Integration of anaerobic digestion and thermal gasification

EUDP 2015-II, project 64015 - 0533

Review Report
September 2017

REPORT

Integration of Anaerobic Digestion and Thermal Gasification

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Hørsholm 2017

Title : Integration of Anaerobic Digestion and Thermal Gasification

Report category : Customer report

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Date of issue : September 2017 (completed 23.09.2019)

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File number : 742.73; H:\742\73 SYNIN2B Eudp\Rapporter\Integration of Thermal Gasification and Biogas Review DGC 2017_final.docx

Project name : Synergi ved integration af biogas og termisk forgasning

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1 Project Status

This review was delivered as part of the national EUDP project “Synergi ved integration af biogas og bioSNG” (2016 – 2018), aiming to demonstrate bio-SNG production by integration of anaerobic digestion, thermal gasification, product gas methanation and biogas upgrading at Madsen Bioenergi I/S. The project is managed by DGC A/S and partners are Frichs Ecotec A/S, Madsen Bioenergi I/S and HMN Gashandel A/S.

Originally, the technology to be developed and commercialized was the heated screw conveyor ‘Sublimator’ design by Frichs A/S (now Frichs Ecotec A/S). Frichs Ecotec, however, was not satisfied with its performance and decided at the end of 2015 to develop a novel electrically heated, fast suspension pyrolysis technology. This was not expected at the time of the project application, and the contents of the project were changed accordingly. During 2016, hot tests were performed with various types of ceramic heating elements that eventually failed. The cause remains unclear, but the failure was most likely due to the harsh operating conditions (frequent startup/shutdown, presence of char and reducing gases, mechanical vibrations). By the end of 2016, the concept was again modified as to recycling part of the product gas for indirect heating by including a gas burner/heat exchanger module. This module is applicable for steam injection and superheating as well, which is required for producing bio-SNG. However, as of September 2017 the project is seriously delayed and the latest design not yet proven.

Looking forward to the methanation step, the main challenge will be the extensive requirement for gas cleaning in order to reduce the rate of catalyst deactivation. Other issues are the design of a pressurized methanation reactor and the energy integration of steam injection/superheating (around 1000 °C) to increase the H_2/CO ratio of the product gas. The complexity (risk) and cost of these and related challenges are well documented in the literature. A simpler setup may be realized by steam gasification of the biochar fraction only, using the (dirty) product gas for process heat. The resulting gas will be cleaner and more readily suitable for methanation. Biological methanation seems promising, as it is a more robust and flexible alternative concerning operation conditions, but reaction rates are much lower due to hydrogen mass transfer limitations. It is not yet clear what types of reactor, microbes, operating conditions, etc. will be applied for optimal performance.

2 Introduction

A report published by the Danish Energy Agency in 2012 discusses future applications of the Danish natural gas grid. One of the conclusions is that using the gas grid for distribution of green gas (i.e. biogas and bio-SNG) would be optimal from a national economic point of view in a future energy system dominated by renewable electricity. Green gas can substitute fossil natural gas and can be stored and used as back-up for RE power as well as for industrial processes and transport fuel.

Small scale, decentral biomass conversion is typically associated with higher specific costs and lower efficiency, but, on the other hand, potential benefits are lower economic risk, security of biomass feedstock supply and the possibility to integrate process heat with local heat demand. Small-scale pyrolysis/gasification (range 1 to 10 MW biomass) may be cost-effective when integrated with anaerobic digestion facilities connected to the natural gas grid. The idea is not new as will be discussed later, and many concepts can be imagined and have been proposed.

One of the challenges in anaerobic digestion is feedstocks containing lignin, such as straw, for which long residence times are required. By gasifying the dewatered and dried solid residue fiber, along with optionally supplementary biomass, the overall gas yield can be improved significantly. In addition, otherwise problematic tar water may be digested, and the biochar/ash is useful as soil amendment.

Production of biogas from manure and other biomass is a mature technology. According to the Danish Energy Agency, the Danish biogas production is expected to increase substantially in the next 15 years from 4 PJ to about 30 PJ. An important driver of this expansion has been the increasing support for the use of biogas for electricity generation and upgrading, the latter was approved for subsidy in 2013. In Europe and worldwide, biogas is mostly used for combined heat and power (CHP) production. Unfortunately, the heat from the CHP unit is wasted as a result of the main focus of most support schemes on electricity production and the lack of heating demand.

Biogas upgrading to natural gas quality has seen substantial progress during the last 10 years in terms of the number of plants in operation, particularly in Germany and Sweden. In Germany, more than 100 upgrading facilities have been installed (of about 7,500 biogas plants), and the government plans to increase this number significantly. The technology is mature; biogas can be upgraded to more than 98 vol-% methane by various methods, typically water scrubbing, amine scrubbing and pressure swing adsorption.

The production of bio-SNG by thermal gasification requires a product gas free of nitrogen (< 1 vol-%). State-of-the-art is indirect (i.e. allothermal) gasification, which avoids using air as gasification medium. Heat for the gasification process is supplied from outside of the gasification reactor and steam is applied as gasification medium. The so-called twin-fluidized bed design has been proven since 2002 (Güssing, Austria) and is now operating commercially in the range ~10 - 30 MWth (e.g. MILENA, Netherland, and GoBiGas, Sweden). However, for small plants in the 1- 10 MWth range with various qualities of feedstock available, pyrolysis technology is probably better suited.

Catalytic methanation of product gas from thermal gasification requires extensive gas cleaning, i.e. nearly complete removal of tar, sulfur species and particulates. In addition, the stoichiometric ratio of H_2 and CO must be controlled within narrow limits by water gas shift and removal of excess CO_2. So far, GoBiGas (Figure 1) is the largest Bio-SNG demonstration facility world-wide (20 MW gas), at which the ‘TREMP’ catalytic methanation process by Haldor Topsøe A/S has been in operation since 2012. Small-scale, catalytic methanation is currently being developed by DTU Mechanical Engineering and others (cf. ‘Mega-Store II’ project).

Biological methanation is a promising alternative with less demanding gas cleaning requirements that has attracted significant interest recently. Some of the methanogenic bacteria (hydrogenotrophes) found in anaerobic digestors convert dissolved hydrogen gas and CO_2 directly to methane. LanzaTech, New Zealand, is commercializing gas fermentation of CO to produce ethanol by means of a naturally-occurring acetogenic bacterium (Clostridium Autoethanogenum). Several research institutes have shown that (simulated) product gas from thermal gasification can be methanized (e.g. DTU

Chemical Engineering and University of Borås). However, there are limitations due to relatively low reaction rates, low solubility of H_2 and CO in water and microbial growth inhibition.

