Life cycle assessment and modeling approaches as a combined evaluation tool for sustainable control strategies at biogas plants

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Abstract

Anaerobic digestion and biogas production can help to meet several targets concerning energy and environmental policy. However, biogas generation is a complex process where many challenges need to be tackled to achieve real sustainable operation. In this regard, better control, monitoring and optimization strategies need to be implemented. This thesis focuses on the combination of Life Cycle Assessment (LCA) and modelling approaches as a tool for a demand driven energy production at the biogas plants. For this reason an extended version of the Anaerobic Digestion Model (AM2) was applied to predict the biogas production under dynamic feedstock loading scenarios. The approach applied in this thesis allows the prediction of different production scenarios and a suitable choice of the one with the most favorable environmental impact. The results are largely dependent on the methodological assumptions made, for instance, the functional unit, the system boundaries, and the method & efficiency of how various feedstock is digested.

If the objective of the optimal design and operation of a biogas production network is the reduction of greenhouse gas (GHG) emissions, the quantification of the impact of each element in the system in a “cradle to grave” sense is required. In order to achieve this, LCA studies need to be performed. The environmental impact vary greatly between the biogas systems studied depending on the feedstock digested and the location of the reference system. Moreover, LCA perspective requires large quantities of operational data. In order to be independent from the availability of data and to predict scenarios for improved operation, the development and application of suitable mathematical models are required. They should be able to describe the main processes with sufficient accuracy, while they keep a low computational burden. There are several potential barriers to a successful implementation of LCA coupled to a suitable modeling approach. It is only feasible after a fair approximation of the entire system and its dynamics that the search for the optimal combination of parameters considering all effects and interactions within the system boundaries. Data of these simulation studies are suitable for the integration into LCA studies. Results of this thesis indicates the importance of the utilization of regionally available feedstock. Flexible feeding management and additional gas storage allow a possible adaptation of the biogas production to the demand together with the CHP capacity. Techno-economic calculations demonstrate that up to 34% flexibility can be gained by biogas storage, while 17% can be

obtained by an adapted feeding regime. Flexibility also ensure an additional revenue of 300,000 €, in spite of the necessary CHP investment costs of 0.17 € kWh^{-1} el. Flexible production allows up to 50% reduction of GHG emissions, however, the process itself requires 16% higher energy input. Overall, a combined application of modeling and LCA would allow the prediction of process behavior in the digesters. This would consequently help to secure the grid stability by means of balanced energy supply against the demand. Moreover, the approach might also assist the countries to reach their climate related goals by allowing to reduce the resulting process emissions.

Keywords: Anaerobic Digestion, Biogas, Life Cycle Assessment, Modeling

Gasspeicherung ermöglichen eine Anpassung der Biogasproduktion an die Nachfrage zusammen mit der BHKW-Kapazität. Techno-ökonomische Berechnungen zeigen, dass bis zu 34% Flexibilität durch Biogasspeicher und 17% durch ein angepasstes Fütterungssystem erhalten werden können. Die Flexibilität sorgt weiter für zusätzliche Einkünfte von 300.000 €, trotz der notwendigen KWK-Investitionskosten von 0,17 € kWh^{-1} el. Schlussfolgernd würde eine kombinierte Anwendung von Modellierung und LCA die Vorhersage des Prozessverhaltens in den Gärbehältern ermöglichen. Dies würde folglich dazu beitragen, die Netzstabilität durch bedarfsangepasste Biogasproduktion zu sichern. Darüber hinaus könnte der Ansatz auch den Ländern helfen, ihre klimabezogenen Ziele zu erreichen, indem sie die resultierenden Prozessemissionen reduzieren können.

Schlüsselwörter: Anaerobe Vergärung, Biogas, Lebenszyklusanalyse, Modellierung

Ertem-Kappler, Funda Cansu, Ökobilanz- und Modellierungsansätze als kombiniertes Evaluationsinstrument für nachhaltige Kontrollstrategien in Biogasanlagen

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Abstrakt

Eine bessere Vorhersage anaerober Gärprozesse in der Biogaserzeugung kann dazu beitragen, mehrere energie- und umweltpolitische Ziele zu erreichen. Die Erzeugung von Biogas ist jedoch ein komplexer Vorgang, bei dem viele Herausforderungen bewältigt werden müssen, um einen nachhaltigen Betrieb zu erreichen. In diesem Zusammenhang müssen bessere Kontroll-, Überwachungs- und Optimierungsstrategien umgesetzt werden. Diese Arbeit konzentriert sich auf die Kombinierung von LCA (Lebenszyklusanalyse) und Modellierungsansätzen als Werkzeug für eine bedarfsangepasste Energieproduktion in den Biogasanlagen. Aus diesem Grund wurde eine erweiterte Version Anaerobes Vergärungsmodells (AM2) zur Vorhersage der Biogasproduktion unter dynamischen Einsatzstoff- und Belastungsszenarien verwendet. Der in dieser Arbeit angewandte Ansatz erlaubt die Vorhersage verschiedener Produktionsszenarien und eine geeignete Wahl desjenigen mit der günstigsten Umweltwirkung. Die Ergebnisse hängen weitestgehend von den methodischen Annahmen ab, zum Beispiel von der funktionellen Einheit, den Systemgrenzen und der Art und Weise, wie der Einsatzstoff vergärt wird.

Die Auswirkungen auf die Umwelt variieren stark zwischen den untersuchten Biogasanlagen in Abhängigkeit von dem vergärten Einsatzstoff und der Lage des Referenzsystems. Um ebenfalls von der Verfügbarkeit von Daten unabhängiger zu sein und Szenarien für einen verbesserten Betrieb vorauszusagen, sind die Entwicklung und Anwendung geeigneter mathematischer Modelle erforderlich. Sie sollten in der Lage sein, die Hauptprozesse mit ausreichender Genauigkeit zu beschreiben, während sie eine geringe Rechenlast behalten. Erst nach einer guten Annäherung des Gesamtsystems und seiner Dynamik wird die Suche nach der optimalen Kombination seiner Parameter unter Berücksichtigung aller Effekte und Wechselwirkungen möglich. Daten dieser Simulationsstudien sind für die Integration in LCA-Studien geeignet. Dabei gibt es mehrere Hindernisse für eine erfolgreiche Umsetzung des kombinierten LCA- und Modellierungsansatzes. Wenn das Ziel der optimalen Planung und Betriebs eines Biogasproduktionsnetzwerks die Reduzierung von Treibhausgasen sein soll, ist die Quantifizierung der Auswirkungen jedes Elements im System in einem "Cradle to Grave" -Sinn erforderlich. Um dies zu erreichen, müssen Ökobilanzstudien durchgeführt werden. Die Ergebnisse dieser Arbeit zeigen, wie wichtig die Verwertung von regional verfügbaren Rohstoffen ist. Das flexible Fütterungsmanagement und die zusätzliche

Eidesstattliche Erklärung

Hiermit versichere ich an Eides statt, dass ich die Dissertation selbständig verfasst habe. Alle benutzten Hilfsmittel und Quellen sind aufgeführt. Weiter erkläre ich, dass ich nicht schon anderweitig einmal die Promotionsabsicht angemeldet oder ein Promotions-eröffnungsverfahren beantragt habe. Veröffentlichungen von irgendwelchen Teilen der vorliegenden Dissertation sind von mir, wie in der vorstehenden Publikationsliste aufgeführt, vorgenommen worden.

Berlin, den 13.08.2018

Funda Cansu Ertem- Kappler

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List of publications

This doctoral thesis is based on the following manuscripts, which have been published in the following peer reviewed publications and will be referred to in the text by their Roman numerals:

I. Ertem, F. C., Neubauer P., & Junne S. "Environmental life cycle assessment of biogas production from marine macroalgal feedstock for the substitution of energy crops." Journal of Cleaner Production 140 (2017): 977-985. doi: https://doi.org/10.1016/j.jclepro.2016.08.041

II. Ertem, F. C., Martínez-Blanco, J., Finkbeiner, M., Neubauer, P., & Junne, S. (2016). Life cycle assessment of flexibly fed biogas processes for an improved demand-oriented biogas supply. Bioresource Technology, 219, 536-544. doi: https://doi.org/10.1016/j.biortech.2016.07.123

III. Arzate, J. A., Kirstein, M., Ertem, F. C., Kielhorn, E., Ramirez Malule, H., Neubauer, P., ... & Junne, S. Anaerobic Digestion Model (AM2) for the Description of Biogas Processes at Dynamic Feedstock Loading Rates. Chemie Ingenieur Technik 89.5 (2017): 686-695. https://doi.org/10.1002/cite.201600176

IV. Ertem F. C., Arzate J. A., Neubauer P, Cruz-Bournazou M. N., & Junne S. Combination of life cycle assessment and modeling approaches as optimization tool for sustainable biogas production (submitted to Renewable Energy Focus Journal of Elsevier)

V. Ertem F. C., Arzate J. A., Neubauer P, Cruz-Bournazou M. N., & Junne S. Combination of extended AM2 and environmental LCA approach: assessment of a demand driven biogas production via feedstock management (submitted to Process Integration and Optimization for Sustainability Journal of Springer)

My contributions to the papers:
Paper I - II: I performed the data collection and calculations, and wrote the paper.
Paper III: I performed much of the data collection, and wrote parts of the paper.
Paper IV: I performed the literature research, and wrote the most part of the paper.
Paper V: I performed the data collection and most of the calculations, and wrote the paper.

List of abbreviations

Anaerobic Digestion	AD
Anaerobic Digestion Model No. 1	ADM1
Anaerobic Digestion Model	AM2
Combined Heat and Power	CHP
Chemical Oxygen Demand	COD
European Power Exchange	EPEX
European Union	EU
Greenhouse Gases	GHG
Life Cycle Assessment	LCA
Life Cycle Inventory	LCI
Life cycle Inventory Assessment	LCIA
Renewable Energy	RE
Renewable Energy Sources	RES
Renewable Energies Sources Act	EEG
Uncertainty Quantification	UQ

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1. Introduction

1.1. Background and motivation of the study

Biogas is an essential part of the renewable energy (RE) sector (Ali et al., 2012; Mao et al., 2015). The European Union (EU) has a very ambitious target to mitigate greenhouse gas (GHG) emissions by the year 2020. The plan "20-20-20" aims to reduce emissions of GHGs and primary energy consumption by 20% compared to the 1990 values, and to increase the RE contribution to energy supply within the EU to 20% (Andersson et al., 2014). It is expected that at least 25% of the EU-27 RE part for 2020 will be provided by bioenergy derived from biogas (Holm-Nielsen et al., 2009). Therefore, the biogas energy production has to be expanded until 2020 (29.5 GW) compared to the 2012 (14.5 GW) (Sun et al., 2015).

Currently, the installation of biogas plants in European countries is rising (Pöschl et al., 2010), although with a different velocity. 14,563 biogas plants with a total installed capacity of 7,857 MW el were operated in Europe in 2014. In 2017, there are almost 9,000 individually operated biogas plants in Germany with different varieties of plant architecture and operations. However, this independent and individual operation is clearly not leading to a maximum output, and optimal yields not necessarily to the most sustainable strategy. For these reasons, and due to the numerous discussions about the eco-friendliness of this technology, it is required to optimize the current biogas production processes by understanding the system in a better way, so that a detection and prevention of system disturbances become possible within a sufficiently short time (Grando et al., 2017; Meyer et al., 2017; Skovsgaard & Jacobsen, 2017). This approach can be combined with a proper objective function, which includes LCA outcomes in order to design a control strategy that indeed minimizes the environmental impact of biogas production.

