ECN System for MEthanation (ESME)

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ABSTRACT: The Energy research Centre of the Netherlands (ECN) has developed and patented a novel concept for the methanation of gas from biomass gasification. The **E**CN **S**ystem for **ME**thanation (ESME) is especially designed for gas from fluidized bed gasifiers such as Bubbling Fluidized Beds, Circulating Fluidized Beds and allothermal gasifiers such as the ECN MILENA process or the FICFB process developed by the Technical University of Vienna. Producer gas from the gasifier must be first compressed to approximately 6 bar (in case of atmospheric gasification) after tar and water removal. The ESME concept is unique because of the smart sequence and the operating conditions of the different units. ESME allows the efficient conversion of producer gas to SNG because the hydrocarbons contained in the producer gas (e.g. benzene, toluene) are not removed but converted, thus being available to be converted to methane. The prereformer catalyst simultaneously reforms aromatic hydrocarbons (e.g. benzene) and produces methane, which has a positive consequence on the heat balance of the prereformer, since the heat released in the exothermic methanation reactions is supplied to the endothermic reforming of aromatic hydrocarbons. Other advantages of ESME include reduced compression cost and no need for gas recycling in the methanation units.

The main parts of the ESME system have been extensively tested under realistic conditions. In October 2014 a duration test of 500 hours was successfully performed with producer gas generated in the ECN MILENA gasifier and cleaned in the OLGA tar removal system. The availability of MILENA during the test was close to 90%, and the availability of the whole methanation system (MILENA + OLGA + ESME) was approximately 85%.

The "raw bio-SNG" produced contains (in dry basis) 52% vol. CO_2, 39% vol. CH_4, 2% vol. H_2, and traces of CO (~130 ppmv) and C_2H_6. The gas composition after the methanation section was found to be at chemical equilibrium. Gas composition remains nearly constant after several hundred hours operation despite variations in the inlet producer gas composition. Catalyst degradation was not observed or near detection limits. The produced bio-SNG should further undergo CO_2 removal (e.g. by amine scrubbing or ECN regenerative dry adsorption), water removal and a last high-pressure methanation step to remove the remaining H_2 and CO prior to injection to the grid.

This milestone paves the way for the scale-up of bioSNG production. In particular, a consortium formed by ECN and a number of partners intends to build a 300 m^3/h SNG pilot-scale facility in the Netherlands.

Keywords: ESME, HDS, innovative concepts, MILENA, prereforming, synthetic natural gas (SNG).

1 INTRODUCTION

SNG (Substitute Natural Gas, or Synthetic Natural Gas) is defined as a gas containing mostly CH_4 (> 95% vol.), with properties similar to natural gas, which can be produced from thermochemical gasification of coal or biomass coupled to subsequent methanation. SNG can be cheaply produced at large scale, and is a storable energy carrier, thus enabling whole year operation independently of fluctuations in demand.

Due to its interchangeability with natural gas, the use of SNG has a number of advantages over the direct use of coal or biomass. SNG can be injected into the existing grid and easily distributed for transport, heat, and electricity applications. SNG can also be efficiently converted in a number of well-established end-use technologies. As natural gas, SNG produces low emissions and has a high social acceptance [1-4].

Methanation of gas from coal gasification processes was demonstrated at large scale in the seventies and many commercial scale installations have been built the last years especially in China. However, producer gas from (low-pressure, medium-temperature) biomass gasification processes has a higher content of large hydrocarbons (e.g. ethylene, benzene) and more diluting CO_2 and H_2O than syngas from (high-pressure, high-temperature) coal gasification processes. Therefore, the gas cleaning technology that is applied for coal gasification is not very suitable for biomass gasification processes.

The overall efficiency of conversion from biomass to SNG can be up to 70% on energy basis [5-7]. SNG is not only an attractive, versatile energy carrier for bioenergy, but also can be used for storage of surplus power from renewable sources (e.g. solar, wind). This is a variant of the so-called "power-to-gas" concept, where excess power produces H_2 that is added to an existing SNG-plant to convert additional CO_2 into CH_4, thus potentially doubling the SNG output from a given biomass input [8].