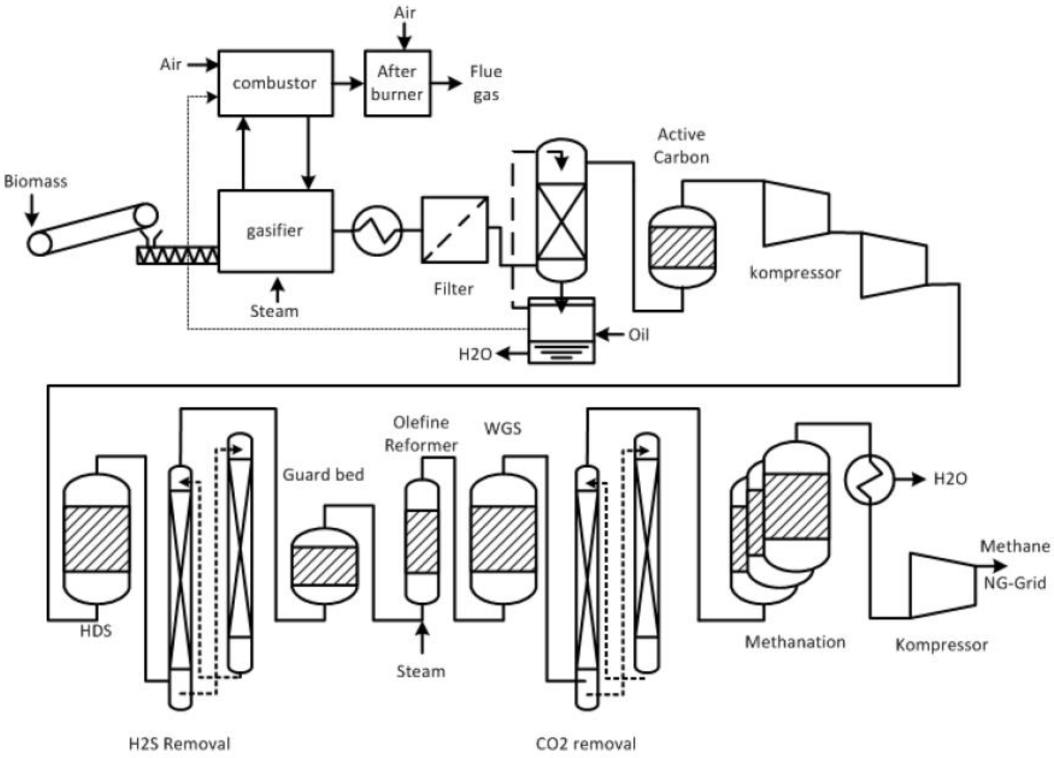

Figure 1 'GoBiGas' 20 MW bio-SNG process (Thunman, 2014), featuring 'TREMP' methanation technology from Haldor Topsøe A/S. Operation has so far been demonstrated with wood pellets, consuming 32 MW fuel, 3 MW electricity and 0.5 MW RME. 11 MW heat is supplied to district heating, of which 6 MW has been upgraded using heat pumps. The bio-SNG is distributed via the local natural gas grid.

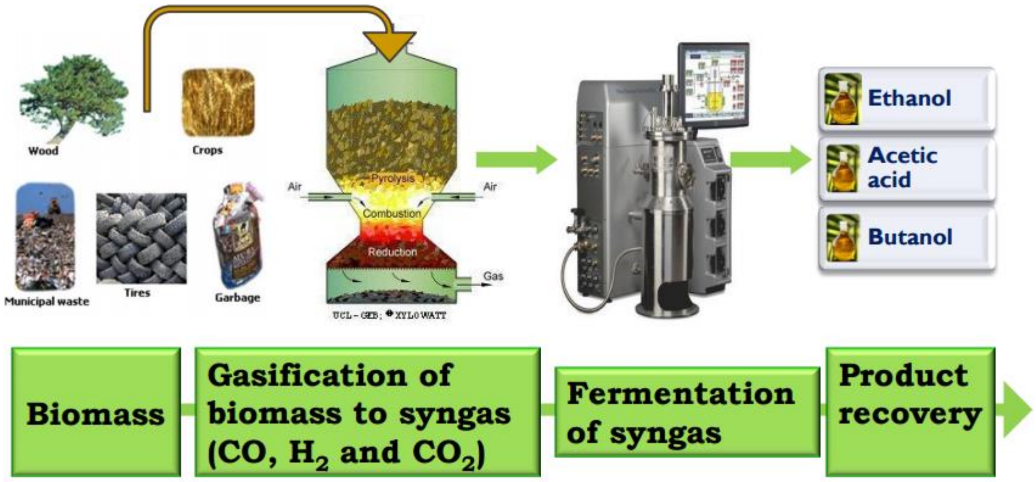

Figure 2 Fermentation of syngas to liquids (Atiyeh, 2009) is being commercialized by LanzaTech (New Zealand) and INEOS Bio (Switzerland).

3 Integration Concepts

Some of the potential synergies that can be identified by integration of anaerobic digestion, thermal biomass pyrolysis/gasification and gas upgrading/grid injection are:

- Dewatered and dried solid anaerobic digestion residues can be used as gasification feedstock.
- The overall capacity of the plant increases due to shorter solids residence time in the digester and/or direct feed of biomass to the gasifier.
- Process heat from gasification can be utilized elsewhere in the digestion, biomass drying and gas upgrading processes.
- Soluble plant nutrients, such as potassium and sulphur that potentially causes corrosion/deposition problems in thermal gasification, are pre-separated into the liquid manure fraction.
- Gasification biochar/ash, containing e.g. phosphorus and calcium, is applicable as fertilizer and for soil amendment.
- Condensation tar water may also be diverted to the digester, increasing overall gas yield.
- Direct gaseous emissions are eliminated.

The concept of integrating anaerobic digestion and thermal gasification was originally proposed in 2008 by Lemvig Biogas and BWSC A/S for CHP, Figure 3 (application for EUDP 2008-II: “Koncepter for termisk/ biologisk samforgasning”, Lemvig Biogas). The project, however, was never initiated for other than technical reasons.

Recently various similar concepts have been discussed by Atiyeh (2009), Frear et al. (2013), Lacroix et al. (2013), Smith and Perez (2013), Hübner and Mumme (2015), Engvall (2015), Bridgwater (2016), Monlau et al. (2016) and Neumann et al. (2016). The proposed concepts mostly differ with respect to the liquid fractions, such as the pyrolysis oil (Hübner and Mumme, 2015) and light tar water with C1-C4 components (Frear et al. (2013), Smith and Perez (2013)). The gas produced is typically applied locally for CHP. Monlau et al. (2016) suggest using the pyrolysis oil for CHP as well. Biochar is generally allocated for soil amendment. Guiot (2013) and Engvall (2015) include electrolysis hydrogen for conversion of CO_2 from biogas upgrading to CH_4 into the overall scheme. Pyrolysis oil and biochar can also be transported and gasified at a central plant, as e.g. in the bioLiq concept (Dahmen et al., 2012). Finally, Fernandez et al. (2014) report that the specific methane production more than doubled by CO_2 enrichment of sewage sludge digestion in 24 h (Fernandez et al., 2014).

Notice that the degree to which tar fractions can be digested or tolerated by microorganisms is not clear, as literature is limited on this subject. Jarboe et al. (2011) and Schwab et al. (2011) studied fermentation/upgrading of pyrolysis-derived bio-oil and concluded that fractionating and detoxification were necessary prior to fermentation. Cyclic organic components such as phenol, cresol (hydroxytoluene) and furfural are well known inhibitants that generally can be tolerated in low concentrations only.

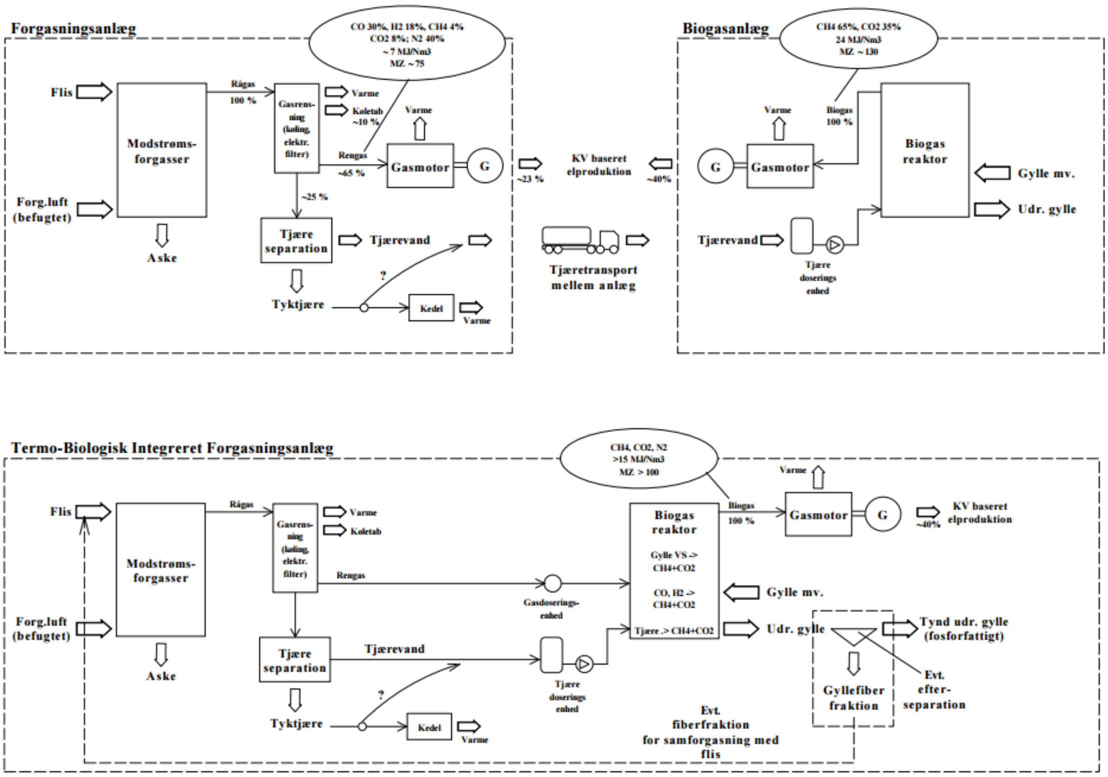

Figure 3 CHP concepts with partial (top) and full (below) integration of wood gasification and biogas production. In the partial concept only tar water is diverted to the biogas reactor. In the full concept degassed manure fiber is blended with wood chips and gasified. Both product gas and tar water are digested. The dense tar fraction is combusted for heat in both cases (Lemvig Biogas, 2008).