Biomass resources are considered as one of the main RE sources, they are expected to provide more than half of the energy demand in the near future (European Renewable Energy Council, 2008). 50-55 % of EU biogas plants´ feedstock is originated from energy crops in spite of growing concerns about using food to produce energy. The utilization of maize as feedstock often results in the highest methane yields per ha of arable land, therefore it is a preferable substrate for anaerobic digestion. This leads to the fact that 90% of biogas plants in Germany run – at least partially - with maize as feedstock (Lüker-Jans et al., 2017).

Several studies have reported benefits of energy crops in terms of the diminution of GHG emissions, air pollution, acidification, or eutrophication (Bacenetti et al., 2013; Brentrup et al., 2004; Buratti & Fantozzi, 2010; González-García et al., 2013; Kimming et al., 2011; Mizsey & Racz, 2010). Nevertheless, recent scientific findings referred that the appealing prices linked to energy crop production are causing the modification of pastures and forests into cropland on a worldwide scale, with a subsequent loss of biodiversity and carbon storage in the biosphere (Lupp et al., 2014). This may yield a negative impact on the global stock and prices of food and lead to increasing quantities of GHGs being emitted to the atmosphere (Ammenberg & Feiz, 2017; Jacobs et al., 2017; Stürmer, 2017). Moreover, it is important to assess the locally available biomass resources, which can be used more efficiently as a source for RE production and a better waste management. Biogas energy potentials of residues and waste were deeply investigated in the past (Lupp et al., 2014). However, there is a lack of knowledge of where to build a biogas plant, what size and how it should be operated in a stable manner, if varying types of local feedstock are applied throughout a week, month or year (Franco et al., 2015; Mol, 2014; Willeghems & Buysse, 2016).

Therefore, it is crucial to evaluate biogas plant operations in a life cycle assessment (LCA) framework to evaluate the real and global environmental outcomes. LCA scrutinizes numerous aspects related to the development of a product and its capability effect throughout a product's life (i.e. cradle to grave) from raw material income, processing, manufacturing, use and final disposal from an environmental point of view. It is widely recommended as a decision making tool to evaluate the real footprint of a process (Baumann & Tillman, 2004).

Anaerobic digestion (AD) is a dynamic multi-stage process involving a wide microbial population structured in several groups of microorganisms, whose composition and dynamics are not understood well or easily measurable. Therefore, a number of challenges must be faced, such as its instability, slow reaction rates compared to aerobic processes, long hydraulic retention time (HRT) requirements (20 - 30 days) (Navia et al., 2002), critical components as sulfide, ammonia or heavy metals (Duarte A, 1982), sensitivity to shock loads, and its complex operation (Hwang et al., 1997; Lin, 1997). The energy content of the gas may also vary. It is dependent on the nature of the substrate. These problems can be reduced through suitable control strategies, which require a convenient mathematical model that describes the most relevant processes of anaerobic digestion (Colussi I., 2012). This model, if properly validated, allows an accurate prediction of the process dynamics. By this, it is possible to design and operate the plant in

such a manner that final objectives (e.g. the minimization of CO_2 equivalents) are achieved. This saves time and money as tests during operation are not easily conducted. This requires that the model has to predict the performance of biogas plants when different substrates or co-substrate ratios are utilized under different loading rates (Edwards & Hamson, 2001).

The combination of the process modeling and LCA methodologies allows a sustainable biogas energy production, which eventually achieves the lowest negative impact on the environment. Therefore, the overall objective of the work described in this thesis was to focus on the integration of LCA and modeling approaches for biogas production, and thus to emphasize the necessity of combining both approaches to evaluate different process designs for a sustainable production with the lowest unfavorable impacts on the environment.

1.2. Overview of papers and outline of the thesis

Papers I-III include the assessment of energy performance and environmental impact of biogas production from a life cycle perspective. The calculations are based on literature reviews and refer to German conditions.

Paper I evaluate the production of biogas by the substitution of energy crops with marine macroalgae. In order to assess environmental friendliness, a life cycle assessment was performed by using the software Simapro. Potential environmental impact categories under investigation were global warming, acidification, eutrophication and the land transformation potential.

Paper II analyses concepts to facilitate a demand oriented biogas supply at an agricultural biogas plant of a capacity of 500 kWh el, operated with the co-digestion of maize, grass, rye silage and chicken manure. Different from previous studies, environmental impacts of flexible and the traditional baseload operation are compared.

A comparative study was conducted in paper III for the simulation of biogas formation at dynamic feedstock loading using maize silage was performed with anaerobic digestion model no. 1 and the anaerobic digestion model 2 (AM2).

Paper IV summarizes the formerly conducted LCA and modeling studies in the area of biogas production, emphasizes good modeling practices, and discusses the potentials of a combination of all these aspects.

Combination of a life cycle assessment (LCA) and modelling approach for demand driven biogas production via a flexible feedstock management is studied in paper V. An extended version of the AM2 model was applied to predict the biogas production under dynamic feedstock loading scenarios. LCA was performed based on SimaPro 7.2 software and Ecoinvent® v2.1

database, while the mechanistic model was implemented in a Matlab® environment.

The next subchapter of this thesis will focus on the renewable energy production, related legal framework and their developments in the last decades. The necessity of a flexible plant operation, a brief overview on the energetic use of biomass and site selection criteria will be depicted. Chapter 3 underlines the LCA methodology and summarizes the LCA studies performed in the biogas field. Further, a demand driven production process will be analyzed from an LCA point of view and impacts of regional differences on the LCA will be described. Chapter 4 reviews the modeling approaches for AD processes and potential combinations of LCA and modeling approaches for a sustainable biogas production. Challenges related to demand based production, combination of LCA and modelling and overall results of papers will be discussed in the last chapter.

2. Role of biogas in Germany

2.1. German renewable energy production

In order to reduce energy imports and GHG emissions, the European Commission set a striving goal of a 20.0 % portion of energy from renewable energy sources (RES) in the EU's gross energy consumption by 2020. This 'RES-Directive' sets compulsory aims for each member country. According to the RES-Directive, Germany is expected to generate 18.0 % of its gross energy consumption from RE by 2020 (Krajačić et al., 2011).

Before the RES-Directive, the German government had already established the Renewable Energies Sources Act (EEG), which was introduced in 2001 (Illing, 2016). This EEG law aimed to establish an expansion of renewable energies by fixed governmental subsidies. A purchase guarantee and the priority feed-in of electricity generated by renewable sources into the grid were included in the EEG to support Germany's energy transition. The EEG guaranteed a continuous fixed feed-in tariff to renewable energy plant operators for electricity fed into the grid over a period of 20 years, which lead a great increase in RE share. In 2014, Germany already had a renewable energy share on gross final energy consumption of 13.7 %, and on gross electricity consumption of 27.4 % (Illing, 2016). Long-term strategies concerning energy security in an economically viable and ecologically sound direction were proposed in Germany's 'Energy Concept' (Szarka et al., 2017). The ambitious targets of the Energy Concept aim to

increase the renewable energy share on gross final energy consumption to 30 % by 2030 and 60 % by 2050. The gross electricity production from renewable energy sources are planned to be increased to 35 % by 2020, 50 % by 2030, 65 % by 2040 and 80 % by 2050. Simultaneously, greenhouse gas emissions are targeted to be reduced by 40 % in 2020, 55 % in 2030, 70 % in 2050 and >80 % by 2050 compared to the base year 1990 (Bundesministerium für Wirtschaft und Technologie, 2010; Szarka et al., 2017).

In total, RE sources – solar, wind, hydropower, and biomass – produced approximately 185 TWh of electricity in 2016 (Szarka et al., 2017). There was no increase in production compared to 2015. Renewables thus made up around 33.9% of public net power supply. The share in gross power supply – including power plants in the processing sector, the mining sector, quarries, and excavation – reached about 32% (Ag Energiebilanzen e.V., 2017)..

In 2016, about 37.5 TWh of electricity from photovoltaic arrays was fed into the grid. At the end of 2016, 40.85 GW PV were installed. In May 2016, the monthly electricity production of PV systems was higher than that of nuclear power plants (Cherp et al., 2017). 78 TWh energy were generated from wind in total. Monthly production of wind power reached a peak in February and was even higher than energy production by hard coal (Weber & Cabras, 2017). For six months, the monthly production of electricity from wind exceeded the production of electricity from nuclear power plants. Onshore wind farms produced 66 TWh el in 2016 (Ag Energiebilanzen e.V., 2017). Offshore wind farms raised their production from 8 TWh el in 2015 to 12 TWh el in 2016. In the North Sea, 10.7 TWh were produced compared to 7.1 TWh in 2015. The offshore wind farms in the Baltic Sea produced 1.3 TWh (0.8 TWh in 2015). At the end of 2016, a capacity of 45.5 GW of wind onshore and 4.1 GW of wind offshore plants were installed. In summary, solar and wind power generators produced 116 TWh in 2016 (Ag Energiebilanzen e.V., 2017). This was sufficient to rank them second after lignite, but ahead of hard coal and nuclear–based electricity generation. Approximately 20.75 TWh were produced from hydropower, a level roughly unchanged year-over-year. About 49 TWh of electricity was generated from biomass, 2 TWh more compared to the year before (Ag Energiebilanzen e.V., 2017).

2.2. Flexibilization of energy generation at biogas plants in Germany

Biogas combustion is one technique for renewable energy production. During the anaerobic process, biomass is metabolized to a gas mixture by microbes. The gas mixture consists mainly of methane (CH_4), which can be transformed to electrical energy and heat by a combined heat and power (CHP) unit (Döhler & Wulf, 2016).

Biogas production has a long history in Germany. A steady increase of installed biogas plants appeared with the introduction of the EEG in 2000. In 2001, 1,300 biogas plants were installed in Germany. This number increased to 3,500 in 2006, and 8,200 in 2012 (Association, 2017). This rapid development appeared due to a certain bonus system in different EEG amendments, enabling biogas plant operators to increase their profits when fulfilling the according requirements. With the EEG 2004, energy crop and CHP-bonuses were introduced. Biogas plant operators gained subsidies for utilizing energy plants and the technical utilization of generated heat of the CHP unit. The EEG amendment of 2009 introduced bonuses for emission reduction and for installations of new techniques. Thus, over the last decades, German industry has become the worldwide technical leader in engineering biogas technique (Illing, 2016). Together with agricultural sector they have taken an exemplary role in this segment. From 2009 to 2011, more than 1,000 biogas plants were installed annually. On the contrary, the expenditure of the grid capacity was too slow: it created a challenge in the control and reliability of the power grid (Moslehi & Kumar, 2010), which is still at risk of power failures. Due to the lack of sufficient grid capacity, the number of wind farms, that were operated at reduced capacity, increased by nearly 300 percent in Germany in 2011. This resulted in a capacity of 407 Gigawatt-hour (GWh) energy loss, or 18 to 35 million euro, respectively (Bürgerinitiative Gegenwind Raven e.V., 2012; Thrän et al., 2015). In response to these, Germany modified the EEG to discourage the production of large AD plants in favor of smaller ones in 2011. AD plants were required to either (i) limit the use of energy crops to a maximum of 600 g kg^{-1} maize per year, (ii) make use of at least 600 J kJ^{-1} of the heat generated from the AD process, or (iii) utilize at least 600 g kg^{-1} manure as feedstock. These and other new requirements on efficiency have resulted in a slowdown of the number of new plants being built, approx. 300 per year.

