis, etc.), crystallization mechanism (induction time, nucleation density, anisotropic growth rates, substrate effects, grain-boundaries, etc.), post-synthetic modification including surface functionalization, ion-exchange, and exfoliation. On the theoretical front, an improved understanding of structure-property relationship is being investigated by ab-initio molecular modeling (density functional theory), as well as by modeling adsorption and diffusion across the nanoporous 2d film. Overall, LAS is developing three distinct membrane platforms, a) single-layer nanoporous graphene films, b) ultrathin polycrystalline MOF films, and c) exfoliated nanoporous 2d nanosheets.

The Geo-Energy Lab – Gaznat chair on Geo-Energy (GEL) is part of the School of Architecture, Civil and Environmental Engineering (ENAC) at the Swiss Federal Institute of Technology, Lausanne (EPFL). The laboratory com-

Figure 1 – Evolution of a hydraulic fracture footprint and width across 3 layers with different in-situ stresses (Constant injection from a well in the middle layer)

Research activities carried out at the Chair Gaz Naturel - Petrosvibri aim to face these aspects with a geomechanical approach by providing solutions through both experimental and numerical analyses. In this context, the Chair is actively involved in several research projects such as the Swiss Competence Center for Energy and Research (SC-CER-SoE) that aims to provide solutions for the energy transition in Switzerland until 2050, and the ELEGANCY project that foresees a CO₂ injection experiment in the underground laboratory in Mont Terri (Switzerland).

bines experimental and theoretical investigations to address fundamentals and applied research problems associated with sub-surface Geo-Energy projects (deep geo-thermal energy, gas storage and production etc.).

We are particularly interested in developing knowledge and technologies to allow more efficient and sustainable fluid injection and withdrawal operations from porous reservoirs located in the upper earth crust.

RESEARCH & DEVELOPMENT PROJECTS SUPPORTED BY GAZNAT

CO₂ CAPTURE BY HIGH THROUGHPUT NANOPOROUS GRAPHENE EMBRANE

Prof. Kumar Varoon Agrawal

The single-layer nanoporous graphene film has the potential to be the ultimate membrane, yielding ultrahigh permeance and attractive molecular selectivity, attributing to its atomic thickness and a remarkable thermal, chemical and mechanical robustness. However, the key issues in the realization of high-performance graphene membranes have been crack- and tear-free transfer of large-area graphene on a porous support, and the incorporation of size-selective pores with a narrow pore-size-distribution. Therefore, our objectives are a) to etch molecular-selective nanopores in single-layer graphene for using nanoporous graphene as a membrane for CO₂ capture, and b) to develop scalable methods for the production of single-layer graphene membranes.

The team has developed a novel nanoporous-carbon-assisted transfer technique for suspending chemical vapor deposition derived graphene on a porous support, leading to crack-free, nanoporous single-layer graphene membranes with a relatively large area of 1 mm² (Figs. 1A and B). The absence of cracks in the membranes allowed

observation of temperature-dependent gas transport from the intrinsic defects. Despite an ultralow porosity of 0.025%, attractive gas separation performances were achieved. The separation performance was stable during multiple thermal cycling (25 - 150 °C), and at least up to a moderate transmembrane pressure difference (7 bar). We also developed an ozone-functionalization based etching and pore-modification chemistry to increase the pore-density and alter pore-size, improving H₂ permeance (up to 300%) and H₂/CH₄ selectivity (up to 150%). Overall, the scalable transfer, pore-etching and pore-modification methods developed in this project are expected to bring the implementation of atom-thick nanoporous two-dimensional membranes a step closer to reality.

