# ECN chapter for book on Synthetic Natural Gas.

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# 9. MILENA – OLGA – SNG (ECN)

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## *9.1 Introduction*

Natural gas provides nearly 50% of the Dutch primary energy consumption. A substitute from renewable sources is needed to meet the goals for $CO_2$ reduction and the share of renewables [1]. Upgrading of biogas from digesters is well developed, but the potential is limited to a few percent of the primary energy consumption. Substitute Natural Gas (bioSNG) by gasification of solid biomass and methanation of the producer gas has large potential, but the technology is less mature. However, as biomass import will be needed, production plants at GW scale may be considered near a harbour.

Feedstock costs can account for up to 50% of bioSNG production costs if biomass is used from sustainably managed sources. That makes high efficiency in the conversion chain of paramount importance. In 2000, ECN evaluated a number of gasification technologies and selected indirect gasification as the best option and started development of MILENA gasification technology. MILENA technology allows significantly higher efficiency in bioSNG production [2, 3]. The design allows operation at large scale and pressure. Present MILENA gasifiers operate at atmospheric pressure. According to our system analysis, that is the best choice for systems smaller than about 50 MW.

The ECN approach is to start with hydrocarbon-rich producer gas, obtained by indirect gasification using little steam and moderate temperatures (~800°C). The producer gas is cleaned and converted into methane, using commercially available catalysts. The conversion involves water gas shift to increase the amount of $H_2$, hydrogenation of higher and unsaturated hydrocarbons, reforming of aromatic hydrocarbons, and methane production from CO and $H_2$. Heat production per mole of methane is reduced when compared to production from CO and $H_2$ only, as hydrogenation of hydrocarbons is less exothermic and reforming endothermic.

Moderate gasification temperatures bring the advantage that fuels can be considered which produce low-melting ash. These fuels can be comparatively cheap, as they are difficult to use in combustion or high-temperature (>900°C) gasification processes. A disadvantage of the applied conditions is the larger production of tar (i.e. heavy aromatic compounds). For bioSNG production, deep tar removal is needed anyhow to prevent catalyst coking. The OLGA tar removal technology developed by ECN is able to remove completely all but the most volatile tar compounds. Tar separated from MILENA producer gas can be used to meet the heat demand of the gasification process, instead of additional fuel or recycled producer gas.

ECN bioSNG research focuses on these two technologies: MILENA indirect gasification and OLGA tar removal. Other important topics are catalytic conversion of organic sulfur compounds, especially thiophene ($C_4H_4S$), and of hydrocarbons such as benzene, toluene and xylene (BTX) or ethylene ($C_2H_4$). BTX and ethylene may be separated from the producer gas instead of converted, if process and market conditions make separation attractive [4].

The aim is to obtain a biosyngas mixture which can be handled by any commercial fixed-bed methanation technology. Final upgrading to gas grid quality is given limited attention. An exception is made for $CO_2$ removal, for which ECN has developed technology using solid sorbents.

The SNG production process considered by ECN involves a number of steps at different pressure levels. Figure 9.1 shows the main process steps. Steam addition or gas recycling may be needed, but are not shown. Processes in the upper line will operate at ambient or mild pressure (< 10 bar). Processes in the middle line will operate at mild pressure. The bottom line involves methanation at high pressure (> 20 bar).

In small systems, the gasifier operates at atmospheric pressure. In future large systems, the gasifier will operate at mild pressure, obviating the need of the first compressor shown in figure 9.1. The outlet pressure of the second compressor will depend on the SNG product specifications to be met. The compression duty is limited by upstream removal of $CO_2$ and water (not shown).

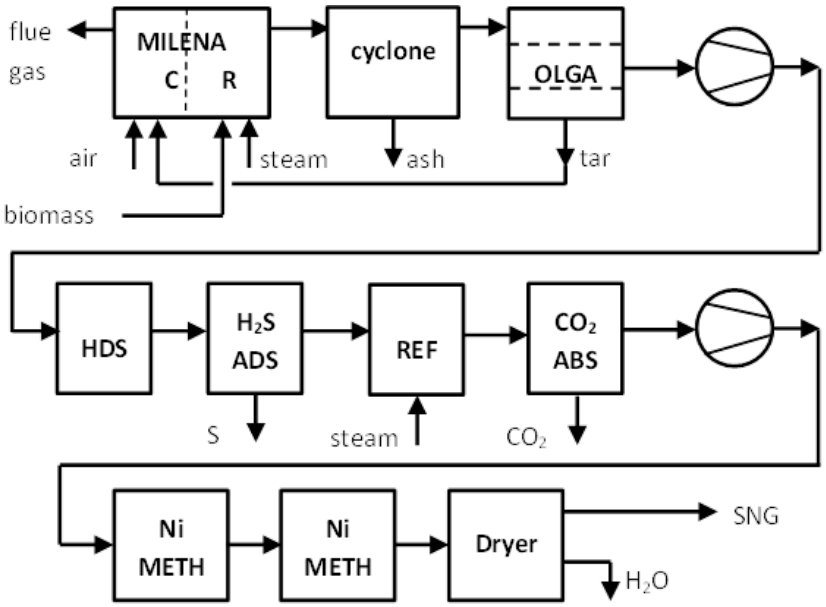


Figure 9.1 *Main steps in the ECN bioSNG process.*

The main steps in the ECN bioSNG process are described in section 9.2. The expected process efficiency and economy are treated in section 9.3. Actual results, the status and plans are described in section 9.4. The outlook for further research and future developments are discussed in section 9.5.