Additional amendments in 2015 have further reduced the feed-in tariffs for new, large AD plants. Meanwhile, AD plants smaller than 75 kW that utilize manure substrates started to receive higher subsidies compared to

other larger AD plants. Finally, the increased energy production due to new AD plants was limited to 100 MW per year. In sum, these changes seek to support small scale plants, drive the use of agricultural residues as feedstock for AD plants and decrease the cultivation of maize monocultures as energy crops on arable land (Sperling, 2017).

Moreover, since it is not possible to produce the same amount of energy from each region, one of the biggest challenges regarding energy is its transport. This emphasizes the importance of site selection criteria, when a new plant is planned (See subchapter 1.5). Energy needs to be transferred to high energy demanding regions. Within the process of transport, energy is lost each year. In order to reduce the energy loss during energy transport, there is a need to construct new high voltage lines, alternating current lines and also to strengthen the present electricity grids and expanding their capacities. In Germany, all these investments are expected to cost more than 10 billion € without the costs of additional underground lines. Upgrading Germany's grid system will cost at least 42 billion € if underground lines were used (Bundesministerium für Wirtschaft und Technologie, 2010; Bürgerinitiative Gegenwind Raven e.V., 2014; EurObserv'ER, 2012; Fachverband Biogas e.V., 2011).

The breakdown of the Fukushima nuclear plant in 2011 and the problems related to the handling of nuclear waste caused many countries to be more cautious than ever before in their approach to nuclear energy (World Nuclear Association, 2011). As an example, the German government decided to shut down all nuclear reactors by 2022, having stopped production in eight already in 2011. The total electricity production fell down to 614.5 billion kWh that year in Germany. The cost of replacing nuclear power with subsidized renewables is estimated by the government to amount to 100 billion €. The parliament approved the construction of new coal and gas-fired plants despite retaining its CO_2 emission reduction targets, as well as expanding renewable energy utilization (World Nuclear Association, 2014). Germany's Federal Network Agency (Bundesnetzagentur) reported that 25 new power plants with a total capacity of 12 GW el were under construction, 67 % powered by black coal and 17 % by brown coal in September 2012. Germany's decision to shut its nuclear plants would create an extra 300 million tons of CO_2 by 2020 due to increased fossil fuel use (Bundesnetzagentur, 2012).

In 2012, 25.3 % of the electricity consumed in Germany was produced from renewable energy that is mainly supported by the EEG, with the use of wind and photovoltaic power accounting for 55 %, and electricity from biomass and hydropower accounting for 45 % (Thrän et al., 2015). Considering the goal of the German Government of phasing out the use of

fossil fuels and the obligation through the Directive of the European Commission 2009/28/EC, an efficient utilization of power from renewable sources is important, thus a cessation of RE generators should be avoided if possible (Ertem et al., 2016a).

The integration of large quantities of intermittent energy sources into energy systems poses the great challenge to balance the provided energy. In this respect, electricity from biomass, particularly from biogas, offers the advantage of high predictability (Hahn et al., 2014). Beyond that, biogas and the feedstock to produce it can be stored and consequently electricity can be generated demand-driven to a certain extent, independent from influences of the weather (sun and wind), in order to balance the intermittent power production from weather-driven RE. Thus, power from biomass, more precisely from biogas, is able to contribute to the integration of large proportions of RE in future energy systems (Mauky et al., 2017).

Based on a flexible biogas production concept, in times of low energy generation by wind or photovoltaics, the power supply will have to be replaced with flexible power generation. When considering biogas production, energetic shortage could be compensated by adequately activating biogas combusting generators (CHPs). However, the realization of demand-oriented biogas plants meets new challenges.

The main goal of most installed biogas plants is to operate at full capacity and to produce maximal electrical energy stable throughout the year. Such biogas plants run with a relatively constant feeding regime. Most biogas plant feedstocks comprise of maize and grass silage. The required retention time for such substrates in the biogas plant is about 100 days, whereas fiber-rich substrates are not fully degraded in this time. The substrate addition to such biogas reactor systems occurs on average 20 times per day (Gemmeke et al., 2009). However, with the introduction of the EEG 2014 and the EEG amendment of 2017, demand-driven biogas production gained increasing importance. With the demand-oriented biogas production, energy should be generated in times of high electrical needs.

Biogas plants may be designed to produce biogas on-demand: these are generally double-stage reactors. Some processes such as ReBi (“Regalbare Biogasanlage”) or IFBB biogas plant (designed for ligno-cellulose rich biomass) can achieve an intraday flexibility of biogas production up to 800 % (Hahn et al., 2014), but these solutions can only be used in the case of new projects.

One simple way to achieve flexible biogas production is to produce biogas in the common constant way and collect the produced biogas in a biogas storage. The biogas storage could be used as backup energy, while

biogas combusting CHP units would produce energy in times of demand. However, such biogas storage capacity is legally limited to a maximum of 50 tons (ca. 39,000 m³ biogas) by the German Federal Pollutant Control Act (BImSchG) (Hahn et al., 2014).

In another alternative, the biogas production of a biogas plant could be regulated by altering the substrate feeding regime or substrate mixture. Ideally, the substrate addition to the biogas plant would result in an increase of the biogas production depending on the individual digestion process parameters, feedstock and microbial consortium. However, a substrate with low energy content per volume would not be a useful choice. As energetic deficits are not always predictable long beforehand, biogas plants with short start-up phases would greatly contribute in such times.

Flexible biogas production in a relatively common biogas plant with 500 kW installed electrical energy and a feedstock composing of manure, maize silage and wheat corn was analyzed by Bofinger et al. (2010). It showed that biogas production can be regulated within a period of several days by a variable feedstock. However, faster biogas production response after substrate addition would be beneficial. Implementing such a fast-adaptable biogas system would require substrates that can be transformed to biogas more rapidly like sugar beet. Sugar beet contains easily degradable sugars and alcohols (after ensiling), which can be metabolized to biogas rapidly and offers similar biogas yield potentials compared to maize silage. However, the mono-fermentation of sugar beet silage can cause process problems by means of acidification and foam formation. The utilization of sugar beet silage as a co-substrate with, for instance, grass or maize silage is highly recommended (Ertem, 2011). Therefore, the regulated input of substrate mixtures with sugar beet silage could reduce the start-up time for biogas production. Changing the substrate mixture might also help to adapt the biogas production (Ertem et al., 2016b; Mauky et al., 2015). However, an optimal biogas production process requires an efficient microbial community in order to deal with changing environmental conditions in form of altering substrate compositions. Therefore, it is in general essential to include a monitoring and process control system into such a concept in order to avoid process failures and thereby economic losses.

2.3. Process monitoring at biogas plants

Process monitoring helps to understand what happens in a biogas plant and help to keep it stable. Under many circumstances, an inhibited microorganism population or a total crash of the entire plant can have greater financial

consequences than the costs of basic monitoring and lost revenue associated with re-establishing a biologically destabilized plant (Habermann et al., 2015).

Several factors can affect the intensity of process monitoring necessary, e.g. scale of biogas plant, economic risk of process instability, frequency of changes in feedstock types, etc. (Enseleit et al., 2017).

Among the process monitoring parameters, there are two different groups (Drosg, 2013). The first group of parameters are early indicators of a process imbalance and they let the biogas plant operator to respond in time before a process imbalance occurs: volatile fatty acids, alkalinity ratio, hydrogen, redox potential, complex monitoring of mixed parameters (like electronic nose). Yet, these parameters do not give straight information of the origin for the process imbalance. For an explanation of the process imbalance, the second group parameters characterizing the process need to be used. The second group are the parameters which describe the process and can regularly help to identify and eliminate the reason of the imbalance: amount and characteristic of feedstock, biogas production and gas composition, fermentation temperature, total solids / dry matter, pH value, and ammonium nitrogen, respectively. These parameters define the state of the overall biogas process. It is necessary to monitor them to detect the potential reasons for fluctuations in the process stability. However, they cannot be used as early indicators for a process imbalance. The reason is that, for example, reductions in gas production or in pH are frequent indications of already ongoing process disturbances. Other parameters, such as changes in H_2 or volatile fatty acid concentration happen before the process turns out to be unstable and let the plant operator to neutralize the situation before a process imbalance happens (Wandera et al., 2018). Nevertheless, some stability complications like for example trace element limitations will demand a more intensive optimization effort and particular expertise will be needed (Drosg, 2013).

Although general guidelines for stability limits of different process parameters can be given, it is always necessary to adapt the monitoring strategy to the specific biogas plant and its feedstock. Many biogas plants will demand detailed process optimization apart from pure process monitoring (Drosg, 2013). This might be achieved by a model predictive control approach that is designated to control production concepts. Currently, there are no control concepts with the target to flexibilize the process and follow a fluctuating timetable of energy demand. A biogas plant serving this flexible market in future will need a control concept, which offers a predictive reaction to future changes in demand. By nature, this will also

avoid additional investments in gas storage capacity by the evasion of excess gas production (Mauky et al., 2015).

2.4. Challenges regarding biomass utilization

Due to the restrictions that the enforcement of other renewable energy sources entails, the enhancement of incentives and minimization of barriers in many countries resulted in the enlargement of biomass use for biogas generation (Pöschl et al., 2010). The substrate input streams of these plants consist mainly of a mixture of manure and energy crops, which can contribute, in some cases, to more than 90% of the total biomass digested in AD plants. The use of organic and food waste as well as industrial waste is still of inferior importance in Germany. In Germany, the majority of digesters are operated with a residence time of 50 –150 days. If mono-digestion of only energy crops or manure would not be feasible, since it would cause process instabilities and require a residence time either above 150 days or less than 50 days (Braun et al., 2008).

In 2010, Germany produced more than 75 million tons of maize, with a cultivated area of 1.85 million ha, representing 30% of the total cultivation area of maize in the EU 27 (Deutsches Maiskomitee e.V, 2014). Furthermore, more than one third of the produced maize (it constitutes 80% of the substrates) was used for biogas production in Germany. Maize for biogas production is therefore the most essential crop for energetic use in Germany, followed by rapeseed for rapeseed oil and biodiesel production (Lupp et al., 2014). For instance, nearly 7% of the arable land was used for biogas substrate production in 2011, but provided only 3% of the national electricity consumption. Due to its comparatively high land requirements and high CO2 avoidance costs, it is important to assess locally available biomass, which can be used with less efforts as a source for renewable energy production and a better waste management. With the aspect of sustainable waste management, the biogas energy potential of residues and waste represent the current focus of interest (Herrmann, 2012; Lupp et al., 2014).

There is an excess amount of biogenic waste, which is locally or seasonally available; however, there is a lack of knowledge on where to build a biogas plant, what size and how it should be operated in a stable manner applying locally accessible feedstock (Mol, 2014). Regions with high amounts of biogas plants create a greater risk by means of nitrate loads. Risks on ground- and surface water by energy crop cultivation are particularly caused due to an excessive reintroduction of digestate for spreading on the agricultural areas close to the plant. Increased N loads in the groundwater are

currently not appropriately measured due to the lack of monitoring networks and long-term flow times (del Río et al., 2017). Therefore, 30% of groundwater bodies are endangered (Mol, 2014).