The Energy research Centre of the Netherlands (ECN) has been working for a number of years on the development of a technology for the efficient production of SNG from biomass gasification. The MILENA indirect gasification and the OLGA tar removal system are the main achievements of this extensive research and development work. The first methanation duration tests were already carried out in 2006. The original goal of these experiments was to test the gas cleaning requirements for methanation catalysts. Recently, ECN has developed and patented a novel technology for the methanation of gas from biomass gasification. The **E**CN **S**ystem for **ME**thanation (ESME) is designed especially for gas from fluidized bed gasifiers such as bubbling fluidized beds, circulating fluidized beds and allothermal gasifiers such as the ECN MILENA process or the FICFB process developed by the Technical University of Vienna. The ESME concept is unique because of the

smart sequence and the operating conditions of the different units. ESME allows the efficient conversion of producer gas from biomass gasification to SNG because the hydrocarbons contained in the producer gas (e.g. benzene, toluene) are not removed but converted, and are thus potentially available to be converted to methane. Another interesting feature of the ESME system is the prereformer, which simultaneously reforms aromatic hydrocarbons (benzene, toluene) and produces methane, thus having a positive effect on the heat balance of the reactor. On the other hand, the compression cost can be reduced with respect to existing methanation processes, since the HDS, prereformer and first methanation units operate at ~6 bar (this first compression step is required for atmospheric gasifiers, but will not be needed in the case of pressurized gasification operating at a similar pressure). Furthermore, the ESME concept does not require gas recycling in the methanation units for temperature control.

The main parts of the ESME system have been extensively tested. A duration test of 500 hours has been successfully performed with producer gas from the ECN MILENA gasifier and the OLGA tar removal system. This paper highlights the main results obtained.

2 EXPERIMENTAL

2.1 Introduction

In October 2014, an endurance test was carried out at the laboratories of the ECN Biomass and Energy Efficiency Unit in order to prove the main parts of the ESME system for bio-SNG production under realistic conditions. Figure 1 shows the layout of the experimental system. Parts not implemented yet include CO_2 and water removal and a final high-pressure methanation step. The main stages of the test rig system are described in the next sections.

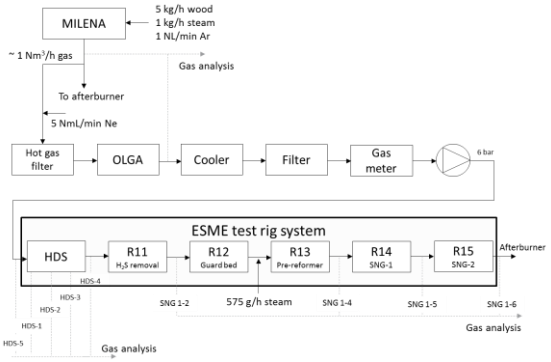

Figure 1: Schematic layout of the experimental facility.

2.2 MILENA gasifier and OLGA tar removal

The indirect ECN MILENA gasifier was used in the endurance test for the generation of producer gas. The main advantages of MILENA include the total conversion of the fuel and the production of a N_2-free gas without the need for an air separation unit in an integrated design. A description of MILENA technology can be found elsewhere [6].

The feedstock used in the gasifier during the endurance test was Rettenmaier Räucher Gold HBK 750/2000 beech wood [9], at an average flow rate of 5 kg/h. Two different fuel bunkers were used during the experiment for the biomass feeding: a 24-hour bunker which allowed continuous operation and a back-up 5-hour bunker used while the 24-hour bunker was refilled. CO_2 (1 NL/min) was used as flush gas in the fuel screw. Steam (0.8 - 1 kg/h) was used as fluidizing gas in the riser. Argon (1 NL/min) was injected as tracer gas for molar balances. In the combustor zone, approximately 110 NL/min primary air was used to oxidise the char circulated from the riser zone. Austrian olivine was used as bed material during the experiment. The lab-scale reactor is provided with heat tracing in order to compensate for heat losses.