## *9.2 Main process steps*

### *9.2.1 MILENA indirect gasification*

The MILENA indirect gasification process is designed to use little steam and yield producer gas rich in hydrocarbons. Table 9.1 shows the producer gas composition on dry basis for a large MILENA gasifier after tar removal. The $H_2$/CO ratio in the producer gas depends on process conditions, but is usually close to 1. The water content is about 35%, depending on gasifier conditions and fuel moisture content. Table 9.1 also shows the contribution of each component to the producer gas heating value, the heating value loss on reaction with $H_2$ to methane, and the expected composition of the bioSNG product after methanation and

upgrading. Not shown in Table 9.1 are contaminants, such as tar, $NH_3$, $H_2S$, HCl and other compounds containing O, N, S and Cl.

Table 9.1 *Composition of tar-free MILENA producer gas (dry basis), contribution to producer gas heating value, loss on reaction with $H_2$ to $CH_4$, and final bioSNG composition.*

| | ***MILENA [vol% dry]*** | ***MILENA [% LHV]*** | ***Conversion loss [%]*** | ***bioSNG [vol% dry]*** |
|---|---|---|---|---|
| **$H_2$** | 27 | 18 | | 2 |
| **CO** | 32 | 25 | 20 | <0.1 |
| **$CO_2$** | 20 | | | 3 |
| **$CH_4$** | 14 | 30 | | 92 |
| **$C_2H_4$** | 4 | 14 | 12 | |
| **$C_6H_6$** | 1 | 8 | 10 | |
| **$C_xH_y$ *** | 1 | 5 | 12 | |
| **$N_2$** | 1 | | | 3 |

* Mainly $C_2H_2$, $C_2H_6$, $C_7H_8$, and small quantities of hydrocarbons with 3 to 5 C-atoms.

The MILENA gasifier (see Figure 9.2) consists of three zones: the gasifier section, the combustion section and the settling chamber. It relies on the use of a bed material such as sand or olivine. The gasifier section operates in fast fluidization mode, with gas velocities around 6 m/s. The combustion section operates in bubbling bed mode, with gas velocities around 0.5-1.0 m/s. The settling chamber is part of the gasifier section where the gas velocity is reduced significantly. From here on, the gasifier and combustion sections will be referred to as riser and combustor.

Biomass is fed by a screw to the bottom part of the riser, where the bed material is fluidized by a small supply of steam or air. Biomass is heated quickly by contact with hot bed material. This produces pyrolysis gas and char and cools the bed material. The pyrolysis gas entrains bed material to the top of the riser, making room for hot bed material to flow from the combustor to the bottom of the riser.

At the top of the riser, gas and entrained solids enter the settling chamber. Here, the reduced gas velocity allows bed material and char to separate from the gas stream. Some dust will be entrained to the gas cooling and cleaning systems. Bed material and char are collected in a funnel and transported via a downcomer into the combustor. More than one downcomer can be applied if required.

In the combustor, the bed material is heated by combustion of char with air. Close to stoichiometric conditions are applied to obtain a high flue gas temperature for maximum heat transfer to the bed material. Secondary air can be injected above the bubbling bed to assure complete combustion and limit $NO_x$ emissions. The low gas velocity leads to a long gas residence time. The combination of high temperature and long residence time makes it possible to use waste derived fuels.

Transport of bed material and char between riser and combustor provides the main contributions to the heat balance. Further contributions may come from e.g. preheated combustor air, additional combustor fuel, recycling part of the producer gas or tar to the combustor, superheated steam or air/oxygen to the riser.

The gasifier operating pressure is limited by the balance between heat and mass transport. Higher pressure reduces the gas velocity and increases the gas density in the riser. The net result is a reduced drag force acting on the bed material, which leads to less bed material

transport to the combustion section. In order to maintain heat transport from the combustor to the riser with less bed material available to carry heat, the bed material has to be heated to higher temperature in the combustor and cooled to lower temperature in the riser. This will limit the operating pressure to about 7 bars.

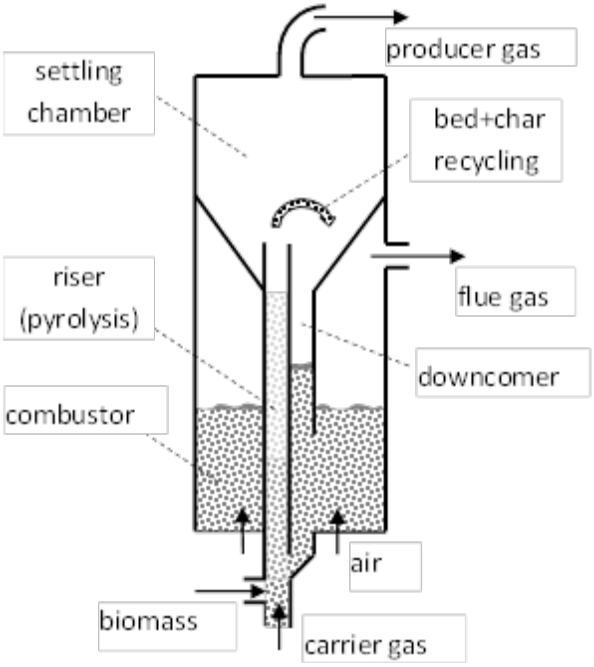


Figure 9.2 *MILENA indirect gasifier with riser, combustor and settling chamber in a single vessel.*

The principles described above are also used in the Battelle [5] and FICFB [6] processes. The actual implementation of the principles in the MILENA process is quite different. Some of the distinguishing properties of the MILENA process are (see also Figure 9.2):

