Final Project Report- SYMBIO (12-132654)

WP1. Process developments for biogas upgrading (Panagiotis Tsapekos and Irini Angelidaki)

Multiple in-situ upgrading experiments were conducted and consequently, a number of publications was generated[1,2,3,4,5]. During the in-situ process specific challenges can be faced, for instance: a) elevated pH due to the bicarbonate consumption and b) increased H_2 partial pressure. These challenges can inhibit methanogenic archaea and also, the interplay between syntrophic bacteria and methanogens. To explore these phenomena, diverse experiments were conducted. At first, co-digestion with acidic substrate was teted to arrest the pH and co-digestion with various substrates or two stage process, where the first stage would have inherent tendency for lower pH. Various substrates (e.g. potato wastewater[2], cheese byproducts[1,5]), at different reactors design (i.e. on stage continuous stirred tank reactors[1], hybrid configuration[4] and up-flow anaerobic sludge blanket[2]) and using dissimilar H_2 distribution devices (i.e. Raschig rings, ceramic sponges[2]) were explored. Although successful upgrading was achieved when pH was controlled, limited process efficiency was achieved at the in-situ process, without pH control with a maximum of 87% CH_4 content using stainless steel diffusers[4]. Parameters as the H_2 injection rate and the mass transfer coefficient (k_La) significantly affected process performance[3]. To increase the contact area between H_2 bubbles and liquid and H_2 transfer coefficient, metallic diffuser followed by ceramic sponge appear as a solution[6]. Members of *Methanomicrobiaceae* family (i.e. *Methanoculleus palmolei* and *Methanothermobacter wolfeii*) were among the predominant archaea, while highly abundant syntrophic bacteria within *Syntrophomonas* and *Coprothermobacter* genera were detected.

For the ex-situ process, improved biomethanation efficiency was achieved. Since the first experimental work, CH_4 content of 89% was achieved using stainless steel diffusers[7]. In accordance with in-situ process, *Methanoculleus* was among the most dominant genera. A comparative study on different reactor configurations was conducted[8]. The process resulted in CH_4 content higher than 98% in the output gas, in either serial upflow or bubble column reactors. It was revealed that gas recirculation rate can increase H_2 utilization, CO_2 removal and thus, improve biomethanation efficiency. Regarding biological aspects, *Methanothermobacter thermautotrophicus* was proliferated at the highly efficient reactors and biofilm was formed during H_2 assisted methanogenesis. In accordance to the aforementioned well-performing systems, more than 96% and more than 97% CH_4 content was succeeded in both trickle filter reactor and reactor equipped with aluminum oxide membrane, respectively[6,9]. Similarly to the previous studies, *M. thermautotrophicus* dominated the archaeal communities and syntrophic bacteria were always detected, demonstrating selection-effect of H_2 on communities composition. In addition, at long-term operation *M. thermautotrophicus* dominated the community after a two years upgrading process[10]. Overall, biological biogas upgrading with CH_4 content higher that 90% was steadily achieved in a number of experimental sets. The promising results were also documented in the PhD dissertation of Ilaria Bassani at DTU. Overall, trickle bed filter was the most efficient reactor configuration ensuring high gas transfer to the liquid phase and supporting efficient biomethanation.

WP2. Process developments for biogas enhancement (Panagiotis Tsapekos, Birgir Norddahl, Irini Angelidaki)

A serial set-up was prepared to couple waste CO_2 –from a biogas reactor treating organic waste (i.e. animal manure) –with exogenous H_2 in an anaerobic reactor containing enriched hydrogenotrophic

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[1] Treu, L. et al. Microbial profiling during anaerobic digestion of cheese whey in reactors operated at different conditions. Bioresour. Technol. 275, 375-385 (2019)

[2] Bassani, I., et al. In-situ biogas upgrading in thermophilic granular UASB reactor: key factors affecting the hydrogen mass transfer rate. Bioresour. Technol. 221, 485–491 (2016)

[3] Lovato, G. et al. In-situ biogas upgrading process: Modeling and simulations aspects. Bioresour. Technol. 245, 332–341 (2017)

[4] Corbellini, V. et al. Hybrid biogas upgrading in a two-stage thermophilic reactor. Energy Convers. Manag. 168, 1–10 (2018)

[5] Fontana, A. et al. Microbial activity response to hydrogen injection in thermophilic anaerobic digesters revealed by genome-centric metatranscriptomics. Microbiome 6:194, (2018)

[6] Bassani, I. et al. Optimization of hydrogen dispersion in thermophilic up-flow reactors for ex-situ biogas upgrading. Bioresour. Technol. 234, 310-319 (2017)