The producer gas composition was online measured by means of micro-GC and gas monitor analysis. The moisture contained in the producer gas was regularly determined from gravimetric measurements of the condensate collected at the gas analysis system. The gasifier temperature was ~830°C, whereas the combustor was kept at approximately 910°C. The regular addition of olivine into the bed to counteract the loss of bed material caused spikes in the bed temperatures. Apart from this, the operation of the gasifier was stable throughout the test.

A slipstream of approximately 1 Nm^3/h producer gas from MILENA was directed to the downstream system. Neon (5 mNL/min) was injected as tracer gas in order to be able to perform molar balances. Producer gas is first removed from dust in a hot gas filter operating at 450ºC, and then directed to OLGA, which is a tar removal system based on oil scrubbing in a series of reactors. It is composed of a collector, an absorber and a stripper. Heavy tars and particles are removed in the collector. The absorber removes light tars, and the oil is regenerated in the stripper (N_2 is used as stripping medium in the lab-scale system). The performance of OLGA was evaluated by guideline and SPA analysis carried out before and after the system to determine the content and composition of tars.

After tar removal in OLGA, most of the water present in the producer gas is removed in a cooler. Then, the gas is passed through a filter for the complete removal of aerosols, compressed to approximately 6 bar and directed towards the ESME system.

2.3 The ESME test rig system

The lab-scale ESME system for the production of bioSNG is composed of six reactors in series, as shown in Figure 1. All reactors are electrically heated in order to compensate for heat losses, and are equipped with pressure sensors and thermocouples along the bed for the determination of the axial temperature profile during operation. Moreover, a number of sampling points for gas analysis allow the measurement of the gas composition all over the system. The gas composition was online measured by micro-GC analysis. Gas bags were also regularly taken and analysed by GC-FPD for the measurement of sulphur compounds.

The first reactor in the ESME system is the hydrodesulphurisation (HDS) unit for the conversion of organic sulphur compounds and the hydrogenation of alkenes and alkynes. Then, the gas passes through a H_2S removal unit (R11) and a guard bed (R12), a prereformer for the conversion of aromatic hydrocarbons (R13), and two methanation reactors (R14 and R15). The large-scale ESME concept includes also CO_2 and water removal and a final high-pressure methanation step. Figure 2 displays the location of the thermocouples and the heating zones in the main ESME lab-scale reactors: HDS, prereformer

and methanation units.

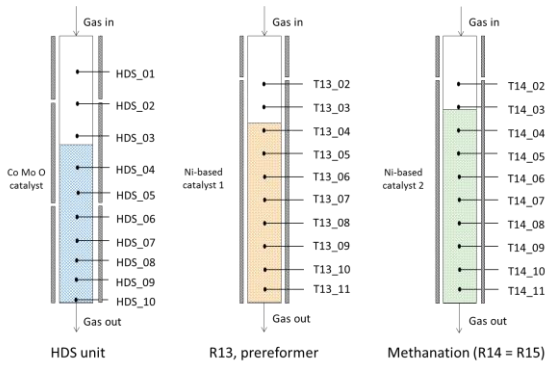

Figure 2: Scheme of thermocouples location in the main ESME lab-scale reactors. Diameter HDS unit: 78 mm; diameter R13, R14, and R15: 56 mm.

The HDS unit consists of a fixed-bed reactor filled with a commercial CoMoO catalyst. The HDS catalyst converts the organic sulphur compounds (e.g. thiophene) into mainly H_2S and COS, and hydrogenates alkanes and alkynes into alkanes (e.g. C_2H_4 and C_2H_2 into C_2H_6). The WGS reaction also takes place in this reactor. The produced H_2S is removed from the gas downstream in a conventional adsorption ZnO bed and a guard bed. The HDS unit is operated at approximately 6 bar. The temperature at the inlet was set at 280°C. The target flow rate of gas entering the ESME system is 11-12 NL/min in order to keep a GHSV (Gas Hourly Space Velocity) of 200-250 h^{-1}.