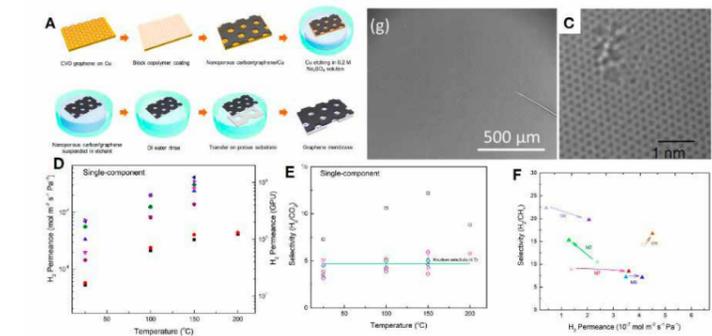


Figure 1 – Synthesis and characterization of nanoporous single-layer graphene membranes. A) High-resolution transmission electron microscope (HRTEM) image of intrinsic defects (nanopores) in single-layer graphene. B) Novel transfer-technique developed at LAS enabling preparation of large-area, crack-free, single-layer suspended graphene. C) Scanning electron microscope (SEM) image of the graphene membrane. D) H₂ permeance from the intrinsic defects (A) in the graphene membrane. E) H₂/CO₂ separation performance from the membrane. Novel pore-tuning method using ozone functionalization leading to either increase in the H₂ permeance or the H₂/CH₄ selectivity or both.

ELECTROCHEMICAL CONVERSION OF CARBON DIOXIDE TO METHANE

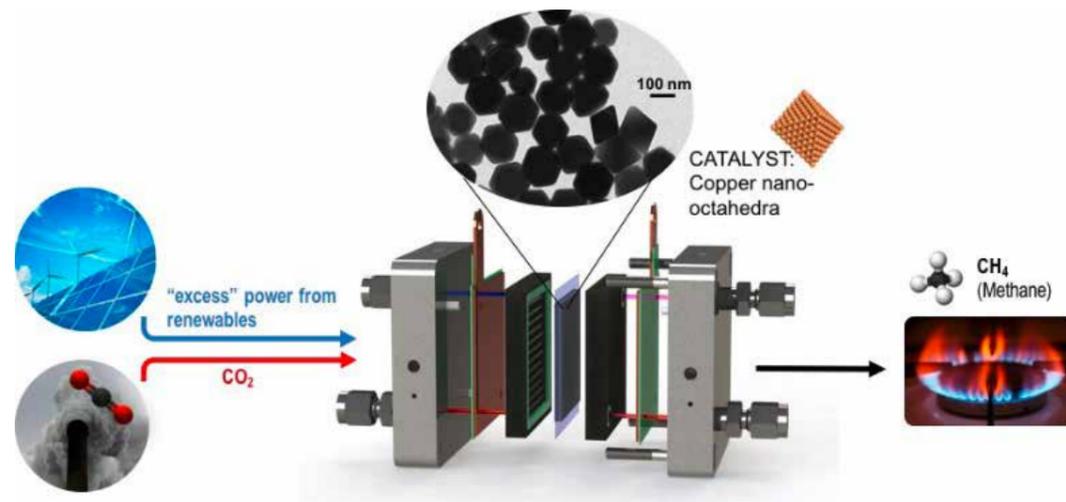
Prof. Raffaella Buonsanti

This proposal focuses on the utilization of CO₂ to produce methane. This conversion is realized in an electrochemical reactor which operates at room temperature and ambient atmosphere in a safe environment. Electrochemical CO₂ conversion is emerging as a sustainable technology, especially if the energy generated from intermittent

renewable resources (i.e. solar) is employed to power the reactor. Such a chemical storage of energy has the potential to be very competitive with high temperature and pressure processes employed today for the production of hydrocarbons (i.e. Fischer-Tropsch process). The proposed research has two major objectives: 1) the identification of one catalyst which is highly active and selective for the conversion of CO₂ to CH₄ and 2) its implementation in a scalable reactor.

During the first year of the project we have identified one promising catalyst which produces methane from CO₂ under the application of a voltage. This catalyst consists of copper and possesses nanometer dimensions and a unique octahedral shape. We have also designed and build a few prototypes for a gas-fed electrochemical reactor.

"Gaznat is allowing my team to translate our basic science into a real technological opportunity. This step is essential to impact society."