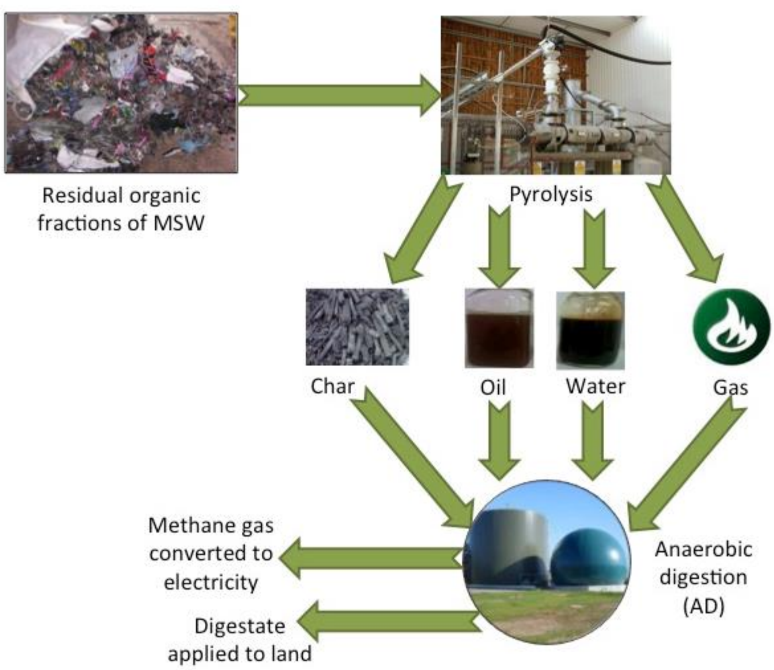

Figure 4 *Increasing energy yield by integration of pyrolysis and anaerobic digestion (www.supergen-bioenergy.net). The pyrolysis products are added to an operational digester fed with conventional substrates. Biochar may act as a carrier for microorganisms and would be incorporated into the solid digestate for spreading on land.*

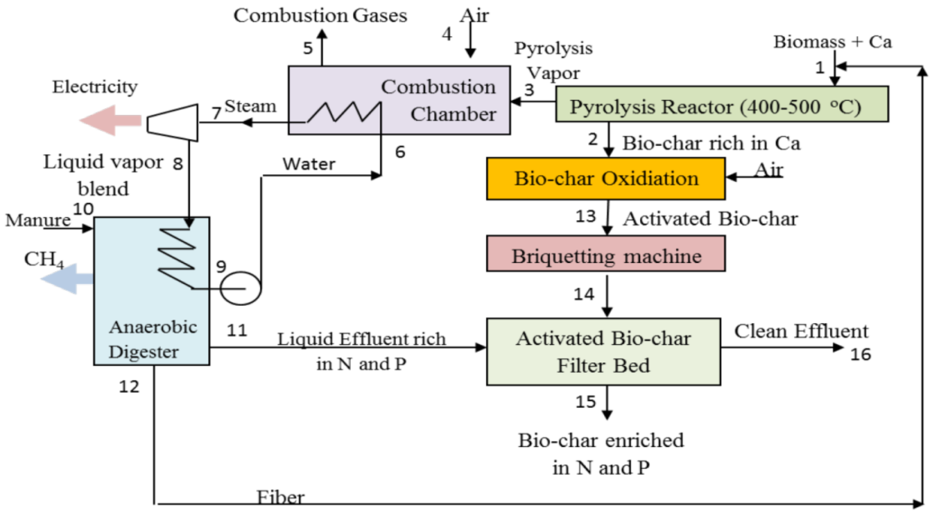

Figure 5 *Integration concept with nutrient activation of biochar (Frear et al., 2013).*

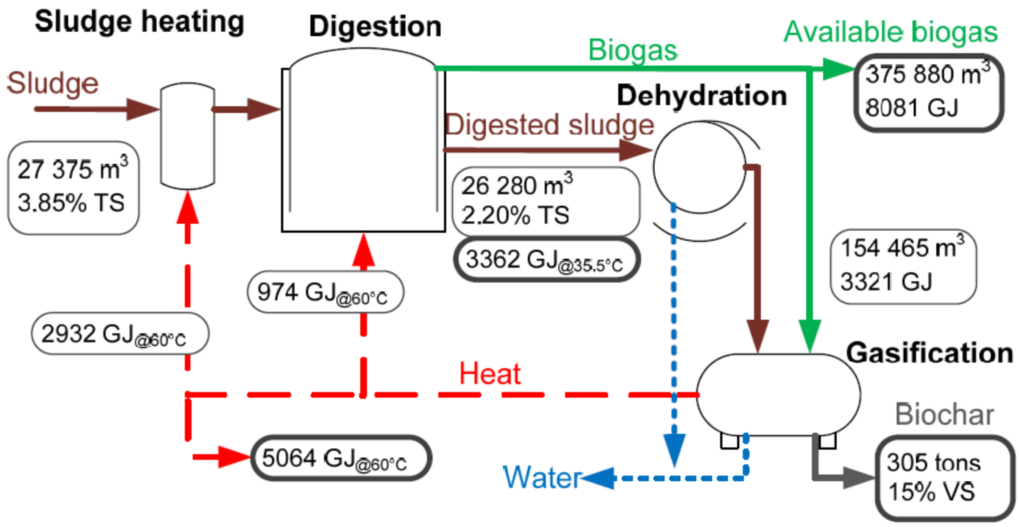

Figure 6 Example of integrated mass and energy streams. Final products are biogas and biochar (Lacroix et al., 2013).

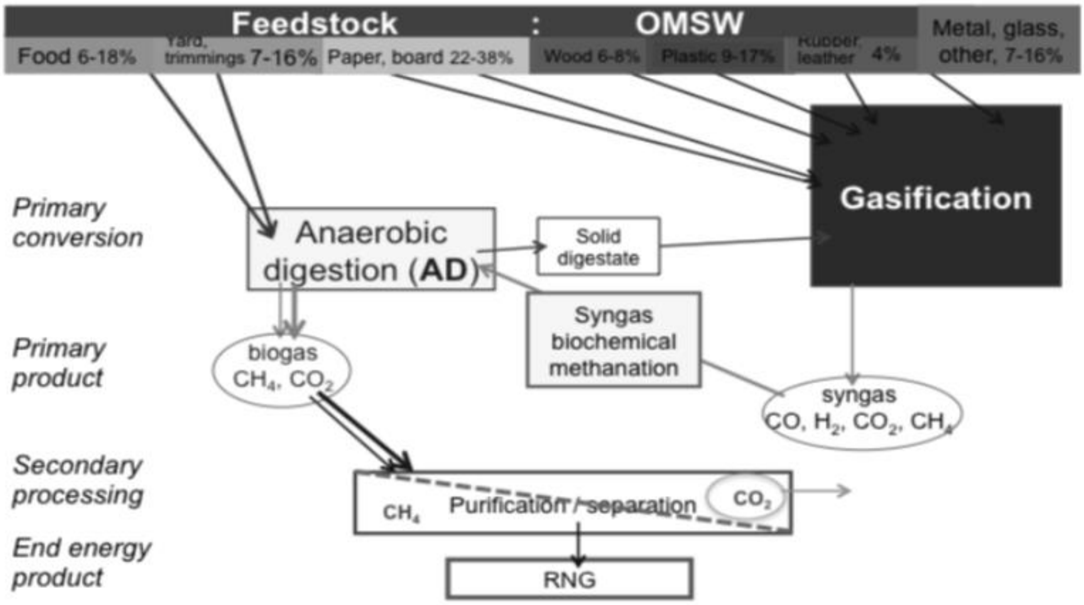

Figure 7 Suggested waste processing biorefinery concept with biological methanation, integrating anaerobic digestion and gasification towards the production of renewable natural gas (Guiot el. al., 2013).

