

Storing bioenergy and renewable electricity in the natural gas grid

1. Storing renewable energy for fluctuation compensation, supply security and grid stability

The goal of future energy systems is a sustainable complete supply based on renewable resources. The final energy sources electricity, heat and fuel should be available at all times without usage restrictions. However, many renewable energy sources, such as wind power and solar energy, provide energy in a fluctuating manner. Energy storage is the solution. Thus, even in times when renewable energy is in short supply (e.g. no wind), the demand can be met.

This paper presents a new approach for seasonal storage of renewable energy. The storage medium in question is SNG – Substitute Natural Gas –, which can be generated via the conversion route „Biogas-to-SNG“, „BioSyngas-to-SNG“ and the new „Wind-to-SNG“ concept.

Generation of substitute natural gas („biomethane“) from biogas is state-of-the-art. Manufacturing processes from biosynthesis gas via biomass gasification are currently in the demonstration phase. The process of generating substitute natural gas from CO₂ and H₂ is new. Fluctuating electricity from renewable energy sources (e.g. from wind power) is used for electrolytic generation of hydrogen, which is converted to methane with CO₂ (e.g. from biogas) or with CO/CO₂ compounds (e.g. from the product gas of the thermo-chemical conversion of biomass) in a synthesis reactor in the wind-to-SNG concept.

Using the existing natural gas infrastructure, the renewably produced, chemical energy source methane is stored efficiently, distributed and

made available for use as required. Bidirectional convertability of electricity and gas facilitates energy storage and electricity grid stabilisation, by providing negative balancing energy if there is surplus electricity by feeding substitute natural gas or by providing positive balancing energy if there is a demand for electricity via conversion of substitute natural gas into electricity.

2. Energy storage: A key component in a sustainable energy system

Of all the renewable energy sources, biomass is the easiest to store, as this exists in material form as fuel. It can be stored seasonally, and is available when required for generating heat, electricity and fuel and therefore suitable for base load coverage. Biomass currently covers approx. 10% of the global energy demand. However, the contribution to global energy consumption could increase to max. approx. 20%. Geothermal energy and run-of-river hydroelectricity, other sources with limited supplies, are also suitable for covering the base load. The great potential of renewable energy sources lies in virtually unlimited solar radiation and in wind energy, although both occur in a highly fluctuating manner and can only be controlled to a limited extent, and therefore require storage.

Only sufficient energy storage can ensure a secure complete supply based on renewable energy sources. The potential and the possible fields of application of the various storage systems depend on the required storage capacity and storage duration, as well as the conversion losses and the costs. Only the expansion of the electricity grids, the bundling of different

ZSW

Dr. Michael Specht
michael.specht@zsw-bw.de

Frank Baumgart
frank.baumgart@zsw-bw.de

Bastian Feigl
bastian.feigl@zsw-bw.de

Volkmar Frick
volkmar.frick@zsw-bw.de

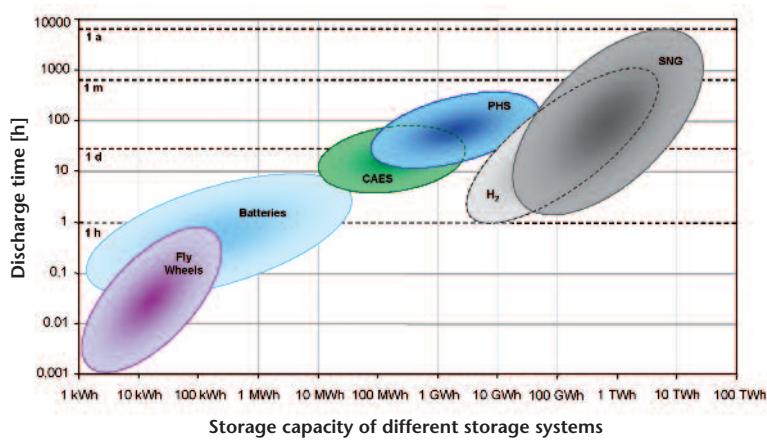
Bernd Stürmer
bernd.stuermer@zsw-bw.de

Dr. Ulrich Zuberbühler
ulrich.zuberbuehler@zsw-bw.de

Fraunhofer IWES

Dr. Michael Sterner
michael.sterner@iwes.fraunhofer.de

**Solar Fuel
Technology GmbH & Co. KG**
Gregor Waldstein
Hofhaymer Allee 42
A-5020 Salzburg
waldstein@solar-fuel.com



CAES: Compressed Air Energy Storage (Druckluftspeicherwerk)
 PHS: Pumped Hydro Storage (Pumpspeicherwerk)
 H₂, SNG: Die Untertage-Ausspeicherung beinhaltet die Rückverstromung in GuD-Kraftwerken (Gas- und Dampf)

