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PRODUCTION OF BIO-METHANE BY GASIFICATION

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Abstract

Compressed Natural Gas (CNG) is becoming more and more important as a transport fuel. Already in 2007, seven million cars were fueled by CNG. The number of Natural Gas Vehicles (NGV's) is increasing rapidly. CNG is a relatively clean transport fuel. The emissions of CO_2, particles and sulfur are significantly lower than for other conventional fossil fuels. Fossil CNG can easily be replaced by CNG produced from biomass (Bio-CNG or Bio-Methane), because the composition of the gas and the heating value are similar. Replacing CNG by Bio-CNG will reduce fossil CO_2 emissions to zero. Bio-CNG even has the potential to become a CO_2 negative transport fuel, because part of the carbon from the biomass is separated as pure CO_2 from the fuel during the production of Bio-CNG. If this pure CO_2 stream is sequestrated, Bio-CNG becomes CO_2 negative.

The production of Bio-Methane or Bio-CNG via digestion has been developed and is implemented (mainly) in small-scale installations. The limited amount of suitable digestible feed stock demands for development of a technology which can convert a wider range of biomass, like wood residue, into Bio-Methane. Gasification is such a route that can convert a wide range of (cellulosic) biomass into CH_4 with a high energetic efficiency.

The Energy research Centre of the Netherlands (ECN) is developing an indirectly heated (allothermal) biomass gasification process (MILENA), optimized for the production of Bio-Methane. The work done at ECN focuses on the development of the MILENA gasification technology for large scale production of gas that can be upgraded into Bio-CNG. ECN also develops and tests the required gas cleaning equipment. The gas from the final gas cleaning step can directly be upgraded into CH_4 by conventional and commercially available methanation catalysts.

ECN has built and tested the Bio-CNG installation on a lab-scale of 6 kg/hour biomass input (30 kW_{th}). A pilot scale unit of 160 kg/hour (0.8 MW_{th}) input is now ready for start-up. The results from the lab-scale installation are promising. The gasifier and connected gas cleaning were operated successfully during several 100 hour duration tests. Progress has been made in selecting the appropriate process conditions to obtain cleaned producer gas that can be sent to a commercial methanation process. The expected final gas composition and heating value are similar to those of natural gas of fossil origin. The main difference is the presence of a few percent of H_2, a gas absent in fossil natural gas or Bio-Methane produced by digestion. It is expected that this small amount of H_2 will cause no technical problems in Natural Gas Vehicles.

The Bio-CNG produced in the ECN lab-scale installation is going to be used to fuel a Natural Gas Vehicle. A demonstration plant of 10 MW_{th} is planned for the near future. The scale foreseen for a commercial single-train Bio-Methane production facility is between 50 and 500 MW_{th} or between 3 and 30 ton/h of Bio-CNG production.

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1. Introduction

The number of Natural Gas Vehicles (NGV's) is increasing rapidly because CNG is less expensive than gasoline or diesel and CNG is a relatively clean transport fuel. Fossil CNG can easily be replaced by CNG produced from biomass (Bio-CNG or Bio-Methane), because the composition of the gas and the heating value are similar.

Biomass is considered a CO_2 neutral fuel, as the amount of CO_2 released on burning biomass equals the amount taken from the atmosphere during growth of the biomass. Replacing CNG by Bio-CNG will reduce fossil CO_2 emissions to zero. Bio-CNG has the potential to become a CO_2 negative transport fuel, because part of the biomass carbon is separated as CO_2 in the Bio-CNG production process. If this pure CO_2 stream is sequestrated, Bio-CNG becomes CO_2 negative.

The production of Bio-Methane or Bio-CNG via digestion has been developed and is implemented (mainly) in small-scale installations. Because of the limited amount of suitable digestible feed stock, there is a demand for development of a technology which can convert a wider range of biomass feed stocks into Bio-Methane. Gasification is a route which can convert a wide range of biomass feed stocks into CH_4 with a high energetic efficiency. Gasification processes can use a variety of non food crops. These include husks, (waste) wood and different energy crops. Dornburg et al. (2007) reported the future world-wide available amount of biomass for energy to be 200 to 500 EJ per year, based on an evaluation of availability studies. Word wide oil consumption was 161 EJ (82.5 million barrels of oil per day) in 2005 according the BP Statistical Review of World Energy June 2006.