PROSPECTS AND BARRIERS TO MICRO-COGENERATION IN SWITZERLAND

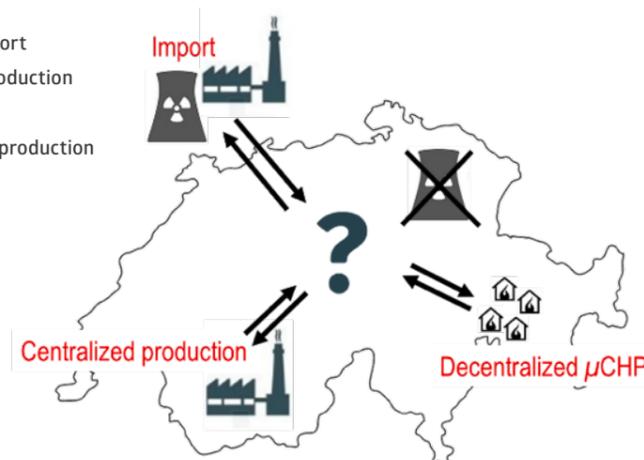
Prof. M. Finger, Network Industry Management (MIR), Prof. P. Thalmann, Laboratory of Environmental and Urban Economics (LEURE), Dr J. Van Herle, Group of Energy Materials (GEM)

Coordination: Dr F. Vuille, Energy Center (CEN), Research engineer, Yann Füllemann

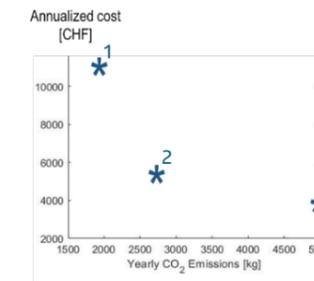
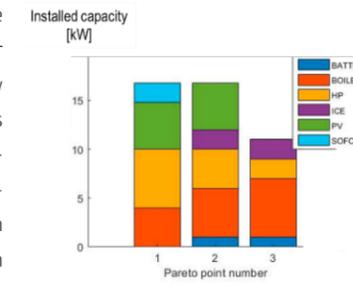
Micro-cogeneration (μCHP) a solution to fill the winter electricity gap

Currently Switzerland consumes more electricity than it produces during the cold months. This situation will worsen in the future with the phase out of nuclear power in Switzerland. The ramp-up of renewables is likely to be insufficient in the medium term to bridge the winter gap. Hence, 3 options are available to close the winter electricity gap:

- Electricity import
- Centralized production in Switzerland
- Decentralized production in Switzerland



The conversion of high temperature heat into electricity in thermal power plants generates large amount of low temperature heat. In centralized plants this heat is generally lost by lack of demand in vicinity of the plant. Conversely, small-scale distributed cogeneration systems, namely micro-cogeneration units (μCHP), might use this waste heat to meet the heat demand from building, and thus benefit from the strong correlation between electricity deficit and domestic heat demand in the cold months. This may reduce significantly the energy consumed and CO₂ emissions as compared to a scenario offering the same service with large thermal power plants and distributed boilers.



Estimating the μCHP potential

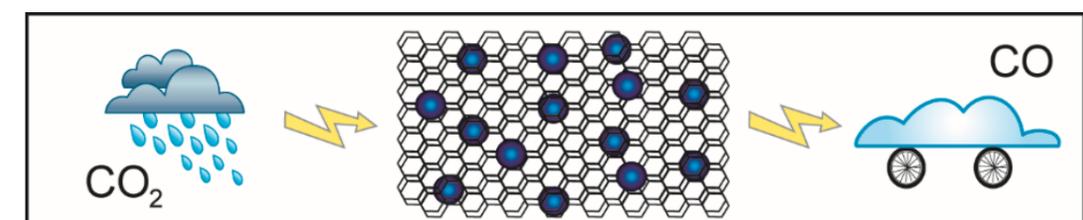
Using an optimisation model, we analyse under which conditions μCHP systems may represent economically viable options for different building typology. Preliminary results indicate that fuel-cell based μCHP units can be viable under certain realistic conditions. We will then extrapolate the results to the Swiss building stock to assess the CO₂ reduction potential and elaborate recommendations for the different stakeholders.

METAL OXIDES AS PARADIGM-SHIFTING CATALYSTS FOR CARBON DIOXIDE REDUCTION

Prof. Xile Hu

Objectives of project: Conversion of carbon dioxide into chemical fuels using electricity generated by renewable energy sources such as solar and wind is an attractive strategy for carbon management. This conversion requires efficient and selective electrocatalysts, which are currently lacking. This project aims to discover and develop a completely new class of electrocatalysts based on non-precious metal oxides. The successful execution of the project is expected to shift the paradigm of research in this area, which is so far limited to a few well-known metals such as gold, silver, copper.