In order to prevent nitrate loads caused by biogas plants, a new amendment was introduced by the fertilizer ordinance. Amendment, in particular, limits the nitrogen content of digestate, which is utilized as fertilizer in farming as 170 kg N/ha. Therefore, regions with high nutrient loads resulting from biogas production will need to transport their digestate to areas with low nutrient loads. Currently, the digestate production creates the most important factor for the economic viability of biogas plants. This challenge might be solved either with control strategies or site selection criteria.

2.5. Site selection criteria for the newly constructed biogas plants

Beside political framework and public acceptance, site selection for biogas plants should be performed under the consideration of multiple criteria. First of all, the transport plays an important role for the location of the plant. According to literature, the biogas plant should be located in a radius of less than 10 km from the available biomass source (Höhn et al., 2014). Moreover, the digestate, which is used as fertilizer in agriculture, should not be transported further than 15 km (Christian, 2008; Gebrezgabher et al., 2010; Poeschl et al., 2012). Transport costs will become important for the profitability of a plant, after the latest amendments in the German Federal Fertilizer Ordinance (DüngeVerordnung and Düngegesetz, 2017), which foresees the increase of the obligatory storage time of digestate from 8 to 9 months and the reduction of permitted nutrients, which originate from digestate per ha agricultural area (50 kg ha^{-1} N and 10 kg ha^{-1} P_2O_5) (von Buttlar & Willms, 2016). Therefore, the agricultural land, which is required for digestate spreading, will be 3 times larger for an average biogas plant with a capacity of 500 kW el (Hansjürgens et al., 2017).

Besides the regional availability, the energy content of the chosen feedstock should also be considered, since it will directly affect the biogas yield. Market prices of the selected substrate and its secondary utilization ways should be considered. Feedstock with low energy content per volume would not be a practical choice (Bartoli et al., 2016; Budzianowski & Postawa, 2017).

The biogas plant generates large amounts of digestate. The amount highly depends on the type of input feedstock, which was selected. Digestate

resulting from the fermentation of agricultural feedstock can be spread as fertilizer. Land spreading requires the assessment of national legislation for the amounts and the period, in which the fertilizer is permitted to be utilized on the agricultural land. In the case of industrial and municipal organic waste, the digestate can be used as fertilizer as well, but certain (national) legislation might limit their application (Bartoli et al., 2016; Hansjürgens et al., 2017; Sieveking et al., 2017).

Due to certain challenges regarding substrate availability and digestate transport, an alternative to a single biogas plant installed on a farm could be a consortium of various farm owners; they may decide to share their production of waste water and byproducts to feed a common biogas plant. This allows an increase in plant power output, and provides the advantages of anaerobic co-digestion compared to digestion of a single substrate (e.g. reduction of technical problems due to the presence of inhibiting compounds in the feed, and a wider availability of feedstock throughout the year). Larger plants can also benefit from the economies of scale, and tend to have lower investment and operational expenses per unit weight of feedstock, however, actual regulations support small scale plants up to a power of 150 kW el.

Besides, suitable sites are defined based on the proportion of heat, which is used among the total heat produced by biogas (Höhn et al., 2014). The transport of heat is cost intensive and energy losses are inevitable as shown in this study. Therefore, based on the generated heat, the biogas plant should be positioned in a radius of 1-2 km on average to the heat customer who has a stable heat demand all over the year at reasonable prices (Höhn et al., 2014). Another possibility is to set up a drying facility for agricultural and wood products to form own heating demand in summer. If the biogas heat is used to replace heating devices which currently work on either crude oil or natural gas, higher price for the heat can be obtained, however, it would still be somewhat lower than the one for fossil fuels.

3. LCA methodology

LCA is a method to assess the environmental aspects and potential impacts associated with a process, product or a system. This system might be a biogas plant including anaerobic digestion process. In a LCA, first of all, an inventory of relevant energy and material inputs are compiled, then the potential environmental impacts are evaluated. At the final stage, the results are interpreted in order to obtain the environmental impacts of the analyzed processes (Guinée, 2002).

LCAs were performed on a huge variety of products and processes. LCA considers the supply of raw materials needed to produce the product, the manufacturing of intermediates and finally the product itself, including packaging, transportation of raw materials, intermediates and the product, use of the product and disposal of the product after use. This sequence is called "Cradle to Grave" assessment. For instance, when a biogas plant is analyzed, LCA starts mostly with the assessment of feedstock: how the feedstock is produced, transported and stored. Then a special attention is given on biogas production at the digesters and the electricity and heat generation from the produced biogas.

LCA might be conducted for several reasons. It can be used to reduce negative environmental impacts and waste, reduce costs, increase efficiency or identify appropriate performance indicators. Furthermore, an LCA creates common metrics that can be compared and shared across the field (Baumann & Tillman, 2004).

According to the ISO 14040 (Environmental management standard of principles and framework for LCA) (Standard) and 14044 (Environmental management standard of the specific requirements and guidelines for LCA) (Iso, 2006a) standards, an LCA is conducted in four steps as illustrated in figure 1. The steps are often interdependent in that the results of one step will instruct how the other steps should be accomplished.

Goal & Scope Definition:

The first step is to clarify the purpose and extent of the LCA. This entails formally determining the functional unit and system boundary. In a multifunctional process assessment, a variety of functional units can be used based on the application of the LCA. For this reason, every LCA study uses different functional units defining the analyzed system or the processes (Hartmann, 2006). Electricity fed into grid is most commonly used functional unit in biogas systems as illustrated in figure 1.

System boundaries in LCAs have to be stated in multiple dimensions: (i) borders between the technological system and nature, (ii) demarcations of the geographical area and time horizon inspected, (iii) boundaries between production of internal tools/energy and production of consumable products, (iv) boundaries between the life cycle of the product, (v) and relevant life cycles of other products (Pieragostini et al., 2014). Within literature, all bioenergy systems were considered from a different LCA approach. Biogas production systems under assessment consider all of the processes involved throughout the life cycle based on their functional unit (Baumann & Tillman, 2004).

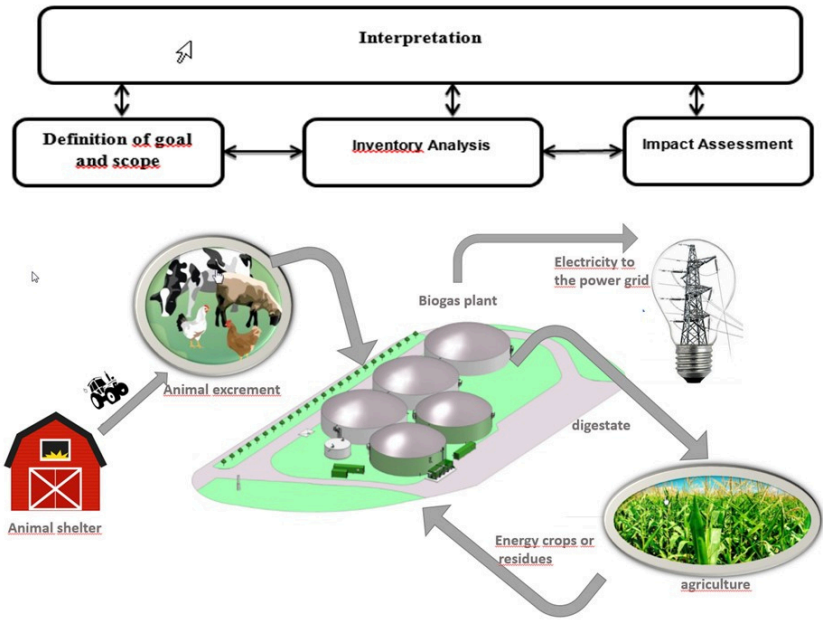

Figure 1. LCA framework based on ISO 14040:2006 Environmental management - LCA - Principles and framework for biogas plants (ISO, 2006b)

Inventory Analysis:

Once the functional unit and system boundary are determined, data should be collected. Inventory analysis entails creating a list of all of the components of the products life cycle that fall within the defined system boundary. LCA includes actual primary environmental impact data. Such detailed LCAs take, on average, three months and cost $10,000-$60,000. They can be completed just after the product is in use and has gone through all stages of its life cycle. This accuracy is worth to be applied for benchmarking or external reporting (such as green marketing) purposes. The resulting Life Cycle Inventory (LCI)

provides a breakdown of all of the energy and materials involved in a product's system at a level of detail that provides a basis for evaluation (Baumann & Tillman, 2004; Yang & Heijungs, 2017).

Impact Assessment:

Once a detailed LCI is created, environmental impacts can be ascribed to its parts, and if desired to the whole system. Life cycle inventory assessment (LCIA) describes the foundation of an inventory of flows from and to nature for a system. Inventory flows comprise inputs of water, energy, and raw materials, and discharges to air, land, and water. The input and output data required for the establishment of the model are collected for all activities within the system boundary, including all of the supply chain (Hartmann, 2006).

The data have to be connected to the functional unit, which is defined in the goal and scope definition. The results of the inventory are an LCI, which supplies information about all inputs and outputs in the form of elementary flow to and from the environment from all the unit processes of the study.

There are four steps to the LCIA process, the first two are considered as mandatory, while the last two are optional: (i) classification, (ii) characterization, (iii) normalization and (iv) weighting, respectively. Classification involves assigning specific environmental impacts to each component of the LCI. It is here where decisions are made during the scope and goal phase about what environmental impact categories are of interest. Once the impact categories have been identified, conversion factors – generally known as characterization or equivalency factors – use formulas to convert the LCI results into directly comparable impact numbers. Some practitioners choose to normalize the impact assessment by scaling the data by a reference factor, such as the region's per capita environmental burden. This helps to clarify the relative impact of a substance in a given context. For instance, if global warming contributions are already high in the context, in which the product is being assessed, a reference factor would normalize whatever the product's global warming contributions are in order to clarify its relative impacts. Weighting is the optional fourth and final step in LCIA, after classification, characterization and normalization. This final step is perhaps the most discussed one. Weighting entails multiplying the normalized results of each of the impact categories with a weighting factor that expresses the relative importance of the impact category. The weighted results all have the same unit and can be added up to create one single score for the environmental impact of a product or scenario. In summary, weighting means applying a value judgement to the LCA results. It is a controversial step, since the chosen weighting factors influence results and conclusions of a LCA (Baumann & Tillman, 2004; White & Shapiro, 1993).

Interpretation:

Although listed fourth, life cycle interpretation actually occurs throughout the whole LCA. It involves the ongoing process of clarifying, quantifying, checking, and evaluating the information used by, and resulting from, the LCI and LCIA phases. The standard that covers the LCA process, ISO 14044, denotes two main objectives (Baumann & Tillman, 2004):

1. Analyze results, reach conclusions, explain limitations, and provide recommendations based on the findings of the preceding phases of the LCA, and to report the results of the life cycle interpretation in a transparent manner.
2. Provide a readily understandable, complete, and consistent presentation of the results of a LCA study, in accordance with the goal and scope of the study.

To achieve these objectives, the ISO standard states that interpretation should cover at least three major elements:

1. Identification of the significant issues based on the LCI and LCIA. Which life cycle stages or components stand out as major contributors to the overall impact? What are the anomalies?
2. Evaluation, which includes completeness, sensitivity, and consistency checks. Is all the information needed for interpretation present in the LCI and LCIA? How reliable is the information related to any identified significant issues? How much do changes in such factors influence the overall results? Are all of the assumptions, data, characterization factors, etc. that were used in the assessment, internally consistent with the overall goal and scope of the LCA? (Guinée, 2002)
3. Conclusions, recommendations, and reporting. A great portion of an LCA's value depends on how its results are communicated to people involved in making relevant decisions, whether engineers, management, marketers, or other parts of the supply chain.