The prereformer unit is a fixed bed filled with a commercial Ni-based catalyst (19 mm diameter x 12 mm pellets) operating at approximately 6 bar. Steam (575 g/h) is added to the gas upstream the reactor. The inlet gas temperature was set at 340°C. GHSV was approximately 2000 h^{-1}. The moisture content of the gas after the prereformer was regularly determined by gravimetric measurement of the condensate collected in the gas analysis system.

The methanation units R14 and R15 consist of fixed bed reactors filled with a commercial Ni-based catalyst (4 mm diameter x 5 mm), different from the prereforming catalyst. The reactors were operated at a GHSV of approximately 2000 h^{-1}.The gas temperature at the inlet of R14 and R15 was set at 230°C and 240°C, respectively.

3 RESULTS AND DISCUSSION

3.1 Overview of the 500-hour test

Table I summarizes the number of operating hours of each of the main units during the endurance test. The system was operated non-stop, with unmanned operation during night shifts and weekends. As can be seen, the whole system (MILENA, OLGA, HDS, prereformer, SNG-1 and SNG-2) achieved more than 500 hours operation.

Table I: Number of operating hours of the system.

Number of operating hours			
MILENA	OLGA	HDS	SNG-2
580	570	560	**515**

MILENA, OLGA and HDS were the first units put into operation in order to carry out measurements of tars and S-compounds using the guideline protocol and SPA analysis over the OLGA and the HDS reactor. The prereformer and the methanation reactors were put into operation approximately 48 hours later, and this was the start of the 500-hour test. After the endurance test, additional tar and S-compounds measurements were performed in the OLGA and the HDS units in order to determine changes in the system performance over time. The availability of MILENA during the test was close to 90%, and the availability of the whole methanation system (MILENA + OLGA + ESME) was approximately 85%.

3.1 Performance of MILENA gasifier

The composition of the producer gas from MILENA is displayed in Figure 3. As can be observed, the CH_4 concentration is very stable, around 12-13% vol. (dry basis). However, the H_2, CO and CO_2 contents show varying trends in time. These changes are explained by the activation process of the bed material, which leads to a decrease in CO concentration and an increase of H_2 and CO_2 concentration over time. Whenever the bed is refilled with fresh olivine (e.g. after shutdown or maintenance), the gas composition gets back to the original values (high CO, and low H_2 and CO_2 values), and progressively tends again to higher H_2/CO ratios over time. The water content in the producer gas (determined gravimetrically from the condensate collected in the gas analysis system) kept around 32% vol. (wet basis) throughout the test. All in all, MILENA showed a stable, reliable operation along the experiment. The main difficulties found were related to the required periodic cleaning of the afterburner.

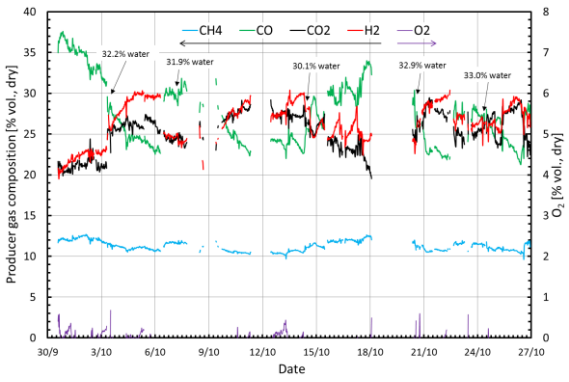

Figure 3: MILENA producer gas composition over the experiment.

3.1 Performance of ESME system

In Figure 4 it can be observed that the pressure over the whole ESME system (from the inlet prereformer to the outlet second methanation step) was kept approximately constant throughout the test around 5.6 bar. The small fluctuations of flow and pressure can have an effect on the temperature profiles of the ESME reactors. On average, the pressure drop $\Delta p_{13\text{-}16}$ also remained constant over time at approximately 30 mbar. This result shows the stability of operation of the whole methanation system.