Figure 1

Discharge time and storage capacity of different electricity storage systems

electricity generators together with consumers and new storage concepts, along with clever management of generation, loads and storage, allow an energy system based on renewable energy sources to be created which can guarantee complete supply at all times.

2.1 Storage options for renewable energy

Most renewable energy is converted to electricity in a transportable form. However, electricity can only be stored directly to a limited extent (e.g. in capacitors). Electricity storage technologies therefore use the following forms of energy:

- Electric energy (supercapacitors)
- Potential energy (hydropower, pumped storage power plant)
- Mechanical energy (compressed air reservoirs, flywheel energy storage systems)
- Electrochemical energy (batteries)
- Chemical energy (fuels)

Pumped storage power plants are generally used for storing electricity for periods ranging from several hours to several days. In the energy industry, such hydroelectric power plants have for decades been the storage medium of choice for intermediate storage of excess electricity and for feeding these capacities back into the electricity grid when needed (peak load coverage). As

their existing capacity and expansion potential are strictly limited by geographical factors and environmental conditions in Germany, they will only be able to contribute to the future integration of renewable energy into the electricity grid to a limited extent.

Compressed air reservoirs operate with output ranges similar to those of pumped storage power plants. However, there are as yet only two systems in operation worldwide.

Storage in flywheel energy storage systems or supercapacitors is limited, particularly with regard to duration and capacity. Therefore, they are primarily used for short-term (<< 1 hour) provision of power to compensate for fluctuations.

Stationary and mobile batteries represent a medium-term (< 1 day) power reserve, although their use is limited by their very low energy and power density and lifetime. The integration of future electric vehicles' mobile batteries into the electricity grid as part of a so-called „vehicle-to-grid“ concept makes it possible to charge vehicles' batteries (energy storage) and systematically feed the energy back into the power grid. This creates large-scale “virtual battery storage”. However, its use is restricted by the availability period of the vehicles and the capacity provided by the vehicle owner. Also, intelligent management of the charging and discharging processes is required (smart grid).

For long-term storage and seasonal balancing of renewable energy sources, currently only chemical secondary energy carriers can be used, such as hydrogen and carbon-based fuels (e.g. substitute natural gas), which can be created from various renewable energy sources. The withdrawal capacities of underground gas storage including conversion to electricity extend into the 10-GW range, with cycle times ranging from days to months (*see Figure 1*). They therefore represent the only conceivable option for seasonally storing renewable energy with a capacity in the TWh range and converting it back into electricity when required. In addition, the chemical secondary energy carriers can be used in other application areas, such as in transport.

2.2 Storage capacities in today's energy system and when expanding electromobility

In today's energy system, energy reserves are provided via the storage of fossil fuels (coal, crude oil and natural gas). The amount of energy thus stored is typically enough to cover several months' consumption. However, this does not apply to electricity. Supply and demand must always be precisely balanced. If supply is largely provided from renewable energy sources, the principal question is: Which storage systems can take the place of fossil fuel reserves?

The figures in *Table 1* illustrate the problems with storing electricity: Generation and consumption must be simultaneous. The available electricity storage capacity adds up to just 0.04 TWh, i.e. the available storage facilities could theoretically satisfy Germany's entire electricity demand for less than 1 hour.

If electric vehicles' batteries are bidirectionally integrated into the grid and coupled with intelligent energy management, both the charging and the withdrawal of energy are possible (vehicle to grid). Batteries have the advantage of a very rapid response time and can thus be activated and deactivated flexibly. Therefore, these

mobile energy storage systems offer the option of providing system services for grid stabilisation, e.g. balancing energy or load balancing. In peak load periods, this energy is available via discharging the traction batteries, which are then charged again during low load periods. This smoothes the electricity load curve and reduces the load on the energy generators, as well as on the grid, depending on the spatial distribution of the storage systems. Assuming that 40 million vehicles are all simultaneously connected to the electricity grid and that each vehicle feeds in 10 kWh, the storage coverage amounts to around 6 hours and is thus many times higher than the capacity installed to date in the form of pumped storage power plants (*Table 2*).