4 Digestate Pyrolysis

A fully integrated digester-gasifier concept necessarily involves thermal treatment of separated and dried digestate. The separator unit is typically a screw press (water removal to approx. 30% w/w dry solids), whereas superheated steam drying is recognized as an energy efficient method for drying to about 10% w/w water or less. Grainwood A/S is an example of a Danish supplier having experience with digestate steam drying. A stable, low water content is a prerequisite for achieving reproducible heating rates and predictable outputs from the pyrolysis/gasification process.

The digestate from Danish biogas plants mainly contains manure fiber. Manure fiber has a high ash content with associated risks of ash deposition and corrosion. In addition, particle sizes are relatively low, making manure fiber unsuitable for conventional fixed bed and fluidized bed gasifiers.

A Danish development, the air-blown, low temperature circulating fluid-bed (LT-CFB) gasification technology (Biomass Gasification Group, DTU) successfully demonstrated gasification of manure fiber in 2006. Operational problems caused by bed agglomeration related to biomass ash melting are largely avoided by operating as low as 750 °C. The technology was later upscaled to 6 MW and fueled with straw pellets, known as the DONG Energy ‘Pyroneer’ process (2011). However, for bio-SNG application the LT-CFB technology has to be converted into oxygen operation. This is currently under development to be tested at BGG, DTU.

Pyrolysis, i.e. heating by an external heat source without feeding air/oxygen, is a robust alternative to gasification that is suitable for a wide range of feedstocks and less demanding regarding fuel preparation. The drawback is lower gas yield and more char, as indicated by Figure 8.

A pyrolysis system named ‘Pursuc’ has been under development by Purfil Aps and Frichs A/S (now Frichs Ecotech A/S) for several years, which is a combined separator, drier/evaporator and auger pyrolysis system (750 °C) for manure processing. The pyrolysis gas is to be used locally for CHP and the char/ash (biochar) as fertilizer/soil amendment. A pilot scale facility is situated at a farm in Havndal near Hadsund. Further development of the

Pursuc system has taken place as part of the project ‘Nima Char’ with partners Frichs Ecotech, Purfil, Radijet Aps (small-scale gas turbines) and Agro Business Park (coordinator). While no full-scale version of the Pursuc system exists, the energy balance has been reported with support from Innovationsnetværk for Miljøenergi (2014).

During 2015, Frichs Ecotech decided to change the reactor type from indirectly heated auger to fast suspension pyrolysis in order to improve heat transfer and temperature control. A demonstration facility is being developed for pyrolysis of chicken manure at the farm Springkilde I/S near Horsens, supported by ‘Grøn Omstillingsfond’, the Danish Business Authority (period 9/2014 – 8/2016). During 2017, Frichs Ecotech continues development of the suspension reactor design with integrated hot filtration and has entered into an agreement with a Chinese customer for treatment of sewage sludge.

While robust and simple in principle, the heat transfer rate is limited with conventional externally heated augers. To solve this problem, a French company, ETIA, has developed an electrically (resistance) heated, flexible auger pyrolysis system, operating up to 800 °C. It is available in capacities from 6 to 3500 liter/hour. ETIA offer customer tests with specific fuel samples at the facility in Compiégne, France (Figure 9). ETIA claims that test campaigns with dried sewage sludge produced about 30-40% char, 50-60% gas and small amounts of pyrolysis oil at 800 °C. ETIA has no data available for biogas digestate, but they offer customer tests (sample requirement about 100 kg of dry sample/test).

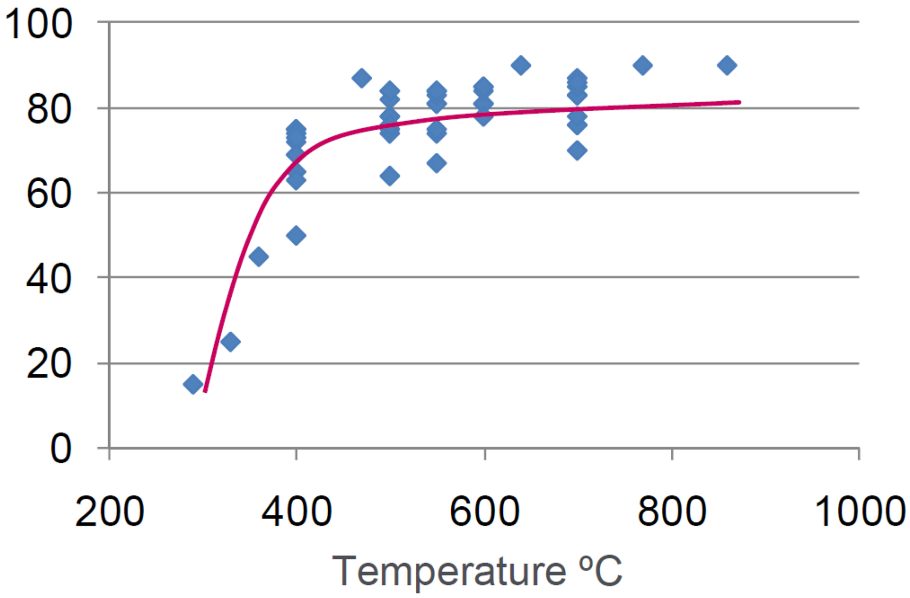

Figure 8 Trend of gas and liquid yields (sum) by thermal pyrolysis,% w/w (Bridgewater, 2010).

Another auger-based concept is marketed by the company ’Susteen Technologies GmbH’ (Sulzbach-Rosenberg, Germany), a spin-off from Fraunhofer-Institut Umsicht: The so-called Thermo-Catalytic Reforming (TCR®) process (Neumann (2016) and patent application by Binder et al. (2015)) where the catalytic effect of the pyrolysis char is exploited (Figure 10).

Figure 9 Direct electrically heated auger pyrolysis, capacity 6-60 L/hour, operating at max. 800°C (ETIA, France)

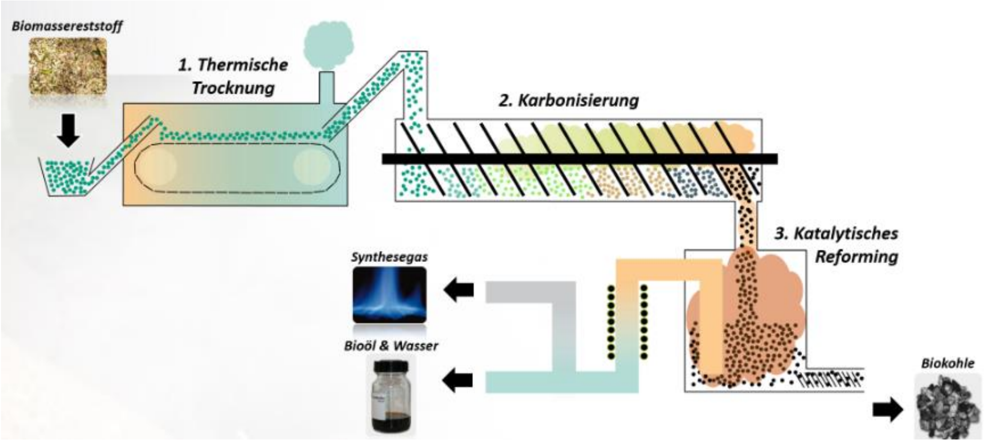

Figure 10 Thermo-Catalytic Reforming concept by Susteen Technologies GmbH.The pyrolysis gas is contacted with the catalytically active biochar.

Finally, an interesting gasification concept ‘WoodRoll’ should be mentioned. The 500 kW test facility has been developed since 2011 by the company Cortus Energy AB, Sweden (Amovic et al., 2014, Marko Amovic & Folkelid, 2017). In principle, similar to the latest concept from Frichs Ecotech, the producer gas is recycled to generate heat for char gasification by means of recuperative, tubular gas burners (Ecothal SER, Sandvik, Sweden). The char is milled into fine powder (< 100 um) before being mixed with steam in an entrained flow gasifier, operating at ambient pressure and 1100 °C. The resulting syngas contains about 60 vol-% H_2, 25 vol-% CO and 10 vol-% CO_2 (dry basis). The composition is mainly controlled by the steam/char ratio and is relatively insensitive of the fuel type. The char conversion rate is, however, naturally influenced by reaction conditions and char reactivity.