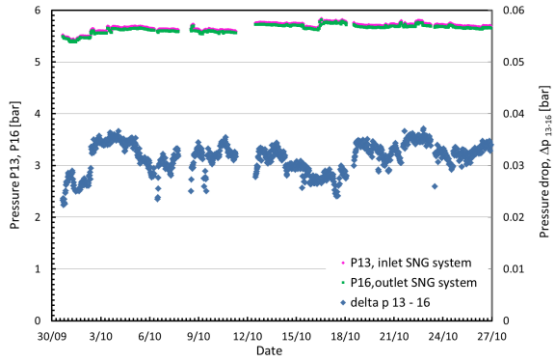

Figure 4: Pressure and pressure drop over the ESME system during the experiment.

Figure 5 displays the average axial temperature profiles of the HDS reactor in different test weeks. As can be seen in Figure 2, T1, T2 and T3 measure the gas phase temperature (empty part of the reactor), whereas T4-T10 are located within the catalytic bed. This is the reason why a steep increase in temperature can be observed between T3 and T4. The graph shows a stable operation of the HDS unit. Organic sulphur compounds (e.g. thiophenes, mercaptans) were converted down to detection limits.

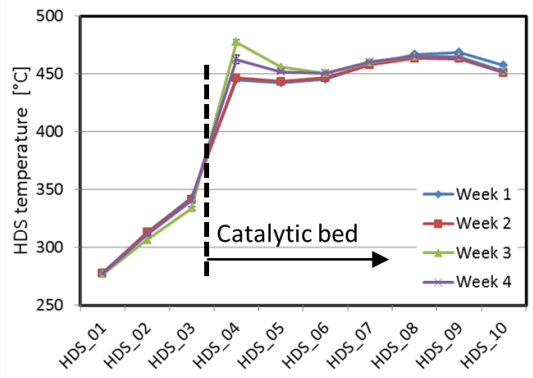

Figure 5: Evolution of HDS axial temperature profile over the experiment.

Figure 6 plots the average axial temperature profiles of the prereformer, R13. T2 and T3 measure the temperature of the inlet gas (empty part of the reactor), whereas T4-T11 are located in the bulk of the catalytic bed. The figure shows in general stable trends except for T5, which gradually exhibits a slight decrease over time, which could be attributed to progressive deactivation of the catalyst, but may also be caused by variations in the pressure or flow over the system (see Figure 4), or changes in the producer gas composition (see Figure 3). Temperatures are also influenced by the external trace heating of the reactor. After 500 h operation, it is not clear from temperature profiles whether catalyst degradation has taken place. In comparison, deactivation of the catalyst was clearly detected after 50-200 hour operation in previous tests performed in 2006 [10]. The water content of the gas at the outlet of the prereformer, determined by gravimetric measurement of the condensate collected in the gas analysis system, was kept approximately constant throughout the test around 45-55% vol. (wet basis).

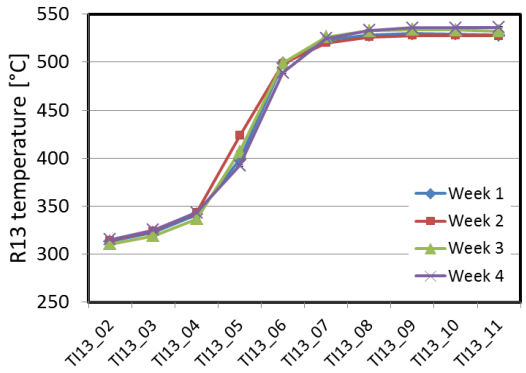

Figure 6: Evolution of the prereformer axial temperature profile over the experiment.

Figure 7 and Figure 8 show the temperature profile over the first and the second SNG reactor, respectively. In both reactors, T2 and T3 correspond to the temperature of the inlet gas (empty part of the reactor), whereas T4-T11 are located within the catalytic bed. In general, a very stable behaviour throughout the test can be observed in both reactors. The slight change in axial temperature profiles are likely due to the effect of the external heating, or to variations in pressure, flow and inlet gas composition.