By incorporating traction batteries, electromobility can thus make a contribution to electricity storage and electricity grid stabilisation. Therefore, in the future it will be possible to use electric vehicles primarily as short-term energy storage systems in order to support grid operation and to bridge short-term fluctuations. However, the existing system does not permit multi-day, let alone seasonal electricity storage, even under the assumption that all current vehicles were replaced by electric vehicles.

		Electricity	Natural gas	Liquid fuels ¹⁾
Consumption	[TWh/a]	615	930	707
Average output	[GW]	70	106 ²⁾	81
Storage capacity	[TWh]	0,04 ³⁾	217 ⁴⁾	250 ⁵⁾
Mathematical storage coverage ⁶⁾	[h]	0,6	2000	3100

1) Petrol, diesel, kerosene

2) Fluctuates greatly seasonally

3) Pumped storage power plants

4) 47 underground gas storage systems (plus 79 TWh under construction/in the planning stage) [1]

5) Stock of petrol, diesel, kerosene und extra light heating oil

6) Relative to the average output

Table 1
Energy consumption and storage capacities in Germany (2008)

		1 million electric vehicles	40 million electric vehicles
Consumption ²⁾	[TWh/a]	1,9	76
Percentage of electricity consumption	[%]	0,3	12
Storage capacity ³⁾	[TWh]	0,01	0,4
Mathematical storage coverage ⁴⁾	[h]	0,15	6

1) Reference year 2008

2) 0.16 kWh/km; 12,000 km/a

3) Available storage capacity per vehicle: 10 kWh

4) Relative to the average output of 70 GW (cf. Tab. 1)

Table 2
Energy consumption and storage capacities via electric vehicles in Germany¹⁾

Current knowledge suggests that the production of secondary energy carriers is a necessary prerequisite for seasonal energy storage. Liquid and gaseous fuels, unlike electricity, can be stored directly and in large quantities. In the fuel market, petrol and diesel are stored for months at a time. The gas storage capacities in Germany are around 5000 times higher than the capacities of pumped storage power plants (*Table 1*). As natural gas can be converted into electricity in modern power plants with an efficiency of almost 60%, the obvious solution is to use gas storage capacity for the storage of renewable energy.

2.3 Capacity requirements for seasonal storage systems

One key question in the event of 100% supply based entirely on renewable energy sources is: How much storage output and storage capacity is required in the German electricity grid, to bridge longer wind lulls for example? Renewable energies used for generating electricity and suitable for covering the base load include bio-energy, geothermal energy, run-of-river hydroelectricity and approx. 10% of the wind power capacity installed. Of this total approx. 18 GW of forecast output in 2050, bioenergy will account for 5 GW, geothermal energy for 4 GW, run-of-river hydroelectricity for 3 GW and the part of the wind energy output which is suitable for covering the base load will be 6 GW, calculated in accordance with [2]. At an average load of 70 GW (*see Table 1*) almost 20 TWh of storage capacity remains, if the remaining output of approx. 50 GW is drawn over a period of 2 weeks. However, only 0.04 TWh are currently available in Germany for electricity storage in pumped storage power plants. For complete supply based on renewable electricity, storage capacities would have to be increased by a factor of around 500!

The only viable option in Germany for the required capacities of around 20 TWh would be chemical energy carriers, which can be stored underground in caverns as gas, for example. In comparison, a reservoir cavern with hydrogen as the chemical storage medium has around 10 to 100 times the storage capacity of the compressed air variant; with renewably generated

substitute natural gas, the storage capacity is even around 30 to 300 times as high (depending on the storage pressure). A comparison with existing and planned natural gas storage facilities shows that these storage capacities are already in place in the existing infrastructure (*Table 1*). From a purely theoretical point of view, 217 TWh of natural gas stored in caverns can be converted into 130 TWh of electricity with gas and steam power plants on a flexible timescale. There are no other storage technologies with capacities in the region of > 10 TWh on the horizon.