It is very important to note that no matter how carefully assembled, analyzed, assessed, and measured, LCAs are never the "real" answer. They require interpretation, which demands for transparency and judgment. The data sources, assumptions, and all other relevant information needs to be transparent to decision makers so that they can understand the full context of results of the LCIA. Deciding among design options is not as easy as just comparing LCIA numbers, whether single- or multi-factor, weighted or not. LCIA results can be a source of insights, but do not stand alone in guiding product development choices. Engineers will need to take them in the context of the other attributes they are trying to optimize, including cost,

manufacturability, performance, and so on. In addition, there are myriad other factors guiding product development decisions not covered by LCAs, including social impacts and acceptance, pricing, political agendas, and regulations (Guinée, 2002).

4. Coupling of model-based process performance simulation and LCA

4.1. Modeling of anaerobic digestion

The general framework for the use of a mathematical model is a 6-step procedure, as depicted in Figure 2 (Donoso-Bravo et al., 2011; Walter & Pronzato, 1997).

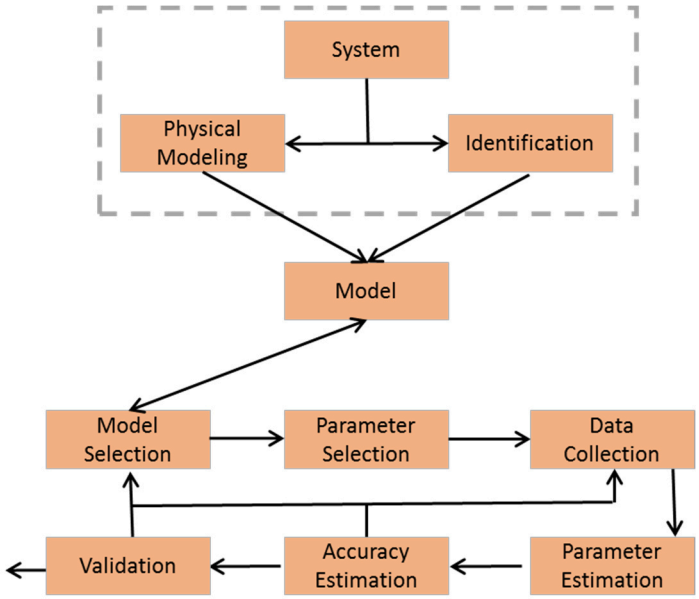

Figure 2. Schematic overview of a dynamic modeling procedure

In the first model selection step, a trade-off should be made between accuracy and model complexity. The latter is determined by the number of state variables and parameters, which are included. A choice has to be made between data-driven or mechanistic models. This initial choice of type and specifics of a model is partially driven by the amount of a priori knowledge and the amount and quality of data available from a system. In case of complex processes with natural process fluctuations like the AD, parameter values can be taken from the literature if the conditions of the experiment are sufficiently similar to the previously reported ones, and/or when the parameter demonstrates little variability (Batstone et al., 2002).

The next step is the parameter selection for calibration. Principally, this selection should be based on an evaluation of the identifiability of the specific

parameters, i.e. the ability to determine parameter values univocally. Identifiability encompasses structural or theoretical components, under the assumption that state variables are known under the consideration of measurement noise and sampling frequency. Several methods for identifiability analyses are available (Walter & Pronzato, 1997). If the identifiability of the parameters cannot be examined, the next best option is to examine the parameter sensitivity. Although the global sensitivity can be calculated (Englezos & Kalogerakis, 2000), analysis of the local sensitivity is more common (Lee et al., 2009; Tartakovsky et al., 2008).

The third step in the modeling procedure is the data collection, i.e. experimental measurements. A specific problem for AD is the challenge of spatial and temporal quantification of the specific microbial populations that are active in the system at any time. Some advanced molecular techniques employed to identify the presence and activity of microbial community members have been developed recently, but are not feasible for a frequent application. Alternative options for dealing with the issues of uncertainty with regards to the biomass include: (i) assuming constant biomass composition (Tartakovsky et al., 2002), (ii) assigning a fixed fraction of consumable solid components to each microbial group (Bernard et al., 2001a), (iii) estimating the initial biomass concentration from a preliminary simulation of the digester or by including them in the parameter estimation (Donoso-Bravo et al., 2011) and (iv), using state-estimators, based on the measurement of other variables (Bernard et al., 2001b; Lopez & Borzacconi, 2009).

Various cost functions or objective functions have been used for the parameter estimation, such as least squares, least-modulus, or maximum likelihood (Donoso-Bravo et al., 2011). Also, a large number of minimization algorithms have been applied: Gauss–Newton, the steepest-descent method, Levenberg–Marquardt (combination of Gauss–Newton and steepest descent), and genetic algorithms, just to denote a few (Englezos & Kalogerakis, 2000; Walter & Pronzato, 1997).

In the subsequent accuracy estimation, the uncertainty is determined. This is expressed by the measurements' covariance matrix and the previously determined sensitivity. Confidence intervals for the estimated parameters have been developed, too (Walter & Pronzato, 1997). If the estimated uncertainty is too large, additional experiments should be performed. The experiment, however, can be optimized in a design of experiments, to deliver the most information on the parameter estimates (Van Derlinden et al., 2010).

In practice, a single test with the intended substrate (for instance sludge) will not yield enough information to determine all the parameters with sufficient reliability. The cause for this problem is that the overall rate of the digestion process is often determined by the slowest process. Typically, the disintegration-hydrolysis is rate-limiting for substrates that contain large

quantities of particulates, while the methanogenesis step is considered to be the slowest for dissolved substrate. In those cases, a proper design of the experiment to estimate the parameter relating the non-limiting kinetics is impossible. As a result, two options are available: perform an additional test, in which intermediate degradation components are added, or rely on previously reported parameters. Finally, the resulting model should be subjected to a validation procedure.

Validation is often reported in terms of the coefficient of determination, R2 (Donoso-Bravo et al., 2011; Palatsi et al., 2010). If the results are not satisfactory, the quality of the data has to be improved by designing new experiments or employing alternative model structures. What is deemed to be 'a good model' is of course dependent on its intended purpose.

In case the model reflects well the true behavior, i.e. a reliable representation of the reality, the obtained residuals of validation of the model should be independent random variables. This can be tested by a Whiteness test, in which a derived form of the residuals should obey a $\chi 2$-distribution. Alternatively, the residuals should not show any correlation between themselves or with past inputs. If the latter were true, this means that a part of the measured output is not reflected by the model. A criterion for evaluation is to check whether the correlation between the inputs and the residuals is significantly different from the correlation within the residuals as well as the inputs (Lauwers et al., 2013).

To use predictive models in engineering design of physical systems, one should first quantify the model uncertainty. Uncertainty quantification (UQ) is the analytic process of determining the effect of input uncertainties (both their magnitudes and sources) on system outcomes. Traditionally applied in engineering reliability analysis, UQ now plays a significant role in predictive model applications as engineers and modelers are increasingly involved in designing or permitting complex systems, including predicting system behaviors through simulations (Arendt et al., 2012; Sun & Sun, 2015).

5. Discussion and conclusions

5.1. Challenges related to demand based production

Biogas production is generally able to supply power in a way that fluctuations of other renewable energy sources such as wind or photovoltaic electricity are balanced. Due to a rising amount of fluctuating renewable electricity producers, keeping the grid stable is a challenge for Germany, and many other parts in Europe, it is an economic burden as well. Therefore, Germany has to export and import energy steadily to keep the grid balanced. Table 1 illustrates energy trade between Germany and its neighboring countries in 2016. As one might easily conclude, the production of electricity is not congruent with the demand and there are periods with a lack or a surplus of electricity in the grid.

Table 1. Power trading between Germany and its neighboring countries in 2016 (entso-e, 2016).

Countries	Energy Import (TWh el)	Energy Export (TWh el)
Netherlands	0.338	24
Austria	3.5	17.8
Switzerland	3	16.1
Poland	16	10.7
Czech Republic	6.1	6.3
Luxembourg	1.4	6.2
Denmark	5.1	5.7

The main challenge for the German electric power system is the local and temporal balance between supply and demand. While spatial imbalances can be managed or diminished by grid expansion, trans-regional temporal imbalances must be solved by other means (Lefebvre & Tezel, 2017). For short periods and alternating imbalances, electricity storage technologies, demand-side management and virtual power plants can be adequate solutions. For longer periods, or to create a permanent surplus of energy over the year for system reliability purposes, only energy conversion to gas (e.g. power to gas) or heat would be adequate solutions. However, they all require cross-sectoral approaches as they connect the electric grid to the actual heat or gas demand. Due to the complexity of the energy generation infrastructure, multiple solutions and different technologies have to be applied. Since about 60 % of the final energy demand in Germany is used for heating and cooling purposes (Lefebvre & Tezel, 2017), thermal energy storage technologies would be a good solution. In this context, electricity is converted into thermal

energy ("power to heat") and used right away or stored for later use (Wei et al., 2017). To compensate the temporal imbalances, future storage technologies may include batteries, fuel cells and electricity storage; compressed air energy storage, large-scale batteries for regional imbalances; hydrogen storage, thermal storage, and pumped hydroelectric storage for long term storage needs (Comodi et al., 2017; Li et al., 2017).

Power production from biogas has a high technical and economic potential (Hahn et al., 2014). In a flexibilization concept on the basis of biogas, the production of electrical energy can be adjusted to the energy demand, and the intraday and spot markets. If a biogas plant owner wants to participate in these markets, certain requirements have to be fulfilled regarding the response time. Medium-term fluctuations in energy demand within hours are compensated by trading on the EPEX Spot SE electricity exchange. The European Power Exchange EPEX SPOT SE operates the power spot markets for Germany, France, Austria and Switzerland (Day-Ahead and Intraday). The price signal of 15 and 30 minute contracts determines a market value for flexibility (Märkle-Huß et al., 2017). Lead-time reductions on the Intraday markets further increase the flexibility of power markets (epexspot, 2018). Depending on weather conditions, electricity producers might be forced to slow down their production ranging from several days to several weeks, or on a seasonal scale. Energy demand has to be sustained by all renewable energy types following the reduction in the capacities of fossil fuel-based power plants.

Installation of an additional CHP and operating it with the already installed CHP is the most common way of flexibilization of the existing biogas plants, although many scientific studies focus on feed management, in which the biological process in fermenters is directly influenced, e.g. by a variable feeding strategy of various feedstock sources with different energy contents. Installation of an external gas storage is another alternative. A further way to flexibilize energy production is to purify biogas into biomethane, although, it is very expensive. Currently, there are about 200 biomethane production plants in Germany. The biomethane (ca. 210,000 Nm^3h^{-1}) is fed into the natural gas grid (Oechsner, 2017).

While the biogas sector grows impressively every year, it has not received the same attention as for example liquid biofuels for transportation. Natural gas powered vehicles have been available for a long time and biomethane plays an important role in the transportation sector (78 % of the produced biomethane). Biomethane production costs vary based on the dominant substrate utilized: between 4 – 7 €c kWh^{-1} from manure, 6.4 – 8.4 €c kWh^{-1} from energy crops, 5.4 – 6.2 €c kWh^{-1} for biodegradable waste, 5 – 8 €c kWh^{-1} for organic waste, 7.5 – 7.7 €c kWh^{-1} for energy crops+slurry (EBA, 2016; Vasco-Correa et al., 2017).