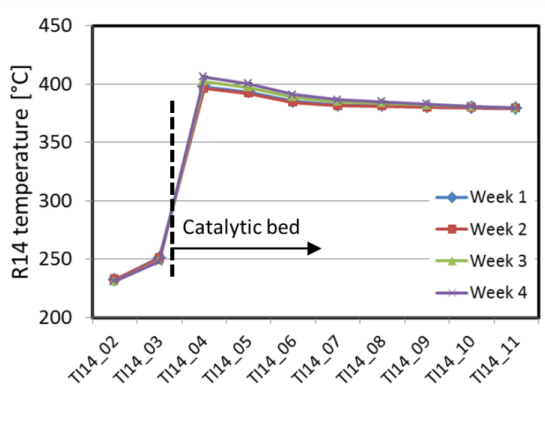

Figure 7: Evolution of the axial temperature profile in the first methanation unit, R14, over the experiment.

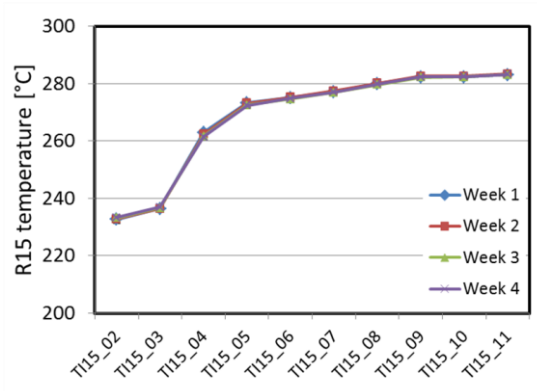

Figure 8: Evolution of the axial temperature profile in the second methanation unit, R15, over the experiment.

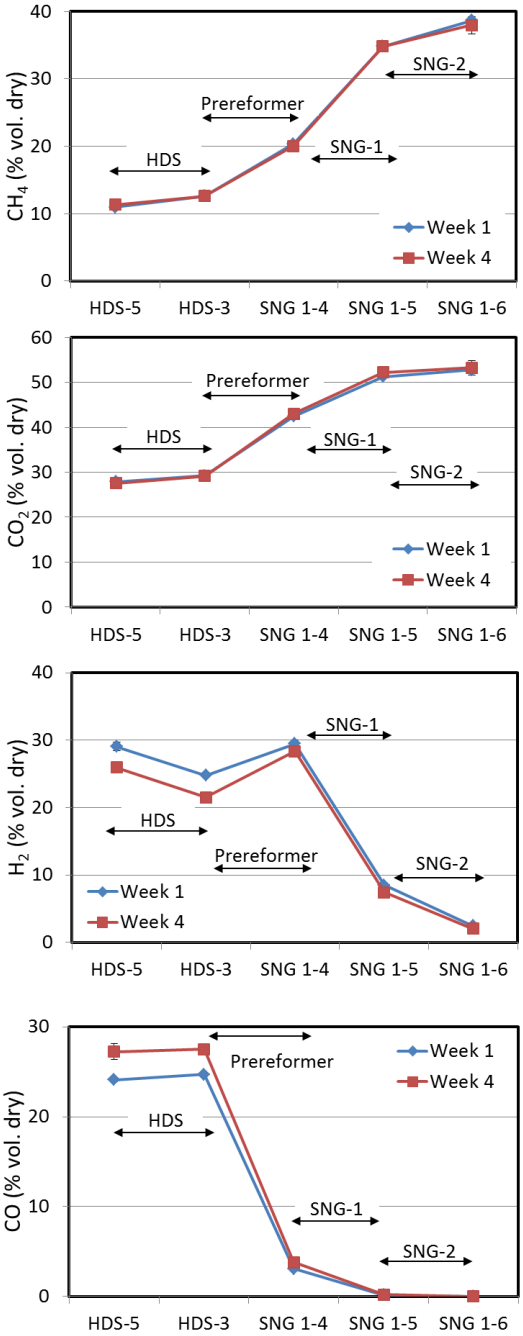

Figure 9: Evolution of the gas composition (dry basis) over the ESME system and over time during the experiment: CH_4, CO_2, H_2, and CO concentration.