- The gasification section is a fast fluidized bed (riser), with fluidization mainly by producer gas. Only a small amount of steam, inert gas or air is needed for initial fluidization.
- The combustion section is a bubbling fluidized bed, with fluidization by combustion air.
- The gasification and combustion sections are placed within a single hull, which makes gasification at moderate pressure (up to about 7 bar) easier.
- Char and bed material are separated from producer gas in a settling chamber and recycled to the combustion section via a downcomer (or several downcomers at large scale).
- Particles which are too small to be separated in the settling chamber are collected by a cyclone or dust filter and can be recycled to the combustion section.
- The process heat demand can usually be covered by combustion of the char and tar separated from the producer gas with preheated air. If more heat is required, some producer gas can be “leaked” to the combustion section by manipulating the pressure difference between the gasifier and combustion sections.
- Low steam use leads to producer gas with high (20 to 60 g/Nm$^3$) tar content, but that is not a problem for OLGA tar removal technology.
- Low steam use leads to producer gas with comparatively low (~35%) moisture content, reducing the cooling demand required to condense water before gas compression and reducing the volume of condensate produced.

### *9.2.2 OLGA tar removal*

OLGA tar removal is a technology specially developed for deep removal of tar. The goal is to be able to use the gas in down-stream processes such as gas engines or catalytic reactors. Figure 9.3 shows a typical OLGA lay-out.

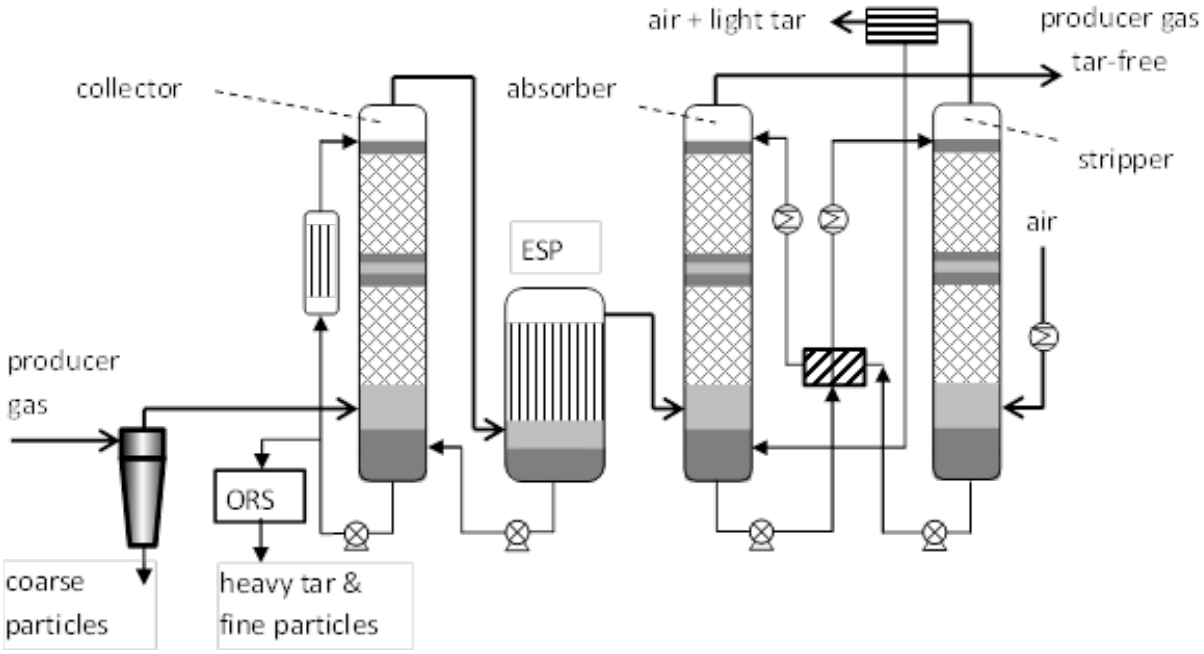


Figure 9.3 *Typical OLGA lay-out with collector, absorber and stripper columns, electrostatic precipitator (ESP) and oil recovery system (ORS).*

The technology is based on the idea that a liquid or solid mixture of tar, dust and water should be avoided at all times. That can be realized if dust is removed at a temperature above the tar dew point and tar at a temperature above the water dew point. In case of MILENA producer gas and at atmospheric pressure, the tar dew point is around 450°C and the water dew point around 75°C. In the current system, a cyclone is used to remove most of the dust from the raw producer gas. Part of the chloride will form KCl, condense onto dust particles and be removed by the cyclone.

OLGA technology comprises several process steps. In the first step, gas is cooled in counter-current by a washing liquid to a temperature above the water dew point. Most of the heavy tar compounds condense and are collected in the liquid, together with most of the dust still present. To avoid plugging, a washing liquid is used which is able to dissolve the condensable tar compounds. Due to the rapid cooling of the gas, aerosols are formed from oversaturated tar vapour and fine dust particles. These aerosols are captured in the wet ESP (Electro Static Precipitator).

In the second step, remaining tar compounds are absorbed in a liquid with affinity for light tar compounds. Even though the column operates above the water dew point, a tar dew point below 5°C can be achieved. Volatile compounds such as benzene and toluene are hardly absorbed and remain in the gas. Water remains in the gas too. It can be removed downstream OLGA by a water scrubber or water condenser.

In the third step, the tar rich absorption liquid is regenerated. Tar compounds are desorbed by heating and stripping with air, nitrogen or steam. Which gas is used, depends on the

location and the integration with the gasifier. The columns used in the three steps are referred to as collector, absorber and stripper.

Key components in the absorption and desorption steps are phenol and naphthalene. The design of the absorber and stripper is such that 99.9% of both is removed and water can be condensed without phenol pollution. The stripper off-gas can be recycled to the MILENA combustor to provide additional heat input for the gasification.