5.1.1. Feeding management

Although biogas plants are traditionally operated with a continuous and constant substrate feed, the biological process in the digester can be regulated with an adapted feeding regime. Feeding management refers to influencing and managing the amount and type of substrate entering into the biogas plant, as different substrate types can be added at different time points and in different amounts to generate the expected gas output. In this way, biogas generation rates can be altered on demand such that the need for gas storage can be optimized and surplus investments can be reduced. In practice, the process is controlled by considering the availability of gas storage capacities (Hahn et al., 2014).

Generally, substrates for biogas production can be characterized by the content of major chemical components (lipids, proteins, carbohydrates and fibers, such as cellulose, hemicellulose and lignin), the microbial biodegradability as well as the relationship of nutrient components to each other. The biochemical methane potential test provides information about the ultimate amount of methane produced from one substrate. The production kinetics can be used to estimate the quantity of biogas that can be produced within a given period (Szarka et al., 2013).

Biological degradation of different types of feedstock varies from several hours (e.g. glycerin, glucose or dairy waste waters) to several weeks (e.g. maize or grass silage). By feeding easily degradable substrates into the digester, the biogas production can be increased. However, still a flexible feeding management is not fully understood, as it is uncertain how anaerobic digestion in fermenters would react under fluctuating conditions. Moreover, it is currently not possible to predict how fast the biogas production might reach the envisaged amount (Hahn et al., 2014).

5.1.2. CHP and gas storage

Besides of feed management, flexibility can be generated through the installation of additional storage capacity, CHP and control-units for the biogas plant (Braun et al., 2017).

A temporary storage of biogas in gas storage facilities provides the possibility to decouple the gas production from the gas utilization. If a larger amount of gas has to be stored, external gas storage units must be built, which cost around 40 € m^{-3} (Ertem et al., 2016a).

In a gas storage management approach, the gas storage is filled and deflated. In order to produce electricity on demand, the produced amount of biogas, the stored amount of biogas and the demand for biogas for the CHP unit(s) have to be known at all time. The aim of the gas storage management is to monitor and control several gas storages. Biogas should be stored near to

the CHP units. Hence, a reliable and sufficient amount of biogas is available and can be used for a controlled electricity production. For this reason, a pressure cascade has to be created. In this pressure cascade, the lowest system pressure should be achieved at the gas storage, which is situated closest to the CHP units (Braun et al., 2017).

For the record of the stored amount of energy in gas storages, the composition, the temperature, the pressure and the volume of the stored biogas have to be known. Since the volume of gases depends on temperature and pressure, it is necessary to refer the volumes to standard conditions. Therefore, a comparison of biogas yields (m^3h^{-1}), volumes and the stored amounts of energy can be conducted. Since biogas is usually saturated with water vapor in internal gas storages, the water content of the biogas has to be considered additionally in order to determine the amount of stored energy. The gas temperature has a significant influence on the storable standardized volume. The temperature of the gas depends on several factors such as the ambient temperature, the type of digester where the gas storage is located (heated or non-heated digesters) and how the solar radiation affects the gas storage.

Investment of an extra CHP for flexible production would cost 0.17 € kW^{-1} depending on the power of the selected CHP. Moreover, additional operational costs of 0.215 € kW^{-1} can be expected (Ertem et al., 2016a). A flexible biogas utilization via CHPs can be achieved in two different ways. One option is the intermitting operation of CHP units at its nominal load, the second option is the part load operation of CHP units. Present engines of biogas CHP units are highly developed and optimized for an operation with biogas. Conventional CHP units in Germany are designed based on the previous funding structure (renewable energies acts of the years 2000, 2004 and 2009), adapted to a base load operation and optimized for a high number of full load hours.

If the CHP unit is intended to run according to the requirements of the grid, a reliable start process is very important. To ensure this, a constant methane concentration of the biogas at the CHP unit inlet is essential. CHP units with combustion can be kept permanently on standby and allow fast response times. The intermitting operation can be carried out according to a defined operating schedule at specific times, on short term price signals or needs. Until the CHP unit reaches its full performance, it is synchronized with the grid and the power output is increased constantly to its maximum. The synchronization with the grid takes between 1 and 2 min, the increase in power is about 1 s kW^{-1} el. A start–stop-operation causes higher material stress to the CHP units than a nominal operation (Wellinger et al., 2013).

Part load-operation of CHPs is another option for the flexible operation. The advantage compared to the intermitting operation at nominal load is that

the flexibility can be reached without additional start processes. In general, biogas CHP units can be operated with up to 40 % of their nominal load. In summary part load-operation leads to an increased engine stress and to a lower efficiency in the biogas utilization. Above a load of 90 %, energy efficiency reaches its maximum [5]. High part load-operating times increase the risk of losing additional electricity market revenues due to the inefficient utilization of the biogas and the higher demand for substrates. An intermitting operation of the CHP unit needs a shorter operating time to produce the same amount of electricity as in part-load operation. For this reason, a longer service life in years of the CHP unit in intermitting operation can be assumed. However, situations like starting problems due to short-term biological problems can arise in which the part load operation seems quite interesting for biogas plants. Especially the heat supply of the biogas plant or external customers can be an important argument for the part load-operation (Braun et al., 2017).

5.1.3. Purification of biogas to biomethane and injection into the gas grid

Another technical approach to achieve flexibility is the upgrading of biogas to the quality of natural gas. The production of biomethane generally allows a separate utilization of heat and power, because biogas plants and CHPs are situated in different places and the gas can be fed into the grid with no time restriction. Therefore, biomethane CHPs are highly suited for sites with a high heat-demand, while the biomethane plant is situated in rural areas where agricultural substrates are available. There are different options for the flexible utilization of biomethane and CHP units: i) Biomethane operated CHP units connected to large scale heat storage and operated at times of high electricity demand (peak load) and therefore also with high prices, ii) Biomethane operated CHP units only designed for peak load electricity supply, without heat utilization (impossible under EEG-2012). The current incentive within the support scheme EEG promotes investments, especially in new and additional CHPs, and/or additional gas storage capacities (O'Keeffe et al., 2016). However, the current price signals of the EPEX Spot SE do not stimulate flexible power generation and forecasting price volatility of EPEX Spot SE over multiple years is very difficult (Grashof et al., 2013).

5.2. Combination of LCA and modeling as a tool for control strategies at biogas plants

While the variability among biogas systems is vast, the results of LCA studies varies widely as well. In the mid and long term, the pressure either on biomass resources for their use as raw materials or energy crops as they conflict with food production is expected to increase significantly due to the

restricted availability of biomass. In this manner, it is important to evaluate all the possible resources. For instance, substituting energy crops with macroalgal biomass might be liable, since it would solve the conflict between bioenergy and food production as depicted in paper I as a part of this dissertation (Ertem et al., 2017).

Furthermore, challenges arise in reflecting the regional features, when LCA is applied on region-based studies of a specific plant, as they must be as close to reality as possible. This issue was addressed in paper iii. The results of this LCA study demonstrate variances among the regions when a same biogas production process was analyzed simply due to differences in regional farming procedures. The link between emissions into the environment and the farming system was indirect, it also depended on other climate variables such as rainfall and temperature. Agricultural production creates the highest source of the global warming potential in any regions analyzed, this was followed by the emissions resulting from transport. These results were supported by outcomes of paper II. This paper analyzed the concepts to facilitate a demand oriented biogas supply at an agricultural biogas plant and compared the environmental impacts of flexible and the traditional baseload operation. Outcomes of the study demonstrated that flexible production could result in lower amounts of emissions.

Several LCA studies were performed to study site-specific concerns. However, the studies were not quite successful at identifying the regions affected by regional activities. There is a need to develop a region-based LCA method, which can mirror the changes of regional characteristics for direct and indirect impacts of corresponding activities. Practical limitations naturally arise when a regionally contextualized LCA is conducted due to limited data availability, modeling capacities, and time constraints. These factors are the reasons why a regionalized LCA is more comprehensive than classic LCA approaches.

Paper IV reviews the current state of art for the latest developments in the LCA and mathematical modeling field and possible challenges that might arise if these 2 approaches are intended to be combined. In order to be able to integrate LCA and process modeling, it is necessary to include GHG formation processes within biogas production, which would make mathematical models more complex. Therefore, special attention should be paid to cover the gap on the lack of data, poor knowledge of anaerobic digestion and the emissions resulting from each processes. As LCA is traditionally a non-dynamic methodology, an interface between dynamic modeling results and inventory flows in LCA is required, together with the conversion of specific inventory items. Particular attention has also to be paid on the dynamics of methane formation to achieve a better control of the total GHG emissions from AD. Since the AD including biochemical hydrolysis is

regarded as the process with the greatest lack of data, modeling should first focus on this part rather than on pre- and post-treatment. Once the system is created in an LCA approach, optimization with mathematical modeling can be performed. This would diminish the negative impacts of biogas plants on the environment and even increase the positive impacts. In the study depicted by paper V, the simulation based on a combined LCA and modeling approach made it possible to increase the biogas production efficiency by 6% when the production was converted from baseload into demand driven production.

In general, the models developed so far were not totally successful in predicting anaerobic digestion operation, failure and possible remedies. The reason behind this fact is the stability problem of AD and the complexity of the whole system. The diversity and customized development of models for applications involving specific substrates limits their widespread implementation.

Regarding the kinetics of hydrolysis, a significant amount of information has been published. However, in most cases, the experimental data were not used for the development of appropriate kinetic models. In order to model the AD of various macromolecules; hydrolysis, acidogenesis and methanogenesis steps should be all considered. The effects of physicochemical parameters such as pH-value, temperature, and mass transfer have been adequately described in the existing models. However, these parameters should be incorporated under a wide range of operating conditions such as a variety of HRT and different organic loading rates. There is also a lack of modeling the system response upon exposure of certain inhibitors such as short-chain carboxylic acids, metal salts, nitrogen components, surface active substances, and others. The complexity of the anaerobic digestion model no. 1 (ADM1) leads to the application of either parameter-reduced versions of the ADM1 or simpler models as, e.g., the anaerobic digestion model AM2. In paper III, the AM2 was evaluated for the application at dynamic process operation, caused by a fluctuating feedstock load and further compared to the ADM1. It was shown that a tradeoff has to be made between model complexity and tractability in order to obtain reliable results: The ADM1 showed to be non-identifiable, if the data is obtained from a usual biogas plant. Taking this into consideration, the implementation of the AM2 in an adaptive framework should be preferred.

Another big challenge for modelers is to adjust the ADM1 or AM2 for a variety of substrates. Therefore, the proper characterization of feedstock required for many of the models is too time-consuming and not practical for the industry. The use of chemical oxygen demand (COD) measurements in AD modeling is not compatible with the data collection scheme of biogas plants, which measures the organic content of the dry matter. The COD is traditionally measured in wastewater treatment, but not at biogas plants.

Future model development should focus on user-specific conditions with additional emphasis on the digestate properties. Furthermore, new advances on the characterization of microbial community composition and full substrate characterization would help to advance mathematical modeling of anaerobic digestion processes and simulate the biogas plant operation more precisely.

LCA, performed for a new process state, requires time as well, a long delay between a process measurement and a control response including LCA would be the result. In these cases, a combined LCA approach for different scenarios based on mathematical modeling can provide predicted operation points independently from the current process state. One of the major questions for the developed tool in this study is the degree of its transferability that it might have for its use in other case studies or in additional areas. In this situation, the configuration of the simulation could be applied to other regions, after a suitable adaptation and calibration. The model structure must be modified to the selected area in terms of, for example, further biomass resources available in the region. More importantly, the model should include regional LCA parameters to decide about the suitability and the sustainability of the concept. It might be also necessary to include further variables within the model in order to capture the actual conditions of the region under study.