The tar content of the raw syngas (at 500 °C) with woody biomass is reportedly in the range 100 – 580 mg/Nm^3, mainly benzene. A relatively high concentration of ammonia (500 – 600 ppm, wet) is found, whereas the sulfur level is very low (< 0.1 ppm, wet) (Amovic and Folkelid, 2017). The development continues with hot gas cleaning for catalytic processing and upscaling of the gasification reactor to 6 MW syngas.

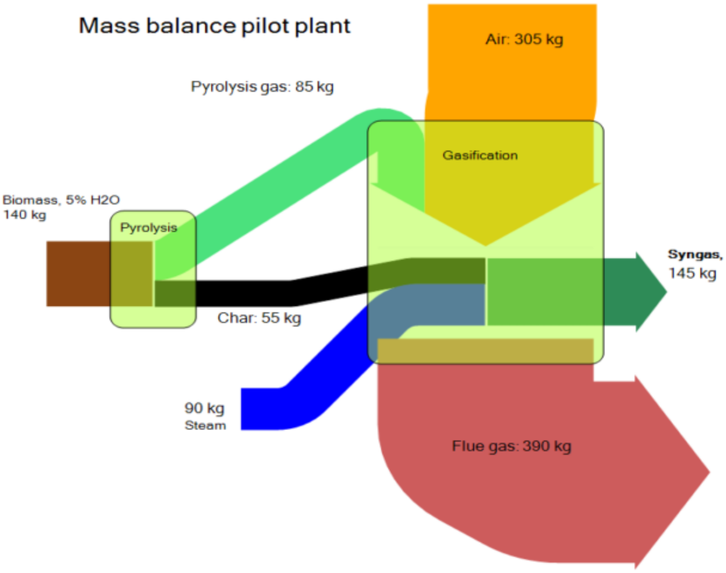

Figure 11 Mass balance of 500 kW syngas WoodRoll test plant (about 620 kW biomass at 5% moisture producing 400 kW char)(Amovic et al., 2014).

5 Pyrolysis Gas Cleaning

Pyrolysis product gas contains significant quantities of condensable tar components, particles and acid gases that must be removed in order to reduce problems in downstream operations, such as clogging of filters, fans, gas pipes etc.

The classical syngas tar removal process includes cooling and condensation followed by biodiesel/rape methyl ester (RME) scrubbing and activated carbon filtration.

The requirement for sulfur removal is extensive for catalytic methanation due to catalyst poisoning. Sulfur species (thiophenes, COS, H_2S) must be reduced to < 10 ppmv levels. COS is converted catalytically to H_2S by reaction with steam, and H_2S can be removed by various methods, such as reaction with iron oxide, scrubbing and adsorption (e.g. activated carbon). Finally, a so-called sulfur guard filter, typically ZnO-based, is installed.

Biological methanation is probably less demanding, but certain tar components have shown to inhibit growth in certain levels and eventually kill the microorganisms (Figures 11 - 14). The study of Hübner and Mumme (2015) also indicate that condensate obtained from 330 °C pyrolysis is less inhibitory than 530 °C pyrolysis condensate (Figure 13). Below a certain threshold, however, the microorganisms may adapt over time to tar exposure.

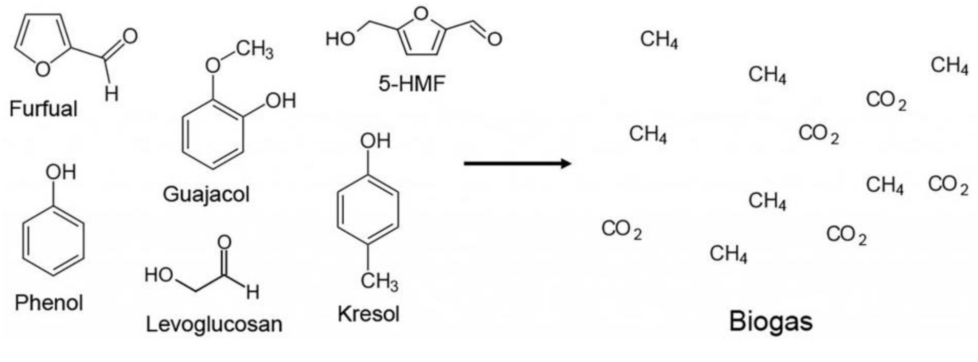

Figure 12 Examples of inhibitory tar compounds (Hübner og Mumme, 2015).

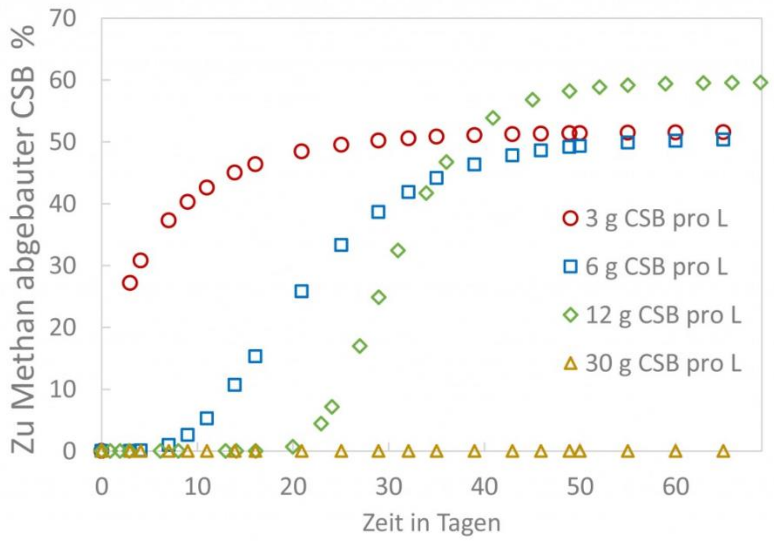

Figure 13 Anaerobic conversion of diluted pyrolysis condensate (Hübner og Mumme, 2015). 'Abgebauter CSB' means 'dismantled chemical oxygen demand'.

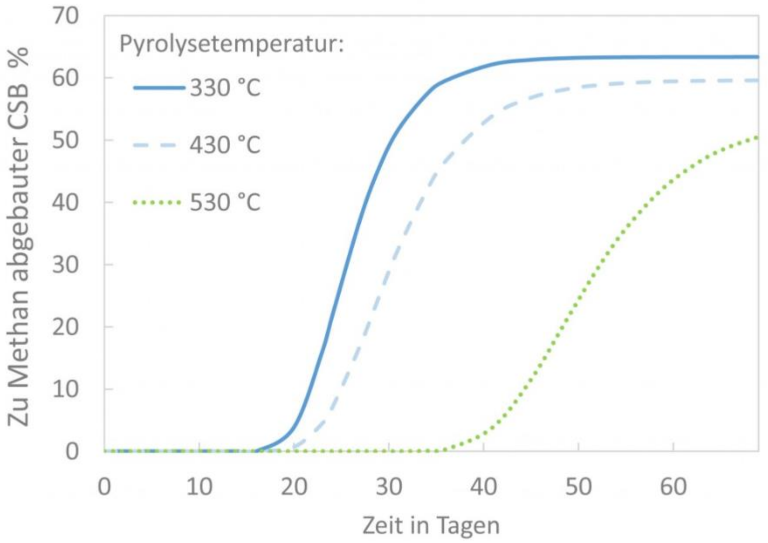

Figure 14 Anaerobic conversion of pyrolysis condensate vs the pyrolysis temperature (Hübner og Mumme, 2015).