For the first separation step, an Oil Recovery System (ORS) has been developed. The function of this device is to separate heavy tar and dust from the lighter tar fraction. This lighter tar fraction is used to maintain adequate viscosity in the collector. Heavy tar and dust are sent to the MILENA combustor to provide additional energy for the gasification.

OLGA effectively removes all tar compounds heavier than toluene. It makes it possible to reuse the energy in the tar for the gasification process and it avoids a waste water problem by separating tar above the water dew point.

### *9.2.3 HDS and deep S removal*

The total sulfur content of producer gas from biomass gasification may vary from about 100 ppmv for clean fresh wood to more than 1000 ppmv for waste derived fuels. The main sulfur compounds in producer gas are $H_2S$ and COS. Other compounds found in significant concentrations (1 – 100 ppmv) are thiophene ($C_4H_4S$), thiols (e.g. $CH_3SH$, $C_2H_5SH$), $CS_2$ and thiophene derivatives which contain one or more (m)ethyl and/or benzyl groups, such as (di)methyl-thiophene, (di)benzo-thiophene etc.

Sulfur binds to nickel methanation catalysts and renders them inactive. The sulfur concentration must be reduced to 0.1 ppmv to obtain a catalyst life of several years. Deep sulfur removal by technology applied in chemical or coal-to-SNG plants is not economic for bioSNG plants smaller than 100 MW, unless they use biomass with high sulfur content. In the latter case, high sulfur removal costs should be compensated by low fuel costs.

Non-aromatic organic sulfur compounds are relatively easy to remove. They are readily hydrolysed to $H_2S$ and then captured by commercially available solid adsorbents or liquid absorbents. Iron oxide adsorbent or scrubbing with amine or a transition metal solution can be used to reach ppmv sulfur concentration. Sub-ppmv level can be reached with zinc or noble metal oxides. Heavy aromatic sulfur compounds can be removed by the OLGA tar removal system. The lighter aromatic sulfur compounds can be bound to metal impregnated active carbon, but BTX bind to active carbon too. That leads to a considerable loss of potential methane output and quick saturation of the active carbon, as BTX are present in much larger concentrations than thiophene.

The ECN approach is to use a commercial hydrodesulfurization (HDS) catalyst for conversion of organic sulfur compounds into $H_2S$, in series with commercial technology for $H_2S$ removal. ECN research focuses on the operating conditions and performance of the HDS catalyst. If sulfided CoMoO is used, a temperature above 350°C is required to obtain sufficient catalytic activity. As the OLGA exit temperature is around 100°C, heat must be supplied.

If gasification is performed at atmospheric pressure, compression of the gas may provide part of the required heat input. However, prior to compression the gas needs to be dried by cooling in order to prevent compressor damage by condensate formation and to reduce the compressor power demand. The relatively low moisture content of MILENA producer gas reduces the cooling duty involved. The cooling and drying step removes some of the producer gas contaminants, notably $NH_3$.

The HDS catalyst also functions as hydrogenation catalyst for unsaturated aliphatic compounds, such as acetylene ($C_2H_2$), ethylene ($C_2H_4$) and propene ($C_3H_6$). Furthermore, the HDS catalyst promotes the water gas shift and methanation reactions, given the right conditions. All these reactions are exothermic. In case of MILENA producer gas, they raise the producer gas temperature by about 200°C. Downstream the HDS reactor, the gas needs to be cooled to allow $H_2S$ capture. The heat removed can be used e.g. to raise the gas temperature between the OLGA exit and the HDS entrance.

Downstream the HDS reactor the only sulfur compound remaining is $H_2S$. A ZnO based solid adsorbent can be applied to obtain the sub-ppmv sulfur concentration required. Operating costs may be reduced by bulk sulfur removal using scrubbing technology or an Fe-based adsorbent. The bulk sulfur removal can be positioned upstream the ZnO adsorbent or upstream the HDS reactor. Downstream the ZnO adsorbent a mixed-metal guard bed can be installed to remove trace compounds left.

### *9.2.4 Reformer*

MILENA producer gas contains about 5% unsaturated aliphatic compounds and 1% BTX. Nickel methanation catalysts exposed to these compounds deactivate by deposition of carbon or polymerization products. Hydrogenation of unsaturated compounds by the HDS catalyst reduces the risk. The reformer contains a dedicated steam reforming catalyst to take care of BTX. A large amount of steam and temperature above 400°C are needed to prevent or reduce catalyst coking.

The steam reforming catalyst also promotes the water gas shift, hydrogenation and methanation reactions. Effectively, the reformer acts as first methanation reactor. Although reforming reactions are endothermic, overall the reactions lead to a temperature rise. The reformer exit temperature is determined by the methanation equilibrium. The mild pressure applied limits the temperature rise, obviating the need for gas recycling. The gas must be cooled for the next step in the process, $CO_2$ removal. Depending on process conditions and requirements, a methanation reactor can be inserted between the reformer and $CO_2$ removal. At this stage, the gas contains only $CH_4$, $H_2O$, $CO_2$, $H_2$, CO and $N_2$. Some $NH_3$ and side products may be present as well.

### *9.2.5 $CO_2$ removal*

Conventional technology for $CO_2$ removal is scrubbing with aqueous solutions of a physical or chemical solvent. Physical solvents require high pressure and/or low temperature, which lead to considerable removal of hydrocarbons such as methane. Therefore, they are not optimal for bioSNG purposes.

