Dynamic Biogas Upgrading for Integration of Renewable Energy from Wind, Biomass and Solar

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Publication date:
2015

Document Version
Publisher's PDF, also known as Version of record

Citation for published version (APA):
Jurgensen, L. (2015). Dynamic Biogas Upgrading for Integration of Renewable Energy from Wind, Biomass and Solar. Department of Energy Technology, Aalborg University.

LARS JÜRGENSEN

DYNAMIC BIOGAS UPGRADING FOR INTEGRATION OF RENEWABLE ENERGY FROM WIND, BIOMASS AND SOLAR

DYNAMIC BIOGAS UPGRADING FOR INTEGRATION OF RENEWABLE ENERGY FROM WIND, BIOMASS AND SOLAR

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Ph.D. Dissertation
Submitted July, 2015

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ISBN: 978-87-92846-64-8

Printed in Denmark by Uniprint

ABSTRACT

The Sabatier process is investigated as a storage scheme for renewable energy. Hydrogen derived from fluctuating renewable energy sources like wind and solar is converted to methane by the hydrogenation/methanation of carbon oxides. Biogas from anaerobic digestion is considered in this study as a high concentrated source of carbon dioxide. By using the Sabatier process, the CO_2 content of the biogas is converted to CH_4, which is a new upgrading process for biogas. By switching between (i) this upgrading process during periods of extensive electricity production from wind and solar, and (ii) combined heat and power production from biogas during periods of electricity demand, bioenergy utilization becomes a dynamic process. In such a process scheme, biomass, wind, and solar could be integrated in a local context.

This thesis aims to demonstrate the feasibility of the dynamic biogas upgrading as a sustainable process for electricity storage and system integration in Northern Germany, i. e. the state of Schleswig-Holstein. A feasibility study was conducted to analyze the energy system in this region and the potential for this process. Process simulation tools were used to prove the product gas properties and the degree of efficiency of the system. Lab-scale and bench-scale experiments where further applied to demonstrate the utilization of industrial waste water for biogas production and the general applicability of biogas in the Sabatier process.

POTENTIAL The analysis of the energy system in Schleswig-Holstein with respect to the sources of electricity, their distribution, and the reasons for feed-in management was carried out to derive the potential of an energy storage scheme based on the use of biogas as a cheap and available carbon dioxide source for the production of substitute natural gas. It was found that there is a need for such a storage scheme in the northernmost four counties of Germany. In these four

counties, 529 mostly farm scaled biogas plants could potentially produce up to $100 \cdot 10^6\,\mathrm{m^3/a}$ SNG (substitute natural gas) using surplus electricity from wind and solar power generation systems availavble from 1600 h/a.

PROCESS SIMULATION The simulation of the whole process using a kinetic reactor model demonstrated the feasibility of the production of substitute natural gas at gas grid standards by a single reactor setup. The Wobbe index, CO_2 and H_2 content, and the calorific value which are key factors for the SNG production, were found to be controllable by the H_2/CO_2 ratio fed to the methanation reactor. Dynamic reactor simulation showed that the process strat-up could be achieved within several minutes to facilitate surplus electricity from renewable energy systems. The heat from the exothermic reaction can be utilized partly at high temperature (approx. 200 °C, e. g. for applications in a biorefinery context) and also at low temperatures (e. g. for district heating).

EXPERIMENTS Using synthetic gas mixtures and real biogas, ammonia and other trace components in the real biogas were observed to have an insignificant effect on catalyst deactivation. Thus, biogas can be used as a feed gas for the Sabatier process without any further pretreatment. However, the removal of hydrogen sulfide using doped char coal and zinc oxides was still necessitated. To produce the biogas used in the methanation experiments, industrial waste water from a local dairy was used as substrate in a novel combination of different anaerobic reactors. A $1\,\mathrm{m^3}$ continuous stirred tank and a 200 l anaerobic baffled reactor in series were used to treat the low strength waste water, showing excellent stability and high COD removal at low residence times. This combination can act as a role model for future biorefinery plants using high diluted waste streams or for the adaption of existing biogas plants using continuous stirred tank reactors, but struggling with process efficiency or stability due to changing feed properties.

RESUMÉ

Sabatier processen er en metode under udvikling for lagring af vedvarende energi. Hydrogen, stammende fra fluktuerende vedvarende energikilder såsom vind- og solenergi, konverteres til metan via hydrogenering/metanisering af kuldioxid. Biogas fra anaerob nedbrydning er tilgængeligt som en højkoncentreret kilde til kuldioxid. Ved at anvende Sabatier processen, kan kuldioxiden i biogas omdannes til CH_4, hvilket en ny proces til opgradering af biogas. Ved at veksle mellem denne opgraderings proces, i perioder med overkuds produktion af elektricitet fra vind- og solenergi, og med kraftvarme produktion, i perioder med et stort forbrug af elektricitet, bliver udnyttelsen af bioenergi en dynamisk proces. På denne måde bliver biomasse, sol og vind integreret i en lokal kontekst.

Denne afhandling har til formål at demonstrere anvendeligheden af den dynamiske biogas opgradering som en bæredygtig metode til lagring af el, samt som system integrering i Nordtyskland, Slesvig Holsten. En forundersøgelse blev udført for at analysere energi systemet i regionen og potentialet af processen. Processimuleringsværktøjer blev anvendt til at dokumentere gas produktets egenskaber og effektivitetsgrad. Eksperimenter, udført på laboratorie skala og bench skala, demonstrerede udnyttelsen af industrispildevand i biogas produktion, samt den generelle anvendelighed af biogas i Sabatier processen.

POTENTIALET Analysen af energisystemet i Slesvig Holsten, i forhold til kilder til elektricitet, deres distribution samt årsager til feed-in management, blev udført for at udlede potentialet for et energilagringssystem baseret på brugen af biogas som en billig og tilgængelig kuldioxidkilde til produktion af et alternativ til naturgas (substitute natural gas, SNG). Det blev konstateret at der er behov for et sådan lagringssystem i de fire nordligste kommuner af Tyskland. I disse kommunerkunne 529 biogasanlæg, hovedsageligt gårdanlæg, poten-

tielt producere op til $100 \cdot 10^6\,\mathrm{m}^3$ SNG årligt, ved at bruge den overskudselektricitet fra vind- og solenergi produktionssystemer som er til rådighed fra 1600 h/a.

PROCESSIMULERINGER Simuleringen af hele processen blev udført ved hjælp af en kinetisk reaktor model og demonstrerede anvendeligheden af den producerede SNG i forhold til gasnet standarder i en enkelt reaktor opsætning. De centrale faktorer for SNG produktion, Wobbe-indekset, CO_2 og H_2 koncentrationen, samt brændværdien, viste sig at være kontrollerbare i form af H_2/CO_2 forholdet indfødt til metaniserings-reaktoren. Via dynamiske reaktor simuleringer blev det påvist, at processen kan startes op på få minutter og håndtere overskudselektricitet fra vedvarende energi systemer. Varmen fra den eksoterme reaktion kan udnyttes dels ved høje temperaturer (ca. 200 °C, f.eks. til processer i bioraffinaderier) og ved lave temperaturer (f.eks. til fjernvarme).

EKSPERIMENTER Ved hjælp af SNG blandinger og reel biogas, blev ammoniak og andre sporstoffer i biogassen påvist at være harmløse i forhold til de-aktivering af katalysen. Med undtagelse af hydrogensulfidfjernelse udført ved hjælp af aktiv kul og zinkoxid eller lignende metode, kan biogas derved anvendes direkte som indfødningsgas i Sabatier processen uden nogen forbehandling. For at producere den biogas som blev anvendt i metaniserings-forsøgene, blev industrispildevand fra et lokalt mejeri og anvendt som substrat i en ny kombination af forskellige anaerobe reaktorer. En $1\,\mathrm{m}^3$ kontinuertligt omrørt tank serie-kombineret med en 200 l anaerob baffle reaktor, blev anvendt til at behandle spildevandet og viste fremragende stabilitet samt høj COD fjernelse ved kort opholdstid. Denne kombination kan fungere som rollemodel i fremtidens bioraffinaderier, som bruger stærkt fortyndede affaldsstrømme, eller til tilpasning af eksisterende biogasanlæg der bruger kontinuerligt omrørte tank-reaktorer og kæmper med at effektivisere og stabilisere processen p.g.a. skiftende kvali af input-materialer.

ACKNOWLEDGMENT

This work would not had been possible without the support of my family, colleges and fellows:

MY FAMILY: Thank you. I love you all.

MY FELLOWS AND FRIENDS Thanks to you all.

MY SUPERVISORS Jens Born, professor at Flensburg University of Applied Sciences, and Jens Bo, associated professor at Aalborg University Esberg: two very genius and motivating experts in and beyond bioenergy.

EHIAZE AUGUSTINE EHIMEN My postdoc, collaboration partner, and my friend.

JOACHIM SCHNEIDER Professor at Flensburg University of Applied Sciences. Thank you for introducing me to academia from my first semester on!

MY PH.D. FELLOW ANE KATHARINA Thank you for joining that journey through the Ph.D. studies and workload and especially for generating all those lovely maps from my data shown in this thesis.

PREFACE/MANDATORY PAGE

This dissertation includes results mainly gained during the three year period of the Large Scale Bio Energy Lab founded by the EU Interreg IVa fund. The program run from 2012–2015 as a trans-boarder cooperation between Aalborg University Esbjerg (AAU), Flensburg University of applied Sciences (FHF, where the main work was conducted) and Europa University Flensburg. The scientific work was supervised by Associate Professor Jens Bo Holm-Nielsen, Ph. D. from AAU and Professor Dr. Jens Born from FHF. The main work was conducted at FHF, coordinated, inspired and supervised by both University, FHF and AAU. This cross-boarder cooperation was very fruitful and the Doctoral School of Science and Engineering (AAU) can be a role model for future Ph.D. programs at the German Universities of Applied Sciences.

The experiments published in the short communication paper presented in chapter **??** were conducted at Queens University Belfast under supervision of Professor David Rooney during an external research stay of three month.

Mainly, this thesis is a comprehension of papers published during the Ph.D. study. Before the presentation of the papers in chapter **??**–**??**, a description of renewable energy systems is given, focusing on the region of Northern Germany and the possibilities for fully integration of biomass into the excising system. From this point of view, the papers will proof the feasibility of the proposed process, giving bioenergy a new role in the energy system.

The papers presented in chapter **??**–**??** are regarded to be an integral part of this thesis, since the major part of the three years of studying is presented in these papers. These papers are:

A Lars Jürgensen, Ehiaze Augustine Ehimen, Jens Born, Jens Bo Holm-Nielsen: *Utilization of surplus electricity from wind power for dynamic biogas upgrading: Northern Germany case study*, Biomass and Bioenergy, 66 (2014) 126–132, `http://dx.doi.org/10.1016/j.biombioe.2014.02.032`.

B Lars Jürgensen, Ehiaze Augustine Ehimen, Jens Born, Jens Bo Holm-Nielsen: *Use Of The Sabatier Process For Dynamic Biogas Upgrading In Northern Germany*, 22nd European Biomass Conference and Exhibition, 881–886, ISBN: 978-88-89407-52-3, `http://dx.doi.org/10.5071/22ndEUBCE2014-3CO.3.5`.

C Lars Jürgensen, Ehiaze Augustine Ehimen, Jens Born, Jens Bo Holm-Nielsen:*Dynamic biogas upgrading based on the Sabatier process: Thermodynamic and dynamic process simulation.* Bioresource Technology 178 (2015) 323–329, `http://dx.doi.org/10.1016/j.biortech.2014.10.069`

D Lars Jürgensen, Ehiaze Augustine Ehimen, Jens Born, Jens Bo Holm-Nielsen, David Rooney: *Influence of trace substances on methanation catalysts used in dynamic biogas upgrading.*Bioresource Technology 178 (2015) 319–322, `http://dx.doi.org/10.1016/j.biortech.2014.09.080`.

E Lars Jürgensen, Ehiaze Augustine Ehimen, Jens Born, Jens Bo Holm-Nielsen: *Hydrogen production using an anaerobic baffled reactor—mass balances for pathway analysis and gas composition profiles.*
Submitted to International Journal of Hydrogen Energy, April 2015, 2015. Revised submission on June 30, 2015.

F Lars Jürgensen, Ehiaze Augustine Ehimen, Jens Born, Jens Bo Holm-Nielsen: *Two-stage fermentation of low-strength dairy wastewater for biogas CO_2 production aimed at synthetic natural gas production*
Submitted to Bioresource Technology, June 29, 2015.

This present report combined with the above listed scientific papers has been submitted for assessment in partial fulfilment of the PhD degree. The scientific papers are not included in this version due to copyright issues. Detailed publication information is provided above and the interested reader is referred to the original published papers. As part of the assessment, co-author statements have been made available to the assessment committee and are also available at the Faculty of Engineering and Science, Aalborg University.

Lars Jürgensen

CONTENTS

LIST OF FIGURES

ACRONYMS

ABR	anaerobic baffled reactor
AD	anaerobic digestion
ADM	anaerobic digestion model
CHP	combined heat and power
CNG	compressed natural gas grid
CSTR	continuous stirred tank reactor
DME	dimethyl ether
EEG	Erneuerbare-Energien-Gesetz (engl. renewable energy act)
EOS	equation of state
gen.	generation
HRT	hydraulic retention time
RE	renewable energy
RES	renewable energy systems
RT	residence time
SD	sustainable development
SNG	substitute natural gas
SR	stoichiometric ratio
SRK	Soave-Redlich-Kwong
STP	standard temperature and pressure
syngas	synthetic gas
UASBR	upflow anaerobic sludge blanket reactor
VFA	volatile fatty acids
WGS	water-gas-shift

Part I

THESIS FRAMEWORK AND BACKGROUND

1

INTRODUCTION

MOTIVATION

The transition of the energy system to a fully sustainable energy based on 100 % renewable energy is one of the biggest challenges mankind will face in the next century. The emission of green house gases and the supply limits of oil and gas forces a transition to the use of renewable energies (RE). Due to uncontrollable risks and the lack of ultimate disposal places, nuclear power is not an option either.

In Germany and Denmark, wind, solar radiation, and biomass are the main sources of renewable energy. The high share of this intermediate supplied renewable energy production[1] results in periods of surplus production in both countries [7, 8]. To effectively manage and integrate this growing share of intermediate power production, new storage processes and re-design of the energy system are needed. In this context, the use of hydrogen as a renewable fuel for the storage of RE is often discussed. The idea of a hydrogen economy however suffers with problems of missing infrastructures, utilization schemes (fuel cells are still under development), and bad physical properties resulting in safety, storage, and transportation issues. Still, electrolysis for hydrogen production remains the only practical link between electricity and chemical energy carriers [9].

H_2 is not a proper fuel.

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[1] Due to the conversation law, energy production is impossible. The term will be used with respect to the kind of energy obtained during its conversion.

In contrast to H_2, compressed natural gas (CNG) is already a very important energy carrier well integrated with existing infrastructure for transportation, utilization and storage. The conversion of H_2 to synthetic natural gas could be facilitated using the Sabatier process, hence overcoming the disadvantages associated with H_2. The Sabatier process is discussed as a storage scheme to facilitate the huge potential of energy storage in the CNG grid.

BIOMASS IN THE CONTEXT OF RENEWABLE ENERGY

Today, approximately 8000 biogas plants are operating all over Germany as a result of high subsidies by the renewable energy act (*Erneuerbare-Energien-Gesetz,* EEG). 77 % of the produced biogas is derived by the digestion of energy crops [6]. When these plants were built, there was no aim to design them according to the needs of alternative substrate utilization (e. g. low-strength industrial waste water, road-side grasses) and no flexible power production was intended by the EEG. Today, prices for substrates has increased due to the high numbers of plants, but the switch to alternative substrates is not that easy. Additionally, the increased electricity production from wind and solar[2] causes the production of surplus electricity, thus there is a demand for flexible power production according the output of the fluctuating generation from wind and solar. Bioenergy could be suitable for demand-led power production, but needs to be integrated in a sustainable way.

Bioenergy has to become flexible.

The production of substitute natural gas (SNG) from biogas is far behind its goal: in 2013, $520 \cdot 10^6$ m^3 was supplied to the compressed natural gas grid, while the goal had been to supply $6 \cdot 10^9\, m^3/a$ in 2020. As a consequence, this goal was dropped during the revision of the EEG by the end of 2014 [10].

The Sabatier process is based on the methanation of CO_2 using renewable hydrogen. The application of such a storage scheme using biogas as CO_2 source might overcome the flexibility problem of biogas plants and would increase the amount of SNG produced

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[2] Photovoltaics is the only conversion technology for electricity production applied in S-H.

from renewable energy and biomass. By using the CNG grid a huge storage potential can be facilitated, even large enough for seasonal storage of large amounts of RE.

SCOPE

The Sabatier process has been used at industrial scale for decades. The application at farm-scale biogas plants needs a different process layout than large-scale methanation plants. The technology has to be adaptable, simple, and robust, i. e. a complex multi-reactor design is not suitable and the catalysts used must not be poisoned by trace substances of the biogas used. Furthermore, the production of biogas should be based on sustainable substrates and it has to be proved, if such an upgrading process can contribute significantly to the integration of fluctuating renewable energy production from wind and solar.

From this point of view, the scope of this thesis is to show the technical feasibility of the Sabatier process to be the missing link between RE production from wind and solar and its sustainable utilization in bioenergy systems. A three step approach was chosen according to the needs stated above: (i) a feasibility study was carried out to determine the potential for storage in Northern Germany, (ii) a process simulation was conducted to determine optimal process conditions and the degree of efficiency in a simple single-reactor process and (iii) experiments were conducted to test the feasibility of using real biogas derived from sustainable substrates for the Sabatier process. The production of biogas using a new anaerobic digestion (AD) concept was a major part of this experimental work. Whereas the simulation was focused on the catalytic conversion and the process layout of the whole upgrading process to produce SNG, the experiments were focused on the utilization of locally available, unconventional substrates for biogas production, and the general suitability of biogas for the Sabatier process.