Figure 9 plots the trends of the main compounds present in the gas along the methanation system. As can be seen, the methane content increases from 12% vol. dry to almost 40% vol. dry. Interestingly, the CH_4 production takes place not only in the methanation reactors SNG-1 and SNG-2, but also in the prereformer. Following similar trends, the CO_2 content increases from 28% vol. dry to 51% vol. dry along the ESME system. This CO_2 should be further removed by conventional processes (e.g. amine scrubbing) or by ECN technology (regenerative dry adsorption) as part of a polishing step (water and CO_2 removal, final high pressure methanation) prior to the injection of SNG to the grid.

The CO present in the gas is totally converted in the system from the initial ~25% vol. dry down to approximately 130 ppmv dry (measured by GC-FID in week 4). The main conversion is achieved in the prereformer, where CO decreases from 25% vol. dry to less than 5% vol. dry, mainly via WGS and methanation. On the other hand, the hydrogen content slightly decreases in the HDS reactor, where it is consumed in hydrogenation reactions, increases again in the prereformer (balance between reforming, WGS and methanation reactions), and is converted up to ~2% vol. dry in the methanation reactors. The main hydrogen conversion takes place in the first methanation step.

The gas composition after the second methanation reactor shows that thermodynamic equilibrium is reached. Lastly, by comparing the trends on the first and last weeks of the test, it can be concluded that regardless of variations in the inlet producer gas composition, there is apparently no change in the activity of the catalysts.

4 CONCLUSIONS

The Energy research Centre of the Netherlands (ECN) has developed and patented a novel technology for the methanation of gas from biomass gasification. The **E**CN **S**ystem for **ME**thanation (ESME) is especially designed for gas from fluidized bed gasifiers such as Bubbling Fluidized Beds, Circulating Fluidized Beds and allothermal gasifiers such as the ECN MILENA process or the FICFB process developed by the Technical University of Vienna. The ESME concept is unique because of the smart sequence and the operating conditions of the different units. ESME allows the efficient conversion of producer gas to SNG because the hydrocarbons contained in the producer gas (e.g. benzene, toluene) are not removed but converted, thus being available to be converted to methane. The prereformer catalyst simultaneously reforms aromatic hydrocarbons (e.g. benzene) and produces methane, which has a positive consequence on the heat balance of the prereformer, since the heat released in the exothermic methanation reactions is supplied to the endothermic reforming of aromatic hydrocarbons. Furthermore, compression costs can be reduced with respect to existing methanation processes, and gas recycling for temperature control is not required in the methanation units.

The main parts of the ESME system have been successfully proven in a 500-hour duration test using producer gas from MILENA gasifier. The availability of MILENA during the test was close to 90%, and the availability of the whole methanation system (MILENA + OLGA + ESME) was approximately 85%. The test has shown that the gas composition after the methanation section is at chemical equilibrium. The "raw bio-SNG" produced contains (in dry basis) 52% vol. CO_2, 39% vol. CH_4, 2% vol. H_2, and traces of CO and C_2H_6. Little or no reduction in catalytic activity has been observed after 500 hours of operation under realistic conditions.

The methane content increases from 12% vol.(dry basis) after the gasifier to almost 40% vol. dry over the ESME system. CH_4 production takes place not only in the methanation reactors SNG-1 and SNG-2, but also in the prereformer. CO is almost totally converted in the system from the initial ~25% vol. dry down to approximately 130 ppmv dry. The main conversion is

achieved in the prereformer, where CO decreases from 25% vol. dry to less than 5% vol. dry. The hydrogen content slightly decreases in the HDS reactor, increases again in the prereformer, and is converted down to ~2% vol. dry in the methanation reactors. The main hydrogen conversion takes place in the first methanation step. Gas composition remains nearly constant after several hundred hours operation despite variations in the inlet producer gas composition. Catalyst degradation was not observed or near detection limits. The produced bio-SNG should further undergo CO_2 removal (e.g. by amine scrubbing or ECN regenerative dry adsorption), water removal and a last high-pressure methanation step prior to injection to the grid.

This milestone paves the way for the scale-up of bioSNG production. In particular, a consortium formed by ECN and a number of partners intends to build a 300 m^3/h SNG pilot-scale facility in the Netherlands.

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