Chemical solvents based on amines can be used at mild pressure. First, the gas must be cooled to the operating temperature of about 40°C. Condensed water must be removed to prevent dilution of the amine solution. Here again some $NH_3$ will be removed. In order to tune the gas composition to the desired $(H_2 - CO_2)/(CO + CO_2) = 3$ ratio, the amine-unit can be bypassed with part of the producer gas stream. The amine absorbent is regenerated by heating. The $CO_2$ stream can be vented, stored or used. A guard bed may be needed to prevent deactivation of downstream catalysts by traces of the chemicals used in the $CO_2$ removal process.

Another option is $CO_2$ removal via regenerative solid adsorbents. The process can be operated at 350-450°C. This novel technology, in development at ECN, is based on the adsorption of $CO_2$ on a solid material at pressures of typically 10-30 bar. After saturation of the adsorbent, low pressure regeneration with steam is applied. As such, the technology

constitutes a hot pressure-swing adsorption (PSA) system for $CO_2$ removal [7]. Compared to amine scrubbing, the energy requirement for $CO_2$ removal with solid sorbents is 25% lower [8, 9]. Because of the inherent WGS activity of the solid sorbent, this hot-PSA system usually has a very high carbon removal rate. To obtain the desired $(H_2 - CO_2)/(CO + CO_2) = 3$ ratio for the downstream methanation, part of the producer gas can be bypassed. Alternatively, the PSA cycle can be tuned to decrease the carbon removal ratio.

#### *9.2.6 Methanation and upgrading*

The final methanation is performed at high pressure, typically 30 to 50 bar, using commercial nickel methanation catalysts. Several fixed beds in series are used, with intermediate cooling, until the residual $H_2$ concentration is below the level required. If upstream conditions are well chosen, gas recycling or steam addition are not needed to moderate the temperature or to prevent carbon deposition.

After the final methanation step, the gas has to be dried to a level that prevents condensate formation in the most severe usage conditions expected. The nearly finished product contains about 95% $CH_4$, some $H_2$, trace amounts of $CO_2$ and CO, and 2.5 times the $N_2$ concentration in the MILENA producer gas. Further treatment will be needed to bring it within the specifications required. Such treatment may involve $N_2$ or LPG addition to lower or raise the Wobbe index, odorant addition to allow quick leak detection, and further reduction of the $H_2$ concentration. If a separate $H_2$ removal step is required anyhow, the number of methanation steps may be reduced. Recovered $H_2$ can be recycled to the HDS reactor or reformer.

### *9.3 Process efficiency and economy*

The economy of bioSNG production has been calculated using different methods and published by various authors. All results are projections and expectations, since there is no full-scale reference bioSNG plant existing at this moment. In any case however, the bioSNG production costs heavily depend on energy efficiency and feedstock costs.

At ECN, an estimate of the investment costs of future large-scale bioSNG plants has been made based on costs of existing plants operating on coal and gas [10]. Differences in technology and scale have been quantified to arrive at a final average estimate: 1.1 billion US$ total capital investment costs for a 1 $GW_{th}$ (input capacity) wood-based SNG plant on the long-term, say 2030. In Figure 9.4, this investment has been translated to different scales using an 0.7 scaling factor. Two bioSNG references are included in the graph: the GoBiGas plant (started up early 2014) in Göteborg in Sweden and the E.On initiative for a larger bioSNG plant (FEED phase in 2014). The investment has been used to determine the production costs of bioSNG. From the figure it becomes clear that scale and the efficiency from biomass to bioSNG are major factors.

The important question is how the cost of bioSNG compares to the alternative of bioSNG. This is not as easy as it sounds, since bioSNG can serve different markets such as power production, transport, heat production and chemical feedstock. One might argue that bioSNG replaces natural gas and therefore should be compared with natural gas, but that is only partly true. Obviously, bioSNG has a low $CO_2$ footprint, which even can be negative (see Section 9.5), and which makes it a different product than natural gas. But there is more. BioSNG serving as a biofuel instead of CNG or LNG (i.e. compressed or liquefied natural gas) replaces other biofuels such as ethanol rather than natural gas. This is true since the EU created a biofuels market through the “biofuels directive” aiming at a certain fraction of fuels to come from renewable sources. BioSNG for power production also has not an easy comparison. In regions where the fraction of intermittent renewable power production is

significant (high share of solar- and wind-power), there is a need for both flexible and renewable power production. BioSNG perfectly fits that picture and therefore creates additional value.

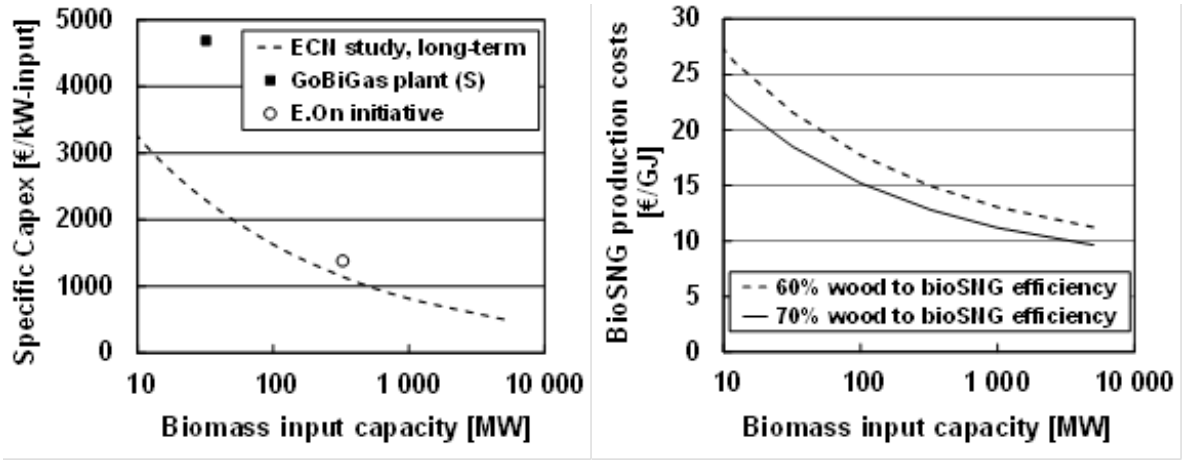


Figure 9.4 *Specific investment costs (left) and bioSNG production costs as function of scale assuming biomass costs of 5 €/GJ, capital costs of 10%/year and 8000 h/y.*