ECN is developing an indirectly heated (allothermal) biomass gasification process (MILENA), optimized for the production of Bio-Methane. The technology is based on fluidized bed gasification. The technology and experimental results have been presented by van der Meijden et al. (2007). Fluidized bed gasification is widely used to produce gas which is fired in gas boilers and gas engines. The gas produced in fluidized bed gasifiers is not directly suitable as a transport fuel (CNG), because the raw gas contains CO, H_2, several hydrocarbons and pollutants like chloride, sulfur, tars and dust. Moreover, most conventional fluidized bed gasifiers produce a gas which contains a large amount of N_2. This makes this raw gas unsuitable for upgrading into Bio-Methane. For Bio-Methane production, such gasifiers have to be operated with pure O_2. Indirect or Allothermal Fluidized Bed gasifiers can operate with air and still produce a gas virtually free of N_2. After removal of the pollutants the remaining mixture of CO, CO_2, H_2, H_2O, CH_4 and other hydrocarbons can be catalytically converted into Bio-CNG.

The work done at ECN focuses on the development of the MILENA gasification technology for large scale production of gas which can be upgraded into Bio-CNG. ECN also develops and tests the required gas cleaning equipment. The gas from the final gas cleaning step can directly be upgraded into CH_4 by conventional and commercial methanation catalysts.

The foreseen scale for a commercial single-train Bio-Methane / Bio-CNG production facility is between 50 and 500 MW_{th} or between 3 and 30 ton/h of CNG.

2. Process description

The overall Bio-CNG production plant exists of the following production steps:

1) A gasifier where solid biomass is converted into a producer gas
2) Gas cooling and tar removal
3) Gas cleaning where the pollutants are removed from the producer gas
4) Catalytic conversion of producer gas into CH_4, CO_2 and H_2O
5) An upgrading step where water and CO_2 are removed and the gas is compressed

The gasifier is an Indirect or Allothermal gasifier based on the ECN MILENA technology (see www.milenatechnology.com). The basis of the technology development was the experience gained by ECN during construction and operation of Bubbling and Circulating Fluidized Bed gasifiers at lab-scale and commercial scale on a wide range of fuels. The Circulating Fluidized Bed technology is now commercially available from Host (www.host.nl). Tar removal is performed with the OLGA technology (www.olgatechnology.com) developed by ECN. The technology is now offered commercially by Dahlman (www.dahlman.nl). The chloride and sulfur removal steps are commercial processes. The catalytic conversion and gas upgrading steps can use commercial processes. The final steps can also be executed partly in reverse order.

The integrated process is schematically shown in Figure 1.