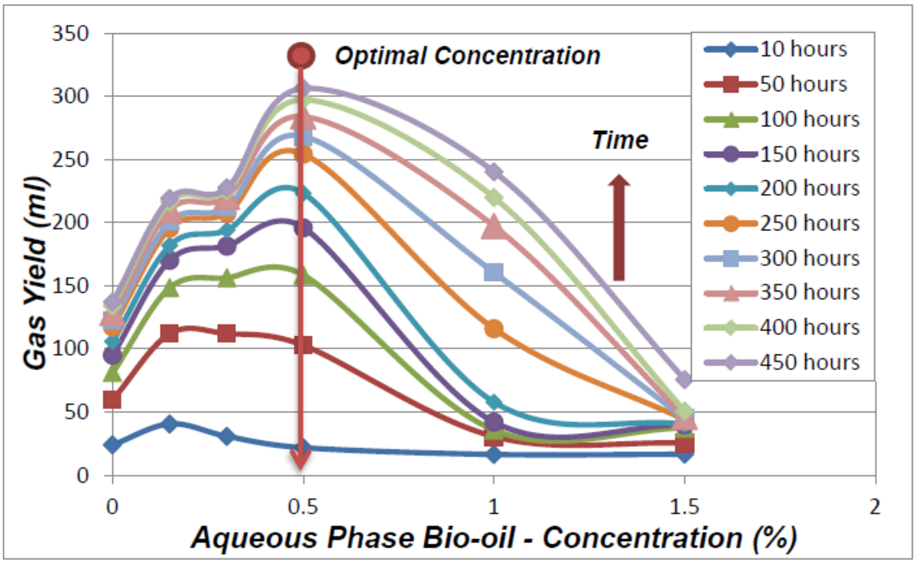

Figure 15 Anaerobic gas yield vs. concentration of aqueous pyrolysis oil fraction (Frear et al., 2013).

High-temperature filtration (< about 1000 °C), optionally with catalyst coating, has been demonstrated for particulate removal and tar reforming, not least in small to medium scale applications (e.g. Repotec, Güssing). Ceramic filters are commercially available in various designs such as candles, bags, and cartridges (e.g. CerX, Figure 16). The latter seems particularly suitable for small-scale gasifiers. It is comparatively open with 10 to 75 µm pore size and 85% total porosity. A catalyst may be added to the fiber surface for e.g. tar reforming.

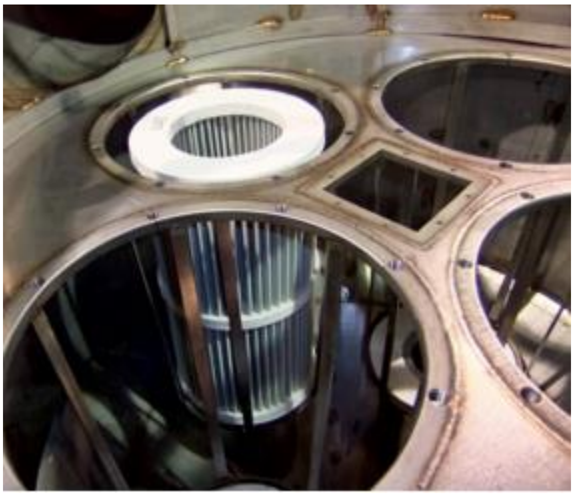

Figure 16 Cartridge filter for small-scale gasifier applications (CerX Ceramic filtration Systems, USA). Available in various lengths and 10” to 30” in diameter.

6 Catalytic Methanation

Large-scale catalytic methanation of syngas (from coal) is progressing mainly in China. It operates at H_2/CO-ratios of approx. 3, temperatures at 200 - 400 °C and pressures of 8-20 bar, producing SNG with 95 vol-% methane or higher. CO_2 is removed (< 5 vol-%), typically using amine scrubbing, prior to methanation. The methanation of CO (and CO_2) is highly exothermic and thermodynamically favored at low temperatures, whereas the reaction rate increases with temperature (diffusion control). A staged recycle layout is necessary to limit the adiabatic temperature rise that otherwise may increase as much as 400 – 600 °C. The active sites of the conventionally nickel-based catalyst age thermally and are poisoned by sulfur, potassium carbonate and arsenious oxide. Caution must be taken to minimize carbon deposition (Jürgensen (2014), Baumhakl, (2014)) and nickel carbonyl formation (boiling point 43 °C, extremely toxic).

In order to reduce the risk of thermal runaway of the conventional SNG process, CO_2 may be removed downstream of methanation (’VESTA’ process patent by Clariant and Foster Wheeler). The concept makes use of the fact that methanation of CO is favoured relative to CO_2, and that the heat capacity of CO_2 is relatively high (acting as temperature damper). The methanation process must be preceded by a water gas shift reactor (WGS, $CO + H_2O = CO_2 + H_2$) to adapt for variations in feed gas composition.

Concerning biomass to SNG development, a consortium of ECN, Dahlman and Gasunie in the Netherlands is developing the ‘ESME’ (patented) methanation system (4 MW SNG demo in Alkmaar planned), building on to the MILENA indirect gasifier and the OLGA gas cleaning concept. The consortium aims at establishing the first commercial unit in 2020 in 50 – 100 MW scale.

Repotec GmbH, well known as gasification technology owner from e.g. the Güssing CHP and the GoBiGas bio-SNG plants, also continues development of bio-SNG technology as part of the ‘GAYA’ R&D project, launched in 2010, with 11 industrial and university partners coordinated by GDF SUEZ. A 500 kW fuel pilot plant has been established near Lyon (France), covering all relevant process steps (biomass treatment, gasification and methanation). Next step is a 10 – 60 MW demonstration plant, planned for 2020.

The two Danish catalytic biogas upgrading projects should be mentioned here as well: ‘MegaStore II Phase 2’, period 7/2016-6/2018 (with partners DTU-MEK, GreenHydrogen, NGF Nature Energy, Biogasanlæg Heden, Fyn) and ‘Electrically Upgraded Biogas’ (with partners Haldor Topsøe A/S, Aarhus Universitet Foulum, DGC et al.).

The goal of MegaStore II is to develop and demonstrate a simple, modular system suitable for mass production at an affordable cost. A proof-of-concept system has been tested successfully at Lemvig Biogas. The gas cleaning unit proved capable of removing sulfur compounds and siloxanes in biogas. The single-pass methanation unit, designed by DTU MEK (Figure 17), operates in excess catalytic CO_2 (similar to the previously mentioned VESTA process) at about 250 °C (claimed self-sustaining) and 8 bar pressure. Next step is upscaling at Biogasanlæg Heden (10 Nm^3/h biogas).

The ‘Electrically upgraded biogas’ project will demonstrate SOEC electrolysis in 10 Nm3 SNG/h scale at Aarhus University Foulum biogas plant (Figure 18). For this purpose, Haldor Topsøe has developed a ‘slim’ single-pass design of the catalytic methanation reactor, improving heat dissipation. The pilot facility is under commissioning.

A simplified methanation process for small-scale bio-SNG was studied by Baumhakl (2014). The entire SNG production process, including indirect gasification with steam injection, gas cleaning (ZnO) and methanation (commercial catalysts) was demonstrated in 5 kW bench scale (wood pellets and lignite, Figure 19). It was concluded that the simplified gas cleaning system was capable of reducing dust, alkalis and inorganic sulfur species to tolerable levels. In addition, light tars were converted during methanation. However, continuous operation was considered uneconomical due to catalyst deactivation by organic sulfur components and the amount of unconverted hydrogen being high. Thus, further improvements of the system are required. Notice that steam injection is required to obtain a H_2/CO ratio of approx. 3 due to the water gas shift equilibrium, approx. 1.5 kg H_2O/kg dry and ash free biomass, Figure 20. Similarly, steam is required to reduce carbon deposition as shown in Figure 21.