Nevertheless, a conflict is arising with regard to the storage of renewable energy in underground storage facilities: the technologies of compressed air reservoirs and gas storage facilities (natural gas, substitute natural gas or hydrogen) are competing with the so-called „storage“ technology CCS (carbon capture and storage), which actually refers to disposal of CO₂ and not storage of energy itself. If the large-scale conversion of fossil fuels into electricity were to involve the dumping of CO₂ in empty natural gas underground storage facilities, the corresponding reservoirs would thus no longer be available for seasonally storing renewable energy.

3. Solution: Substitute natural gas (SNG) as a storage medium for renewable energy

The renewable energy carrier SNG can be produced in a variety of ways. Primary resources include

- „Wet“ biomass for anaerobic fermentation (biogas to SNG)
- „Dry“ biomass for thermochemical gasification (biosyngas to SNG)
- Renewably generated electricity for electrolytic production of hydrogen in combination with carbon (di)oxide from various biogenic and non-biogenic sources (wind to SNG)
- Combination of the abovementioned methods

The individual paths are explained below.

3.1 Biogas to SNG

In anaerobic fermentation of biomass, raw biogas with the main components CH₄ (50 – 70 vol.%) and CO₂ (30 – 50 vol.%) is produced. It also contains steam, minor components H₂S, NH₃, and depending on the type of pre-desulphurisation, also N₂ and O₂. Treatment of the raw biogas to SNG is implemented by removing water, the minor components and the main component CO₂, until it reaches the quality required for feeding (substitute gas quality) for the maximum concentration of the gas components and the combustion properties. CO₂ is removed in existing plants via pressure swing adsorption or various scrubber systems. The residual gas created in treatment is generally used to generate heat for the fermenter in a burner or in a gas motor for combined electricity/heat generation.

3.2 BioSyngas to SNG

If solid fuels are not burned but gasified, the result is a combustible gas which can be used for a variety of purposes. The fuel reacts with air, oxygen and/or steam, and the raw gas required is created. Its composition depends on the gasification method, the process conditions and the materials used. Ideally, the gas is not diluted with nitrogen, an inert component (gasification with air). Main components include H₂, CO, CO₂, H₂O and (depending on the gasification temperature) CH₄. Minor components such as sulphur compounds, ammonia, tars and dust loads must be removed from the gas.

To create SNG via biomass gasification, the AER (Absorption Enhanced Reforming) process developed at ZSW has ideal properties for downstream methanation due to its high H₂-content of > 60 vol.%. In this reaction, CO

and CO₂ are converted to methane via the hydrogen present in the gas (Equation 1 – 3). This requires a defined H₂/CO/CO₂ ratio, provided no gas conditioning/gas separation is required. Thanks to its configurable stoichiometry [3], its components and the CH₄ part already present, the AER product gas is ideal for creating SNG, as no other process steps are required after primarily quantitative conversion and after separation of reaction water. If synthesis gases from gasification with non-adjusted H₂-content are used, downstream CO₂ separation is absolutely necessary.

3.3 Wind to SNG

The „Production of C-based fuels from CO₂ and H₂“ topic has been the subject of research at ZSW since the end of the 1980s with the objective of storing renewable energy [4 – 6]. New aspects of the wind to SNG concept are the use of existing gas grid infrastructures for storing and converting the generated fuel to electricity, and in particular the use of wind-generated electricity, the further expansion of which is currently restricted by the capacity of the electricity grids. However, solar electricity or any other type of renewable electricity can be used for the process.