[7] Bassani, I., et al. Biogas Upgrading via Hydrogenotrophic Methanogenesis in Two-Stage Continuous Stirred Tank Reactors at Mesophilic and Thermophilic Conditions. Environ. Sci. Technol. 49, 12585–12593 (2015)

[8] Kougias, P. G. et al. Ex-situ biogas upgrading and enhancement in different reactor systems. Bioresour. Technol. 225, 429–437 (2017)

[9] Porté, H. et al. Process performance and microbial community structure in thermophilic trickling biofilter reactors for biogas upgrading. Sci. Total Environ. 655, 529–538 (2019)

[10] Treu, L. et al. Two-year microbial adaptation during hydrogen-mediated biogas upgrading process in a serial reactor configuration. Bioresour. Technol. 264, 140–147 (2018)

methanogens[7]. The set-up was tested at mesophilic and thermophilic conditions in which the produced biogas composed of 69.7% and 67.1% CH_4, respectively. Subsequently, at the second reactor dominated by hydrogenotrophic methanogens, 99% and 92% of the external H_2 was utilized at mesophilic and thermophilic conditions, respectively. Hence, the final bio-methane quality overpassed the lower threshold of 90% CH_4 composition at the output, at both temperature levels. The experimental set-up was operated for two years in DTU to ensure repeatability of the process and establishment of a successful method for biological biogas upgrade at long-term operation[10]. Interestingly, after two years the biomethanation efficiency was even higher (>98.7%) validating the preliminary results. It worth mentioning that the serial configuration set-up is under operation for almost six years and still has similar biomethanation performance (Fig. 1).

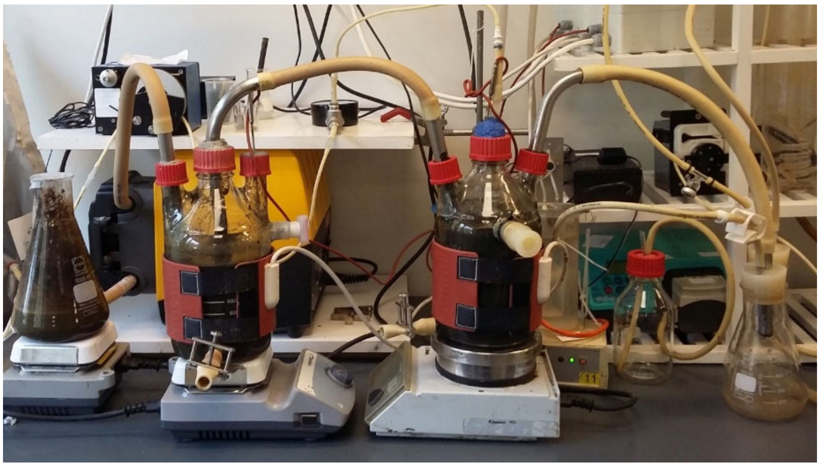

Fig. 1. Serial configuration for hydrogen-mediated biogas upgrading at long-term process (□6 years)

Concerning the microbial aspects of the process, the long-term operation indicated a proliferation of homoacetogenic bacteria and syntrophic acetate-oxidizers. In addition, the most abundant archaea during the initial experimental phase[7] (i.e. *Methanoculleus thermo-hydrogenotrophicum*) were substituted by *Methanothermobacter thermautotrophicus*, as a result of microbial population dynamics[10]. Overall, it is clearly indicated that bio-methane of high heating value can be biologically produced. The obtained results can pave the way for biomethanation establishment as a novel energy carrier via grid injection to partially substitute natural gas. A series of experiments carried out at CBE-SDU, where different diffusers made of porous hydrophobic polymer material were tested as distributors of gas mixture (composed of H_2, CO_2, and CH_4) in glass column filled with a clear liquid simulating the content of a biogas digester with respect to viscosity and general hydrodynamic behavior. The outcome of this set of experiments was a design comprising hollow fibres of polypropylene (PP) giving an optimized distribution of the gas mixture in the liquid[11]. The design enabled the best contact with maximal gas hold-up and minimal mass- transfer between gas molecules and active microorganisms affecting the process, where H_2 and CO_2 react forming methane following the reaction eq. shown below.

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad \Delta G^o = -130.7 \text{ kJ/mol}$$

Later experiments showing the method in a laboratory model of a biogas digester documented process efficiency with PP hollow fibre diffusers. The results were submitted in a scientific paper and documented in the PhD dissertation of Gossaye Tirunehe. The method resulting from the experiments was further patented as presented in the patent listed in deliverables section.