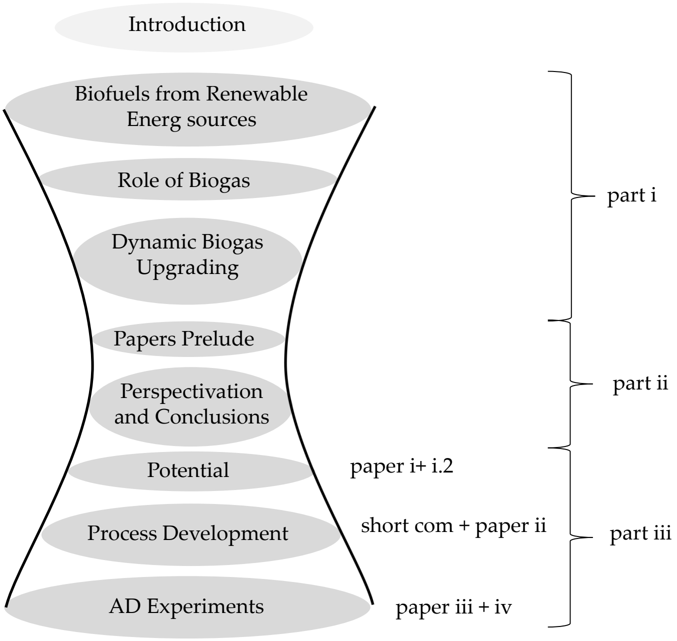

Figure 1: In part i, the boundary conditions for renewable energy systems are described followed by the role of biogas in such systems and the idea of using the Sabatier process for the dynamic biogas upgrading process. Part ii presents the paper prelude, perspectivations and discussion of the thesis, while part iii presents the published and submitted papers containing the scientific work.

THESIS STRUCTURE

This thesis is structured into three parts as shown in figure 1:

1. In part i, the boundary conditions for the Sabatier process are analyzed: From a global view on the energy system, a zoom into Germany and later into Schleswig-Holstein is done to identify the current issues and problems facing the integration of RE and the production of biofuels. From this perspective, possibilities for novel biogas plant concepts are reviewed, including flexible power production and new reactor configurations. At the end of part i, the Sabatier process and its theoretical background is given.
2. Part ii contains the introduction to the papers published or submitted during the Ph. D. period and finally ends with the conclusion and further perspectives of this thesis.
3. In part iii, the published or submitted papers are presented.

2

BIOENERGY AND RENEWABLE ENERGY SOURCES

2.1 RENEWABLE ENERGY SYSTEMS

The necessity and urgency of the transformation of the global energy system is well known. High efforts are needed to limit the global warming to 1–2 °C above pre-industrial level (2 °C scenario), including agriculture and industrial practice, changes in regulations, solid waste management, a movement towards greater efficiency, and progressing towards renewable energy as an alternative for non-renewable fuels [11].

2.1.1 *Global Changes and Challenges*

90 % of the world's primary energy demand is consumed in the region of North America, Europe, and Asia [12]. According to the International Energy Agency (IEA), just 13.5 % of the global energy supply was based on renewable production in 2012, mainly bioenergy (10.0 %) and hydropower (2.5%) (see fig. 2) [2]. Only 38 % (i. e. 3.8 % of the total primary energy) of the bioenergy were produced by modern technologies [1]. Modern bioenergy utilization is the production of high-quality energy carrier like electricity or biofuels [13]. In 2012[1], 20 % of the electricity production worldwide came from renewable energies, mainly from hydro (78 %), on-shore wind (10 %) and bioenergy (8 %). Photovoltaic (PV), geothermal, and off-shore wind power production were at minor levels. In 2011, biofuels pro-

3.8 % *modern bioenergy worldwide.*

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[1] Newest data published recently by the IEA.

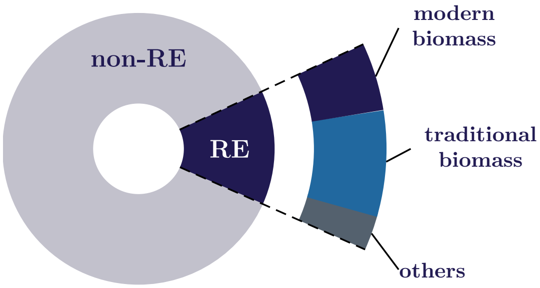

Figure 2: World's primary energy supply: Only 13.5 % is supplied from RE, the rest comes from non-RE (including nuclear). Modern bioenergy contributes just by 3.9 %, today (according to [1, 2]).

vided 2.6 % of the global transportation energy consumption. Only first generation biofuels where produced in considerable amounts at that time, e. g. ethanol from sugarcane in Brazil and oil-crop based biodiesel [3].

To reach the goals set by the 2 °C scenario, the energy sector and non-energy sectors (industry, buildings, etc.) have to be transformed towards a sustainable global energy system. The green house gases released by energy production and industrial processes have to be cut by half until 2050. Therefore, renewable power production has to be increased by 124 % and biofuel production by 209 % by 2020 [3]. As shown in figure 3, bioenergy, PV, and wind power are to be increased by several hundred percent. Especially the goals for wind and biomass are consistent with the findings published by the IPCC [1, p. 300, 595], thus the rapid growth of these sectors has to be expected to continue in the next years and decades.

All sectors have to contribute.

Figure 4 shows the contributions from all sectors to this goal until 2025 by means of GHG emission savings. In this context, bioenergy and biomass are able to cover parts from the power, industry, transport, and building [14]. In industry, biomass can be used as a renewable feedstock for the production of a wide range of chemicals, e. g. by fermentation (lactic acid etc.), chemical reaction (oleochemicals) [15] or by syngas routes [16]. To mitigate the CO_2 emission from the building sector, the extended use of heat from combined

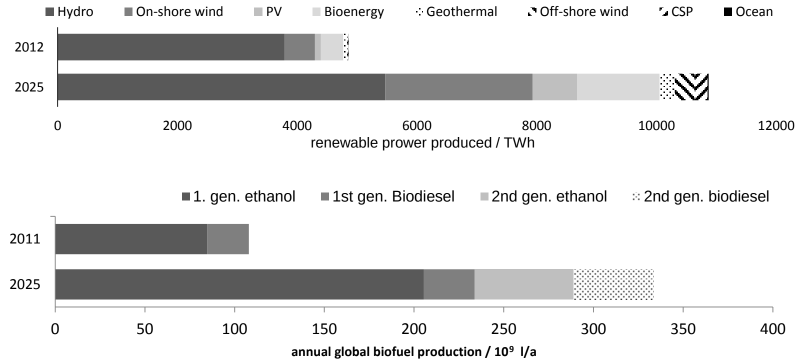

Figure 3: Global increase in renewable power and biofuel production to reach the 2 °C goal, data published by the IEA [3].

heat and power (CHP) production for heating and cooling is important [17]. The use of wood products can reduce the embedded energy of buildings and capture the CO_2 which is adsorbed during photosynthesis [18].

Rapidly growing populations and increasing life standards will result in a higher energy demand as shown in figure 4. The transition of the global energy system goes hand-in-hand with sustainable development (SD) and a safe and sustainable energy pathway is essential for SD [19]. SD is often defined by its three pillars of economic, social, and environmental considerations [20]. Due to its importance for RE and the transition of the energy system, the relationship between SD and RE has been described as [1, p. 710]:

> "The relationship between RE and SD can be viewed as a hierarchy of goals and constraints that involve both global and regional or local considerations. Though the exact contribution of RE to SD has to be evaluated in a country specific context, RE offers the opportunity to contribute to a number of important SD goals: (1) social and economic development; (2) energy access; (3) energy security; (4) climate change mitigation and the reduction

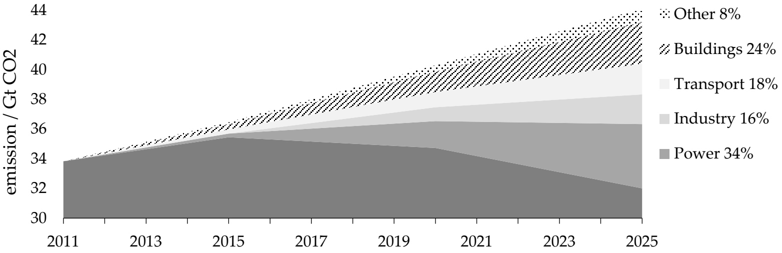

Figure 4: Contribution from all sectors to GHG emission savings to limit the average global temperature increase to 2 °C, data published by the IEA [3].

> of environmental and health impacts. The mitigation of dangerous anthropogenic climate change is seen as one strong driving force behind the increased use of RE worldwide."

RE: think global, act local.

This quote demonstrates the complexity of renewable energy development. To minimize global warming local and regional efforts have to be carried out as a tool for climate change mitigation. In the following, we will zoom into the study region by taking a look at the European strategy, the *Energiewende* (which already has become an international term, German for the transition of the ES) in Germany, and the local structure in the study region Schleswig-Holstein. It will be shown, that an integration of the local biogas sector into the existing energy system by dynamic biogas upgrading will contribute to sustainable development.

2.1.2 *RE in the European Union*

To fulfill this goal, the European Union (EU) started several initiatives to reduce GHG emissions, setting targets for RE production and binding targets to reduce CO_2 emissions from cars [21]. Here, the target for RE production is of special interest. The EU set the goal of 20 % (27 %) renewable energy production in the year 2020 (2030). Following the pathway set by the current polices, 24.4 % will be reached in 2030. Unfortunately, this goal is not obligatory for the member states [22].

During the recent decades, several countries in the EU started promotion strategies for renewable electricity. In 1979, Denmark was the first country supporting wind power and biogas with investment subsidies. It took ten years, until Germany followed this role model by paying investment subsidies as well as feed-in tariffs for wind and PV installations. In the following years, the United Kingdom (1990), Sweden (1991), Austria (1992) and other countries initiated similar programs [23].

Currently, different subsidy programs are existing in the EU member states, regulated by the directive 2009/28/EC. The goals for 2020 are summarized as 20/20/20: 20 % share of renewable energy (including 10 % biofuels in the transportation sector), 20 % renewable energy supply for heating and cooling in buildings and 20 % improvement in energy efficiency [24]. In 2011, the EU committed to the 2 °C goal by endorsing the international Copenhagen Agreement. In order to reach this goal, the GHG emissions in the EU are expected to be reduced by 80–95 % in 2050 [25]. Recently, the European Parliament set an important goal for the implementation of 2nd gen. biofuels: the share of 1st gen. biofuels is limited to 7 % of the energy consumption in the transportation sector, now. Thus, alternative biomass sources and technologies for next gen. biofuels have to be stimulated. 18 month after this directive enters into force, the member states have to set own national targets for the share of next gen. fuels [26].

20/20/20 is the EU energy policy for 2020

2.1.3 *The Situation in Germany*

It took until the 1990s, when the first studies for large scale renewable electricity generation were published. Before then, publications about RE were more of a descriptive charater [27] and RE production had been seen as a solution for decentralized, small-scale off-grid solutions [28]. The oil crises in 1973/1974 and 1979/1980 and the nuclear catastrophe in Chernobyl changed the public awareness of RE. Wind energy was boosted for the first time in the early 1990s

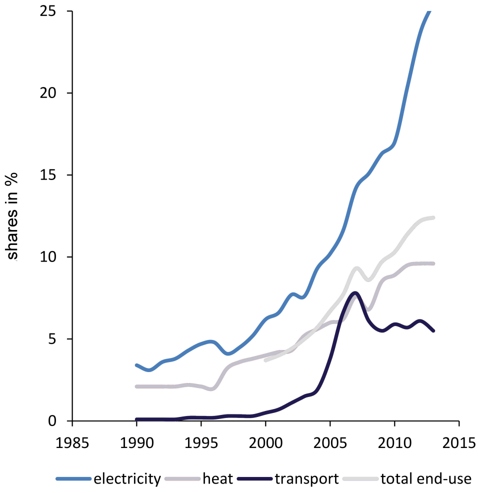

Figure 5: Development of RE in the different energy sectors since 1990 in Germany (data from [4]).

by the *Stromeinspeisungsgesetz* (StrEG, electricity feed-in law). From 2000 on, PV and biogas energy production broke through due to subsidies and investment programs mainly under the renewable energy act [29].

Figure 5 shows the development of RE in the electricity, heat, and transportation sectors from 1990. Today[2], 25 % renewable electricity is produced in Germany from RE sources, mainly wind (8.2 %), PV (5.2 %) and biogas (4.6 %). In the heat sector, 9.6 % was produced from RE, mainly from solid biofuels use in residential houses (4.6 %) and industry (1.4 %). However, just 0.9 % heat was produced from biogas. Upgraded Biogas contributed to the biofuels used in transportation only by 1.5 % [4]. The large share of RE in the German energy system caused several problems like surplus power production [30] and decreasing social acceptance (e. g. by noise, smell, asteteics etc.) [31]. By the high number of decentralized electricity production units from wind and solar, bottlenecks in the electrical grid are

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[2] 2013, newest data published by the Federal Ministry in 2015 [4].

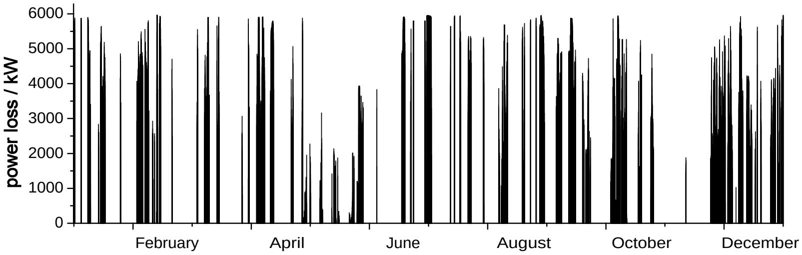


Figure 6: Yield loss (black area) in 2011 due to feed-in management of a wind farm with four turbines and a total capacity of 6 MW located near Lindewitt (countie of Schleswig-Flensburg, data provided by Dirkshof, Reußenköge).

caused, thus RE generation has to be curtailed by the grid provider to prevent failures. Since 2009, every RE generation unit $> 100\,\text{kW}$ has to be equipped with remote control systems for curtailment by the grid provider. Any power loss caused by this curtailment or feed-in management has to be paid by the grid provider, who caused the bottleneck [8].

Figure 6 shows the yield loss of a 6 MW on-shore windfarm in S-H caused by feed-in management in 2011. Here, the situation appears drastic, but in 2013, 555 GWh (increase of 44 % compared to 2012) of surplus production was reported to have resulted in $43.7 \cdot 10^6$ € reparation. This corresponds to 0.44 % of the annual renewable electricity production. The reasons are bottlenecks in the transportation grid, as well as in the distribution grid and 95 % taking place in the northern states [32].

Curtailment is increasing due to RE production

2.1.4 *Schleswig-Holstein*

The region of South Denmark and S-H (see fig. 7) can be seen as a model region for studying renewable energy systems. In both regions, even nowadays high shares of renewable energy from wind, solar, and biomass are implemented. In April 2015, S-H produced 66 % of its own electricity demand from renewable sources [33]. For

Figure 7: The state of Schleswig-Holstein and its counties surrounded by the North Sea and the Baltic Sea.

2025, the goal of S-H's government is to reach 300 % renewable electricity production [34].

300 % renewable electricity in S-H, by 2025!

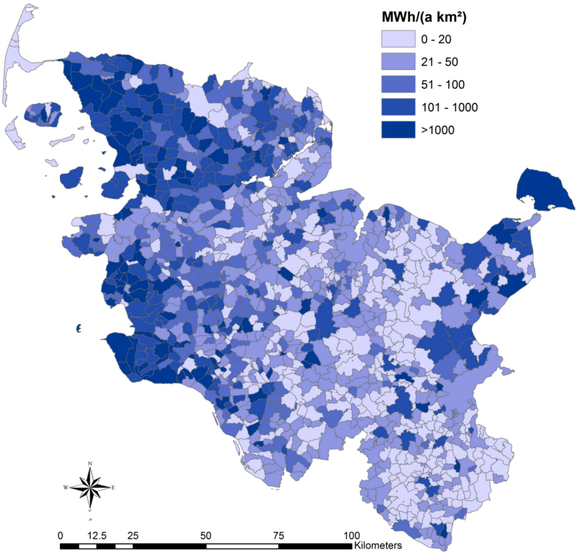
Today's energy system is built on a demand oriented, centralized supply structure. Nowadays, renewable electricity is produced decentralized from fluctuating sources like wind and solar [35]. Figure 8 shows the location of renewable electricity generation in S-H. Typically, the electrical grids in these regions are weak and may suffer with the export of such high amounts of electricity [36]. With this situation, RE generation units are curtailed by the grid operator to provide grid stability. In 2012, 346 GWh renewable electricity was lost by this feed-in management in S-H (see paper i.2 on page **??**). It can be seen, that the main production is located at the west coast and in the north next to the Danish border. Due to the ongoing re-powering of on-shore wind turbines, some studies assume up to 1900 h/a of surplus production in Northern Germany, causing 1.1–13 TWh (depending on the scenario assumed) of surplus production [37].

Currently, over 700 farm-scale biogas plants are operating in S-H, shown in figure 8(b). The electricity production from wind and PV is overlapping with a high biogas plant density, i. e. biogas is often available next to fluctuating RE production. Additionally, a well developed CNG grid exists in S-H (not shown here). It is established by law, that any biogas plant has to be connected to the CNG grid up to 10 km, if it is requested by the plant owner and no technical obstacles are present [38].