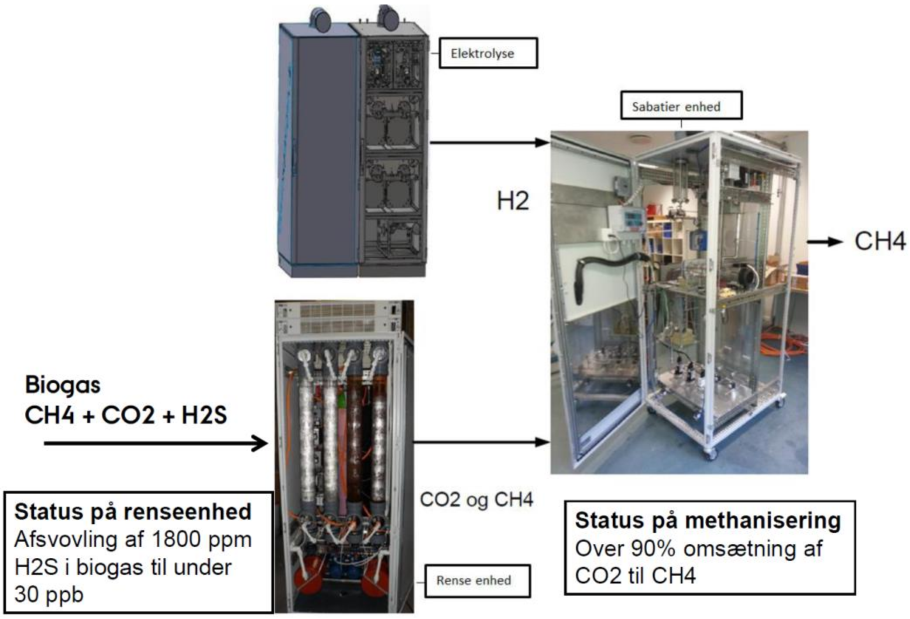

Figure 17 Small-scale modular biogas methanation unit ('Mega-Store II' project, DTU Mechanical Engineering et al.).

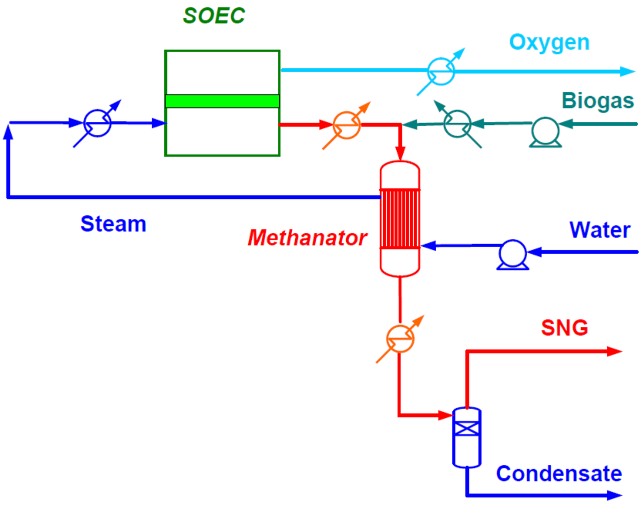

Figure 18 Layout for electrically upgraded biogas with SOEC electrolyser (Haldor Topsøe et al.).

Figure 19 *Bench-scale bio-SNG test rig (5 kW fuel) with indirect gasifier. The methanation catalyst operates around 250 °C, 5 bar pressure (Baumhakl, 2014).*

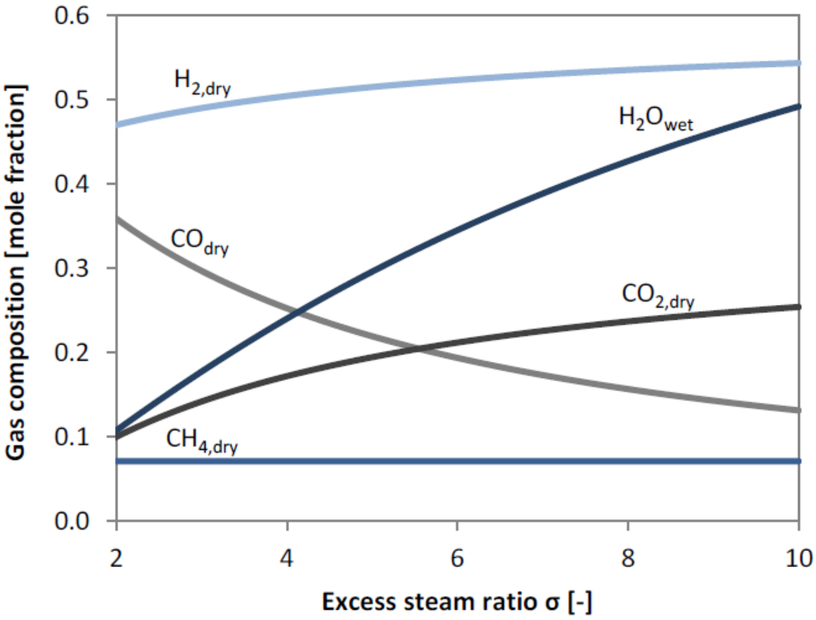

Figure 20 *Calculated equilibrium of wood gasification (dry basis, 800 °C, 2 bar) vs. excess steam ratio (relative to the stoichiometric requirement of approx. 0.2 kg* H_2O/kg_{daf} *wood) (Baumhakl, 2014).*

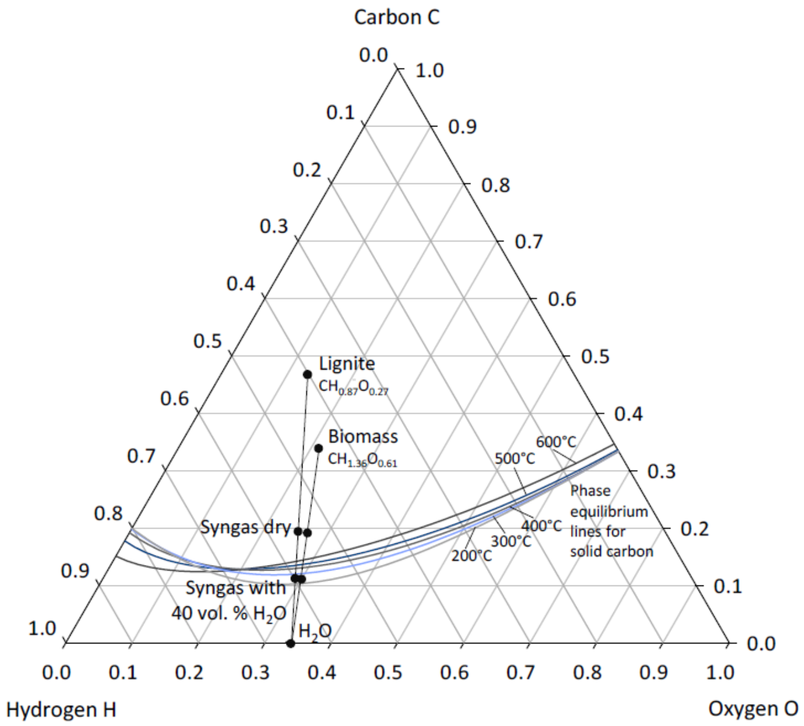

Figure 21 Equilibrium lines for solid carbon formation. Solid carbon can be deposited in the area above the lines at equilibrium (Baumhakl, 2014).

Finally, a metallic honeycomb methanation reactor design was developed as part of the ‘DEMO-SNG’ KIC InnoEnergy project, with partners Karlsruhe Institute of Technology (KIT), DVGW (Germany), KTH and Cortus Energy AB (Sweden). The monolith reactor (Figure 22), also known from mobile exhaust gas cleaning, is effective for exothermal reactions in small-scale (Buchholz, 2013). Product gas from the WoodRoll gasifier, discussed previously (section 4), is directed to the DemoSNG pilot plant designed by KIT (Figure 23). The thermodynamic efficiencies of 3 process configurations of WoodRoll technology with methanation were simulated by Biacchi (2015): 1) no heat recovery, i.e. product gas provides heat to the gasifier, pyrolysis and drying steps, 2) heat from methanation supplied to a steam cycle for electricity generation, and 3) heat supplied to the drier for particularly wet biomass feed. The biomass-to-methane efficiency was found to range from 55% (case 1) to 66% (case 3) (Biacchi, 2015).