WP3. System analysis and technological, environmental and economical assessment (Abid Rabbani, Henrik Wenzel, Panagiotis Tsapekos and Irini Angelidaki)

A technology catalogue is compiled for hydrogen-assisted biogas upgrading technologies, constituting projections for CO_2 hydrogenation, electrolysis, methane and CO_2 storage technologies. The catalogue builds on top of existing catalogues from the Danish Energy Agency and Energinet.dk evaluating electricity and heat, local heat generation, alternative fuels, H_2 technologies and advanced biofuels. It is noted that a considerable part of the technologies is now in the development phase. Hence, today's price and performance -as well as future estimations are associated with a high level of uncertainty. Table 1 summarizes the Danish biomass potential and biogas potential estimates based on the available biomasses.

[11] Tirunehe, G. & Norddahl, B. The influence of polymeric membrane gas spargers on hydrodynamics and mass transfer in bubble column bioreactors. Bioprocess Biosyst. Eng. 39, 613–626 (2016)

Table 1. Overview of CH_4 potentials from the literature as well as estimated potential for future

	Potential (PJ/year)	Estimated biogas production from type of biomass (PJ/year)			
		2020	2025	2030	2040
Slurry & manure	16	5	6	12	20
Straw	32	1	5	15	45
Deep litter	7	0.7	3	6	7
Industrial & other residual waste	8	8	8	8	8
Discarded crops	-	0.3	0.4	0.6	0.9
Source separated organic household waste & green waste		2	6	6	6
- of which source separated organic household waste	*5*	*2*	*5*	*5*	*5*
- garden/park waste	*1*	*0*	*1*	*1*	*1*
Green agricultural waste		1	2	7	7
- of which beet tops and other tops	*3*	*0*	*1*	*3*	*3*
- grass from natural areas	*3*	*1*	*2*	*3*	*3*
- border zones and ditch edges	*1*	*0*	*0*	*1*	*1*
Total		**16**	**30**	**55**	**94**

The Danish biogas production potential from the available biomasses is significantly larger than today's scale of production. From the estimated production of approx. 18 PJ biogas/year in 2020, production is expected to increase to 25 PJ/year up to 2025 within the framework of the current subsidy scheme and with the establishment of the already planned biogas plants. The production can potentially further increase to 40 PJ biogas/year in 2030 and 60 PJ biogas/year in 2040, which corresponds to the use of all projected amount of slurry in Denmark at the time. Moreover, there is a possibility to include a vast amount of residual biomass in the biogas, in particular straw residues, raising the potential up to 90 PJ biogas/year. This potential can be further increased by methanation of biogas-CO_2 with H_2 with the SYMBIO approach up to a limit of 160 PJ of biogas/year assuming that all appropriate biomass is used, and all biogas is methanised. In the longer term, other CO_2 sources can also be included in H_2 methanisation and ultimately the CO_2 of the atmosphere. Thus, there is no upper ceiling for CH_4 production. Several analyses of whole energy system design were done to serve as a platform for understanding the role of H_2 in hydrocarbon production, including hydrogenation of CO_2 in biogas and further conversion of external CO_2 using the microbial conversion approach as in SYMBIO. An energy system vision paper is produced to signify an integrated system design philosophy[12]. The central element of this vision is that a main input to the community's supply of hydrocarbons in the future renewable energy system is biogas. There may be several other avenues for parts of society's need for specific carbonaceous substances, but the largest demand for hydrocarbons for transport fuels and chemicals/materials is produced in this vision from biogas as a raw material, including biogas-CO_2 reacted with H_2 to CH_4. Figure 3 below illustrates a process flow diagram of the vision.

Bio-methane, being storable, have a key role in supporting the balancing and integration of the energy system, i.e. not only provide transport fuels, but also support the balancing of the fluctuating renewable electricity production from wind and solar power. Also, the inherent and unavoidable process heat from conversion processes can be effectively utilized for residential heating and cooling. A deeper system analysis was elaborated for further revealing and quantifying the role of H_2 in the system[13]. The study is an in-depth review of detailed energy system design solutions for fully renewable energy systems and a synthesis of system design principles and their implications for the biomass dependency of the renewable energy system. The study advances the understanding of biomass dependency of renewable energy systems, and it shows the requirements for the system design in order to stay within a sustainable level of biomass demand.