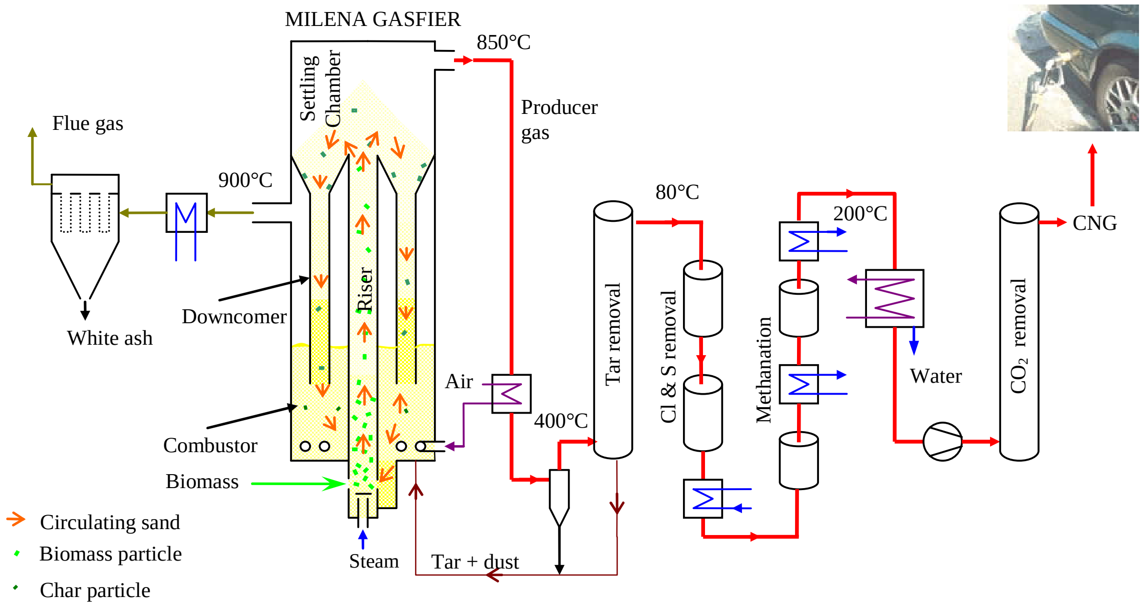

Figure 1. Simplified scheme of Bio-CNG system

The gasifier contains separate sections for gasification and combustion. The gasification section consists of three parts: riser, settling chamber and downcomer. The combustion section contains only one part, the combustor. The arrows in the gasifier figure represent the circulating bed material. The processes in the gasification section will be explained first.

Biomass (e.g. wood) is fed into the riser. A small amount of superheated steam is added from below. Hot bed material (typically 925°C sand or olivine of 0.2 – 0.3 mm) enters the riser from the combustor through a hole in the riser (opposite of biomass feeding point). The bed material heats the biomass to 850°C. The heated biomass particles degasify; they are partially converted into gas. The volume created by the gas from the biomass results in a vertical velocity of approximately 6 m/s, creating a “turbulent fluidization” regime in the riser and carrying over of the bed material together with the degasified biomass particles (char). The vertical velocity of the gas is reduced in the settling chamber, causing the larger solids (bed material and char) to separate from the gas and fall down into the downcomer. The producer gas leaves the reactor from the top and is sent to the cooling and gas cleaning section. The typical residence time of the gas is several seconds.

The combustor operates as a bubbling fluidized bed (BFB). The downcomer transports bed material and char from the gasification section into the combustor. Tar and dust, separated from the producer gas, are also brought to the combustor. Char, tar and dust are burned with air to heat the bed material to approximately 925°C. Flue gas leaves the reactor to be cooled, de-dusted and emitted. The heated bed material leaves the bottom of the combustor through a hole into the riser. No additional heat input is required; all heat required for the gasification process is produced by the combustion of the char, tar and dust in the combustor.

The hot producer gas from the gasifier contains several contaminants such as dust, tar, chloride and sulfur, which have to be removed before the catalytic conversion of the gas into Bio-CNG. All fluidized bed gasifiers produce gas which contains some tar. Tar compounds get sticky when the gas is cooled, which makes the gas very difficult to handle, especially in combination with dust. The producer gas is cooled in a heat exchanger, designed to treat gas which contains tar and dust. The heat is used to pre-heat combustion air. Tar and dust are removed from the gas in the OLGA gas cleaning section. The OLGA technology is described by Boerrigter et al. (2005). The OLGA gas cleaning technology is based on scrubbing with liquid oil. Dust and tar removed from the producer gas are sent to the combustor of the MILENA gasifier. The cleaned producer gas, containing mainly CO, CO_2, H_2, CH_4, C_2H_4 and C_6H_6, is catalytically converted into a mixture of CH_4, CO_2, H_2O and some residual H_2. Commercial techniques, like the Selexol process, can be applied to remove CO_2 and H_2O. The compressed final product can be used as transport fuel in Natural Gas Vehicles or, eventually, can be injected into the gas grid.