In summary, the costs of producing bioSNG can be and has been estimated by different parties. Clearly the costs depend heavily on scale, efficiency and biomass costs. The question whether it is attractive or not is more difficult to answer, since it concerns a new product that serves many markets, each with its typical requirements and alternatives. Looking at the various bioSNG initiatives of parties around the globe (but mainly in Europe), one might say that there clearly are attractive markets for bioSNG [11].

## *9.4 Results and status*

### *9.4.1 MILENA*

The MILENA development is aimed at commercial application at a size between 5 and several hundred MW of biomass input. That is why first a design was made for a 10 $MW_{th}$ plant from which designs for smaller systems are derived. Experimental work for the MILENA development is performed in a 30 $kW_{th}$ (~6 kg/h biomass) lab-scale facility and an 800 $kW_{th}$ (~160 kg/h biomass) pilot plant.

The lab-scale installation was taken in operation in 2004 and has been used for more than 6000 hours. The reactor wall can be heated externally to compensate for the relatively high heat loss. The fuel particle size has to be in the range of 1 – 3 mm, because of the size of the feeding screw and riser reactor.

The MILENA pilot plant was to replace a 500 $kW_{th}$ CFB gasifier, which was used for ten years. The goal was to realize an installation for experiments under realistic 'commercial' conditions, i.e. no external heat supply to the reactor wall and larger fuel particle size. The upper size limit was put at 15 x 15 mm, based on experiments with the 500 $kW_{th}$ CFB gasifier. The pilot plant was taken in operation in 2008 and has been used for approximately 1500 hours, in combination with the pilot scale OLGA gas cleaning.

Several fuels were tested in both installations. Most of the experimental work was done with wood and demolition wood, but several other fuels, such as RDF, soya residue, sunflower husk, lignite, sewage sludge and high ash coals were tested as well.

After the first tests with the MILENA pilot plant, the HVC Group (a Dutch waste processing company) joined ECN to develop the MILENA technology for bioSNG production. The first plan was to build a 10 $MW_{th}$ MILENA gasifier, in combination with OLGA gas cleaning and a gas engine. The aim was to demonstrate the gasification technology and to supply a continuous slip stream of cleaned gas to a methanation test rig. Subsidy for the production of electricity from renewable sources was expected to help cover the cost of the demonstration plant. The plant would be located in Alkmaar, next to an HVC site and not far from the ECN site in Petten. The Dutch company Royal Dahlman was involved in engineering of the demonstration plant for both the MILENA gasification and the OLGA tar removal technology.

The development involved several duration tests with demolition wood in the ECN pilot plant. These tests were performed in 2010 and 2012 and resulted in a number of modifications and an updated design for the commercial scale gasifier. When the subsidy scheme for renewable energy production was changed, plans for the demonstration plant had to be adapted. In 2013 Gasunie (a large Dutch gas company) joined the consortium to demonstrate the MILENA technology for SNG production. It was decided to go for a slightly smaller (4 MW) demonstration plant producing SNG. In 2014, subsidy for bioSNG production and injection into the grid was granted. This provides a sound economic base for realization and operation of the demonstration plant.

In 2013 Royal Dahlman acquired a license for the MILENA gasification technology. In 2013 a large experimental program was carried out for Royal Dahlman within the framework of a project financed by the British company ETI. The data is used for basic engineering of a commercial scale demonstration plant using RDF fuel. In 2014 it will be decided if the project will be continued. Several other projects using different fuels are in preparation as well.

The Indian company Thermax is constructing a demonstration plant based on the MILENA and OLGA technology in India. The fuel is a residue from the soya crop. Fuel tests were performed in the ECN lab-scale installation. The gas will be used in a gas engine. Commissioning of the demonstration plant is scheduled for 2014.

### *9.4.2 OLGA*

Currently, four OLGA systems have been built and been in operation on different scales and downstream various gasifiers. From 2001, Dahlman has been involved in the technology development and construction of OLGA systems. In 2006, Dahlman and ECN signed a license agreement. An overview of systems realized is given in Table 9.2.

**Table 9.2** *Overview of OLGA systems*

| Location | Lab ECN (NL) | Pilot ECN (NL) | Moissannes (Fr) | Tondela (Pt) |
|---|---|---|---|---|
| **Capacity ($Nm^3/h$)** | 2 | 200 | 2000 | 2000 |
| **Construction** | 2001 | 2004 | 2006 | 2010 |
| **Front end** | BFB / MILENA | CFB / MILENA | PRMe gasifier | CFB |
| **Application** | Fuel cell<br>SNG test rig | Boiler<br>Gas engine<br>Micro gas turbine | Gas engine | Gas engine |
| **ORS included** | no | no | no | yes |
| **ESP included** | no | yes | yes | yes |

The lab scale OLGA has the highest accumulated number of operating hours. It has also been tested with the largest variety in product gases. Ranging from pyrolysis gas with several hundreds of grams/$Nm^3$ tar to high temperature gasification with tar levels down to 10 gram/$Nm^3$. In all cases the overall removal efficiency of the lab scale OLGA is in the

range of 95 – 99%. The lab-scale system has been modified several times. It is still used, especially for research on difficult fuels and cost reduction.