[12] Wenzel H, et al. Vision for en bio-methan og electro-methan platform for fremtidens kulbrinteforsyning. ISBN: 978-87-93413-15-3 (2019)
[13] Mortensen, AW, et al. The role of electrification and hydrogen in breaking the biomass bottleneck of the renewable energy system. Energy and Environmental Sciences (Submitted November, 2019)

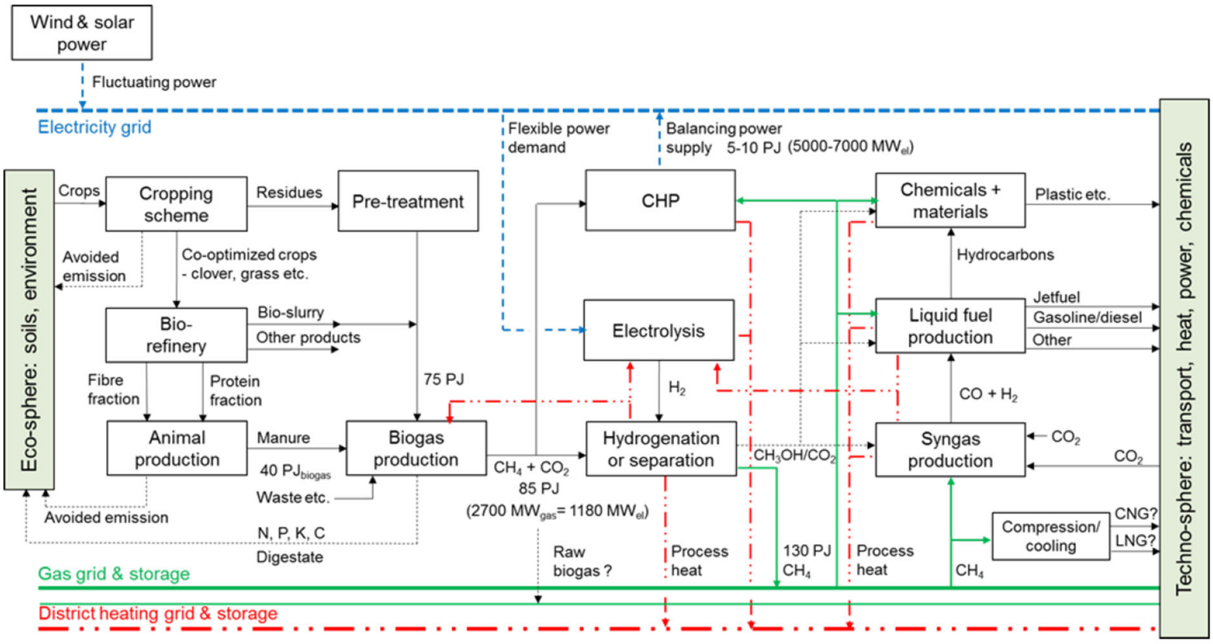

Fig. 3. Energy system design vision for biogas and hydrogenated biogas-CO_2 for the future hydrocarbon supply. Green lines indicate CH_4 flows, red lines indicate heat flows and blue lines indicate electricity flows. Dotted lines indicate optional alternative flows

Especially, the study reveals the possibility and necessity of heat and transport sector electrification and of electrolysis and H_2 integration into the system to reduce biomass dependency to a sustainable level, e.g. hydrogenation as in the SYMBIO concept. Figure 4 below represents a key finding of the study and shows the solution space and correlation between the system's demand for biomass versus the production and integration of H_2 into the system.

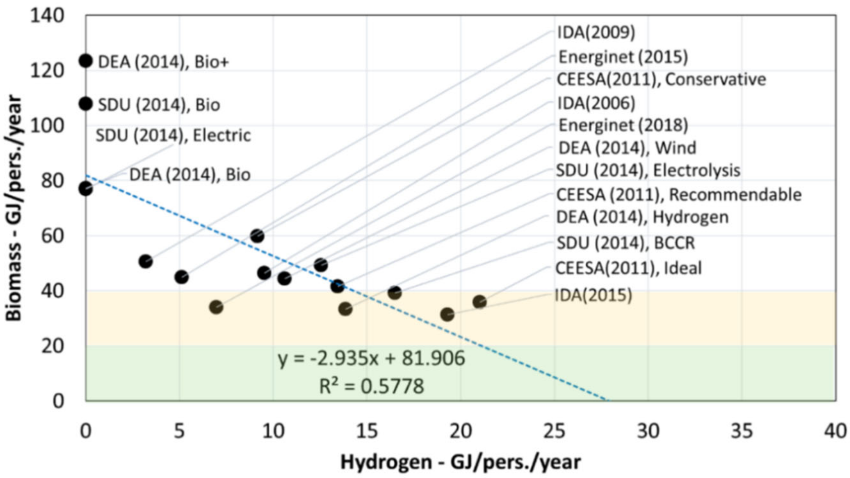

Fig. 4. The relation between biomass and H_2 integration for all the 16 scenarios under thorough investigation based on the raw data from the studies. The green area indicates the sustainable technical potential of biomass on a global scale and the reddish area indicates the Danish biomass potential