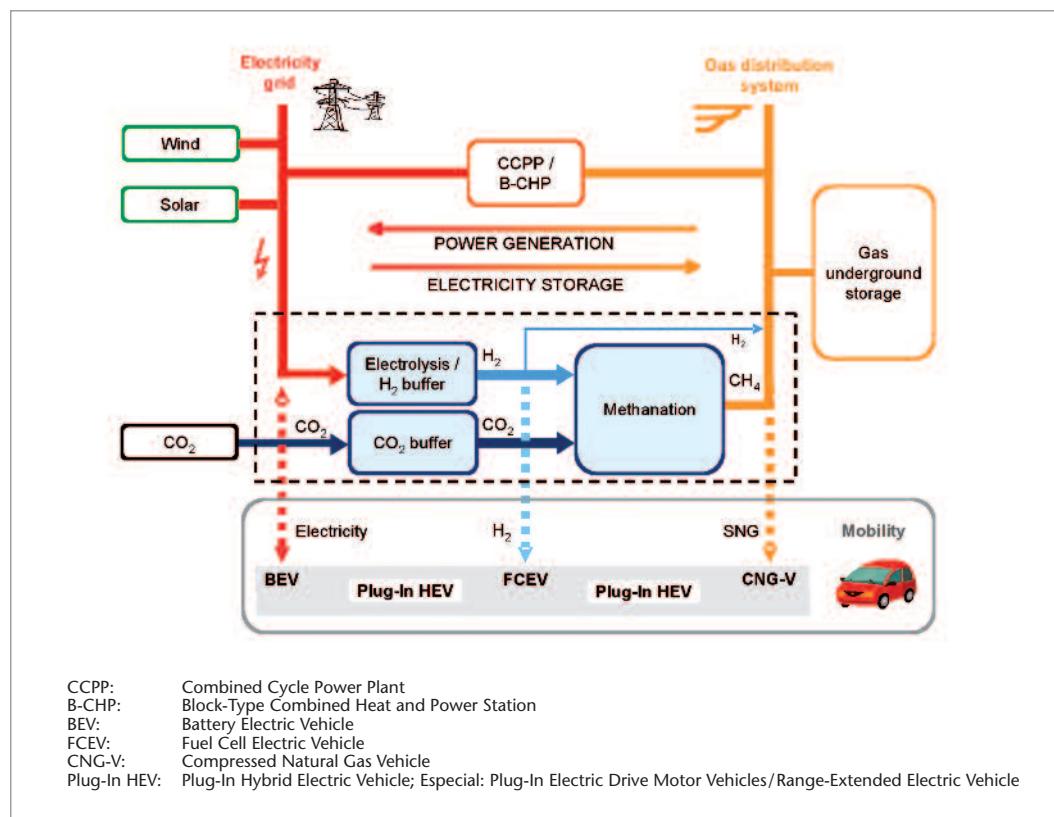
The basic principle of the wind to SNG concept is the bidirectional linking of the existing infrastructure units (the electricity grid and the gas grid) with the goal of establishing a new way of managing loads and generation, which enables high proportions of fluctuating electricity generation from renewable energy sources to be accommodated in the energy system. To date, this link only exists in terms of generating electricity from natural gas (gas to power), but not vice versa (power to gas). The new concept is based on storing electricity which cannot be fed into the grid for reasons of grid stability, or

Methanation reactions			
3 H ₂ + CO	→ CH ₄ + H ₂ O(g)	ΔH _R = -206 kJ/mol	(Equation 1)
4 H ₂ + CO ₂	→ CH ₄ + 2 H ₂ O(g)	ΔH _R = -165 kJ/mol	(Equation 2)
CO-Shift-Reaktion			
H ₂ O(g) + CO	→ H ₂ + CO ₂	ΔH _R = -41 kJ/mol	(Equation 3)

Equations 1 to 3

Figure 2

Wind to SNG concept for bidirectional coupling of the electricity and gas grids with a link to the mobility consumption sector



cheaply available electricity (e.g. at times when a large amount of wind power is available), in the form of substitute natural gas. One key goal is to enable the planning and control of the feed from wind farms. The principle is shown in *Figure 2*.

The concept envisages firstly using electrolysis to convert „excess“ electricity from fluctuating sources into hydrogen, then into substitute natural gas in a subsequent synthesis step with CO₂ (and/or CO). The energy efficiency for this is > 60 % ($\text{kWh}_{\text{SNG}}/\text{kWh}_{\text{el}}$).

A wind to SNG system can accommodate excess wind power by initiating electrolysis and can store it temporarily as SNG in the natural gas grid. In times when less wind power is available, or when the demand for electricity is higher, the electrolysis level can be reduced by means of systematic reduction or deactivation of the electrolysis. In order to ensure that there is sufficient electricity generation power – even during periods of low to no wind – a combination of the wind to SNG system with a gas or

combined heat and power plant is a suitable concept, whereby conversion to electricity does not have to be implemented at the location of the wind to SNG system.