The results of the paper V prove that the introduced approach (combined LCA and mathematical model) supports decision making of biomass utilization in a regional scale and its use for demand driven energy production, through analyzing quantitative changes of environmental indicators, energy demands/generation and substrate characteristics. The approach therefore allows a sustainable regional development. The developed dynamic tool is a powerful method, it can thus provide useful decision support, especially when used as a priority-based screening of potential regional development programs for a new energy supply. By changing the conditions in the model, operators can find a way to prevent high emissions, but still avoid inefficiencies of the biochemical conversion process. This will reduce GHG and keep a profitable process.

Sometimes operators are faced with a decision that requires trade-offs. For example, what if they run the plant longer between turnarounds or when the substrate is limited? It's a difficult decision to make. The combination of modeling and LCA approach can help operators to better understand operating limits and optimal maintenance schedules to maximize plant profitability. This approach can be beneficial in many ways: it can help policy makers to decide where to build a newly designed biogas plant, how to operate the plant in order to reduce the negative environmental impacts resulting from the operation, how to reach future political targets related to

renewable energy production and emission reductions. It also provides fundamental and practice-relevant insights for the integration of newly planned biogas plants into regional economic cycles as well as national smart grid systems. This would be a greater interest for Mediterranean countries especially for island regions, as each year power supply are subsidized with billions of funds, which is a great burden on the society. Replacement of current diesel generators with renewables (particularly biogas production from biogenic residues) can substantially improve the economy and reduce the dependence of big power companies on these islands.

6. References

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Hypotheses

I. Future climate goals can only be met, if renewable energy sources are all considered and coupled together

II. Biogas production is generally able to supply power in a way that fluctuations of other renewable energy sources such as wind or photovoltaic electricity are balanced, consequentlyCO2eq emissions can be reduced.

III. Most commonly applied flexibilization way for industrial biogas plants is to produce biogas in the common constant way and collect the produced biogas in a storage and combust it at CHPs during the times when energy demand is the highest.

IV. In the mid and long term, the pressure either on biomass resources for their use as raw materials or energy crops as they conflict with food production is expected to increase significantly due to the restricted availability of biomass and arable land. Closed regional carbon cycles under consideration of biogenic residual material is one way to counteract this problem.

V. There is a need to develop and apply more intensively region-based LCA methods. However, there are practical limitations for trying to develop and conduct such regionally contextualized LCA approaches, such as data availability, modeling capacities, and time constraints.

VI. Better control strategies, technologies related to system monitoring and process optimization need to be developed in order to tackle challenges raised during biogas production via anaerobic digestion.

VII. Environmental LCA evaluations are relevant for marketing strategies, managing supply chains, and political decision-making as long as the data sources, assumptions, and all other relevant information are transparent to decision makers so that they can understand the full context of results.

VIII. The combination of modeling and LCA approach allows operators to adapt their energy production on a demand base from the regionally available feedstock mixtures, while the system efficiency is increased and negative impacts on the environment are decreased, as well. The approach can also help policy makers to decide where to build a newly designed biogas plant, how to operate a biogas plant in order to reduce the negative environmental impacts resulting from the operation, how to reach future political targets related to renewable energy production and emission reductions.

IX. In order to be able to combine LCA and modeling approaches, and take the benefit of simulating processes to gain data rather than making a lot of experimental observations on a local scale with much effort, it will be necessary to include GHG formation processes, which make models even more complex.

X. One of the major questions for any developed tools is the degree of transferability that it might have for its use in other case studies or in additional areas.

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Environmental life cycle assessment of biogas production from marine macroalgal feedstock for the substitution of energy crops

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ABSTRACT

The central objective of this paper is to evaluate the production of biogas by the substitution of energy crops with marine macroalgae: mixture of brown (20%) and red algae (80%) as feedstock in an industrial scale biogas plant. This plant operates with the co-digestion of maize (27%), grass (54%), rye (8%) and chicken manure (11) and produces 500 kWh energy. In order to assess environmental friendliness, a life cycle assessment was performed by using the software Simapro. Potential environmental impact categories under investigation were global warming, acidification, eutrophication and land transformation potential.

Our results determine the affirmative impact of the codigestion of algae with chicken manure on the emission reductions: 52%, 83%, 41% and 8% lower global warming, acidification, eutrophication and land transformation potentials, respectively per 1 MJ of energy generation, moreover, 84% and 6% lower acidification and land transformation potentials per kg of feedstock.

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1. Introduction

Biomass resources are considered as one of the main renewable energy sources and expected to provide more than half of the energy demand in the near future (European Renewable Energy Council, 2008). Nevertheless, some studies suggest that intensive exploitation of arable land for the cultivation of energy crops may yield a negative impact on the global stock and prices of food and will lead to increasing quantities of greenhouse gases (GHG) being emitted to the atmosphere (Fargione et al., 2008; Johansson and Azar, 2007; Searchinger et al., 2008). For that reason, alternative sources of biomass for energy generation that would be both economically competitive and environmentally-friendly are required. Considering its high photosynthetic effectiveness, fast biomass growth and resistance to contaminations (heavy metals), algae appears as a competition to typical energy crops (Aitken et al., 2014; Alvarado-Morales et al., 2013; Lardon et al., 2009). Macroalgae has been harvested from the sea. Brown macroalgae dominate the harvest with twice the volume of red macroalgae. Green macroalgae (seaweed) are less valuable and are not harvested in significant amounts (Werner et al., 2004). According to Yokoyama et al. (2007), 0.9% of Japan's required CO_2 mitigation according to the Kyoto protocol could be achieved by farming macroalgae on a large scale. However, it has to be considered that burning or decomposing macroalgal biomass will only recycle carbon. In this respect, the application of macroalgae to produce energy appears to be a promising practice to complement energy supply based on biomass. This paper presents an assessment of the consequences for the sustainability of biogas production, when the energy crops are (partially) replaced with macroalgae (brown and red algae) as feedstock at an industrial scale biogas plant in Northeast Germany.

As macroalgae attracts quite a lot interest for biofuel production, this paper focuses on the macroalgae harvest from the regions or areas nearby the coast for biogas production and its replacement with energy crops. In many countries, an excessive natural growth of macroalgae has been observed as result of the progressive eutrophication of coastal water by excessive amount of N, P, CO_2 and insufficient amount of dissolved O_2. Macroalgae consume these nutrients for biomass growth. Collection of this biomass from beaches would result in clean beaches and altered impacts of eutrophication. This biomass could also represent a potential substrate in biogas plants as has recently been suggested by many authors (Allen et al., 2013; Bucholc et al., 2014). Current bioenergy projections are based on feedstock such as corn, soya bean and sugar cane, which are also food commodities. Energy and agricultural markets are closely linked, and due to their size the

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movements in energy markets affect agriculture more than vice versa. Therefore, algal biomass offers a number of advantages, especially the use of otherwise nonproductive land (in our case, no arable land use, due to harvest of beaches), and some others (Subhadra and Grinson, 2011). In case of integrated concepts, in which biogas production is coupled to a biorefinery concept, certain algae can be used for the production of other liquid and gaseous fuels like biohydrogen, see for a review e.g. (Kumar et al., 2015). Then, biomass residues of these processes might be used as feedstock for a final biogas production, before those are applied as fertilizer.

2. Methods

Life cycle assessment (LCA) is a method that evaluates the environmental impacts of a system by collecting an inventory data related to inputs and outputs. On the next step, it assesses the potential environmental effects of those inputs and outputs. As a last step; it interprets the results of the inventory and impact assessment based on the aim of the study (ISO, 2006). The standard ISO 14040:2006, which gives the basis for LCA procedures, was pursued in this study. The study analyses the Northeast region of Germany, which is characterized by sandy or loamy soil. The amount of rainfall is approx. 20% lower in comparison to other regions in Germany. That is why the inventory data, including the digestate composition, emissions, operation style of the biogas plant, agricultural management for crop cultivation, regional properties of the soil and climate conditions, are chosen to be descriptive for the area. The outcomes of this study may be further used for other geographical areas only after a suitable revision of data.

2.1. System boundary

Fig. 1 indicates both systems investigated: firstly the current production system with energy crops, and secondly, the alternative production system with the co-digestion of macroalgae and chicken manure. The analyzed systems involve the collection/production and storage of feedstock, anaerobic digestion, storage/handling of digestate, electricity and heat generation from biogas, and lastly the transportation.

2.2. Life cycle inventory analysis

Inventory Analysis is a stepwise methodology for measuring the energy and raw materials necessary, atmospheric and waterborne emissions, solid wastes, and other releases for the entire life cycle of the system. The inventories include all main process steps and contain resources used, as well as emissions to the air, water, or surrounding land until biomethane is released to the gas grid.

The amount of feedstock, biogas production and methane ratio, and electricity consumption were observed continuously at the plant during one year, in this case 2012. Material flows that could not be determined at the plant were calculated based on the assumptions from literature. The rest of the calculations were performed depending on the database of Ecoinvent 2.2 (the Ecoinvent Centre, Switzerland) (Hans-Jörg Althaus et al., 2010).

2.2.1. Determination of feedstock amounts/compositions and functional unit

The quantity of macroalgae to substitute energy crops was determined based on biogas yields. Characterization of feedstock, the total solid (TS), organic total solid (oTS) and the biogas yield

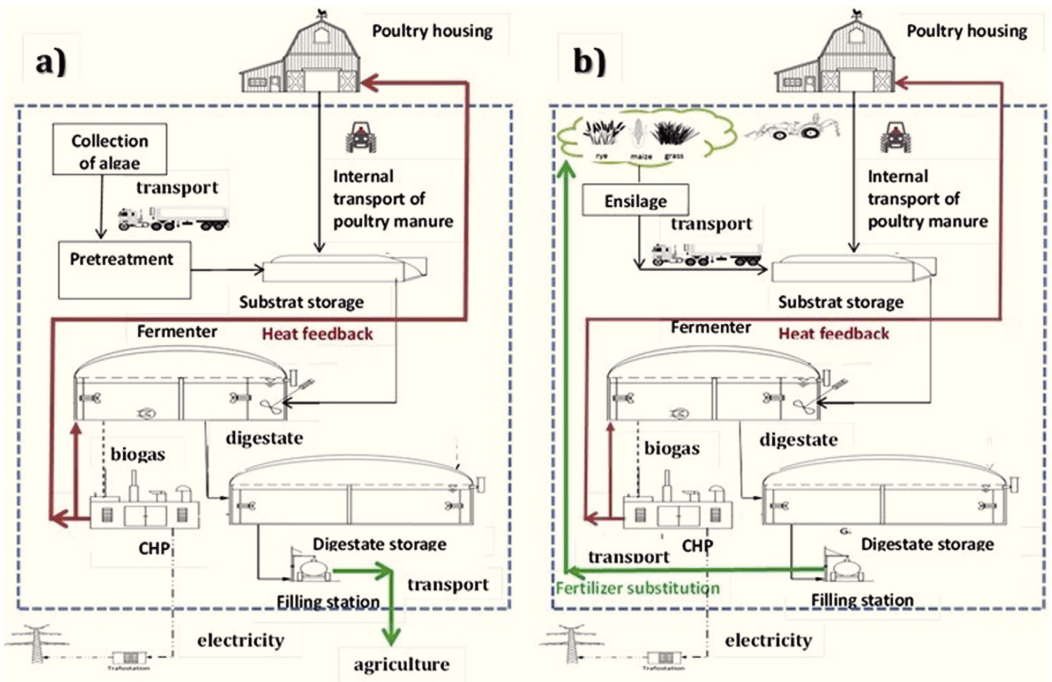

Fig. 1. System boundary: Energy production from the co-digestion of chicken manure with a) Macroalgae and b) Energy crops. Adapted from (KTBL, 2014). The arrows indicate material and energy flows.