Progress made and upcoming objectives: We have developed two types of non-noble metal catalysts. The first one is ultra-small tin monoxide (SnO) nanoparticles (smaller than 3nm) on carbon black. The selectivity of CO formation on previously reported Sn-based catalysts is lower than 20%. Our SnO catalyst shows selectivity to CO about 40% and gives also much faster reaction rate than previous catalysts. The second type is a metal-carbon (M-C) catalyst with metal single atoms embedded in carbon matrix.



This catalyst shows very high selectivity to CO (> 80%) and extremely high formation. This catalyst is among the most active catalysts ever developed. Our work on the first catalyst is published (Angew Chem Int Ed 2018); the work on the second catalyst led to a Patent application.

The next step is to further develop metal-carbon catalysts for highly selective and efficient electrochemical CO₂ reduction.

DEVELOPMENT OF A ROBUST AND INEXPENSIVE PHOTOELECTROCHEMICAL CELL FOR THE ARTIFICIAL PHOTOSYNTHESIS OF SOLAR FUELS FROM CO₂ – “TOWARDS THE ARTIFICIAL LEAF”

Prof. Kevin Sivula

The objective of this project is to develop the light harvesting materials for a photoelectrochemical type “artificial leaf” technology, which consists of semiconductors capable of harvesting visible light directly coupled to catalysts used to increase reaction rates and tune product selectivity.

A main challenge to date has been the identification of semiconductors and catalysts that are robust, non-toxic, and earth abundant. Our project addresses this challenge by using a light harvesting materials based on copper iron oxide (CuFeO₂) in the delafossite crystal phase, which has been identified by our lab as a promising photocathode material.

The ultimate goal of the project is to build a device capable of reducing carbon dioxide with high selectivity for methane or methanol at the photocathode while an oxidation reaction (water oxidation to produce O₂ for example) occur at the photoanode as shown in Figure 1.

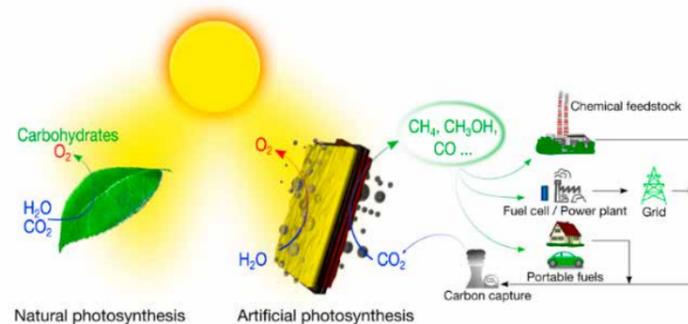


Figure 1 – Comparison between natural and artificial photosynthesis. Solar fuels (e.g. methane) produced from highly efficient artificial photosynthesis are envisaged to be used as chemical feedstock, in power plants or household/transportation use.

During the first stage of the project we have focused on addressing the challenges with the CuFeO₂ photocathode. There are three main processes that must occur to drive solar fuel production on the photocathode, (1) light absorption (2) electron transport to the semiconductor interface and (3) electron extraction via the catalytic formation of the fuel. While the CuFeO₂ semiconductor is known to be robust and inexpensive, and can perform steps (1) and (2) well, we have identified that step (3) is limited by surface defects causing poor charge extraction. Deposition of diverse defect-passivating overlayers as well as coatings of different catalysts are currently under investigation to overcome this limitation. Using a CuCrO₂ overlayer treatment, a performance improvement has been observed, and the deposition of catalysts have also indicated that a clear increase in the electron extraction is possible in the presence of CO₂. The robustness and the effectiveness of these treatments should be improved for the implementation of CuFeO₂ as a viable photocathode.

Our future work will mainly focus on the improvement of the stability of both catalysts and semiconductor assemblies.