The ECN development focuses on high overall efficiency, because biomass is seen as a valuable resource. Figure 2 shows a simplified overall balance for an Bio-CNG system based on MILENA gasification. Only the major flows are shown. Air and steam added to the gasifier are not shown. The gross efficiencies given are indicative. Overall efficiency varies by moisture content of the biomass, level of system integration, definitions used and process pressures.

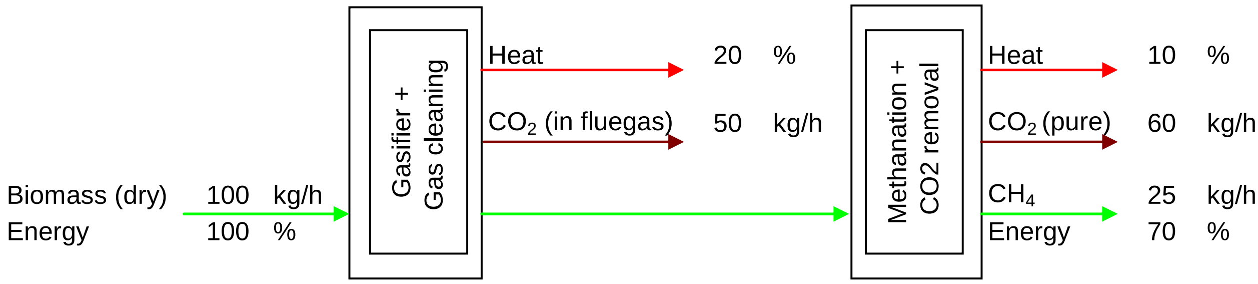

Figure 2. Indicative mass & energy balance Bio-CNG system

Carbon dioxide is released from the system at two locations. The CO_2 in the flue gas is a diluted stream and is normally vented after cleaning. The CO_2 stream from the CO_2 removal section after the methanation is nearly pure and therefore available as usable product. Heat available from the system can be used for biomass drying, which improves the system efficiency. The typical moisture content of the biomass (wood) fed to the gasifier is 25 wt%.

A popular alternative Bio-Fuel is Fischer Tropsch Diesel produced by gasification of biomass in a high temperature oxygen blown Entrained Flow gasifier. Biollaz and Stucki (2004) report an average overall net efficiency from biomass to Fischer Tropsch Diesel below 50%. The goal set by ECN for Bio-CNG production is an overall net efficiency above 70%. Process simulations based on data from the lab-scale installation show such an efficiency to be achievable.

3. Experimental results

ECN produced the first Bio-Methane in 2004, using a conventional oxygen blown fluidized bed gasifier. The lab-scale MILENA gasifier was built in 2004. The installation is capable of producing approximately 8 m_n^3/h methane-rich medium calorific gas with high efficiency. The lab-scale gasifier is coupled to a lab-scale gas cleaning installation and a methanation unit. The entire system operates at atmospheric pressure. Figure 3 shows the MILENA lab-scale gasifier and the OLGA tar removal equipment. The two bunkers on the left are used to feed the fuel (small wood particles) to the gasifier.

Figure 3. Photos of Lab scale MILENA (left) and OLGA (right) installation

The methanation unit consists of a number of sections with commercial catalysts operating at different temperatures for optimum conversion speed and efficiency. The first long-duration test was executed at the end of 2006. The producer gas from the biomass gasifier was converted into CH_4 and CO_2. Figure 4 shows the measured gas composition downstream the methanation unit (before CO_2 removal). The test proved that the system was capable of converting producer gas into CH_4, CO_2 and H_2O. The gas composition was near the expected chemical equilibrium concentrations. After approximately 10 hours of operation the first sign of catalyst degradation was noticed (as a local drop in temperature). The remaining catalyst was capable of converting the producer gas into CH_4 for another 60 hours.