The wind to SNG concept is also easy to integrate in the existing energy system. A particular advantage compared to other options is the use of the natural gas grid with its high storage and transport capacity. While a high voltage direct current transmission is restricted to outputs < 7 GW, gas pipelines can reach up to 70 GW. High wind power yields can be stored both seasonally and transported long distances with high energy transmission levels. For conversion to electricity, gas power stations with electric efficiencies of up to 60% are ideal. With an increasing amount of renewable energy in the electricity grid, Germany requires the construction of these high-efficiency power stations to be able to react rapidly to load fluctuations. By contrast to nuclear and coal-fired power plants, gas power stations can be regulated quickly and easily.

Also worthy of note, is the particular degree of flexibility regarding use options of the stored energy, because not only can SNG be converted back into electricity, it can also be used in the heating market or the fuel market. The latter is of particular interest in the context of the planned increase in the proportion of renewable fuels in transport area.

The wind to SNG concept has various interfaces to the mobility area ("wind to tank" in *Figure 2*), as three regenerative energy carriers for vehicles can be provided:

- (Stored) electricity for battery-powered electric vehicles (BEV)
- H₂ for fuel cell vehicles (FCEV)
- SNG for natural gas vehicles (CNG-V)

The chemical energy carriers H₂ and SNG are also suitable for plug-in hybrid vehicles (plug-in HEV), with which short distances can be travelled purely electrically – H₂ or SNG are only used for longer distances via conversion to electricity in a "Range extender".

Hydrogen from electrolysis of wind to SNG systems can be distributed via H₂ grids and be made available for mobility. On the other hand,

hydrogen can also be provided via decentralised generation at petrol stations by reforming SNG using the existing infrastructure, without requiring a large-scale distribution infrastructure for hydrogen.

3.4 Biogas/Wind to SNG

The carbon dioxide required for methanation can be provided from a variety of sources (CO₂ separation on conversion of fossil fuels to electricity, lime/cement production, chemicals industry processes etc.). As an "off gas", CO₂ is created when converting biogas to biomethane (CO₂ separation). As this biogenic CO₂ is not associated with climate-relevant emissions, it is particularly suitable as an educt for methanation (*Figure 3.1*). Alternatively, CO₂ from biogas can also be used directly without previous separation, by feeding the biogas directly to a methanation unit (*Figure 3.2*). The connection of a wind farm/biogas/wind to SNG system to locations where bottlenecks in the electricity grid cause delays in adding wind power is an optimal combination (e.g. in coastal areas where a lot of new offshore wind power is installed).

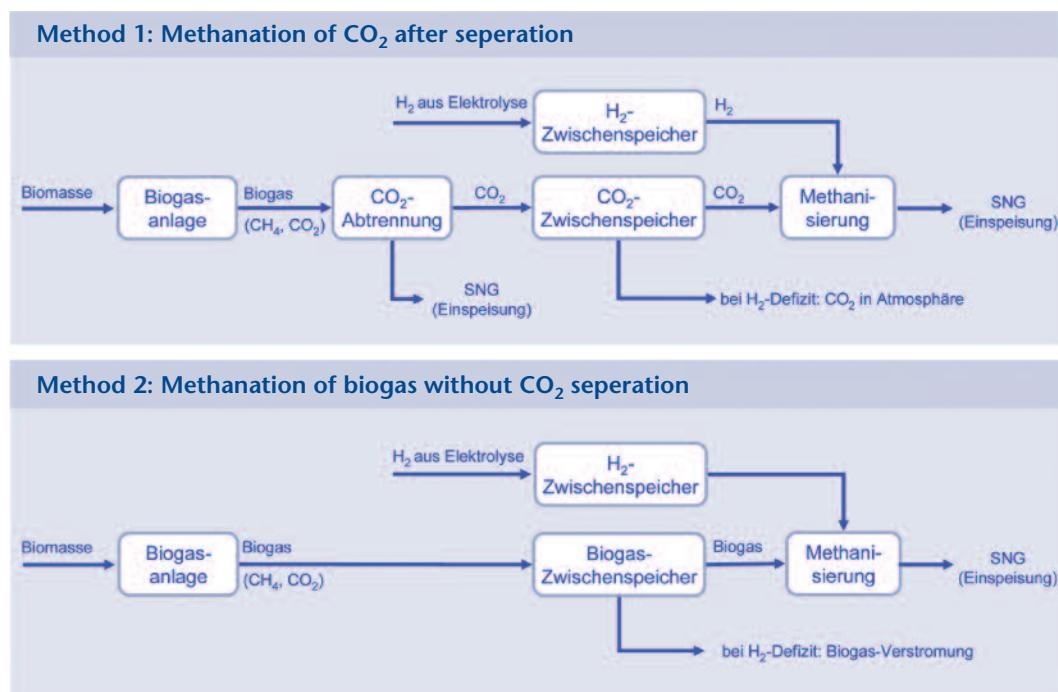


Figure 3
Increasing the methane yield from biogas systems by adding H₂ and subsequent methanation