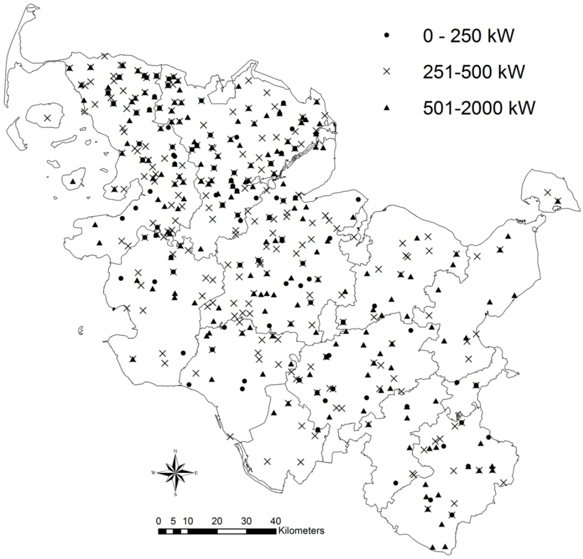
In paper i and i.2 presented in chapter **??** on page ?? and chapter **??** on page ??, the ES in this region is described in detail.

2.2 ELECTRICITY PRODUCTION IN RENEWABLE ENERGY SYSTEMS

The transition to an energy system with high shares of fluctuating renewable energy production requires energy storage options since RE sources are not static: The production of heat and electricity from solar radiation follows a daily profile depending on the height of the sun above the horizon. Wind follows a seasonal profile with higher wind speeds in the winter time [39]. Most energy crops can just be



(a) Electricity production density from wind an PV.



(b) Location of all biogas plants.

Figure 8: Renewable energy production from wind, biogas and PV in S-H.

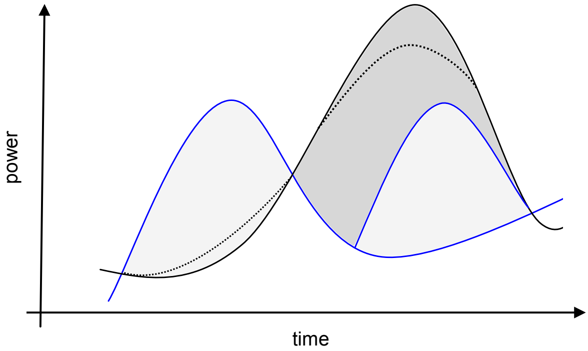


Figure 9: Schematic possibilities for load dispatching in ES with high share of renewable energies [5]. The blue curve is the power output of RE, the black curve is the grid load. RE storage are charged and discharges (light gray area), additional production management (dark gray) and peak shaving/demand side management (dashed line) are applied to secure grid stability.

harvested once a year and have to be stored during the whole year. For example, crop biomass is conserved by lactic acid fermentation resulting in silage [40]. In contrast, the energy demanded by the consumer follows strict weekly and daily profiles.

Integration of RE is needed

The task to be solved for the transition of conventional energy systems to 100 % renewable is to fit the energy output to the energy demand, whether if it is electricity, heat, or transport fuel. All three kinds of energy (electricity, heat, chemical energy/fuels) are in close conjunction with each other. Anaerobic digestion is a great example for this synthesis: crop biomass (e. g. maize) harvested once a year is converted by AD to a gaseous fuel and utilized in CHP systems. The electricity is fed to the grid and the heat is fed to district heating network or other applications. If no heating network exists, the heat produced during CHP generation might be lost. Figure 9 shows the possibilities to fit the production and demand of electricity to secure grid stability. Storage of RE can be used to shift production from periods of low load and high production to periods of low production and high load (gray area). Demand side management can be used for peak shaving, i. e. to reduce the maximum load. Thus, the capacity of the whole system can be reduced. The lag of energy has to be provided by controllable production processes, e. g. biomass-fired CHP systems [41].

A wide range of technologies currently exist and/or are in development for smoothing the transient energy output from renewable energy systems by production and demand side management and to improve energy efficiency, as well as sensitizing initiatives to involve the end user into energy savings [42]. The smart grid technology, where producers, consumers, and grid providers are connected to each other in an intelligent way, is a great example of how to integrate RE [5]. In this context, the smart home and smart metering concepts have to be mentioned, since they are the core elements of future RES enabling the participation of the consumer/generation side [43]. Future RES will contain several of such solutions in combination, depending on the existing infrastructures and the renewable energy sources available. Focusing on Schleswig-Holstein, the main renewable energy sources are energy crops currently used for CHP production from anaerobically derived biogas, wind, and solar radiation. The main infrastructure consists of an electrical grid, which once was built to supply the sparsely populated region with energy and a well extended natural gas grid.

A wide range of technologies are available for the storage of energy. The systems can be classified by the form of energy stored [44]:

- mechanical, e. g. pumped hydro power, flywheels or compressed air energy storage systems,
- electrochemical , e. g. batteries or flow batteries,
- chemical, e. g. hydrogen, SNG or DME,
- electromagnetic, e. g. supercapacitors ,
- thermal energy storage, i. e. as sensitive or latent heat.

These energy systems are highly different in their characteristics. Response time, rated power, storage capacity, storage time, energy density, efficiency, and the form of the released energy need to fit to the requirements of the energy systems where they are installed. For example, flywheels can only be used to store a very limited amount of electricity over short periods due to low energy density and high self-discharging rates at minimum 20 %/h [45]. By flywheels, it is possible to provide electricity to the grid within seconds to balance stochastic wind and load variations and to improve power quality [46]. Obviously, such a system has its limitations when it comes to long term storage, energy transportation (e. g. from an remote site for RE generation to consumers), or application in the transportation sector.

Large-scale renewable energy generation often takes places in remote and sparsely populated areas, where wind farms and solar installations can be built [36]. The energy has be transported to industrial sites and cities, because the demand within those regions are often far below the production. Schleswig-Holstein is an example for such a situation. The county of North Frisia (see figure 7 on page 16) is producing more than 340 % renewable electricity even today [33]. The electricity produced has to be exported to the south of Germany.

Summing up, in Germany's ES, technology for seasonal storage (due to the seasonal wind speed profile) and energy transportation (due to the high RE capacity in the north) are needed. To reduce the capacity of the grid required to utilize 100 % of the generated electricity, the local utilization should be as high as possible. Beside electricity, there is a big demand for heat and fuels from RE as well. In the following section, the use of synthetic fuels and biofuels for renewable energy utilization, storage, and transportation will be discussed.

2.3 SYNTHETIC FUELS, BIOFUELS AND THEIR ROLE IN ELECTRICITY STORAGE

Since a significant amount of energy is consumed in the transport sector, the transition of the energy system requires alternative transport fuels and solutions for electricmobility (e-mobility will be not discussed here). Usually, biofuels are divided into first and second generation biofuels. Whereas first generation biofuels like bio-ethanol and bio-diesel are derived directly from oil seeds, wheat, sugar cane etc. by extraction or digestion, second generation biofuels are derived from ligno-cellulosic biomass by advanced processes like biochemical/hydrothermal processes, thermochemical gasification and synthesis. Often, first gen. biofuels have been discussed to have production issues, like competition for land and water used for food and fiber production, government subsidies to compete with petroleum products and widely varying GHG mitigation. Such problems limit the potential of first gen. biofuels. Second gen. biofuels are produced from non-food feedstocks like agricultural byproducts, residues, and waste [47]. A wide range of conversion technologies exist for the production of second gen. biofuels, e. g. gasification, (hydrothermal) liquefaction or pyrolysis. Fuels from algae often referred as third and fourth gen. biofuels [48], but will not be discussed in this thesis.

Syngas offers many possibilities

Once the feedstock is converted to synthesis gas (syngas, a mixture of H_2 and CO_2), it can be converted to a wide range of materials and products, since the use of syngas is well established in the chemical industry [49, p. 555ff]. Fuel production from syngas is well known since the 1920's. Fischer and Tropsch discovered the Fischer-Tropsch synthesis and within 10 years commercial plants were operating in Germany [50][3]. In 1902, P. Sabatier and J.-B. Senderens discovered the synthesis of methane by hydrogenation of carbon oxides [51], which was used in industrial application for the removal of CO in ammonia plants [52].

Such conversion routes can act as a link between renewable electricity production and transport fuels by utilizing renewable hydrogen. The CO needed to provide carbon component of the syngas can be derived from biomass or separated from air. Fuels derived by this route will be referred as next generation biofuels here.

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[3] At that time, the circumstances for commercialization have been special due to the horrible political situation in Germany.

2.3.1 *Hydrogen from Renewable Electricity*

In the context of energy storage, hydrogen is often discussed as the energy carrier of future energy systems [53, 54, 55]. Using electrolysis, renewable electricity can be utilized from the grid and converted to chemical energy in the form of H_2. Currently, three different technologies are mainly available for the electrolysis of water: alkaline electrolysis (with a liquid electrolyte), polymer electrolyte membrane electrolysis (with an acidic ionomer electrolyte), and high-temperature steam electrolysis (with a solid oxide electrolyte). Polymer electrolyte and alkaline electrolysis are available at different commercial scales. Both struggle for implementation due to the use of noble metals or bad gas quality when working under partial load [56].

In this thesis, the research and development work in the field of electrolysis will not be reviewed in detail. However, there is a consent in literature that the investment and operation cost for H_2 from electrolysis will decrease during the next years, so, H_2 will become available for a certain price [57]. This thesis therefore assumes the availability of cheaper H_2 for use in the proposed system.

2.3.2 *Production of next Generation Biofuels utilizing renewable Hydrogen*

The implementation of H_2 into existing energy systems is limited by missing infrastructure for storage, transportation, and utilization (e. g. by fuel cells). Stored at a pressure of 20 MPa, the energy density is approximately seven times lower compared to CNG and 18 times to diesel respectively, making hydrogen an unattractive transport fuel [58].

Whereas electricity has to be accommodated by the grid intermediately [59] and hydrogen suffers due to low energy density, safety issues, and missing infrastructure, most biofuels fuels can be stored easily. As a drop-in fuel, they fit perfectly into the existing energy system [60]. Liquid biofuels can be stored and transported in tanks. The energy density of synthetic liquid biofuels, e. g. derived by Fischer-Tropsch-processes or hydrothermal liquefaction, is several ten-folds higher compared to batteries [61]. SNG can be stored and transported by natural gas facilities, i. e. CNG grids, tanks, and caverns. The storage capacity of SNG is the highest of all systems currently discussed [44]. In Germany, the storage potential is assumed to be 300 TWh by means of electricity stored in the gas [62].

SNG offers the highest storage capacity

First and second generation biofuels can be produced by a wide range of processes (e. g. AD, pyrolysis, gasification, hydrothermal liquefaction etc.) from a wide range of plant based materials (e. g. manure, energy crops, wood, municipal solid waste). Even if biofuels can overcome the disadvantages of first gen. biofuels mentioned above, they are often independent from (the intermediate output of) the electrical grid. By introducing renewable hydrogen into the synthesis of biofuels, a coupling of the bioenergy sector and the electricity sector in a sustainable way is gained. Here, biomass has to be seen as an energy carrier as well as a carbon carrier.

During the transformation of biomass to biofuels, a certain share of the carbon is released as CO_2. Looking at Fischer-Tropsch synthesis from biomass, only 23–41 % of the carbon is converted to the produced liquid fuel [63]:

$$CH_{1.6}O_{0.7}+aO_2 \rightarrow b\text{-}(CH_2)\text{-} + cCO_2+dH_2O.$$

In the case of AD, it is [64]:

$$\begin{aligned} C_nH_aO_b + (n - a/4 - b/2)\ H_2O \rightarrow \\ (n/2 - a/8 + b/a)\ CO_2 + (n/2 + a/8 - b/a)\, CH_4, \end{aligned} \quad (1)$$

if glucose is used a substrate, this results in 50 % carbon transferred to the product (CH_4). By utilizing the CO_2 released during this process, all carbon can be transferred to the product, multiplying the yield per area. Additionally, the product/energy carrier has a higher volumetric energy density compared to pure H_2. As pointed out in section 2.1.4, there are a large number of biogas plants available in Northern Germany, where curtailment of RE systems takes place. In the following chapter, possible contributions from the biogas sector in S-H for the implementation of large shares of fluctuating RE production are reviewed.

3

BIOGAS IN CONTEXT OF ACHIEVING 100 % RENEWABLE ENERGY

Today, biogas has to be seen mainly as a first gen. biofuel in Germany, since 77 % percent comes from energy crops which are grown only for energy production purposes (see section 3.1). Since the energetic use of biomass has the lowest value chain utilization [65], a novel role of the existing biogas plants according to the needs of future RES (e. g. storage and flexible production) would increase the value chain utilization of biomass.

Figure 10 summarizes the challenges of the bioenergy sector in context to a sustainable development towards 100 % RE:

FUEL VS. FOOD The use of energy crops which compete with food crops is not sustainable with respect to an increasing world population and high costs. However, a demand exists for transportation fuels and bioenergy has to deliver the carbon component at least (see section 2.3).

UTILIZATION OF WASTE STREAMS To overcome the food vs. fuel debate, potential waste streams from municipals and industry and byproducts from agro-industries have to be considered.

HEAT Today, heat from RE is just 9.5 % of the total heat consumed in Germany [4]. Heat from bioenergy processes can be used to increase this share.

SMART GRID INTERACTION Bioenergy processes has to be operated according to the grid load caused by fluctuation RE. Additionally, storage capacities can be provided, when the Sabatier

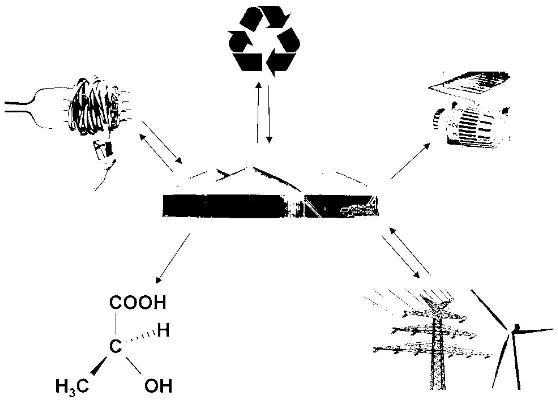

Figure 10: The boundary conditions for the development of AD: (i) the food vs. fuel discussion, (ii) waste streams as new substrates and fertilizers as byproducts, (iii) heat supply from biogas plants, (iv) the electrical grid with high shares of fluctuating RE and (v) the demand for new, green chemical products.

process is applied, as it will be demonstrated in the following chapters.

NEW BIOREFINERY PRODUCTS In future RES, the chemical industry has to be based on a sustainable C-source. Products derived from biorefinery processes can contribute to this development. In AD, the upgrading of the digestate to fertilizers is an important topic already.

In this chapter the opportunities for a novel role of biogas in Germany is discussed according to those challenges. The focus is on the grid interaction using flexible generation concepts.

3.1 STATUS QUO

On a global scale, biogas production is manly used in two ways: (i) in developing countries, biogas is produced in small, household-sized digesters to produce gas for lighting and cooking [66] and (ii) in

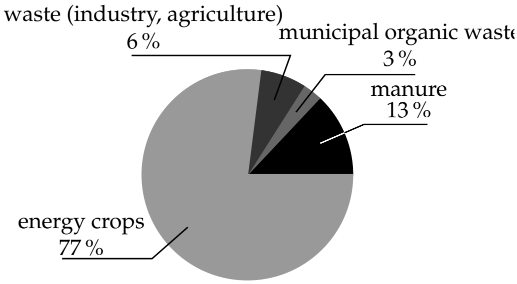

Figure 11: Substrates used for biogas production in Germany in 2014, energy based (data published by DBFZ) [6]

industrial countries to produce electricity and SNG from waste and energy crops [12]. While more than half a million domestic biogas plants are operating in Asia and Africa, the potential of large scale system utilizing manure, waste, and other organic sources is mainly unused. The reduction in GHG emission by utilizing such substrates is assumed to be more than $1.6 \cdot 10^{12}$ kg CO_2 equivalent per year [66].

Half of the electricity and SNG production from farm- and industrial-scale biogas plants takes place in Europe. In 2013, roughly 15 GW installed capacity were installed worldwide, with 8 GW installed in Europe [67]. Due to the EEG, Germany was the main producer of biogas with 3.5 GW installed capacity in 2013 and 3.7 GW forecasted in 2015 [68]. Due to the revision of the EEG in 2014, the fast increase during the recent years will not continue. The increase is now limited to 100 MW per year. However, the branch association *Fachverband Biogas* expects the increase to be even less due to missing subsidies [69].

The current biogas production in Germany is based mainly on energy crops. Figure 11 shows substrates used in German biogas plants, today. Since there are no subsidies for newly built biogas plants, future biogas plants in Germany have to utilize substrates, which are cheap or even free, i. e. organic waste from municipalities, industry, or agriculture. The already built biogas plants are using granted fed-in tariffs, but many are struggling with increased prices for substrates due to high competition in the market. Thus, new plant concepts have to be developed to make biogas attractive for projects without any subsidies. This can be new products from biorefinery concepts (e. g. H_2 or lactic acid), new reactor concepts to utilize unused substrates (e. g. dairy waste water), or to offer new grid services like storage of surplus electricity or control power.

3.2 THE CHANGING ROLE OF AD

Anaerobic digestion is a multi-purpose technology of biomass utilization and will have an important role in future energy systems [70]. The origin of the biogas technology is the treatment of waste water. In 1920 the first anaerobic digester was built by Karl Imhoff in Essen, Germany for the treatment of sewage sludge. The first agriculture biogas plant was built in 1948 in Odenwald, Germany for convenient power supply. Due to the low price of fossil fuels, early agriculture biogas plants experienced shut downs. With the oil crisis in the 1970's, AD increasingly became part of the scientific and industrial research. At the beginning the focus was on the processing on semi-liquid manure to derive a fertilizer with lower environmental impacts compared to the untreated manure [31]. From there on, AD became a multi-purpose technology for the following needs [65]:

- Environmental protection: reduced risk of diffuse N pollution like NO_3 leaching and increased NH_4 available for take up into plants and crops,
- Agriculture products: better control of ammonia emissions, easier management of P_2O_5/fiber separation and reduced applications of mineral fertilizer,
- Health improvement: bio-security from pathogen reduction,
- Waste reduction: reduction of disposed waste in landfills.