FRICITION: FAULT REACTIVATION DURING CO₂ SEQUESTRATION

Prof. Marie Violay

Which “fluid cocktail” for a safe CO₂ geological sequestration?

Here, as case study, we investigate this question using a new experimental method for evaluating the risk of 1) CO₂ leakage and 2) induced seismicity, provoked by fault reactivation during geological CO₂ sequestration. Our experiments stimulate CO₂ injections into a reservoir-cap rock system bounded by faults at different state of stability. Fluid pressure, flow rate injection, injection strategy effects on fault stability will be investigated, in order to find the good ‘fluid cocktail’ for CO₂ geological sequestration. These data will provide new constraints on the reservoir permeability evolution in case of fault reactivation and will shed new light on the physics of induced earthquakes mechanics, by recording the micro-seismicity while testing the deformation.

So far, experiments simulating intact reservoir have been performed. First results show that the strain and acoustic emission event rates are exponential functions of the applied stresses on the sample. Pore fluid oscillations at small periods do not seem to affect the sample strength, even for amplitudes as high as 8 MPa. However, a hydraulic fatigue mechanism seems to occur at very high period of oscillations.

Future experiments are planned on faulted samples and fault gouge samples which are more representative of natural reservoirs.

GAZNAT AND EPFL A COLLABORATION FOR FUTURE ENERGY TECHNOLOGY

Prof. Andreas Züttel

Laboratory of Materials for Renewable Energy (LMER), Institute of Chemical Sciences and Engineering (ISIC), Basic Science Faculty (SB), École polytechnique fédérale de Lausanne (EPFL) Valais/Wallis, Energypolis, Sion, Switzerland

Empa Materials Science & Technology, Dübendorf, Switzerland

The Laboratory of Materials for Renewable Energy (LMER) works on the materials for the storage of renewable energy, which appears in the form of electricity. The storage of electricity in batteries is very limited due to the low energy density of batteries and therefore the large amount of material needed. Alternatively, hydrogen production by electrolysis and storage of hydrogen in hydrides offers a much higher (>10 times) energy density. Furthermore,

the reduction of carbon dioxide with hydrogen and the synthesis of hydrocarbons lead to compounds e.g. methane or alkanes, that are well known and stored by established technologies. Two collaboration projects with Gaznat are ongoing where we investigate the synthesis of methane from renewable energy and a new method to produce methane and heat for the gas expansion station. A common patent about a new highly efficient methanation reactor was filed recently.

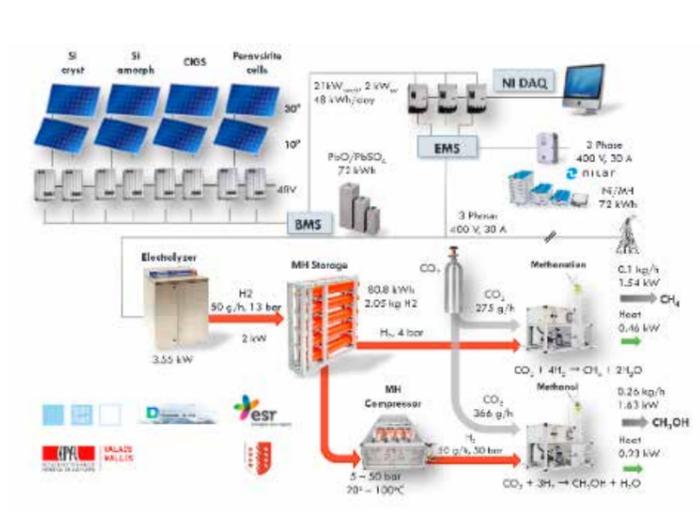


Figure 1 – The Small Scale Demonstrator in Sion (SSDS). URL: www.ssd.sps.epfl.ch

The project "Small Scale Demonstrator in Sion (SSDS)" demonstrates the entire energy chain from photovoltaics (20 kWp) through battery storage, hydrogen production and storage, compression and finally synthesis of methane and methanol. The objectives are to investigate the energy flows and storage capacities, to investigate the behavior of the components and to produce data for the modeling of energy systems. The project SSDS is financially supported by Gaznat.