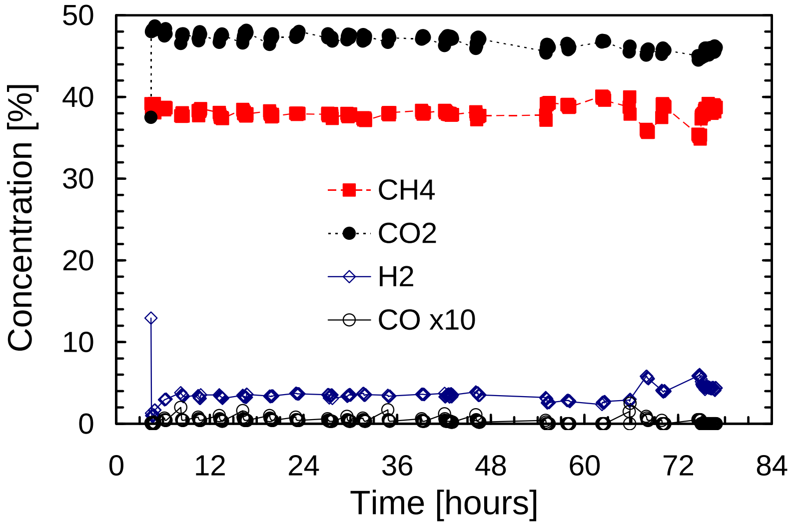

Figure 4. Gas composition before CO_2 removal

The 2007 program was mainly devoted to preventing the deactivation of the catalyst. During a run in the beginning of 2008 the catalyst was tested for 200 hours on gas from an air blown fluidized bed gasifier. The results from these tests were promising. Only some minor deactivation could be observed after 200 hours.

The gas composition shown in figure 4 would not suffice to meet natural gas standards. The methanation has to be performed at increased pressure or reduced temperature to obtain more complete conversion and reduce the H_2 content. Finally, CO_2 and H_2O (not specified in the dry gas composition) have to be removed, and the final product compressed to the pressure required for Bio-CNG.

The N_2 concentration in the producer gas from the gasifier has to be minimized, because this N_2 will end up in the final product. Nitrogen is an inert gas which lowers the heating value of the gas and increases the compression duty. For instance, a N_2 concentration of 5 vol% in the dry producer gas from the gasifier will result in a Bio-CNG N_2 concentration of 19%. Inert gases (including CO_2) in natural gas are limited to 5% according the Swedish standard for biogas as vehicle fuel. The amount of CO_2 in the final Bio-CNG can easily be reduced to approximately 1.5%, so the maximum allowable N_2 concentration, next to CO_2, in the producer gas from the gasifier is approximately 1%. Tests were done to minimize the N_2 concentration in the gas from the MILENA gasifier. The N_2 concentration was reduced to 1% by purging the fuel bunkers with CO_2 and injecting CO_2 between the combustion and gasifier section of the MILENA gasifier. Tests with the pilot scale installation are required to verify whether this relatively low N_2 concentration is also achievable in larger installations.

The calculated final Bio-CNG composition, produced from a gas containing 1% N_2 is given in Table 1. The left column shows the composition of the producer gas from the gasifier after tar removal.

Table 1. Expected gas compositions and net heating values (LHV) of MILENA producer gas (after tar removal) and Bio-CNG versus those of Dutch standard natural gas (Slochteren)

		Producer gas	Bio-CNG	Slochteren
CO	[vol%]	17.1	0.0	0.0
H_2	[vol%]	19.3	4.2	0.0
CO_2	[vol%]	12.9	1.7	0.9
H_2O	[vol%]	36.6	0.0	0.0
CH_4	[vol%]	9.0	90.1	84.8
N_2 + Ar	[vol%]	1.0	3.8	14.3
C_2H_y	[vol%]	3.4	0.0	2.9
C_3H_8 C_4H_{10}	[vol%]	0.0	0.0	0.6
$C_6H_6 + C_7H_8$	[vol%]	0.6	0.0	0.0
LHV	[MJ/m_n^3]	10.4	32.8	31.7