During the last two decades CHP generation from AD became an important part of the renewable energy sector. Due to high subsidies for biogas production from energy crops, the number of plants grew from 20 in 1990 to 1043 (2000), 4100 (2008) [31] to approx. 8000 in the year 2015. The installed electrical power is expected to be 4054 MW producing 27.88 TWh electricity per year. Just 156 plants currently produce upgraded biomethane [68][1]. With the EEG 2014, energy production from energy crops is not any longer substituted, thus the growth of the biogas sector will be limited in the future.

Approx. 8000 *biogas plants in Germany*

In the past, CHP production from AD was seen as a constant base load production without any flexibility. Since 2012, the flexible electricity production from biogas has been supported in Germany. It is expected that AD would offer a wide range of options for flexible production like substrate management, storage of intermediates, gas and heat storage, SNG production, or plant pooling [71].

3.3 THE BIOREFINERY CONCEPT FOR NEW SUBSTRATES AND PRODUCTS

The biorefinery concept aims to integrate biomass conversion systems in such a way that resource-efficiency, sustainability, and economical benefits are maximized. The term biorefinery correlates to fossil fuel refineries, where a wide range of products are produced from crude oil and thereby, waste streams are avoided [72]. Often, the only product of conventional biogas plants is biogas for CHP generation. Since the focus in such systems is mainly on the primary product, less attention is paid to the side streams. In potato processing for example, 80 % of the processed crop is non-starch [73]. In other processes, only up to 15 % is utilized in the main product stream, e. g. in the production of saccharose, cellulose, biogas, or biodiesel. By only focusing on the main product, different kind of side-products (often classified as waste), are more or less utilized, e. g. high quality glycerol, C-source for all kinds of fermentation processes, and fertilizers [74]. According to the needs of RES, the biorefinery concepts can be expanded to processes which use sustainable H_2.

Figure 12 shows the integration of the biomass, industry, and energy sector. AD can be used in such biorefinery schemes for the

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[1] Numbers are predicted for 2015

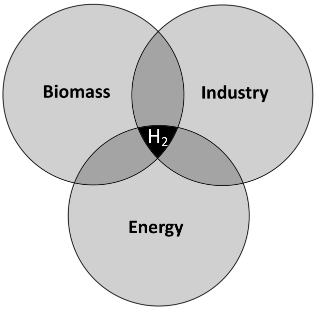

Figure 12: Integration of the biomass, energy, and industry sector: H_2 produced from fluctuating RE used in biorefineries to produce new products for the industry or energy sector (e. g. pharmaceuticals, biofuels etc.) can act as a link.

treatment of complex waste stream from industrial processes. By using renewable electricity for H_2 production, the energy sector is embedded in this scheme. Or, if cheap surplus electricity is available, bioenergy can be used to produce H_2 for energetic or industrial use. Many other combinations are possible. In the following, just a short description of a special type of reactor for AD and the production of bio-hydrogen is given.

3.3.1 *The Anaerobic Baffled Reactor*

Crop biomass is an expansive substrate

The high costs for energy crops are the main hindrance for biogas production. On an average 500 kW farm scale biogas plant using mainly maize silage, Balussou *et al.* calculated the substrate costs to be 7.5 ct/kWh out of 18.8 ct/kWh total production costs [75]. In practice, the substrate cost are even higher: The average production costs in Germany are 17 ct/kWh [76] and the average substrate costs are 42 ct per cubic meter CH_4 for the use of maize silage[2] [77]. With the high heating value of 10 kWh/m^3 and a degree of efficiency of 40 %, the substrate costs are calculated to be $> 60\,\%$! Thus, alternative

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[2] Maize silage is the cheapest energy crop available [77].

substrates and new products (including grid services, i. e. storage or provision of control power) have to be found to increase the cost efficiency of biogas plants. New substrates for the substitution of expensive energy crops can often be found in side-streams of large-scale agro-industry or other industrial sectors.

In AD, alternative substrates may require pretreatment to ensure the biodegradability of the feedstock, process adaption (e. g. different pumps, if feedstocks with a high fiber content are used) or even other reactor concepts than the conventional CSTR. Low-strength waste water is often treated in high rate anaerobic digesters like upflow anaerobic sludge blanket (UASBR) or biofilm reactors. These types of reactors are based on different hydraulic (HRT) and solid retention time distribution, thus a backing of the slow growing methongen bacteria is ensured.

The anaerobic baffled reactor (ABR) is known as a high rate anaerobic digester mainly used in developing countries as septic tank for on-site sanitation [78]. In the recent two decades many papers were published reporting the ABR as an excellent anaerobic digester for low- and high-strength waste water [79, 80, 81] and for the treatment of complex waste streams as well. Due to the construction of the ABR as a series of up-flow and down-flow sections, this reactor types enables an internal phase separation, i. e. different process parameters can be maintained in the different compartments of the reactor. This enables even hydrogen production at low residence times, reported by many research groups in the recent years [82, 83, 84]. Nowadays, the industrial applications are limited mainly to waste water treatment. [78].

However, the high rate anaerobic reactor concepts reach their limits, if the substrate contains high levels of fat or solids. Solids with a higher density than water will sink and accumulate in the first chamber. Whereas fat will build swimming layers [78]. In both cases the organic components are hard to be accessed by the microbial community.

Combination of reactor concepts to utilize other substrates

To overcome this disadvantages, several combinations had been tested. One possible combination never reported in the literature before is the combination of the CSTR and the ABR in series. First, the macromolecules are degraded in a hydrolysis stage at low pH carried out in a CSTR. Secondly, the ABR will be able to treat the high volume flow. The stirring of the CSTR will reduce the tendency of swimming layer formation and settling of solids. Details of this concept are investigated and presented in paper iv on page **??**.

3.3.2 *Production of Biohydrogen*

In recent years the possibility of hydrogen production by anaerobic digestion has been increasingly discussed in scientific literature [85]. This process, also known as *dark fermentation*, is possible due to the nature of the anaerobic degradation of polymers via four steps: hydrolysis, acidogenisis, acetogenesis and methanogenesis. By lowering the pH value below 6.0–6.5, the methanogenic bacteria can be inhibited, thus H_2 production via the hydrolysis and acidogenesis step can be released to the gas phase [84]. The H_2 is produced during the formation of the volatile fatty acids (VFA), for example acetic and butyric acid synthesis from glucose, as presented in equations (2) and (3) [86]:

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \tag{2}$$

$$C_6H_{12}O_6 \rightarrow CH_3\left(CH_2\right)_2COOH + 2CO_2 + 2H_2. \tag{3}$$

The production of biohydrogen is not of much interest with regards to flexible biogas production. But integrated into a biorefinery approach it can be applied for the production of other value-added compounds [87].

3.4 BIOGAS PLANT CONCEPTS FOR FLEXIBLE POWER PRODUCTION AND STORAGE

The idea of flexible production of biogas can be implemented in different ways. In the following, different ideas for a flexible power production by anaerobic digestion will be presented and evaluated.

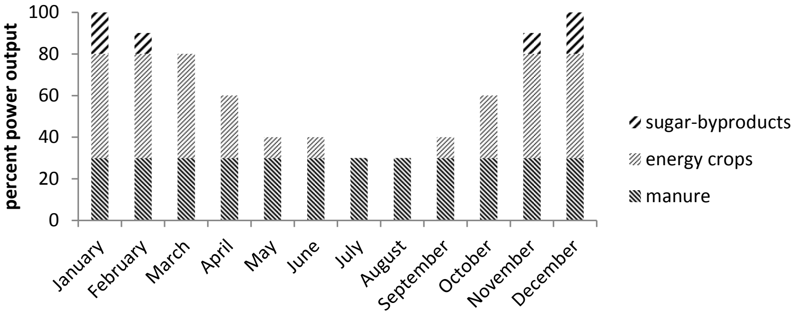

Figure 13: Flexible power production on an annual basis of a heat-led biogas plant in Denmark.

Reactor gas space storage option

In Germany, the common AD reactor is a CSTR equipped with a gas tight single or double membrane roof. This roof can be used to store the produced gas [88]. The capacity of this solution is limited to 4–6 h [89]. This storage capacity is already used during periods of feed-in management and by plants which are paid with a market and/or flexible premium.

Additional gas storage

As soon as the shut down time exceeds 4–6 h, additional gas storage capacity is needed. In principle, the storage of biogas is a mature technology, since it can be stored at low pressure in plastic bags sized up to 16, 000 m^3 or pressurized in steel tanks [89]. However, both options are not used in Germany at large scale. Some biogas plant manufacturers are offering storage systems based on the double membrane roof, e. g. FARMATIC Anlagenbau GmbH in Northern Germany.

Flexible Feeding

Due to the long residence time in AD (up to 100 d), a flexible biogas generation is difficult. Figure 13 shows flexible biogas production on an annual basis[3] by varying the amount and composition of the substrate. Since the feed-in tariffs for Danish biogas plants are lower compared to biogas plants in Germany, the plant is heat-led to run more economically. To provide the required heat in the winter, even expensive substrates like high-yielding industrial by-products (e. g. from sugar processing or fish oil etc.) can be fed for a short period.

A feeding strategy to meet the daily electricity demand is more difficult. In lab scale and simulation studies using the anaerobic digestion model 1 (ADM1), feeding strategies were investigated. The feeding strategy is strongly dependent on the substrates used due to their different kinetics of degradation. Thus, there is a dead time between changes in the feeding and changes in the gas production. However, some studies have reported feeding strategies resulting in demand oriented gas production using substrates with different degradation kinetics and without effecting the long term process stability [90]. Grim *et al.* simulated demand-oriented power production using a modified ADM1. An increased income from electricity production of 6–10 % seems to be possible under Swedish conditions, i. e. using the Swedish day ahead spot market [91]. No scientific literature is present which reports experiences with flexible feeding on full-scale. In general, experiments using full-scale plants are reported very sparely. The economic risk is high due to loss in income, when the stability of the reactor is not given. It has to be assumed, that flexible feeding leads to a decreased capacity factor, because the plant often is not operated at full load.

Liquid products storage

The AD process can be split up into four different steps as shown in figure 14. The idea is to store the liquid products from the hydrolysis and acidogenesis, i. e. manly VFA, and fed them into a discontinuous process according to the biogas demand. This split process is possible due to the different conditions of the microorganisms involved: while hydrolysis and acidogenesis are fast in kinetics with optimum conditions at low pH values, acetogenesis and methanogenesis are

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[3] Data from AL-2 Agro A/S, Mr. Preben Nissen

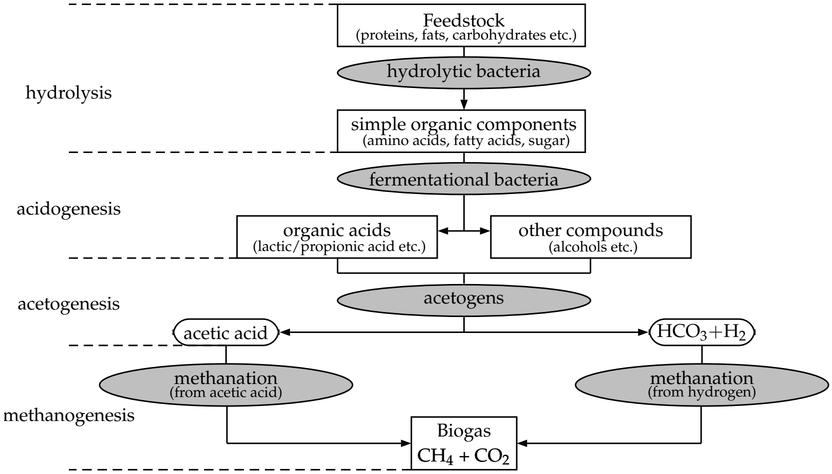


Figure 14: The anaerobic digestion of organic matter for biogas production can be devided into four steps (according to [40]).

relatively slow in kinetics with optimum conditions at elevated pH values [92].

To ensure a fast response when the liquid products are fed for demand oriented biogas production, a fixed bed reactor is chosen in such plant configurations. The solid fraction is removed and fed to a CSTR. Currently, such plant configurations are being investigated by different research groups and no full research papers are published yet, except for a review mentioning the plant configuration [89]. This concept could be of special interest for biorefinery concepts, when hydrogen is produced in the first stage and organic acids are recovered from the liquid fraction, the remaining liquid (weak in concentration) can be utilized in such a dynamic way using fixed bed reactors.

Combined biogas and hydrogen storage

To enable positive and negative control power from the biogas plants, the electrolyzer can be located next to the biogas plant. During periods of surplus electricity production (or whenever the electricity price drops under a certain level), the electrolyzer can be started to store the electricity as chemical energy in hydrogen. The hydrogen is pressurized (if necessary) and stored in tanks. The biogas CHP plant is expected to not be operating during those periods (or even earlier) as well. The biogas from the digester has to be stored as described above.

To utilize the stored energy, the hydrogen is mixed with the stored biogas and used in the CHP plant. Biogas-fed internal combustion engines are able to operate under a wide range of H_2 addition $> 30\,\%$ [93] resulting in high generating efficiency and low NO_x emissions [94]. Instead of biogas-fed CHP plants, fuel cells can be used for such a system as well [95]. The advantage of using it next to a biogas plant is the usage of the existing CHP plant, but comes with a low efficiency.

In-situ methanation

Hydrogen produced at the biogas plant site can be converted in-situ to CH_4 by the so called hydrogenotrophic methanogens [96], i. e. the conversion takes place directly in the anaerobic reactor. The reaction is equal to the Sabatier reaction and occur in AD as shown in figure 14:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O. \tag{4}$$

The advantage of CH_4 is its established infrastructure for storage, transport, and utilization as discussed before. In lab scale studies, methane concentrations up to 90 % were gained via the injection of hydrogen into a CSTR-type anaerobic reactor [97] and 94 % using an UASB-type reactor [98]. In large scale systems, such an injection might be very difficult. Full scale AD are not that well mixed as lab scale systems. The gas-liquid mass transfer is the limiting step [97], and it is difficult to ensure full conversion of the injected hydrogen.

To avoid limitations by the gas-liquid mass transfer, the hydrogen can be produced directly in the liquid phase by inserting electrodes into the anaerobic reactor. Recently published research studies indicate high CH_4 concentrations (98 %) [99]. Other studies are reporting increased COD removal by 50 % and increased methane production by 26 % during the co-digestion of switchgrass and cow manure [100]. Both studies were carried out at lab scale.

During in-situ upgrading on large scale and long term, fouling of the electrode surfaces and the hydrogen gas disperser (necessary to ensure small hydrogen bubbles by injection) will occur. If fouling problems are minimized or reduced to an acceptable level, in-situ upgrading might be a feasible technology to be combined with other separation technologies to produce SNG. This combination is neccessary, because the electrolyzer have to run in transient mode according to the fluctuating output of renewable energies. Thus, a static upgrading is not suitable.

Chemical methanation

Instead of in-situ upgrading, the produced biogas can be converted to SNG in chemical reactors using the Sabatier reaction:

$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O. \qquad (5)$$

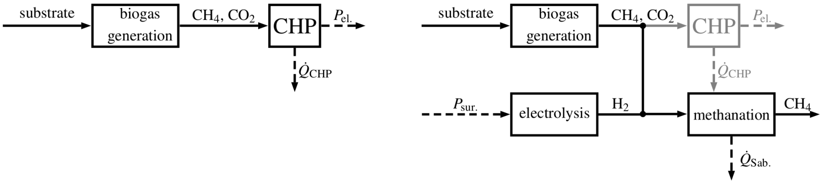
Instead of separating the CO_2 fraction, it is converted to CH_4 which is already present in the raw biogas.

The Sabatier reaction is usually catalyzed by Nickel and Ruthenium catalysts [52, 101]. The chemical equilibrium of this reaction is far on the right hand side [102, 103] and experimental investigations have shown that CO_2 and H_2 can be nearly completely converted with selectivity close to 100 % [104].

Combining a chemical reactor for CO_2 conversion together with the already existing CHP infrastructure, the upgrading process is thus dynamic with respect to two process states:

1. During periods of electricity demand the CHP generates electricity P_{CHP} and heat $\dot{Q}_{\text{CHP}}$ from the biogas resulting from the anaerobic digestion process (figure 15a).

2. During periods of excess wind energy, the surplus electricity from renewable energies $P_{\text{sur.}}$ is used for the production of hydrogen (via electrolysis). The hydrogen is then used for the conversion of the biogas CO_2 content to bio-SNG using the Sabatier process (figure 15b).



(a) (b)

Figure 15: Simplified process of dynamic biogas upgrading: (a) Production of heat and electricity by CHP plant during periods of electricity demand. (b) Production of bio-SNG during periods of excess electricity production.

The implementation of the dynamic biogas upgrading scheme would therefore provide opportunities for:

1. the use of the produced gas for bio-SNG production,
2. the exploitation of the exothermic reaction of the upgrading process for heat supply to connected consumers, and
3. switching between both process , where positive and negative control power is provided to the electrical power grid operator.

The technologies associated with the dynamic biogas upgrading are not novel. This configuration provides a completely new role of biogas and biomass in the current energy system: From a constant producer totally independent of any demand to a fully integrated link between energy production from fluctuating renewables and the energy demanded by the grid/consumer. The full idea of the dynamic biogas upgrading is described in paper i on page **??**.

Dry reforming using induction heating

Once a syngas is produced, a wide range of synthesis routes are available to produce different bulk chemicals like H_2 by the water gas shift reaction, Fischer-Tropsch fuels, methanol, SNG, or oxoaldehyde.