Figure 4
Container-integrated wind to SNG system with electrolysis stack [1] and methanation device [2]



In an initial technical implementation phase, the installation of a 10 MW wind to SNG system in conjunction with a biogas plant is planned, in which the biogas is methanated to SNG without CO₂ separation by adding H₂. The system is to be commissioned in 2012.

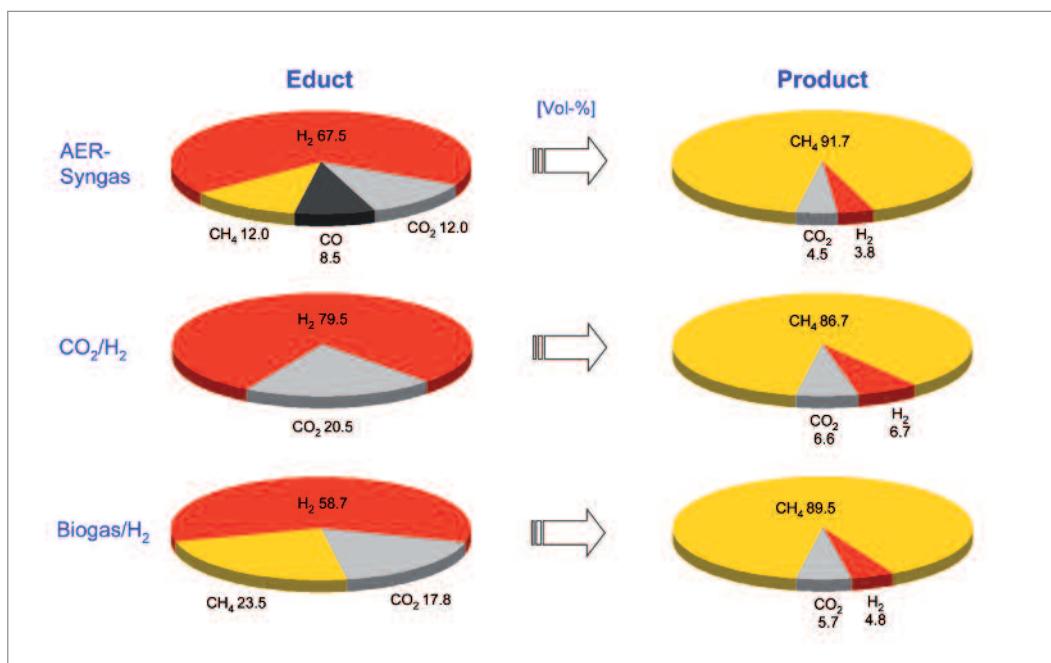
3.5 BioSyngas/Wind to SNG

In a further version, biogenic gases from thermochemical gasification should be used, whose stoichiometry is not adapted to the subsequent SNG generation. Addition of H₂ to the gasification gas allows virtually complete conversion of the biogenic carbon to fuel carbon. This facilitates significantly more efficient use of biogenic resources for the fuel yield. Another aspect is the use of the oxygen produced during electrolysis for biomass gasification.

4. Experimental results

At ZSW, a variety of fixed bed reactors for SNG generation up to a power class of 50 kW was built and tested. Due to the exothermic energy from methanation and the quality requirements for the gas properties for feeding into the gas grid (H₂ < 5 vol. %, CO₂ < 6 vol. %), there are special requirements for the reaction management and the reactor concept. This is taken into account in the reactor geometry, the reactor cooling concept and the activity profiles set for the catalyst packing beds.

Figure 5
Gas composition of the educt and product gases on methanation
Reactor system: Fixed bed; Ni-based catalyst;
 $T = 250\text{--}550^\circ\text{C}$; $p_{abs} = 8$ bar; space velocity = 5000 1/h); reaction paths: AER syngas → SNG; CO₂/H₂ → SNG; Biogas/H₂ → SNG



The target is a maximum conversion level in a single-phase reactor system without requiring downstream gas conditioning. As an alternative, reactor concepts with intermediate condensation/water separation are being investigated.