In 2004 the pilot OLGA was taken into operation downstream an air-blown CFB gasifier. The gas flow was 100 times larger than in the lab scale OLGA. Notable difference is the wet ESP in the line-up, which is not present in the lab scale OLGA. In a 700 hour duration test with the CFB gasifier, tar removal efficiencies of up to 99% were achieved [12]. The installation was partly modified to accommodate gas from the MILENA indirect gasifier, which produces the same gas volume but about twice as much tar. In 2010 and 2012 duration tests of 250 and 500 hours were performed. Despite tar concentrations of 60 – 70 gram/$Nm^3$, OLGA managed to effectively remove 97 – 99% of the total amount of tar.

In 2006, the first commercial OLGA demonstration system was commissioned by the French company ENERIA for a plant in Moissannes [13]. The system showed good performance when wood and wine residue were used as fuels. Upstream OLGA dust concentrations up to 1,500 mg/$Nm^3$ and tar concentrations up to 11,000 mg/$Nm^3$ were measured. Downstream OLGA a series of aerosol (oil & fine dust) measurements were carried out with a filter at 70°C. The total amount of aerosols (dust, tar & oil) was far below the detection limit of 25 mg/$Nm^3$. The key tar compounds phenol and naphthalene were sufficiently removed, i.e. remaining phenol was below the detection limit and naphthalene reduced by 99%. The cleaned gas was used in a Caterpillar gas engine to produce 1.1 $MW_e$.

In 2010, the second commercial OLGA system was installed in Tondela for the Portuguese company Iberfer. Gas produced by a CFB gasifier from chicken manure and wood chips is cleaned by an OLGA system and applied in again a 1 $MW_e$ Caterpillar gas engine. The OLGA performance has been further improved. The gas tar content (excluding BTX) is reduced from 16 g/$Nm^3$ dry gas to 63 mg/$Nm^3$, i.e. the system removes 99.6%. The key tar compounds phenol and naphthalene are reduced by more than 99.9%.

In 2014, another OLGA system will be realized in India. The other projects mentioned in section 9.4.1, notably the RDF gasifier and the Alkmaar SNG demonstration plant, will also include an OLGA system.

### *9.4.3 HDS, reformer and methanation*

In 2006 ECN completed a test rig consisting of the lab-scale MILENA, OLGA, sulfur and chloride adsorbents, hydrogenation, reformer and methanation reactors [14]. The system operated at atmospheric pressure and was designed for a producer gas flow of 1 $Nm^3$/hr, i.e. about 5 kW. Test runs of up to 200 hours were performed. The first experiments showed quick catalyst deactivation and plugging by soot formation. The problems were reduced considerably by changes in operating conditions.

Another problem encountered was slip of organic sulfur compounds, i.e. mainly thiophene. Adsorption of these compounds by active carbon was studied and proved feasible. However, the use of active carbon is not an attractive solution because of the large amounts of benzene and toluene which are adsorbed too. Regeneration of active carbon is an option if the recovered stream of BTX and thiophene can be used or sold [4]. In the present market conditions, ECN prefers to keep BTX in the producer gas and convert BTX into SNG.

The alternative for thiophene removal is conversion to $H_2S$, followed by $H_2S$ removal. To that end, in 2007 an HDS reactor with CoMoO(S) catalyst was added to the SNG test rig. The reactor is externally heated to obtain approximately adiabatic conditions. Tests were performed using 0.3 to 1 $Nm^3$/hr gas containing 100 to 200 ppmv $H_2S$, 5 to 10 ppmv COS, about 10 ppm $C_4H_4S$ and about 1 or 2 ppm each of $CH_3SH$ and $C_2H_5SH$.

At atmospheric pressure, catalytic reactions start when the gas temperature reaches about 350°C. The temperature rises quickly, due to heat produced by exothermic reactions. Figure 5 shows the effect of temperature on the reactions. Between 450 and 500°C, the water gas shift (WGS) reaction reaches thermodynamic equilibrium. Conversion of thiols and COS takes place in the same temperature window. Hydrogenation of $C_2H_4$ needs slightly higher temperature and clearly depends on gas hourly space velocity (GHSV). Thiophene conversion follows the same trend.

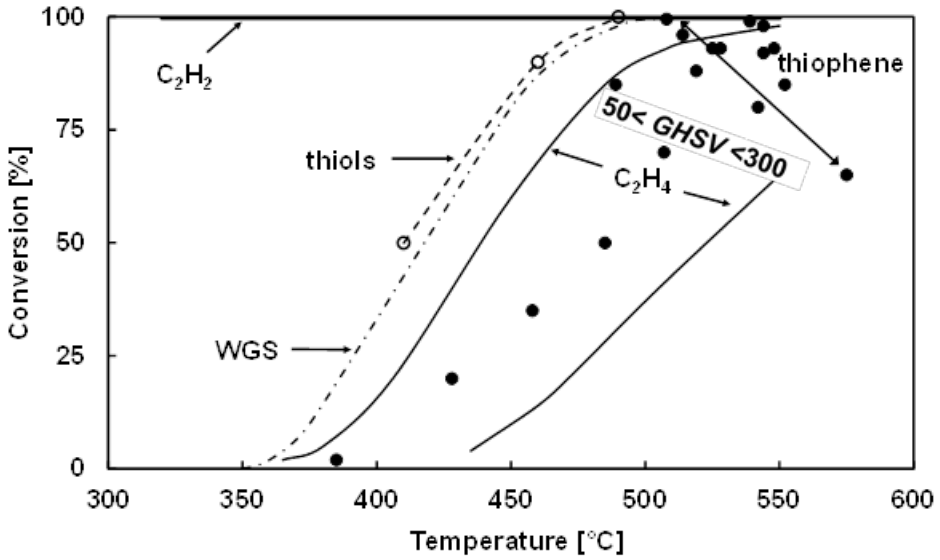


Figure 9.5 *Temperature dependence of reactions in HDS reactor for MILENA producer gas at 1 bar and gas velocities of 50 to 300 $hr^{-1}$.*