As mentioned before, the H_2 concentration in the Bio-CNG can be lowered by increasing the methanation pressure or decreasing the methanation temperature. The example given in Table 1 is for a methanation pressure of 30 bar and a temperature of 280°C. There are commercially available catalysts which can operate at lower temperatures. If required, residual H_2 can be removed by catalytic oxidation. The CO_2 concentration in the Bio-CNG can be lowered by increasing the CO_2 removal rate from 98% to higher values, but this will increase electricity consumption. The amount of inert gases (CO_2 and N_2) in the final Bio-CNG is slightly above the Swedish standard of 5% for biogas as vehicle fuel, but the amount of inert gases is far below the concentration in the Dutch standard “Slochteren” natural gas. The concentrations of chloride and sulfur in the final Bio-CNG are far below the concentrations set in different standards, because the producer gas is extensively cleaned before the catalytic conversion step.

The MILENA gasifier technology is scaled up from 30 kW_{th} to 800 kW_{th}. The new 800 kW_{th} pilot scale gasifier replaces the previous ECN 500 kW_{th} Circulating Fluidized Bed gasifier named BIVKIN. The new pilot scale MILENA gasifier will be coupled to the existing producer gas cooler, OLGA tar removal, wet scrubbers and a boiler. The producer gas could also be used in a gas engine. At present time there is no gas engine available for tests at ECN, since the testing program was finished with a long-duration test of 700 hours. We consider a gas engine on cleaned producer gas to be too much of a commercial technology to justify further experimental work. The results of the 700 hours test, in which the OLGA pilot installation was tested that will be used for the new MILENA pilot, were reported by Verhoeff et al. (2007).

The basic and detailed engineering of the MILENA pilot plant was done by ECN. The construction of the reactor vessel was done by HoSt BV, together with Klaas Zijlstra Metaalbewerking BV. The OLGA tar removal pilot plant was built by Dahlman. The OLGA technology was developed by ECN and is now licensed to Dahlman. Dahlman has built a 4 MW demonstration unit in France and is preparing several larger scale units for commercial plants all over the world. The MILENA technology is not licensed yet, because the pilot plant is not operational yet. ECN plans to license the MILENA technology when we have operated the Milena pilot reliably for some time. Figure 5 shows photos of the MILENA and OLGA pilot installations.

Figure 5. Photos of Pilot scale MILENA (left) and OLGA (right) installations

4. Future activities

The start-up of the MILENA pilot is now scheduled for the summer of 2008. Essential repairs of leakages found during pressure testing have caused some delay. Later this year, the existing pilot scale OLGA gas cleaning will be connected. Next year, further gas cleaning, a pressurized methanation unit and final product upgrading will be realized. We plan to have a natural gas vehicle running on Bio-CNG produced from wood in 2009.

Preparations are underway to realize a 10 MW_{th} demonstration plant, based on ECN MILENA and OLGA technology. The gas will be converted into Bio-Methane which can be injected into the gas grid, or used as transport fuel (Bio-CNG).

5. Conclusions

Results from the lab-scale MILENA gasifier coupled to the lab-scale OLGA gas cleaning are promising. The technology is tested extensively and results are up to expectations. The MILENA technology is ready for up-scaling. The 800 kW_{th} MILENA pilot plant will be taken into operation during the summer of 2008. The pilot plant will be connected to the pilot-scale OLGA at the end of the year. When results from this pilot plant are according to expectations a 10 MW_{th} demonstration plant will follow.

Research on upgrading of the cleaned producer gas to Bio-CNG is still ongoing. Progress is made in increasing the lifespan of the catalyst. Additional long-duration tests are scheduled to verify if the improvement suffices for a commercial process.

The upgraded gas produced by gasification of (waste) wood is in principle suitable for use as Bio-CNG, the heating value is above the Dutch “Slochteren” standard. The most important deviation from natural gas or Bio-methane produced by upgrading Biogas from a digester is the small amount of H_2 in the gas. It is expected that this will give no technical problems. A demonstration with a car on Bio-CNG from the MILENA gasifier is scheduled for 2009.

6. Acknowledgements

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