Today, these routes are using oil, coal, or natural gas as raw material converted into syngas by steam reforming [49, p. 552ff]. These routes can be built on biomass utilization as well using gasification processes [105]. However, such biofuel production systems are always stand alone systems and not integrated into the electrical grid. But there is one way to store electrical energy in syngas without using electrolysis: Pérez-Camacho *et al.* described a process for syngas production from biogas using dry-reforming in a catalytic reactor heated by induction. The dry reforming of methane

$$CH_4 + CO_2 \rightleftarrows 2CO + 2H_2 \qquad \Delta H^\circ = 247\,\mathrm{kJ/mol}, \tag{6}$$

is highly endothermic and takes place at temperatures up to 860 °C. The quick response of induction heated reactors enable the utilization of fluctuating renewable energy [106]. The idea is to use the derived syngas for dimethyl ether (DME) production[4], which is possible by the following reaction using CuO-ZnO-AL_2O_3 catalysts [107]:

$$3CO + 3H_2 \rightleftarrows CH_3OCH + CO_2 \qquad \Delta H^\circ = -246\,\mathrm{kJ/mol}. \tag{7}$$

It is obvious, that the energy stored by the dry reforming (6) is released during the DME synthesis (7). No storage is achieved, but the induction heating can cover the losses during the transformation into a liquid fuel.

Looking at the potential of such a process, a standard farm scale biogas plant with 500 kW installed electrical capacity, can utilize an average surplus power of 350 kW for induction heating, which is 1/8 of the rated power output of on average on-shore wind turbine currently installed in S-H [108].

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[4] Oral information from Dr. David Rooney.

4

BIOGAS UPGRADING USING THE SABATIER PROCESS

4.1 CONVENTIONAL BIOGAS UPGRADING

Biogas can be purified and used as transportation fuel or for injection into the CNG grid by various technologies. According to the IEA, currently 380 biogas upgrading plants are in operation. By far, most of these plants are installed in Germany (160 plants) with an average raw biogas input of $1155\,\mathrm{m}^3/\mathrm{h}$ set into operation between 2008 and 2014. Further 52 biogas upgrading plants are under operation in Sweden and 50 in the USA [109]. The investment cost is strongly dependent on the capacity of the plant. The smallest size in Germany have production capacities of $250\,\mathrm{m}^3/\mathrm{h}$ [109], which is also the lowest size costs are reviewed for [110].

Conventional biogas upgrading technologies are derived from conventional gas separation. The biogas CO_2 fraction can be removed by processes like membrane separation, pressure swing absorption, water scrubbing, or other chemical absorption methods [111].

According to the plant size necessary for economic feasibility and the technologies used, conventional biogas upgrading comes with major disadvantages:

1. Big biogas plants need a huge substrate flow. Often, energy crops are necessary to provide such huge material flows. The use of energy crops comes with several disadvantages as described in section 2.3.

2. None of the conventional biogas upgrading technologies are linked to the electrical grid, i. e. the operation of such systems does not provide any advantages for the integration of RE.
3. Due to the methane slip of these technologies (i. e. methane, which is release to the atmosphere with the separated CO_2), the sustainability can be decreased strongly [112].

4.2 METHANATION OF CO_2—THE SABATIER PROCESS

4.2.1 *Introduction*

The methanation of carbon oxides, according to its discoverer also known as the Sabatier process, is available in nearly every ammonia plant since the 1960s to remove trace substances of carbon oxides in the feed gas [52]. The first and only commercial plant for SNG production from coal was set to operation in 1984 producing up to $4.81 \cdot 10^6\,\mathrm{m}^3/\mathrm{d}$ [113]. Since 2009, it is proposed as a process for storage and transportation of renewable hydrogen [114].

4.2.2 *Catalysts for Methanation of CO_2*

Due to their extensive use in ammonia plants, methanation catalyst are commercially available and have been studied extensively. Nickel and Ruthenium catalysts show the best activity and selectivity. Iron catalysts have also been studied, but due to their tendency to build C–C bounds, their specificity is worse. Whereas the activity of Ruthenium is higher compared to Ni, the price for Ruthenium is much higher as well. For most applications Ni catalysts are sufficient, but Ru catalysts found some limited special applications, e. g. when CO concentrations have to be limited to < 1 ppm [52]. Other catalytic systems have been studied as well, e. g. Pt or Rh based. Various oxides have been studied as support, including SiO_2, TiO_2, Al_2O_3 and more [115].

Ni catalysts are used in standard applications, when carbon deposition can be avoided and thermal stability is given. To increase the resistance against carbon deposition, Ni catalysts are promoted with ceric oxide (CeO_2) [116]. To avoid a difficult process setup, a usable methanation catalyst has to be reduced at low temperature (typically approx. 300 °C) and should have a long life use (8–10 years, depending on feed-gas poisoning) [52]. Summing up, Ni catalysts are suitable for the methanation of biogas at low temperature, but the sulfur content of the feed gas has to be removed and the pressure has to be increased to avoid deactivation.

Deactivation of Catalyst during Methantion of CO_2

In general there are six different mechanisms for catalyst deactivation reported in literature [117]:

1. poisoning,
2. fouling,
3. thermal degradation,
4. vapor compound formation accompanied by transport,
5. vapor-solid and/or solid-solid reactions and
6. attrition/crushing.

In the methanation processes, only the first two mechanisms are considered to appear, because of the low reaction temperature. Poisoning could be caused by trace substances like H_2S, whereas fouling is caused by carbon decomposition on the catalyst particles.

CARBON DECOMPOSITION Carbon decomposition on Ni catalyst used in methanation or steam reforming takes place on the Ni surface or in the pore mouths. In the first case the active catalyst side is blocked, in the second case deactivation is caused by physical breakdown of the catalyst. It was found that there are up to four different species of carbon which can be built [118]:

1. well-ordered graphitic deposits,
2. carbon whiskers,

3. non-orientated deposits and
4. various carbides.

The considered reactions for the production of carbon are [119]:

$$\begin{aligned} 2CO &\rightarrow CO_2 + C && (8) \\ CH_4 &\rightarrow 2H_2 + C && (9) \\ CO + H_2 &\rightarrow H_2O + C && (10) \\ CO_2 + 2H_2 &\rightarrow 2H_2O + C && (11) \end{aligned}$$

Reaction (8) is called Boudouard reaction and (9) is called methane thermolysis. These two reactions are considered to be the main source of carbon formation in methanation of CO_2 and reforming of methane at high temperatures [120]. Reaction (9) is not the main source of carbon during methanation of CO_2, due to its low equilibrium constant. The main source of carbon at the reaction temperature of 250 °C is reaction 8 [119].

Trimm reported the mechanism of carbon formation and decomposition on Ni-catalysts. No carbon is decomposed if the rate of gasification exceeds the rate of dissolution/decomposition [121]. This is the case for temperatures below 600 K. However, decomposition of carbon on Ni-catalysts in methanation of CO_2 is an often reported problem. This behavior is explained by interaction of the support with the metal crystallites [117] and can be minimized by the addition of CeO_2 [122].

POISONING As with most transition metals, Ni-catalyst are strongly poisoned by sulfur containing compounds. Even a few ppm can reduce the catalyst life time dramatic [123]. Less attention had been taken to investigating the influence of ammonia on methanation catalysts, but its well known that ammonia is a common poison for acid solids such as silica-alumina in cracking and hydrocracking reactions and on Ni-catalysts in hydrogenation reactions [117]. However, Effendi *et al.* found no effect of ammonia on the activity of Ni-catalysts in steam reforming of model biogas. The results had been announced to be published [124], but never had been published.

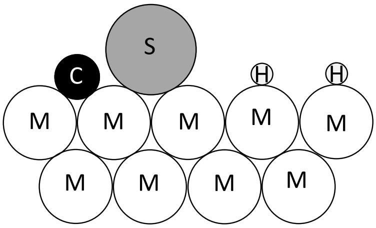

Figure 16: Conceptual model for deactivation of a catalyst by strong chemisorption of sulfur on a catalyst: active sites are blocked, thus the adsorpted and activated reactants could not react.

The mechanism of deactivation by poising had been described to be manifold (see fig. 16): (i) a strongly adsorbed atom blocks a few reactions sites, (ii) this atom modifies the electronically properties in its nearest neighbor atoms. (iii) Changes in the surface structure are possible and influence the activity in surface sensitive reactions. (iv) The adsorbed poison blocks access of absorbed reactants to each other and (v) and prevents or slows their surface diffusion [117].

On the other hand it is reported that small amounts of sulfur in the feed are necessary to maintain Ni-catalyst activity and life in steam reforming. This is explained by the way that the nucleation of carbon requires a larger number of active nickel surface sites than the main reactions [125].

4.2.3 *Kinetics*

Various studies have been published using different catalysts, experimental conditions, and reactors. In 1975, 14 kinetic models were reviewed including very simple zero-order reaction models and very complex LHHW models [126]. Earlier studies developing simple rate equations neglected rate limitations by diffusion and adsorption and more complex models were developed using so called intrinsic kinetics [127].

In 2009, the most detailed experimental approach on methanation kinetics on Ni catalysts was published within the *methane from wood* project, conducted by Kopyscinsky at the Pau-Scherrer-Institute, Switzerland. The LHHW rate equations developed showed excellent agreement with Kopyscinsky's experimental data and were used in the simulations presented in paper ii on page **??**. Kopyscinski assumed the methanation of CO_2 as a linear combination of the water gas shift reaction (WGS) and the methanation of CO. The hydrogenation of an absorbed carbon species was found to be the rate limiting step. The reaction rate is not inhibited by CH_4 and CO_2, which is of special interest for the methanation of biogas, since biogas contains an initial concentration of approx. 60 % CO_2. H_2O is inhibiting the reaction rate [128], thus it is often removed between different reactors in the process schemes shown in section 4.2.5.

The rate equations were used in the form of

$$r_{\mathrm{CO}} = k_{\mathrm{CO}} \cdot \frac{K_A p_{\mathrm{CO}}^{0.5} p_{\mathrm{H_2}}^{0.5}}{\left(1 + K_A p_{\mathrm{CO}} + K_B p_{\mathrm{H_2O}} p_{\mathrm{H_2}}^{-0.5}\right)^2} \tag{12}$$

$$r_{\mathrm{WGS}} = k_{\mathrm{WGS}} \cdot \frac{K_C p_{\mathrm{CO}} p_{\mathrm{H_2}}^{-0.5} p_{\mathrm{H_2O}} - p_{\mathrm{CO_2}} p_{\mathrm{H_2}}^{0.5} K_3^{-1}}{\left(1 + K_A p_{\mathrm{CO}} + K_B p_{\mathrm{H_2O}} p_{\mathrm{H_2}}^{-0.5}\right)^2}, \tag{13}$$

where r_{CO} and r_{WGS} are the reaction rates of the methanation of CO and WGS reactions, respectively, $K_{\mathrm{A,B,C}}$ are combinations of absorption constants of intermediates present in the reaction system, p_i is the partial pressures of component i and K_{WGS} is the equilibrium constant of the WGS reaction (15). p_i is calculated from the EOS and the absorption values. All other variables are a function of the temperature as shown in paper ii.

The reaction rate r can be expressed as

$$r = -\frac{\partial c}{\partial t},$$

thus equation (12) and (13) are coupled, temperature dependent, non-linear differential equations, which have to be solved during the process simulation. Using a tubular reactor model like Aspen plus' RPLUG model, r has to be expressed as function of the reactor length z by substitution of t:

$$\begin{aligned} z &= t \cdot c \\ &= t\frac{\dot{V}}{A}. \end{aligned}$$

Now, r is expressed by

$$r = -\frac{\partial c}{\partial\left(z \cdot \frac{A}{\dot{V}}\right)},$$

which makes the problem even more difficult from a numerical point of view, because the volume flow $\dot{V}$ is not constant over the reactor length z, due to changes in the number of moles by the methanation of CO_2 (5) and temperature changes. Aspen plus uses a one-dimensional reactor model including a grid. The rate equations are discretized and solved at every grid note. In the region of high gradients in concentration and temperature, the number of grid notes has to be increased by the user to ensure stable simulations.

4.2.4 *Thermodynamics of Methanation*

GENERAL REFLECTIONS Thermodynamic analysis helps to understand complex reaction systems such as methanation of CO_2. As it is well known, the methanation of CO_2 is a complex reaction network with numbers of side reactions [127]. Carbon deposition by reactions (9)–(11) is of peculiar interest to determine boundary of carbon formation in the reactor. The formation of coke drastically reduce the catalyst life. Side products like CO and C_2H_6 have to be avoided or minimized to a certain level given by the specifications for natural gas grids.

In the following, the basic equations needed for the calculation of chemical and phase equilibrium of the reaction system are described, but before some general thoughts about the sensitivity of the Sabatier reaction equilibrium can be made by using the Le Chatelier's principle. The methanation of CO_2 as shown in (5) is an exothermic gas-phase reaction with a change in volume. Due to its exothermic nature, low temperatures are favorable. The decrease in volume results in higher pressures to be favorable for high conversion. However, low temperatures result in slow kinetics and high pressures are expensive to realize due to enhanced safety issues and power consumption by compression. In paper ii, process simulation tools are used to address these issues and the simulation results confirm these reflections. However, the formation of coke in the process needs to be addressed, since coke is one of the main reasons for catalysts deactivation.

REACTION SYSTEM The thermodynamics of methanation is of peculiar interest to understand the behavior of reactions systems by calculating the chemical and phase equilibrium. The main number of research papers on this topic published recently investigate the methanation of CO. A fewer number of papers was published on the methanation of CO_2. However, the reaction system is the same for both processes and the following reactions are involved [102, 103]:

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \qquad \Delta H^\circ = 247\,\mathrm{kJ/mol} \tag{14}$$

$$CO_2 + H_2 \rightleftharpoons 2CO + H_2O \qquad \Delta H^\circ = 41\,\mathrm{kJ/mol} \tag{15}$$

$$2CH_4 + CO_2 \rightleftharpoons C_2H_6 + CO + H_2O \qquad \Delta H^\circ = 106\,\mathrm{kJ/mol} \tag{16}$$

$$2CH_4 + 2CO_2 \rightleftharpoons C_2H_4 + 2CO + 2H_2O \qquad \Delta H^\circ = 284\,\mathrm{kJ/mol} \tag{17}$$

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2 \qquad \Delta H^\circ = 136\,\mathrm{kJ/mol} \tag{18}$$

$$CO + 2H_2 \rightleftharpoons CH_3OH \qquad \Delta H^\circ = -90.6\,\mathrm{kJ/mol} \tag{19}$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \qquad \Delta H^\circ = -49.1\,\mathrm{kJ/mol} \tag{20}$$

$$CH_4 \rightleftharpoons C + 2H_2 \qquad \Delta H^\circ = 74.9\,\mathrm{kJ/mol} \tag{21}$$

$$2CO \rightleftharpoons C + CO_2 \qquad \Delta H^\circ = -172.4\,\mathrm{kJ/mol} \tag{22}$$

$$CO_2 + 2H_2 \rightleftharpoons C + H_2O \qquad \Delta H^\circ = -90\,\mathrm{kJ/mol} \tag{23}$$

$$H_2 + CO \rightleftharpoons H_2O + C \qquad \Delta H^\circ = -131.3\,\mathrm{kJ/mol} \tag{24}$$

$$CH_3OCH_3 \rightleftharpoons 3CO + 3H_2 \qquad \Delta H^\circ = 258.4\,\mathrm{kJ/mol} \tag{25}$$

$$3H_2O + CH_3OCH_3 \rightleftharpoons 2CO_2 + 6H_2 \qquad \Delta H^\circ = 136\,\mathrm{kJ/mol} \tag{26}$$

$$CH_3OCH_3 + H_2O \rightleftharpoons 2CO + 4H_2 \qquad \Delta H^\circ = 204.8\,\mathrm{kJ/mol} \tag{27}$$

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \qquad \Delta H^\circ = -37\,\mathrm{kJ/mol} \tag{28}$$

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \qquad \Delta H^\circ = -165\,\mathrm{kJ/mol} \tag{29}$$

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \qquad \Delta H^\circ = -206.2\,\mathrm{kJ/mol} \tag{30}$$

Nikoo and Amin performed a performed a thermodynamic equilibrium analysis of dry methane reforming (see eq. (14)) in view of solid carbon formation [103]. Aspen plus was used to solve the reaction system by direct minimization on the Gibbs free energy method. An important key for equilibrium analysis is to choose an appropriate property method, i. e. the equation of state (EOS). Nikoo and Amin used the Soave-Redlich-Kwong (SRK) model and found results in good agreement with experimental values. The equilibrium constants were calculated as well. For all reaction involving carbon decomposition, i. e. (21)–(24), low values for K were found. Thus, the decomposition of coke in the dry reforming of methane can be controlled by temperature, pressure and feed composition. However, the analysis was not done in the temperature range relevant for methanation of CO_2, i. e. from 200–400 °C, H_2/CO_2 ratios equal to 4 and pressure up to 20 bar.

Gao *et al.* analyzed the thermodynamics of the methanation of carbon oxides using the CHEMCAD software and compared the results to experimental values [102]. The equilibrium analysis were carried out with respect to temperature, pressure, ratio of CO_2/H_2 and the influence of trace substances in the feed gas such as H_2O, O_2, CH_4 and C_2H_4. Conversions of CO_2 near to one and high selectivity near to one were found at low temperature (200–250 °C) even at atmospheric pressure. Formation of CO by reaction (15) leads to higher yields off CO and methane production is decrease drastically. Methane fraction is close to zero over 600 °C. High carbon yields are found for $H_2/CO_2 < 4$. The suppression of carbon formation by stoichiometric feed compositions is explained by reaction (21); thus the hydrogenation of carbon is exothermic it takes place spontaneously. If no hydrogen for the hydrogenation of solid carbon bound to the catalyst surface is available accumulation will take place. The formation of solid carbon is well known as a problem especially on Ni-catalyst even at optimal conditions. This deviation from ideal behavior is discussed in section 4.2.2. The effect of H_2O on the methanation of CO_2 was studied over a range of 4–10 % at stoichiometric conditions. The conversion of CO_2 was just slightly decreased with no influence on CH_4 selectivity. The influence of CH_4 in the feed was not investigated. For the methanation of biogas, similar analyzes have to be done, extending the temperature range to 200 °C and taking the CH_4 content of the biogas into account.