A complete container-integrated wind to SNG system in the 30 kW power class was developed as commissioned by the Solar Fuel Technology company. It contains electrolysis, methanation and control electronics including a filling module for natural gas vehicles (*Figure 4*). The system is used to study load profiles for grid control. After completion of the test phase, the wind to SNG system will be operated at a biogas plant. The biogas will be methanated directly (without previous CO₂ separation) according to process version 2 in *Figure 3*.

The results of SNG generation from educt gases AER syngas, CO₂/H₂ and biogas/H₂ are shown in *Figure 5*. The reactor was operated with comparable operating parameters in all three cases. After a single reactor run, the concentrations remain below limit concentrations for H₂ and CO₂ in the generated SNG for the educt gases AER syngas and biogas/H₂ after drying without further gas conditioning. For the CO₂/H₂ educt gas, these limit concentrations are slightly too high, but can be complied with via reduction of the gas load and/or pressure increase.

The fundamental suitability of the wind to SNG concept for energy storage and grid control was proven. With a far less complex process compared to Fischer-Tropsch or methanol synthesis, SNG can also be produced in decentralised applications, distributed via the natural gas grid, stored and used in accordance with demand.

5. Conclusion

The various methods for producing SNG from renewable energy and the use options in different consumption sectors offer opportunities for a merging of the electricity grid, gas grid and mobility energy sectors. Electricity and SNG can be converted to one another bidirectionally and have a fully-established infrastructure with seasonal gas storage capacity. Also, H₂ can be created decentrally from both energy carriers, without having to rely on a widespread H₂ distribution system with high infrastructure costs. The concept presented possesses the following outstanding features:

- SNG generation permits seasonal storage of renewable energy. While the storage capacity of the electricity grid is currently only approx. 0.04 TWh – with a storage coverage of less than one hour –, the storage capacity of the gas grid in Germany is over 200 TWh with a storage coverage of months.
- The wind to SNG concept can provide positive and negative balancing energy to stabilise the electricity grid (conversion of SNG to electricity and increasing/decreasing electrolysis).
- By expanding wind energy (in particular offshore), in future, high wind power levels will be available more and more often, which cannot be absorbed fully by the electricity grid, but as SNGs in the existing gas grid.
- SNG generation from CO₂ and H₂ is, unlike bio-SNG, not subject to surface limitation due to the cultivation of biomass.
- SNG can be produced from various forms of renewable energy (biomass, wind/solar electricity, etc.).
- Combining the resources of biomass and electricity from renewable energy allows biomass carbon to be transferred almost completely into fuel carbon, thus increasing the coverage of fuels from biomass significantly (e.g. doubling the methane yield from a biogas plant).

Literature

- [1] R. Sedlacek, Erdöl Erdgas Kohle 125, Nr. 11, S. 412 (2009)
- [2] M. Sternér, N. Gerhardt, Y-M. Saint-Drenan, A. von Oehsen, P. Hochloff, M. Kocmajewski, P. Lindner, M. Jentsch, C. Pape, S. Bofinger, K. Rohrig, Studie für Schluchseewerk AG, Fraunhofer IWES, Kassel, www.schluchseewerk.de/105.0.html (2010)
- [3] J. Brelochs, T. Marquard-Möllenstedt, M. Specht, U. Zuberbühler, S. Koppatz, C. Pfeifer, H. Hofbauer, Int. Conf. on Poly-Generation Strategies, Wien, 1-4 Sept. (2009)
- [4] A. Bandi, M. Specht in „Landolt-Börnstein“, Energy Technologies, Subvolume C: Renewable Energy, VIII/3C, p. 414 (2006)
- [5] M. Specht, U. Zuberbühler, A. Bandi, Nova Acta Leopoldina NF 91, Nr. 339, S. 239 (2004)
- [6] M. Specht, A. Bandi, K. Schaber, T. Weimer in „CO₂ Fixation & Efficient Utilization of Energy“, Y. Tamaura, K. Okazaki, M. Tsuji, S. Hirai (Eds.), Tokyo Institute of Technology, Research Center for Carbon Recycling & Utilization, Tokyo, Japan, p. 165 (1993)