The tests showed that thiophene in producer gas could be reduced to below 0.5 ppmv, but the allowed GHSV was too low for practical purposes. In 2011 a test rig was built to study HDS performance at higher pressures. To simulate conditions for a pressurized gasifier, gas was first dried by cooling to 5°C, then compressed to the required pressure, and finally steam was added to restore the moisture content. Results for thiophene conversion differed from those shown in Figure 9.5 only by the GHSV values, which could be increased linearly with pressure.

In 2013 the test rig was extended to allow testing of reforming and methanation at higher pressure too. The test rig is used to obtain and check design parameters for the SNG demonstration plant to be built in Alkmaar. The equipment also allows simulation of gas recycling and Power-to-Gas (P2G) operating conditions.

## *9.5 Outlook*

Although indirect gasification of biomass for the production of bioSNG is in its first phase of implementation, developments for the longer term are ongoing. These developments are targeted to make the process even more efficient in terms of energy, economy, and $CO_2$-reduction.

*Pressure*
The lab and pilot MILENA gasifiers operate near atmospheric pressure. Demonstration and commercial size gasifiers will operate at slightly elevated pressure. In general, pressurized gasification improves the energy efficiency, as pressurizing solid fuels consumes less energy

than producer gas compression. Specific investment costs can be reduced, as reactor size decreases with pressure.

In case of a bioSNG plant, gasification at elevated pressure could result in a higher methane yield. That would benefit the overall efficiency to bioSNG, but tests showed no significant increase in methane yield at pressures up to 5 bar. The main benefit is the lower demand for steam to suppress coking in the reforming reactor (see Figure 9.1), as water formed in the gasifier remains in the gas phase. In case of atmospheric gasification, water vapour in the gas inevitably is condensed in the gas cooling/compression stage prior to reforming and thus has to be added again as steam.

The benefits of higher pressure come with a few penalties. A pressurized indirect gasifier needs air compression for the combustion reactor. The disadvantage can be turned into an advantage if an expansion turbine is fitted in the flue gas outlet, provided an appropriate turbine is available. Another penalty relates to the practical problems of pressurized biomass feeding, which translate into reduced availability and additional investments.

As explained in section 9.2.1, there is an inherent limit to the operating pressure of an indirect gasifier. That limit is incorporated in the ECN bioSNG process design shown in Figure 9.1. A design requiring higher pressure downstream OLGA, would still require condensation of water vapour and thus lose an important advantage of indirect gasification at elevated pressure. At present, there is insufficient experience with the process to be able to tell at what size the theoretical cost and efficiency advantages of pressurized gasification will outweigh the increased technical complexity.

*Co-production*
Indirect gasification shows superior efficiency to bioSNG since a large part of the gas produced by the gasifier itself already is methane. The gas also contains significant amounts of other hydrocarbon molecules, such as BTX and ethylene, which are converted into methane in the system shown in Figure 9.1. BTX and ethylene add up to 25% of the heating value of the raw gas, but they require special attention, because of their tendency to form coke on catalysts. However, BTX and ethylene are valuable chemicals too [4]. That is why ECN is developing technology to separate BTX and ethylene rather than convert them to methane. Research is ongoing to increase the yield of valuable chemicals in gasification, with the aim to further improve the business case of co-production of bioSNG and chemicals.

*BioCCS (BECCS)*
BioSNG production results in a large flow of essentially pure $CO_2$. The amount of $CO_2$ roughly equals the bioSNG production on a volume basis. The $CO_2$ stream may be vented to the atmosphere, from which it was recently taken by growing plants, but may also be stored. When applied to reduce $CO_2$-emissions from processes using fossil fuel, Carbon Capture and Storage (CCS) involves considerable costs and efficiency loss. As $CO_2$ separation is an integral part of the bioSNG process, CCS combined with bioSNG production (BioCCS or BECCS = Bio-energy with Carbon Capture and Storage) hardly involves an energy penalty. That makes BioCCS a relatively efficient and cheap method to reduce $CO_2$ concentrations in the atmosphere. BioCCS is a way to go far beyond $CO_2$-neutral [15].

*Power-to-Gas*
Balancing power production and demand is becoming more difficult when a growing share of power production comes from intermittent renewable sources such as wind and solar PV. One of the options for large-scale storage of temporary excess power is the production of hydrogen by water electrolysis, a concept called Power-to-Gas (P2G). Hydrogen can be used as such, or made to react with $CO_2$ to produce fuels, which fit more easily in the existing infrastructure.

As a bioSNG plant produces large quantities of essentially pure $CO_2$ as a co-product in the process (see above), it offers a smart way to accommodate hydrogen. In a bioSNG plant, hydrogen can be added to produce additional methane and consume $CO_2$ that otherwise would have to be separated and be lost as a carbon source. The P2G concept integrated with the bioSNG process involves limited additional costs. It only requires additional capacity and flexibility in the last part of the bioSNG process, and saves on the expense of $CO_2$ separation [16].

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