BASE EQUATIONS The composition at chemical and phase equilibrium is determined by its search for the minimum of the Gibbs energy. This procedure is widely used in analysis of reaction system. This procedure has great advantages because only the Gibbs energies at the considered temperature and the elemental formula of the involved compounds are needed [129, p. 552].

The composition of a chemical system in equilibrium can be determined by the knowledge that the Gibbs energy is at its minimum. The Gibbs energy G of a gaseous mixture can be expressed as

$$G = \sum_i \mu_i n_i \tag{31}$$

at given a temperature and pressure. Here μ_i is the chemical potential of the component i and n is its amount of substance. The chemical potential can be express in terms of the fugacities f:

$$\mu_i = \mu_i^0 + RT \ln \left(\frac{f_i}{f_i^0} \right)^{\nu_i} . \tag{32}$$

By introducing (32) into (31), the Gibbs energy of a gaseous reaction system can be written as

$$G = \sum_i n_i \mu_i^0 + n_i RT \ln \left(\frac{f_i}{f_i^0} \right)^{\nu_i} .$$

Because pure carbon appears in the reaction system for methanation of CO_2, the phase equilibrium between the solid carbon phase and the gaseous phase has to be determined. Starting point for all phase equilibrium calculation is that the fugacities of each species in each phase, i. e. the fugacity of the solid and the gaseous phase are the same [130]:

$$\bar{f}_i^{\mathrm{G}}(T, P) = \bar{f}_i^{\mathrm{S}}(T, P), \tag{33}$$

where S and G indicate the solid and gaseous phases and $\bar{f}$ means the partial molar fugacity. For a pure solid phase it is $\bar{f}_i^{\mathrm{S}} = f^{\mathrm{S}}$ and $i = 1$ is chosen for the solid component. By introducing the definition of the activity coefficient γ_i into (33), the carbon mole fraction x_1 is introduced:

$$\bar{f}_1^{\mathrm{S}}(T, P) = x_1 \gamma_1(T, P) f_1^{\mathrm{G}}(T, P),$$

which can be solved for x_1, now:

$$x_1 = \frac{\bar{f}_1^{\mathrm{S}}(T, P)}{f_1^{\mathrm{G}}(T, P)} \cdot \gamma_1(T, P). \tag{34}$$

If the heat of fusion $\Delta_{\text{fus}}H(T)$ is available, the fugacity ratio can be calculated by

$$\ln \frac{\bar{f}_1^{\text{S}}(T,P)}{f_1^{\text{G}}(T,P)} = \\ -\frac{1}{RT}\left(\Delta_{\text{fus}}H(T)\left(1-\frac{T}{T_m}\right)+\int_{T_m}^{T}\Delta C_p \mathrm{d}T - T\int_{T_m}^{T}\frac{\Delta C_p}{T}\mathrm{d}T\right).$$

Using this expression in (34), leads to

$$\gamma_1 \ln x_1 = -\frac{\Delta_{\text{fus}}H(T)}{RT}\left(1-\frac{T}{T_m}\right)-\frac{1}{RT}\int_{T_m}^{T}\Delta C_p \mathrm{d}T+\frac{1}{R}\int_{T_m}^{T}\frac{\Delta C_p}{T}\mathrm{d}T. \tag{35}$$

The activity coefficient γ_1 and the fugacity f_i can then be calculated by Aspen plus using the SRK EOS. Thus, the amount of carbon built in a gaseous system in equilibrium with a solid carbon phase can be determined.

The equations shown above are implemented and solved in Aspen plus by the model RGibbs, which is able to solve simultaneous phase and chemical equilibria. As a theoretical model applied to solve the thermodynamic equilibrium as shown above, catalyst, reaction kinetics and transport processes are not taken into account.

4.2.5 *Reactors and process schemes*

Due to the Sabatier reaction being strongly exothermic, heat removal from the reaction mass is the main specification for the construction of methanation reactors to avoid temperature peaks in the catalytic bed. Furthermore, mass transfer and equilibrium limitations have to be avoided [131]. Therefore, different process schemes have been developed including adiabatic fixed bed reactors with intercooling [132], fixed bed isothermal reactors, fluidized-bed reactors [113], micro-channel reactors [133], membrane reactors [134] and slurry reactors [135].

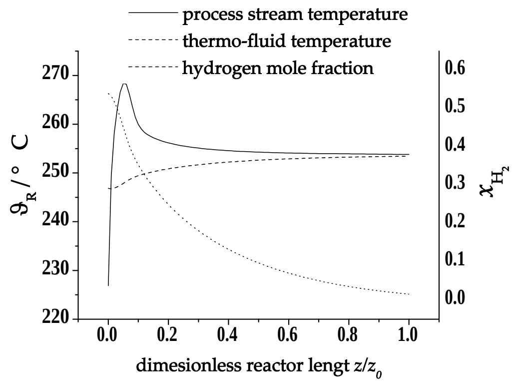

Figure 17: Typical longitudinal temperature and conversion profile in a catalytic multi-tubular reactor. Taken from paper ii.

FIXED-BED ADIABATIC REACTOR The chosen reactor configuration strongly depends on the context where it is supposed to be used. In large decentralized applications, cascades of adiabatic fixed bed reactors with inter-cooling and recycling are preferred [113]. Here, such simple reactors with a limited conversion can be used. To reach a high overall conversion, a complex process design can be chosen due to the economy of scale in such systems [136].

FIXED-BED MULTI-TUBULAR REACTOR To overcome the disadvantages of adiabatic reactors (thermal stress, limited conversion in a single reactor), mutli-tubular reactors are often used for highly exo- or endothermic reactions. On an industrial scale, reactors containing up to 20 000 pipes are used, e. g. in the low-pressure synthesis of methanol. The operational efforts for catalyst replacement is high compared to other reactor types. Typically, a longitudinal temperature profile is observed in tubular reactors including peak temperatures at the entrance of the reactor (see fig. 17). According to limited heat transfer in the catalytic bed, axial profiles have to be considered too [137, p. 356]. In the 1970's, the Linde AG (Germany) proposed using a complex multi-tubular, isothermal reactor for SNG production. Today, this reactor is used in methanol production [113].

Recently published simulation studies for the application of mutlitubular reactors for low-temperature methanation of coke oven gas (a small-scale application compared to coal gasification plants) focused successfully on the limitation of this peak temperature [138], as well as for the utilization of syngas derived from the gasification of biomass [131]. As well, multi-tubular reactors (or similar plate-reactors) have been used in the first bench-scale plants for the methanation of CO_2 separated from biogas [139].

FLUIDIZED BED REACTOR To overcome disadvantages of fixed-bed reactors in heat and mass transfer and the difficulties of catalyst removal, fluidized-bed reactors have found wide applications in industry. The fluidization causes a uniform temperature profile and a broad residence time distribution, thus the reactor volume has to be higher compared to fixed-bed reactors to reach equivalent conversions. On the other hand, the fluidization comes with different disadvantages, like difficulties in scaling-up and modelling [140].

Several bench-scale methanation reactors were built on this principle [113], but are under development and suitable only for large-scale applications [141].

MICRO-CHANNEL REACTOR Micro-channel reactors are structured, heterogeneous catalytic reactors. The catalyst is supported on a metallic support with high thermal conductivity. Channels for heat recovery can be integrated into the support resulting in excellent temperature control. Micro-channel reactors with Ni catalysts have been applied successfully for the methanation of syngas [142]. Due to the easy scale-up and scale-down, micro-channel reactors offer great advantages in decentralized applications [143].

SLURRY REACTORS The methanation catalyst can be suspended in heat transfer liquid [144] or in ionic liquid [145] to enhance heat transfer. Such slurry reactors are supposed to be a suitable solution for small scale applications, due to its dynamic stability and the robustness against fluctuations in the feed gas composition [146], but only lab scale experiments and no long term operation was done until now [144].

4.3 METHANATION OF BIOGAS

The *status quo* of the technologies needed for the conversion of CO_2 into CH_4 using renewable hydrogen is available and the framework for a large-scale implementation in Northern Germany is given. Different reactor concepts had been used successfully at industrial, pilot, or lab scales. Renewable electricity is available and there is a demand for storage technologies in the coming years. Biogas is currently available as a source of high concentrated CO_2. However, there are still some hindrances to overcome. The industrial scale for methanation plants so far is not suitable for methanation of biogas coming from an average biogas plant in Northern Germany. Further downscaling has to be done to fit the sizes required to match the biogas production and methanation. The complex process designs used at industrial scales are not suitable for small-scale applications. A simple and robust process is therefore needed. Electrolysis is needed to be available at a certain (low) price. This last key factor is often discussed in the context of hydrogen as an energy carrier of the future and due to development and mass production of electrolysis systems, the price is expected to decrease drastically during the coming decade [147].

Since 2013, the first biogas upgrading plant using the Sabatier process is operating in Germany. The plant was built by the company Etogas GmbH on behalf of the Audi AG. The nominal power input is rated to be 6.3 MW. As source of CO_2, the off-gas of a conventional biogas upgrading plant is used [148]. The full-scale plants were announced to be 20 MW. However, the cmpany later changed its strategy to offering turn-key plants in multiple of 1.2 MW using different CO_2 sources (raw biogas included) [148]. Our aim was to investigate the main differences between the processes as applied so far (as described above) and the process suitable for the methanation of biogas at farm-scale biogas plants which are:

SCALE The process has to fit the scale of farm-scale biogas plants, which is several magnitudes smaller compared to industrial applications as described above.

DYNAMICS The process has to be dynamic with respect to the intermediate output of renewable energy production from wind and solar, while conventional chemical processes run constantly.

BIOGAS CH_4 CONTENT The CH_4 content in raw biogas may influence equilibrium conversion and the kinetics of the Sabatier reaction, thus it is questionable if sufficient conversion can be obtained using a simple process design.

BIOGAS TRACE SUBSTANCES The trace substances in raw biogas, e. g. H_2S, NH_3, and siloxanes may deactivate or poison the catalyst. With exception of H_2S, these trace substances have not been investigated in previous studies.

BIOGAS PRODUCTION The biogas sector is facing high substrate prices and new reactor configurations are required for the utilization of alternative substrates. Unutilized streams are often available from food industry, but not presently utilized because of missing process technology, such as modified high rate anaerobic reactors.

The simulations and experiments conducted during this thesis addressed these topics.

4.3.1 *Study Simulation*

To demonstrate the feasible use of biogas for the Sabatier process, equilibrium calculations as well as full process simulations have been conducted. The aim of the equilibrium simulation was to find optimal process parameters and to investigate the influence of the biogas CH_4 fraction on the possible conversion from a theoretical point of view. The optimal choice of the process parameters is important since carbon occur as a side product in such gas reactions. Carbon is one of the main factors contributing to the deactivation of catalysts used as mentioned above. Such equilibrium calculations never have been reported for the methanation of biogas before. The results are presented in paper ii on page **??**. By optimal choice of temperature and pressure, high conversions were obtained and the formation of carbon suppressed.

The process scheme for the methanation at farm-scale biogas plants should be simple and connected to the (district) heating system which is supplied by the CHP plant. Figure 18 shows the flow sheet used for the full process simulation. It includes compression of the biogas, while the hydrogen used is already delivered pressurized by the electrolysis. A heat recycle is used to preheat the gas. The multi-tubular reactor is cooled by a thermo-oil, which transfers the heat to the heating system. To maximize the energy efficiency, another heat exchanger is used to cool the product gas as much as possible. Finally, ground heat exchangers are used to cool the gas down to ambient temperature. The throttle and the last cooler shown in this figure are just included to gain the product gas properties at STP. By using such a process, the dynamic biogas upgrading becomes feasible at a smaller scale.

The simulation showed high conversion up to 98 % and, even more importantly, good fuel properties of the produced SNG. By using such a process scheme, the heat produced by the exothermic reaction could be utilized at high temperature level directly from the reactor, and at low temperature level from the product gas. In this simulation, only heat utilization for district heating is assumed, but other heat integration schemes are possible as well, e. g. in future biorefinery concepts.

The multi-tubular catalytic reactor reactor used in the steady-state simulation was transferred to Aspen Dynamics to investigate the reactor start-up dynamics, since the proposed process has to run in dynamic operation according to the intermediate output from renewable energy production, i. e. wind and solar. To avoid carbon decomposition during hot stand-by in periods of direct biogas utilization by CHP, the reactor is assumed to be filled with hydrogen to flush out the carbon containing gases, i. e. CH_4 and CO_2. Similar to this shut-down procedure, where a lot of gas not suitable for SNG utilization is produced, a start-up procedure was simulated. In this start up procedure, the gas mixture of biogas and H_2 was supplied to the reactor filled with H_2 (hot stand-by).

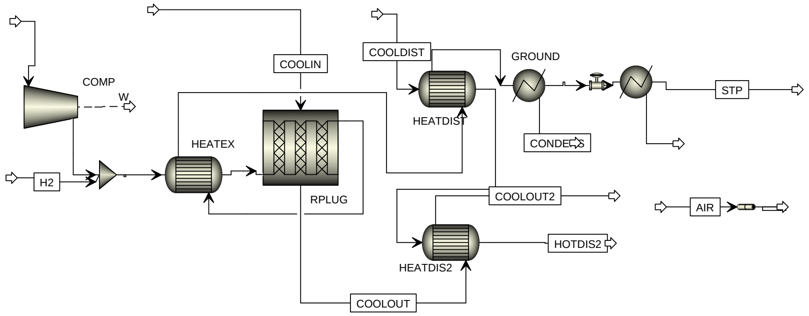

Figure 18: Aspen plus flow sheet for biogas upgrading using a single reactor configuration including heat recovery for district heating. The last heat exchanger and throttle valve before the `STP` stream and the `AIR` stream are needed for the simulation (see paper II).

4.3.2 *Experiments*

The experiments conducted during this thesis aimed to prove the simulation results, as well as to investigate the influence of biogas trace substances, and the possibilities for alternative substrate utilization using novel reactor concepts, i. e. the combination of the CSTR and ABR in series. Lab scale experiments were chosen to investigate the influence of NH_3, as one of the major trace substances in biogas, on the methanation catalyst. The experimental results indicated a slightly positive effect of ammonia on the deactivation, thus the process layout without any gas pretreatment (with exception of H_2S removal) is suitable with respect to the biogas NH_3 content.

A complex experimental setup was installed to investigate the biogas production from low-strength dairy waste water as an alternative substrate and to varify the simulation results (see figure 19). This setup contains two anaerobic digesters, gas storage and conditioning (drying, desulfurization, and compression), and a catalyst test plant.

One 1 m^3 CSTR and one 200 l ABR are available for biogas production. Since the installation of the ABR, several test trails have been performed using different substrates, including the usage of starch

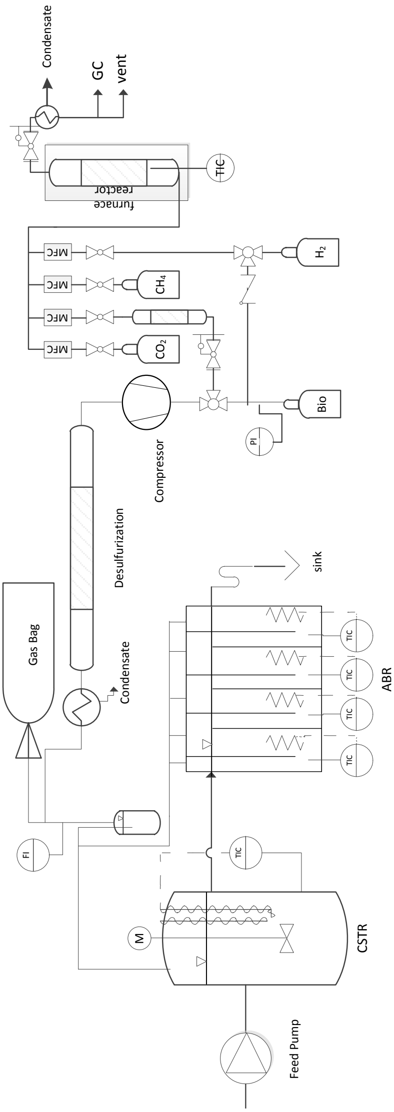

Figure 19: Test facility installed at the end of 2014 containing a two-phase anaerobic digestion system, gas conditioning and compression and a catalytic methanation reactor.

as a model substrate as presented in paper iii on page **??**. For the treatment of low-strength dairy waste water, the ABR was combined with a CSTR in series, this was since the ABR often struggled with process stability and solid accumulation during the test trails. This combination comes with several advantages, e. g. the handling of solids and fats in the CSTR and its role as a buffer tank in this combination. Using this combination, low strength dairy waste water was utilized successfully for biogas production aimed at the catalyst test plant. This combination of CSTR and ABR was not reported before this study.

The produced biogas was collected by a piping system connected to the CSTR and the ABR head gas space. The gas spaces of both reactors are slightly pressurized to approx. 20 mbar by dip tube as shown in figure 19. The gas flow is measured by a drum counter and stored in gas bags with a total volume of 180 l (or to atmosphere, if the gas storage is filled or not used). From here, it is compressed to 11 bar and transferred on demand to the biogas bottle using a membrane compressor. A filter for desulfurization, filled with doped charcoal, and a drying unit was installed between the gas bags and the compressor to avoid passing of the dew point while compression. Due to the limitation of the compressor's outlet pressure (11 bar), the addition of H_2 directly to the biogas bottle was provided, if experiments at higher pressures are to be conducted.