The specific role of biomass conversion technologies for agricultural straw residues was studied comparing anaerobic digestion (AD) and ethanol fermentation[14], further elaborating on importance of efficient utilization of available bio-resources and the significance of hydrogenating biogas-CO_2. These systems are compared in terms of cost-efficiency, biomass demand, system integration capabilities and flexibility in producing transport fuels, use of hydrogen, balancing of electricity grid and ability to integrate process heat in addition to ensure synergy with the agriculture sector. Using agricultural straw residues for AD, results in the lowest biomass demand for the overall system.

[14] Mortensen AW, et al. The system integration aspects of biomass conversion technologies – a case of agricultural straw residues for anaerobic digestion and ethanol fermentation. Manuscript ready for submission (2019)

Moreover, Rabbani and Wenzel[15] presented an integrated energy model of the Island of Funen, Denmark by utilizing traditional national gas grid for the upgraded bio-methane and assess the system capacity to assimilate electricity, heat, transport, industry and agriculture sectors. By switching between power generation from biogas when electricity prices are high and upgrading when prices are low, establishes a concurrent and cost-effective dual-mode solution, in addition to identifying peak wind shaving, electrolyser capacities, shares of energy supply and demands for each sector, bottlenecks in the grid, gas compression and pressures, conditions and ratio of bio-methane imports and exports. Overall, an energy system based on biogas using cheap electricity for H_2 provision can be a promising alternative to avoid huge demands to produce energy from biomass. A combination of hydrogen-assisted biological upgrading with bio-trickling filter and amine scrubber, showed a competitive upgrading cost when compared to other conventional alternatives in the techno-economic analysis of ten upgrading technologies[16].

WP4. Upscaling of the process (Panagiotis Tsapekos and Irini Angelidaki)

Based on the results of previous WPs, trickle bed reactors were shown as an efficient reactor system for biomethanation process[9,17]. Thus, an integrated trickle bed unit was constructed at pilot-scale (68 L working volume), filled with porous packing material and placed in project's collaborator WWTP (BIOFOS, Avedøre) (Fig. 5). A serial set-up was designed to couple waste CO_2 –from a pilot biogas reactor fed with organic waste –with exogenous H_2 in the trickle bed unit. The AD reactor was fitted with a stainless steel top plate, which supported the vertical low speed mixer, gear motor, safety and pressure valve and a safety level sensor. Process temperature was maintained by pumping hot water through a stainless steel coil fitted inside the reactor using an electric flow heater and circulation pump. Reactor content was mixed by low speed gear motors fitted with two impellers operating in a 5 min on/off mode. Two eccentric pumps were used to pump influent and effluent operating five times per day for 60 s each time. Prior to each feeding, an equal amount of effluent was removed from reactors working volume. Biogas from the reactor was measured continuously using a diaphragm gas meter. At steady conditions, the amount of produced biogas was known and so, the exact amount of CO_2 to be fed to the upgrading unit was calculated. For gas supply to the upgrading unit, a H_2 line was installed, while the gas flow was controlled via automated flow controller. For start-up phase, thermophilic hydrogenotrophic inoculum was collected from lab-scale tests. The needed micro- and macro- nutrients for the hydrogenotrophs were provided from sieved and pasteurized digestate. Both reactors were controlled by an electrical panel connected with a PC in which LabView was installed. The complete set-up was assembled in line with ATEX regulations and the entire facility was ATEX protected.

Fig. 5. Pilot-scale operation at BIOFOS WWTP in Avedøre

The reactor was operated at gas retention time of 10 h, without applying gas recirculation in order to avoid extra operation costs. Process monitoring showed that the CH_4 content reached more than 90% in the gas output since the first two weeks of operation. Hence, the high performance of the ex-situ pilot reactor was shown in thermophilic conditions for the bioconversion of H_2 and CO_2 to bio-methane.

[15] Rabbani A. et al. An integrated gas grid model for upgraded biogas in future renewable energy system. 2nd Intl. Conf. on Smart Energy Systems and 4th Generation District Heating. (2016)

[16] Fischer, A.Techno-economic analysis of biogas upgrading technologies. Master's thesis, SDU (2018)

[17] Angelidaki, I., et al. Biogas upgrading and utilization: Current status and perspectives. Biotechnol Adv 36: 452–466 (2018)