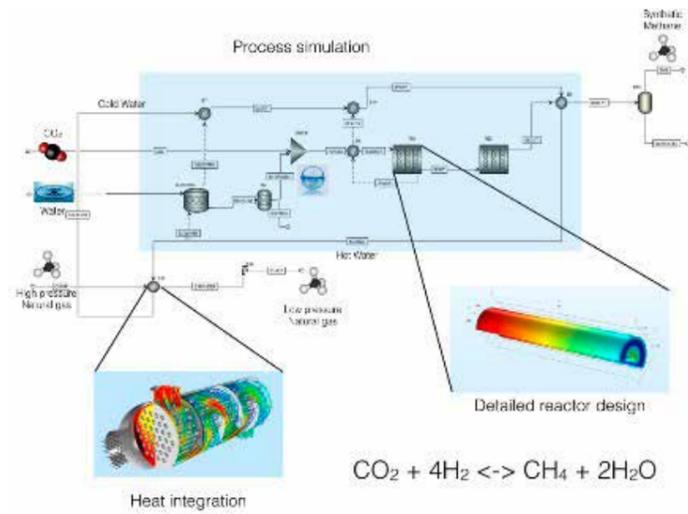


Figure 2 – Synthesis of Methane and Heat Recovery (SOMAHR)

The project "Synthesis of Methane and Heat Recovery (SOMAHR)" is a CTI project in order to develop a methane reactor for the heat production in the gas expansion stations. Instead of burning methane, methane is synthesized from CO₂ and hydrogen and the heat produced in the reactor is used to compensate the expansion heat of the natural gas. In this project Gaznat is the industrial partner financing >50% and LMER EPFL is the academic partner.

The global energy demand in the past 50 years has increased by a factor of 8 and is continuing to increase. More than 80% of the energy demand is covered by fossil fuels, e.g. coal, oil and natural gas. However, we know today that the fossil resources are limited and the combustion and emission of CO₂ has an effect on the global climate.

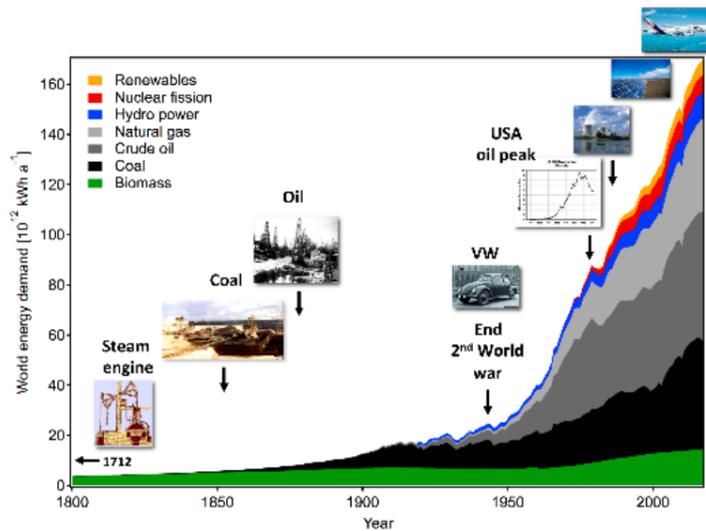


Figure 3 – Development of the global energy demand according to Jean-Marie Martin-Amouroux, IEPE, Grenoble, France

The contribution of renewable energy to the global energy demand is still small, however the installed peak power of photovoltaics is increasing exponentially and will reach the world energy demand of 2017 in 2025. This development is only possible if the intermittent renewable energy can be stored in large quantities.

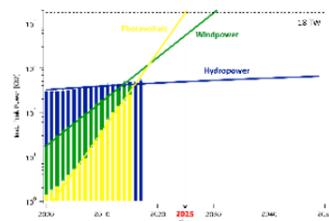


Figure 4 – Development of the installed peak power in photovoltaics, wind power and hydro power according to <http://cleantechnica.com/2016/08/17/10-solar-energy-facts-charts-everyone-know/>

The production of hydrogen and the reduction of CO₂ to hydrocarbons including synthetic methane represent key technologies for the coming years. The storage, transport and distribution of hydrogen and methane will play a very important role in the conversion of the energy economy from fossil to renewable energy.



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