To prove the results of the equilibrium calculations, i. e. the influence of the process parameters, and to investigate the influence of biogas trace substances, a fully automated catalyst test plant was installed as shown in figure 19. This test facility was manufactured by AP Miniplant GmbH & Co. KG, Germany. It was designed not only according to the needs as stated above, but as well as a mult-purpose test plant enabling a wide range of process parameters. Additional to the pipe reactor shown in figure 19 the possibility for including a double-walled oil-cooled reactor was provided to demonstrate the simulation results from the multi-tubular reactor used in the simulations in later studies. A detailed piping and instrumentation diagram is shown on the following page.

Very important for the choice of this layout was the possibility of using synthetic and real biogas. The synthetic biogas is used mixed from gas bottles providing highly purified gases whereas the biogas compressed to the biogas bottle contains all trace substances. This plant was set into operation in the end of 2014, therefore just a few numbers of experiments have been carried out in this thesis period. A 2^k design[1] of experiments has been used to prove the simulation results of the equilibrium analysis (using synthetic biogas) and two long term trials have been conducted to demonstrate the suitability of biogas as a feed-gas for the Sabatier process (one reference using synthetic biogas and one trial using real biogas). The methodology of these experiments is shown in paper iv on page **??**. The wide range of the process parameter (pressure up to 20 bar, temperature up to 500 °C (pressureless up to 950 °C) enables the plant use for a wide range of processes, e. g. the synthesis of methanol and the dry-reforming of methane.

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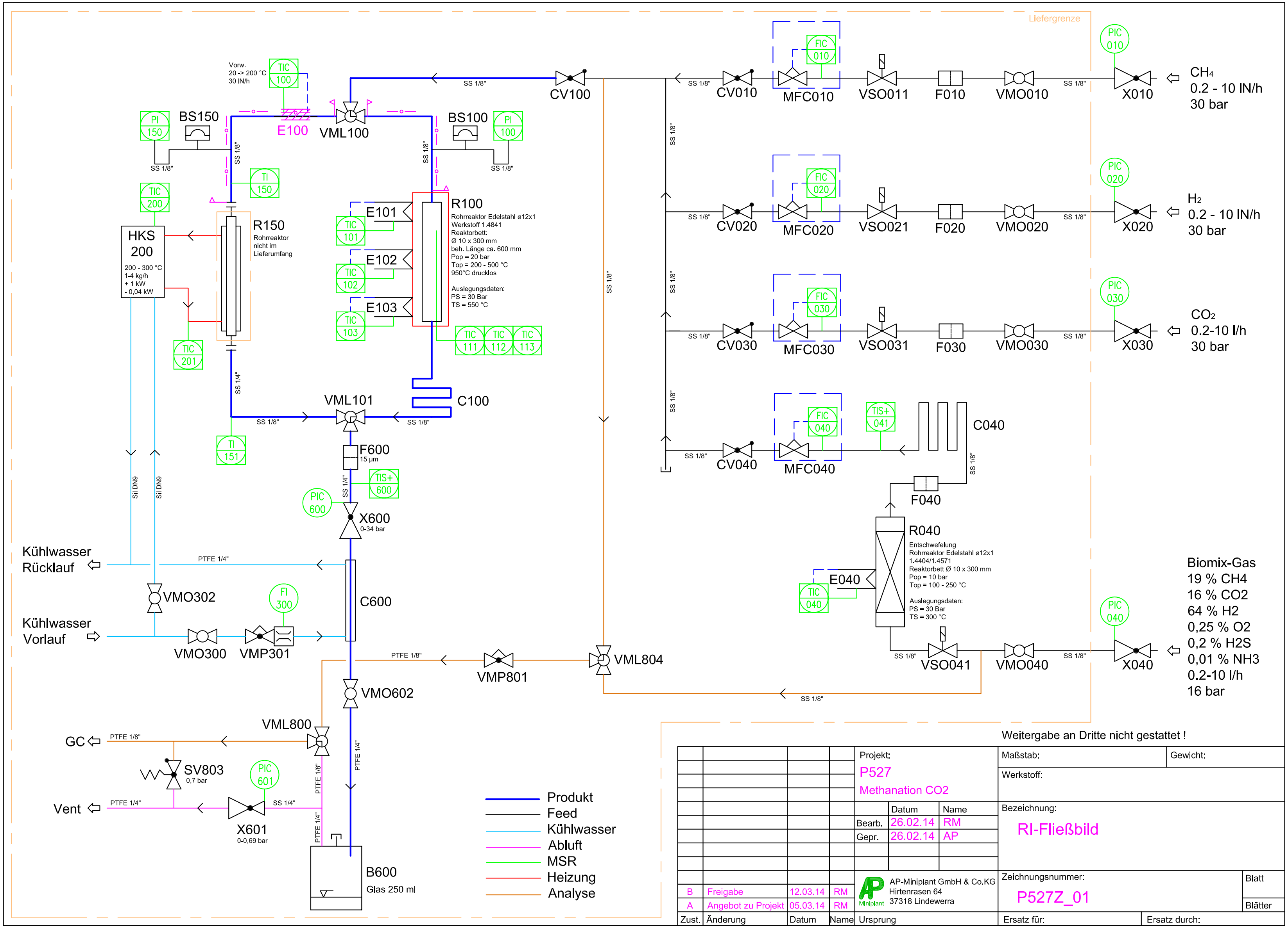
[1] $k = 4$—four variables: pressure, temperature, stoichiometric ratio, and retention time.



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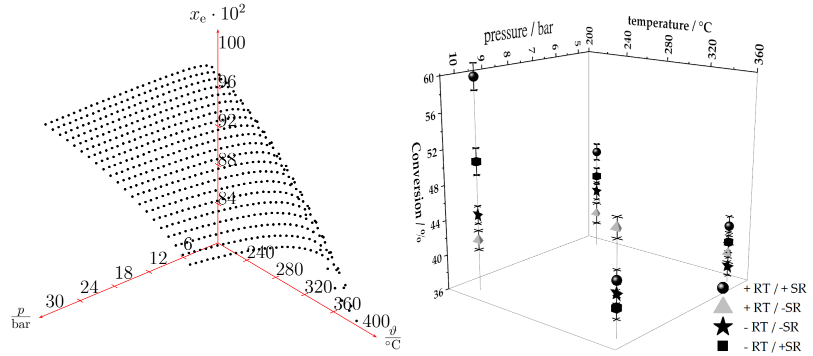
4.3.3 *Comparison of Experimental and Simulation Results*

Since no simulation of the influence of the biogas trace substance is possible, only a comparison of the trials using synthetic and real biogas is possible as shown in paper iv. According to the simulation results as shown in figure 20(a), the lower and upper temperature values were chosen to be 220 °C and 350 °C, since conversion < 90 % was found in this range. For pressure the range was chosen to be 6–10 bar. Elevated pressure is needed to avoid coke deposition and to decrease the extensive non-linear influence of temperature as show in figure 20(a). The upper bound was chosen according to the maximum outlet pressure of the biogas compressor in the experimental setup.

The stoichiometric ratio (SR) of H_2/CO_2 was shown to be an important variable to control the product gas fuel properties in paper ii, the limits chosen were 3.6 and 4. Since these experiments were carried out in a continuous pipe reactor with finite residence time (i. e. with equilibrium not obtained), the residence time (RT) was chosen as the fourth parameter with the lower and upper limit of 17 s and 28 s respectively.

Figure 19(b) shows the results of the experiments considering the influence of the process parameters: In general, the results from the simulation are confirmed (note: the equilibrium analysis was carried out over a wider range of pressure and temperature causing different scales in the graphs shown). With increasing pressure increasing conversion was observed, while decreasing conversion was found for increasing temperature. For low temperature and low pressure, relatively low conversion was found which could be explained by slow kinetics under these process conditions. The kinetic influence becomes visible when the experiments with changing RT but with a constant SR are compared (i. e. ▲/● for high SR and ■/★ for low SR). Higher RT caused higher conversion, indicating that the reaction did not reach equilibrium, i. e. steady state within the reaction time. The relatively low conversion of approximately 60 % indicates this as well. The chosen retention time of 17–28 s was relatively lower then the 164 s used in the simulation of the multi-tubular reactor. The result of the experiment conducted for high temperature, high



(a) (b)

Figure 20: Influence of process parameters: (a) some simulation indicating equilibrium conversion depending on temperature and pressure and (b) and some experimental results varying temperature, pressure, stoichiometric ratio (SR), and retention time (RT), where $+$ is the upper boundary (SR$=$ 4, RT$=$ 28 s) and $-$is the lower boundary (SR$=$ 3.6, RT$=$ 17 s) in the design of experiments. Note: the simulation/equilibrium analysis was carried out over a wider range of temperature and pressure so the scale of the x- and y-axis are different.

pressure, high retention time, and low SR has to be seen as an outlier, since no reasonable explanation can be found. As it is exacted by Le Chatelier's principle, an increase of the stoichiometric ratio should result in an increase of the conversion.

Summing up, excellent agreement of the simulation and experimental results could be obtained considering the limitation of the experiments by kinetic influences, i. e. the usage of a continuous reactor with finite reaction time.

Part II

PAPERS PRELUDE, PERSPECTIVE AND DISCUSSION

5

PAPERS PRELUDE

The aim of this thesis was to combine anaerobic digestion and the Sabatier process in a sustainable and integrated way, with respect to the existing energy system in Schleswig-Holstein. The work conducted during the Ph. D. period can be divided into three different topics as shown in figure 21:

CASESTUDY In a detailed feasibility study, the energy system in Schleswig-Holstein was analyzed and a methodology was developed to determine the potential of the dynamic biogas upgrading. The methodology and first results have been published in paper i presented in chapter **??** on page ??. Updated and more detailed results had been published in paper i.2[1] presented in chapter **??**.

SIMULATION Aspen plus and Aspen dynamics had been used to simulate the dynamic upgrading process. A simple single-reactor process design using a Langmuir-Hinshelwood-Hougen-Watson (LHHW) model has been developed and analyzed with respect to fuel properties of the produced SNG, process efficiency and start-up time. The results are published in paper ii presented in chapter **??**.

EXPERIMENTS Experiments covering AD and the Sabatier process have been performed during the Ph. D. period. Lab-scale experiments focusing at the influence of ammonia as a biogas

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[1] Conference proceedings of the 22nd European Biomass Conference and Exhibition 2014, Hamburg, Germany.

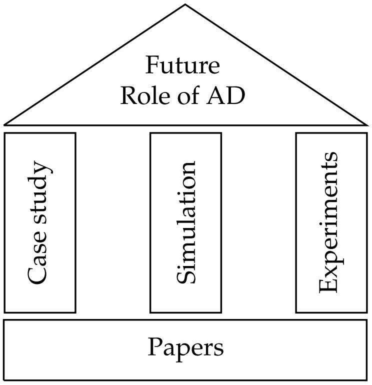

Figure 21: The vision of the future role of bioenergy presented in part i is founded on three pillars: a case study, process simulations, and experiments. The results are published in the papers presented in part **??**.

trace substances had been performed (chapter **??** on page ??) as well as AD processes for the production of H_2 and organic acids as biorefinery products (chapter **??** on page ??) and the treatment of unutilized waste streams. As a result of all experiments, a continuous biogas process was installed using dairy waste water including a fully automated catalyst test plant for future projects (chapter **??** on page ??).

All three pillars are drawing a consistent picture of AD as sustainable part of future RES, using the Sabatier process and the hydrogen generation by electrolysis as missing link. In the following, the papers of each pillar is summarized in a short chapter, and finally the conclusions and perspectives are given in chapter 9.

6

POTENTIAL IN THE STUDY REGION

6.1 PAPER I—DEVELOPMENT OF A METHODOLOGY AND FIRST ANALYSIS OF THE ENERGY SYSTEM IN SCHLESWIG-HOLSTEIN

TITLE Utilization of surplus electricity from wind power for dynamic biogas upgrading: Northern Germany case study

AUTHORS Lars Jürgensen, Ehiaze Augustine Ehimen, Jens Born, Jens Bo Holm-Nielsen

STATUS: Published in BIOMASS AND BIOENERGY, 66 (2014) 126-132

Abstract

The methanation of CO_2 has been increasingly discussed for the potential long term storage of electricity and for facilitating grid load management. Using the regions of northern Germany as a case study, the feasibility of CO_2 conversion from biogas plants and its integration in existing natural gas grid was examined in this study. Furthermore the material and energy fluxes of in the methanation process, were evaluated to provide expression for the quantities of excess electrical energy which could be potentially stored using the biogas integrated systems. The study results showed that with 480 biogas plants in the region would be able to utilize up to 0.7 TWh surplus electricity could be used to produce $100 \cdot 10^6\,m^3$ at standard temperature and pressure of upgraded methane per year.

6.2 PAPER I.2—UPDATED AND ENHANCED DATA

TITLE Use of the Sabatier Process for Dynamic Biogas Upgrading in Northern Germany

AUTHORS Lars Jürgensen, Ehiaze Augustine Ehimen, Jens Born, Jens Bo Holm-Nielsen

STATUS: Published in the conference proceedings of the 22nd European Biomass Conference and Exhibition 2014, Hamburg, Germany. 881-886.

Abstract

Approximately 8000 farm scale biogas plants are present in Germany which produce electricity (mainly using energy crops as substrates). The potential role of biogas plants in energy systems penetrated by high amounts of fluctuating renewable energy production is discussed in this paper. Today the production of renewable energy from wind, solar, and biomass in Northern Germany (i. e. the state of Schleswig-Holstein, S-H), leads to situations where production exceeds the demand and transport capacity. The analysis of the energy system in Schleswig-Holstein with respect to the sources of electricity, their distribution and the reasons for feed-in management was carried out to derive the potential for an energy storage scheme based on the use of biogas as a cheap and available carbon dioxide source for the production of substitute natural gas. It was found that there is a need for such a storage scheme in northernmost four counties of Germany. In these four counties, 529 mostly farm scaled biogas plants could potentially produce up to $100 \cdot 10^6\,\mathrm{m}^3/\mathrm{a}$ SNG using surplus electricity from wind and solar power generation systems available from 1600 h/a.

7

FLOWSHEET DEVELOPMENT OF THE DYNAMIC BIOGAS UPGRADING PROCESS

7.1 PAPER II—FINDING OPTIMAL PROCESS PARAMETER, EFFICIENCY AND FUEL PROPERTIES USING PROCESS SIMULATION

TITLE Dynamic Biogas Upgrading based on the Sabatier Process: Thermodynamic and Dynamic Process Simulation

AUTHORS Lars Jürgensen, Ehiaze Augustine Ehimen, Jens Born, Jens Bo Holm-Nielsen

STATUS Published in Bioresource Technology 178 (2015) 323–329

NOTA BENE Accidentally, this paper was marked as short communication by Elsevier. Instead, the short communication shown in chapter **??** on page ?? was published as full research paper. This mistake was caused during submission, reviewing, and publication at the same time in the same special issue.

Abstract

Using thermodynamic equilibrium analysis, kinetic reactor modeling and transient simulation, an integrated approach regarding the operation of a biogas based-Sabatier process was examined in this study. Furthermore the startup of a heterogeneous methanation reactor was investigated on a lab scale to proof simulation results. The simulation of the whole process using a kinetic reactor model

demonstrated the feasibility of the production of substitute natural gas at gas grid standards by a single reactor setup. The Wobbe index, CO_2 content and calorific value, which are key factors for the SNG production, were found to be controllable by the H_2/CO_2 ratio fed the methanation reactor. A H_2/CO_2 ratio between 3.45 and 3.7 was found to be optimal for producing product gas with high calorific value and high Wobbe index. Dynamic reactor simulation proofed, that the process can be started up within several minutes to facilitate surplus electricity from renewable energy systems.

8

EXPERIMENTS

8.1 SHORT COMMUNICATION—PROOFING AMMONIA AS A HARMLESS BIOGAS TRACE SUBSTANCE

TITLE Influence of trace substances on methanation catalysts used in dynamic biogas upgrading

AUTHORS Lars Jürgensen, Ehiaze Augustine Ehimen, Jens Born, Jens Bo Holm-Nielsen, David Rooney

STATUS Published in Bioresource Technology 178 (2015) 319-322

NOTA BENE Accidentally, this paper was pubslished as full research paper by Elsevier. Instead, the full research paper shown in chapter **??** on page ?? was published as full research paper. This mistake was caused during submission, reviewing, and publication at the same time in the same special issue.

Abstract

The aim of this work was to study the possible deactivation effects of biogas trace ammonia concentrations on methanation catalysts. It was found that small amounts of ammonia led to a slight decrease in the catalyst activity. A decrease in the catalyst deactivation by carbon formation was also observed, with ammonia absorbed on the active catalyst sites. This was via a suppression of the carbon formation and deposition on the catalyst, since it requires a higher number of active sites than for the methanation of carbon oxides. From the

paper findings, no special pretreatment for ammonia removal from the biogas fed to a methanation process is required.

8.2 PAPER III—A MULTI-PURPOSE REACTOR FOR NEW AD CONCEPTS

TITLE Hydrogen production using an anaerobic baffled reactor—mass balances for pathway analysis and gas composition profiles

AUTHORS Lars Jürgensen, Ehiaze Augustine Ehimen, Jens Born, Jens Bo Holm-Nielsen

STATUS Submitted to International Journal of Hydrogen Technology

Abstract

This study investigated pathways for anaerobic hydrogen production from biomass at low pH values, also known as dark fermentation. A 200 l bench scale anaerobic baffled reactor with four internal compartments was used for hydrogen production from wheat starch. The liquid fermentation products and hydrodynamic characteristics were analyzed using high performance liquid chromatography, tracer studies and gas analysis. A mean residence time of 29 h and a feed strength of 4 g_{COD}/l resulted in a total gas production of 230 l/d containing 42 % of hydrogen and 11 % of methane. The gas collected from the different compartments highly differed in composition showing a partial phase separation, with maximum H_2 concentrations of up to 60 % observed in the first compartment. 49 % and 44 % of the total H_2 produced were derived during the formation of acetic and butyric acid respectively. Just 8 % of the H_2 was produced during propionic acid synthesis. Concentrations up to 1 g/l lactic acid built by the bifidum pathway was also observed.