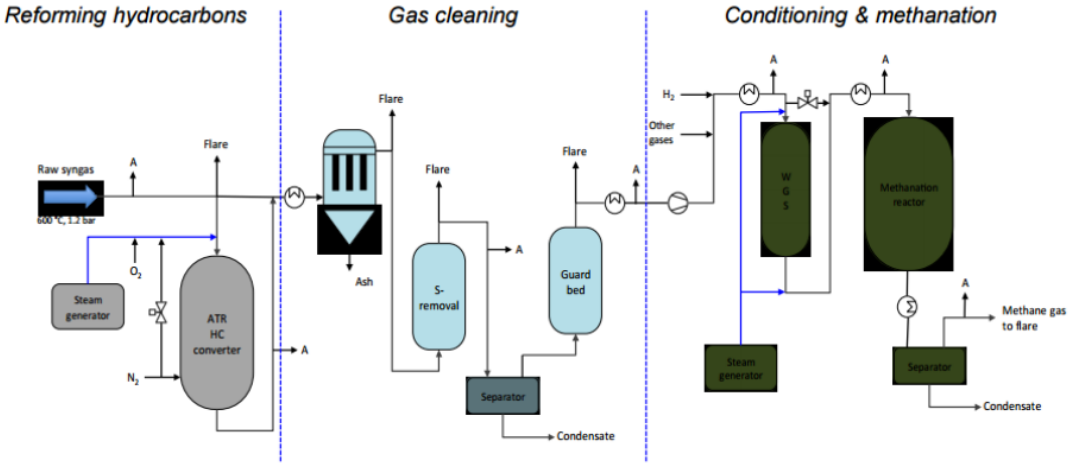

Figure 22 Outline of the 'DEMO-SNG' containerized gas cleaning, conditioning and methanation system (12 x 2.4 x 2.4 m). A side stream of 12-14 Nm^3 (430 °C) product gas is extracted from the 500 kW WoodRoll gasifier (Engvall, 2015).

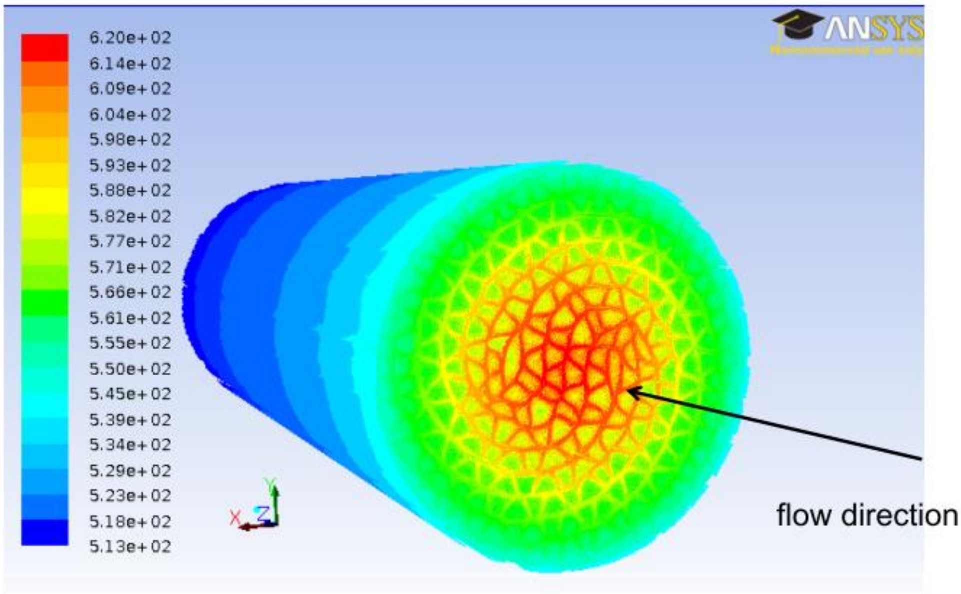

Figure 23 CFD-simulation of temperature profile (in Kelvin) of a honeycomb reactor element. Dimensions are 100 mm length and 35 mm outer diameter (Buchholz, 2013).

7 Biological Methanation

Some microorganisms found in nature and anaerobic digesters are able to convert dissolved hydrogen into methane directly (hydrogenesis) or indirectly via acetic acid (acetogenesis). Likewise, carbon monoxide can be converted via acetic acid to methane. Both mesophilic and thermophilic sludges have obvious methanation potential (Luo and Angelidaki, 2012)

Biological methanation of syngas seems promising for small scale application with potentially lower capital and operating costs than the catalytic alternative. The process is energy efficient (metabolic, low temperature), flexible regarding H_2/CO ratio, highly selective, tolerant/adaptive to inhibitors and various (more valuable) liquid products may be obtained as well. On the other hand, there are limitations due to e.g. low reaction rates, low water solubility of hydrogen and CO and growth inhibition.

Currently there is significant R&D activity in biological methanation, mainly of biogas. Among Danish projects can be mentioned ‘BioUpgrade’ (DTU et al.), ‘Synferon’ (DTU, DGC et al.), ‘BioCat’ (BIOFOS, Audi, HMN Gashandel et al.), ‘ElectroGas’ (SDU, Landia A/S et al.), ‘FutureGas’ (DTU, DGC et al.) and not least the activities at DTU Biosustain (Redl et al., 2016). ‘Synferon’ focuses on syngas fermentation and will install a 5 kW fuel lab-scale gasifier at DGC. In ‘ElectroGas’, Landia will address the low solubility of hydrogen using ejector technology (Figure 24).

Expanding capacity for bio-SNG production, Audi has recently partnered with Schmack Carbotech (subsidiary of Viessmann Group) for biological biogas methanation. The first pilot facility was established in 2015 in Allendorf (Germany), running at 5 bar pressure.

Figure 24 'GasMix' system for hydrogen injection to biogas reactors (Landia A/S).

Fermentation of syngas (from natural gas reforming and waste gasification) and to liquids (e.g. ethanol, acetic acid, butanol) has attracted some commercial investments. Actors in this field are LanzaTech (New Zealand), Ineos Bio (Indian River BioEnergy Center, Florida) and Synata Bio (formerly Coscata).

LanzaTech is now focusing on steel plant and other industrial off-gases containing CO, for which a 10-year co-operation agreement was signed with Siemens Metals Technologies in 2013 worldwide. However, LanzaTech has also been actively demonstrating the compatibility with other feedstocks, including biomass derived syngas (Figure 25 and Figure 26). LanzaTech also recently acquired indirectly heated gasifier technology and other assets from Range Fuels, Georgia (US), planning to produce ethanol and 2,3-butanediol from wood. Both products can be formulated into jet fuel by LanzaTech partner firms.

Figure 25 Mobile plant to demonstrate the syngas fermentation of biomass derived syngas (LanzaTech).

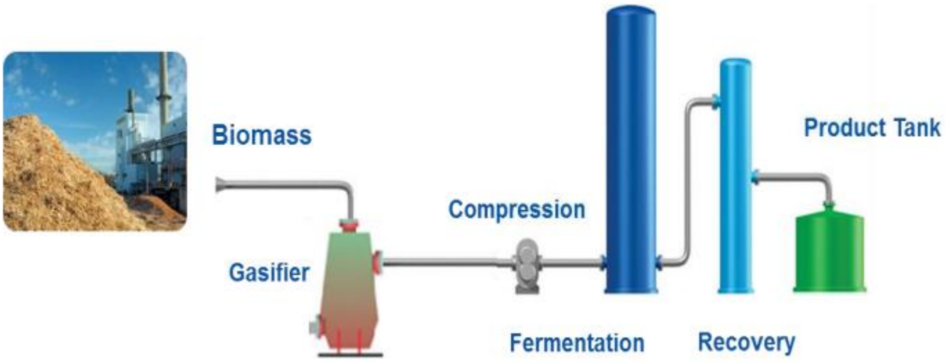

Figure 26 Outline of LanzaTech's syngas fermentation process.

The solubility of H_2 and CO in water is 1.1 mg/l and 11.3 mg/l, respectively, at 60 °C, which is very low. Consequently, it is generally accepted that gas-liquid mass transfer is rate limiting for biological methanation, which means that the conventional stirred reactor is not suitable. Various other reactor designs, including cell immobilization, have been proposed to increase mass transfer area and reduce film thickness of the gas-liquid-biofilm interface (e.g. Youngsukkasem (2015) and Westman (2016)). The classic trickle-bed reactor (filter material 305 m^2/m^3) seems well performing, obtaining a production rate of about 1 Nm^3 CH_4/m^3 bed/day. It is, however, diffusion limited as well (Burkhardt, 2012). The system must be pressurized to improve performance significantly, as shown by Dröge (PFI Biotechnology, 2016), who reports a production rate of 8.6 Nm^3 CH_4/m^3 bed/day at 64 °C and 6 bar (initial pressure) in a batch reactor with gas recycle (Figure 27). Due to the consumption of more moles of H_2 and CO_2 than of CH_4 generated, the pressure (and hence reaction rate) decreases significantly during the course of reaction.

Figure 27 Pressurized, trickle-bed reactor with gas recycle (Dröge, 2016).

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