8.3 PAPER IV—LOCAL INTEGRATION OF INDUSTRY, BIOENERGY AND RE

TITLE Two-stage fermentation of low-strength dairy waste-water to produce biogas as CO_2 source for local utilization of renewable hydrogen by the Sabatier process

AUTHORS Lars Jürgensen, Ehiaze Augustine Ehimen, Jens Born, Jens Bo Holm-Nielsen

STATUS Submitted to Bioresource Technology

Abstract

Anaerobic digestion of low-strength dairy waste water has been used for the production of biogas as a source of high concentrated CO_2. By using hydrogen from renewable energy sources located next to the production side, the CO_2 fraction of the produced biogas is used to store surplus electricity by the Sabatier process, which converts the biogas CO_2 fraction to CH_4, i.e. synthetic natural gas. A two-phase pilot scale process had been established within 90 d using a 1 m^3 continuous stirred tank reactor and an 200 l anaerobic baffled reactor in series. The system was fed at constant retention time of 1.6 d and, according to a changing feed strength, various organic loading rates between 1.25–4.50 g/(l·d). The average COD removal was 82 % with a biogas yield of 0.26 l/g_{COD}. The use of the derived biogas for the Sabatier process to convert sustainable hydrogen into methane showed no disadvantages compered to synthetic gas mixtures.

9

PERSPECTIVES AND CONCLUSION

9.1 FUTURE RESEARCH PERSPECTIVES

In future RES, bioenergy will be needed for renewable fuels, storage, and balancing of electrical grids penetrated by high amounts of fluctuating electricity production from wind and solar and as a C-source for the chemical, pharmaceutical, and other high valued products industry. New substrates have to be utilized to overcome the disadvantages of energy crops for the production of first generation biofuels. The combination of the Sabatier process and the AD technologies offers possibilities to fulfill these requirements. Both technologies have been proven for many decades; the Sabatier process is used at an industrial scale, whereas AD is used at farm scale at thousands of of farms though Germany. Now, the Sabatier process has to be scaled down to fit the requirements of decentralized C-utilization from biomass and bio-waste. AD now faces the problem of high prices for energy crops and new plant concepts are required to enhance the value-adding of biomass conversion and bio-waste utilization.

The biorefinery approachis expected to be boosted in the mid-term future to satisfy the demand for new value-added products from biomass. Such biorefineries have been set into operation the last years, e. g. the Maabjerg biorefinery in Holstebro, DK. Here, AD is used as a problem solver for the potential nutrient overloading on the fields due to the heavy agro-industry in this region. Combined with an upcoming second generation ethanol plant utilizing the large amounts of straw in this region, such a system will demonstrate the sustainable combination of agro-industry, bioenergy and fuel production for the transportation sector. Even using such integrated approach, the fiber fraction from both processes (mainly containing lignin) is incinerated in the local CHP plant. Currently, a wide range of processes are under development to utilize such streams to produce high value chemicals and fuels. For example, hydrothermal liquefaction can be used for the conversion of the lignin remaining in the digestate of AD in biorefineries [149]. The nutrients leaving the processes can be recovered for fertilizer production, another possible and valuable product from biorefineries [65]. Furthermore, for the utilization of alternative substrates, new reactor and plant concepts are necessary. As it was demonstrated in this thesis, several smart possibilities exist for the utilization of locally available waste streams currently unused or even disposed expensively.

Beyond the biorefinery as described above, the future aim of bioenergy will be the balancing of the electrical grids, i. e. to operate according to the load from fluctuating RE. As described in section 3.4 on page 32, the concepts discussed are mainly based on the flexible use of the derived biogas in CHP systems. However, in future biorefineries, hydrogen will be used for different purposes, e. g. for biocrude upgrading from hydrothermal liquefaction [149]. In the next decades, more biorefinery concepts will come up including dynamic processes for the utilization of renewable energy. Since biomass is a highly concentrated carbon source, which is available in rural areas, just like the production of renewable energy, this synergy will be taken more into account.

In the next years and decades, synthesis routes like the Sabatier process, as well as Fischer-Tropsch, dimethyl ether and methanaol synthesis, etc. will be developed for decentralized application. All those processes need C as an feedstock. Since biomass is the only renewable highly concentrated C-source, these processes have to be developed in context of bioenergy, i. e. in small scale. Here, the economy of numbers might help to overcome the disadvantages of small scale systems, compared to large scale system, which are feasible due to the economy of scale [74].

We have seen the electrical grids and the homes getting smart, but often bioenergy is operating independent from the main renewable energy sources in the grid: wind and solar. In future RES, bioenergy has to be smart enough to take the best advantage of such systems. Today, bioenergy is mostly used to substitute fossil energy, e. g. by the production of transport fuels which can be blended into gasoline or as solid fuels to substitute coal in Danish CHP plants [150]. But future energy systems will are expected to look and operate differently. Electricity will become the main carrier of primary energy, because all renewable energies come as mechanical, thermal, or radiation energy which will be converted to electricity in the first place, with the exception of biomass [9]. Since the specific energy yield per area from PV and wind is several times higher compared to energy crops grown on the same area, it will not be used as a source of renewable energy in the first place [151]. In this context, energy production from biomass will just be an additional goal. The main goals will be the disposal of waste water, manure, and other waste streams and the application in biorefineries [60]. Here, hydrogen consuming processes like the Sabatier process will deliver additional advantages to operate such systems in context with the fluctuating primary energy sources. Since hydrogen is currently the only practical link between renewable energy and the electricity sector [9], the development of electrolysis and the development of hydrogen consuming decentralized biorefineries during the next decades is crucial to fitting the bioenergy sector into future RES.

Biomass will not be grown for energy purposes!

The experimental setup installed in the end of the thesis period can be used for long term experiments demonstrating biogas as a suitable feed-gas to synthesis processes. First experiments demonstrated the suitability of dairy waste water for biogas production and its use in the Sabatier process. To optimize the Sabatier process, new high active catalysts are needed, which cannot be developed at the campus of FHF, thus cooperation with other high qualified institutes will be fruitful. The expertise in the biogas production from unutilized substrates and the experimental setup implementing realistic conditions offers the possibility for testing new catalysts. New reactors can be tested using the thermo-oil provided in this experimental setup. The optimization of the catalyst used, the process parameter, and the reactor configuration will be crucial for the production of product gas at CNG standards.

9.2 CONCLUSIONS

Potential in Schleswig-Holstein

The integrated approach described in this thesis demonstrates that the dynamic biogas upgrading using alternative substrates and novel AD concepts to be a feasible process for the utilization of renewable hydrogen with a big potential in Schleswig-Holstein. A detailed methodology was developed based on materials and energy flows using the actual amount of biogas produced. In 2014, more than 750 biogas plants were operating in S-H corresponding to 320 MW capacity. Out of this, 529 plants are located in the counties North Frisia, Schleswig-Flensburg, Rendsburg-Eckernförde, and Ostholstein, where a major part of curtailment takes place[1] due to overloaded transformer and bottlenecks in the lines. Using the well-developed CNG grid in this region, up to $0.1 \cdot 10^9\,\mathrm{m}^3/\mathrm{a}$ SNG can be supplied to the natural grid by establishing the Sabatier process at every biogas plant. The establishing of the process at every plant might be unrealistic, but compared to $520 \cdot 10^6\,\mathrm{m}^3$ SNG produced by conventional biogas upgrading in Germany in 2014 [10] it demonstrates the huge potential of the proposed upgrading scheme. The former goal for 2020 had been the supply of $10^9\,\mathrm{m}^3/\mathrm{a}$ of SNG. Facing the huge deficit of the current production and this goal, it had been canceled by the revision of the EEG in 2014. Still, the goal of 10 % biofuels in transportation sector remains and SNG from the dynamic biogas upgrading process can contribute to that goal in a sustainable way.

Beside the large amount of SNG produced by the dynamic biogas upgrading, a huge amount of approx. 220 MW positive and 600 MW negative control power becomes available. This control power is feasible available on medium voltage grids where it is needed to avoid the previously mentioned reasons for^power curtailment. Thus, the Sabatier process offers more options than just energy storage, such as

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[1] Curtailment takes place in Dithmarschen and Steinburg as well, but was not taken into acount due to an existing H_2 infrastructure.

- conversion, storage, and transport of surplus electricity without long transport ways,
- provision of control power on medium voltage grids allowing a capacity reduction of the lines built in the near future, and
- allowing flexible electricity generation from biomass by the management of biogas utilization by CHP production or upgrading.

Power to gas processes like the Sabatier process have to become part of the mid-term national and European grid development plans taking the special situation in S-H and Denmark into account.

Process design for decentralized small-scale application

The large-scale industrial processes used for the Sabatier process are not suitable for decentralized application due to their complexity. The simple process layout focusing on a single-reactor technology was seen to work fine in simulation. The product gas properties are even suitable for gas injection into high heating value gas grids (H-grids). However, the gas composition does miss the specification for H-grids, which limits the total amount of other gases than CH_4 to 5 %. The specifications for L-grids are easily fulfilled. From the point of fulfilling the fuel properties (heating value and Wobbe-index), the specifications for H-grids should be changed. The limitation of the other gases than CH_4 has to be changed according to safety issues, e. g. a maximum H_2 concentration meet all safety issues.

The H_2:CO_2 ratio has been shown to be a key variable for the process control to maintain product gas properties. Previously studies always assumed stoichiometric H_2:CO_2. The use a sub-stoichiometric ratios might lead to enhanced carbon deposition on the catalyst (see section 4.2.4 on page 47). By thermodynamic equilibrium analysis, it was shown that C deposition can be suppressed at low temperature and enhanced pressure. This has to be verified in long term experiments. New catalysts might help to overcome the disadvantage of Ni catalyst in C deposition and low activity at low temperature. The online measurement of the feed and product gas composition to control the H_2:CO_2 ratio, might be an obstacle to overcome. Further simulation should concentrate on the accuracy of the measurement needed to ensure constant product quality.

The chosen process layout was able to utilize the heat generated in the exothermic reaction at high (i. e. $>$ 200 °C) and low (approx. 100 °C) temperature. The generated heat can be used for district heating, which is often necessary when the CHP unit is not working or other purposes even in high temperature applications. In future biorefinery concepts this will be of interest.

Biogas from renewable substrates as CO_2 source

The experiments performed in lab- and pilot-scale demonstrate the feasibility of the process. AD and the methanation of synthetic and real gas mixtures had been performed. The ABR was shown to be a suitable reactor for the utilization of unused biomass streams and even for the production of bio-hydrogen from starch containing waste water. Even if the production of bio-H_2 is not of interest for the dynamic biogas upgrading, it can be considered as an important part in biorefinery concepts in areas where no surplus electricity from the grid is available.

In combination with conventional CSTR reactors, the treatment of low-strength waste water becomes possible. In the 200 d lasting experiment, the shock loading resistance of such a system was demonstrated. The CSTR can act as buffer tank, hydrolysis stage, and solves the problem of swimming layers and settlement of solids in the ABR. This concept might be a role model for existing biogas plants suffering with high substrate prices. The upgrading of conventional biogas plants by an additional ABR can offer the possible use of alternative substrates and process stability and efficiency, enhancing the plant efficiency or leading to a reduction in the demand for energy crops as a co-substrates for the treatment of manure. Once again, AD is demonstrated as a multipurpose technology suitable for so much more than just energy crop utilization.

In lab-scale using synthetic gas mixtures, ammonia was shown to be a harmless biogas trace component. No previous studies had been carried out on the influence of ammonia on such systems. In pilot-scale experiments using real biogas, this result was verified. The use of real biogas derived by AD of dairy waste water cannot ensure that the biogas contains every possible trace component like they would appear when manure, maize silage, or deep-bedding material (e. g. used in cowsheds) is used. Since these compounds are difficult to detect (e. g. siloxanes), further experiments should try to analyze their amounts and influence on the methanation process.

With minor exceptions, the technical obstacles are clear and can be overcome during the next years. To put it in a nutshell, some more insecurities have to be overcome: policy is asked to develop a frame work to enable first demonstration plants. The economic feasibility depends on factors like the price, taxes, and allocation which has to be paid. Here, planning reliability is needed. In addition, the regulations for business cases and quality standards for the produced gas have to be clarified. Over the coming years, the course has to be set for the Sabatier process to become an important part of the future RES. Ideal candidate regions for the demonstration of this technology are the state of Schleswig-Holstein in Germany and West Denmark.

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FULL PUBLICATION LIST

PEER REVIEWED JOURNALS

1. Lars Jürgensen, Ehiaze Augustine Ehimen, Jens Born, Jens Bo Holm-Nielsen: *Utilization of surplus electricity from wind power for dynamic biogas upgrading: Northern Germany case study*, Biomass and Bioenergy (2014), 66 (2014) 126–132.
   `http://dx.doi.org/10.1016/j.biombioe.2014.02.032`

2. Jürgensen, Lars, et al. "Influence of trace substances on methanation catalysts used in dynamic biogas upgrading." Bioresource Technology (2014).
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3. Jürgensen, et al. *"Dynamic biogas upgrading based on the Sabatier process: Thermodynamic and dynamic process simulation".* Bioresource Technology (2014).
   `http://dx.doi.org/10.1016/j.biortech.2014.10.069`

4. Lars Jürgensen, Jens Born, Jens Bo Holm Nielsen, David Rooney: *Einfluss von Ammoniak als Biogasbestandteil auf Methanisierungskatalysatoren*. Chemie Ingenieur Technik, 2014, 86, No. 9, 1347–1365.
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5. Lars Jürgensen, Ehiaze Augustine Ehimen, Jens Born, Jens Bo Holm-Nielsen: *Hydrogen production using an anaerobic baffled reactor—mass balances for pathway analysis and gas composition profiles.*
   International Journal of Hydrogen Energy (2015).
   `http://dx.doi.org/10.1016/j.ijhydene.2015.07.068`

6. Lars Jürgensen, Ehiaze Augustine Ehimen, Jens Born, Jens Bo Holm-Nielsen: *Two-stage fermentation of low-strength diary waste-*

water to produce biogas as CO_2 source for local utilization of renewable hydrogen by the Sabatier process.
Submitted to Bioresource Technology

PAPER AND PROCEEDINGS

1. Lars Jürgensen, Ehiaze Augustine Ehimen, Jens Born, Jens Bo Holm-Nielsen: *Use Of The Sabatier Process For Dynamic Biogas Upgrading In Northern Germany*, 22nd European Biomass Conference and Exhibition, 881–886, ISBN: 978-88-89407-52-3, `http://dx.doi.org/10.5071/22ndEUBCE2014-3CO.3.5`.
2. Lars Jürgensen, Ehiaze A Ehimen , Jens Born, Jens Bo Holm-Nielsen, David Rooney: *Influence of trace substances on methanation catalysts in dynamic biogas upgrading,* Progress in Biogas III, September 10–12, 2014, Stuttgart.
3. Lars Jürgensen, Ehiaze A Ehimen , Jens Born, Jens Bo Holm-Nielsen: *Dynamic Process Simulation of Dynamic Biogas Upgrading using the Sabatier Process,* Progress in Biogas III, September 10–12, 2014, Stuttgart.

ORAL PRESENTATIONS AND POSTER

The presenter is marked by a star.

1. Presentation: L. Jürgensen*, N. Tröger, A. Kruse: *Hydrothermale Karbonisierung (HTC): Einfluss der Prozesstemperatur auf die Produkteigenschaften*. Jahrestreffen des ProcessNet-Fachausschusses Hochdruckverfahrenstechnik Fulda, 4.-5.März 2010.
2. A. Kruse*, L. Jürgensen, O. Sahin, K. Stelzel, N. Tröger, D. Wüst: *Hydrothermale Karbonisierung: Einfluss der verwendeten Biomassen auf die gebildeten Strukturen und der Verbleib von Heteroatomen.* 2. Fachtagung Hydrothermale Carbonisierung (HTC) Schweiz, Wädenswil, CH, 23.September 2011.

3. Presentation: Jens Born, Lars Jürgensen*: *Innovating Biogas Technology—Process Efficiency, Gas-Upgrading and Complementary to Fluctuating Renewable Energy Systems*, New Energy Husum 2012.
4. Presentation: Jens Born*, Lars Jürgensen: *Dynamic Biogas Upgrading as a novel tool for production and demand management in electricity production from biomass*, LSBEL-Biogas Konferenz, September 2013.
5. Presentation: Lars Jürgensen*, Jens Born: *Methanation for Dynamic Biogas Upgrading—Potentials in South Schleswig*, New Energy Husum 2014.
6. Presentation: Lars Jürgensen*, Ehiaze Augustine Ehimen, Jens Born, Jens Bo Holm-Nielsen: *Use Of The Sabatier Process For Dynamic Biogas Upgrading In Northern Germany*, 22nd European Biomass Conference and Exhibition 2014, Hamburg.
7. Poster: Lars Jürgensen, Ehiaze A Ehimen , Jens Born, Jens Bo Holm-Nielsen, David Rooney: *Influence of trace substances on methanation catalysts in dynamic biogas upgrading,* ProcessNet Jahrestagung, September 30–Oktober 2, Aachen.
8. Plenary presentation: Lars Jürgensen*, Ehiaze Augustine Ehimen, Jens Born, Jens Bo Holm-Nielsen: Dynamic Biogas Upgrading for local integration of waste water treatment, biomass, wind and solar. 23nd European Biomass Conference and Exhibition 2014, Vienna.