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Table 1
Characteristics of the feedstock.

Feedstock	Macroalgae	Maize silage	Rye silage	Grass silage	Chicken manure
TS (% FM)	24.8	33	25	35	40
oTS (% TS)	80	95	89	90	75
Gas yield (m^3t^{-1} FM)	993	270	245	255	225
Methane content (%)	60	52	53	53	55

TS: Total Solid; oTS: organic Total Solid; FM: Fresh Matter.

were determined based on literature (Ertem, 2011; FNR, 2010; KTBL, 2014) (Table 1).

The functional unit (FU) provides a logical basis for comparing the environmental performance of alternatives (ISO, 2006). The main function of these bioenergy systems is the anaerobic digestion of feedstock for biogas production in order to co-generate electricity and heat. Therefore, two FU were chosen: 1 kg of feedstock mixture fed into the digester and 1 MJ of energy production from biogas. The selection of these FUs is in agreement with other biogas LCA studies (Bacenetti et al., 2012; Dressler et al., 2012; Poeschl et al., 2012a).

2.2.2. Feedstock

The total 7227 tons of energy crop were cultivated on 360 ha of agricultural areas yearly: 2190 tons of maize, 657 tons of rye and 4380 tons of grass (based on wet weight). While maize and rye were harvested once a year, grass was harvested three times a year and then ensiled for 6 months. Although it is suggested that ensiling may increase the methane yield and use of correction factors might cause overestimated methane yields (Herrmann et al., 2011; Kreuger et al., 2011; Pakarinen et al., 2011), it is accepted in this study that the changes in wet weight and total solids during ensiling are small and the loss of energy is negligible.

Table 2 provides an overview of the required input for cultivation of energy crops. Emissions from herbicide applications were calculated based on data from Tenuta and Beauchamp (1996), and Lal (2004). Following the ensilage, crops were transported to the biogas plant. Emissions from ensilage were estimated based on data provided by Institut für regenerative Energietechnick Fachhochschule Nordhausen (2013). The transport (12 km) was conducted with a truck consuming 40 L h^{-1} Diesel. The Diesel consumptions of all the vehicles used in the system were provided by the biogas plant owner.

In order to replace the energy crops, 1400 tons of macroalgae with a C to N ratio of 15:1 were collected from German coast of the Baltic Sea. The most common algae types lie on the beaches around the Baltic Sea is filamentous red algae as also determined by Trelleborg municipality (Gradin, 2015). The collected samples consisted of 80% red algae and almost 20% brown algae mixed with some other residues (less than 1%). Algae was harvested from the shore in early September (it starts lying on the beach since April) by The DM Truxor 4700B amphibian with a fork attachment, a collection capacity of 45 m^3h^{-1} and which consumes 12 L Diesel h^{-1}. The vehicle can operate both on land and in water. As proven by WAB Projects, collected samples are almost completely free of sand, although the machine moves quite slowly (Municipality, 2011). The collected algae were transported (150 km) by a 40 ton capacity truck. In order to have a successful anaerobic digestion, the C to N ratio of feedstock mixture should range from 20:1 to 30:1 (Carver et al., 2011; Mata-Alvarez et al., 2000). Macroalgae has typically lower C:N ratio and high S content (1%) and therefore it was important to co-digest with a feedstock high in N and low in S content (0.31%), e.g., chicken manure to achieve adequate values of C:N ratio and sulphur amount. The high sulphate concentration can lead to the formation of H_2S which results in inhibition of methane production; foul odours; sulphur dioxide emissions on combustion of the biogas; and a corrosive environment (Milledge et al., 2014). For that reason, 912.5 tons of annually produced chicken manure (C to N ratio of 30:1 due to its high straw content) were utilized. The feedstock mixture consisted of 40% manure and 60% macroalgae (based on wet weight). The feedstock mixture had a C to N ratio of 21:1 and 0.72% sulphur content (FNR, 2010). The manure was carried by a tractor to the storage (up to 3 months store). The loading capacity of the tractor was 250 kg and the Diesel consumption was 40 L h^{-1}. Nitrogen-based emissions during storage of chicken manure were estimated based on data from Wathes et al. (1997), Nicholson et al. (2004) and Koerkamp (1994). It was assumed that the storage process results in a release of 10% of the ammonium content to the atmosphere.

Table 2
Basic data for the cultivation of the crops.

	Maize	Rye	Grass	
Dates				
Sowing	1st of May	1st of October		1st of April
Harvest	20th of September	20th of June		Harvest 1: 1st of April; Harvest 2: 1st of July; Harvest 3: 1st of October
Input (kg ha^{-1})				
Seed	28	110	40	
Herbicide	3	3	1	
N fertilizer	166	130	38	
P_2O_5 fertilizer	72.7	75	70	
K_2O fertilizer	180	170	220	

Cultivation data of crops are real data of the plant.

2.2.3. Pre-treatment of algae

Macroalgae contain different types of carbohydrates depending on genera. Brown seaweeds lack of easily fermentable sugars. For this reason, it would not be feasible pursuing a standard AD. On the other hand, green and red seaweeds have high levels of easily accessible sugars. Those are represented by floridian starch and xylan in red macroalgae and starch in green macroalgae (Montingelli et al., 2015). The higher amount of red algae therefore could boost the AD process. Therefore, no pretreatments for the breakdown of the carbohydrates were necessary for this study. However, mechanical pre-treatment was applied as described by Alvarado-Morales et al. (2013). The system consists of milling and grinding of harvested macroalgae (particle size 0.5 cm). The energy consumption was estimated to be 38 kWh per ton of dry macroalgae. Moreover, the electrolytic recovery method for heavy metal removal was utilized as described in Stopić et al. (2007). The yearly energy consumption was determined as 61 MW.

Baltic Sea has a salinity of 2 PSU (practical salinity unit and 1 PSU = 1 g L^{-1}) (Matthäus and Ulrich Lass, 1995). Low salt concentrations can stimulate microbial growth, but high salt concentrations ($\geq$10 g L^{-1}) are known to inhibit anaerobic systems through an increase of osmotic pressure or dehydration of methanogenic microorganisms (Barbot et al., 2015). The collection of macroalgae

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brings along the salinity problem, occasionally. Since the salinity in Baltic Sea is quite low and a possible inhibition of microbial growth through increased salt concentration in the bioreactor was ruled out by Wiese and Konig (2009), in this study the salinity is accepted to create no challenge for the digestion.

2.2.4. Anaerobic digestion

3 digesters with a total volume of 4500 m^3 are operated at the biogas plant. The digesters are temperature-controlled at 42 °C, culture broth is retained for 170 days. A 1% share of total biogas produced at the digesters assumed to leak into the atmosphere. Electricity for the plant operation was supplied from the electrical grid. Biogas was burnt in a 500 kW Combined Heat and Power, which is assumed to run 8552 h per year. 35% of the produced heat was used for temperature control of the digesters and 65% to the chicken housing.

2.2.5. Digestate

Digestate was stored at the plant or near the agricultural field. The storage process resulted in emissions of CH_4, N_2O and NH_3, which vary depending on the seasonal temperature and the nutrient composition of the digestate. The emissions were estimated according to data from De Vries et al. (2012), (Faulstich and Greiff, 2008); Jülich (2008) and Lukehurst et al. (2010).

The digestate provided N, P, and K (De Vries et al., 2012) for the energy crop production. It was transported to the agricultural areas by a truck of a capacity of 40 tons. The quantities of mineral fertilizers that are potentially substituted by the digestate were determined based on the digestate properties and fertilizer exchange values. In addition, the digestate compositions were determined based on the decomposition rates of the feedstock mixture, and organic N available (De Vries et al., 2012; KTBL, 2014).

Digestate is spread by splash plate into arable land. Methods as described by Brentrup et al. (2000) were followed to determine the fertirrigation emissions caused by digestate spreading. Fertirrigation stands for the combined utilization of fertilizers and water. The main difference from normal fertilization is that in this method, fertilizers are added in soluble forms at low amounts but high frequency, which also allows to save large amounts of water (Lucena, 1995). In the system where macroalgae codigested with chicken manure, there were no possibility to have a closed loop, which allows digestate to be used back in the agriculture as fertilizer, because there is no crop production takes place. Therefore, in this system, the digestate is evaluated at the closest agricultural areas in the same region; however its application is extracted from the system boundary.

2.3. Life cycle impact assessment

The function of the life cycle impact assessment step is to pile up the data gathered in the inventory. First, a classification of impact categories is performed, typically replicating a joint mechanism of environmental risk (e.g. global warming and acidification). In the characterization step, the environmental operation listed in the inventory table is translated into points in regard to each impact category (Tukker, 2000). These points deliver an estimation on the relative intensity on an environmental impact category (Goedkoop et al., 2009). To enable the comparison of feedstock, environmental impacts were calculated based on FU.

A combination of impact categories was considered depending on the type of process: global warming (GWP) in kg CO_2-eq, acidification (AP) in kg SO_2-eq, eutrophication (EP) in kg P-eq, and land transformation (LTP) in m^2. GWP is used within the Kyoto Protocol as a metric for weighting the climatic impact of emissions of different GHG's (Shine et al., 2005). Acidification potential accounts for acidification caused by SO_2 and NO_x. Many nitrogen compounds, which are added as fertilizer, acidify soil over the long term because they generate nitrous oxide and nitric acid during the process of nitrification. The production systems were modelled in the Simapro 7.3.2 (PRé Consultants, 2008) by using the Ecoinvent 2.2 database. The effects of emissions in the environment were assessed for a 100-year period, in accordance with the ReCiPe midpoint hierarchist method v.1.06. Midpoint results help to improve the understanding of the complexity of the impacts to emissions to air, water and soil to impact categories. Positive values indicate increased environmental impacts.

3. Results

LCA studies were performed within the system boundaries as shown in Fig. 1. Fig. 2 illustrates the comparison of LCA characterization results (For a detailed overview, see Appendices). When energy production is considered (FU: 1 MJ of energy production), the substitution of energy crops with macroalgae would result in 67%, 95%, 65% and 73% lower GWP, AP, EP and LTP, respectively, due to the avoidance of digestate spreading. When the amount of feedstock for energy production is considered (FU: 1 kg of feedstock fed into the digesters), it can be seen that macroalgae would result in 22% and 15% higher EP and GWP. The different functional units lead to varying results, which underlines the importance of the consideration of relevant FU based on the necessities; either the bioenergy production or the amount of feedstock consumed.

When macroalgae were used, the greatest emission contributor were the digesters (44% of GWP, 32% of AP and 40% of the EP). If the current operation (co-digestion of energy crops with chicken manure) was investigated, it is seen that the digestate spreading contributes the highest to acidification, eutrophication and particulate matter formation potentials due to high nitrate and phosphorous emissions. Crop production creates the highest LTP due to arable land use for bioenergy production, followed by transport. Fuel combustion emissions of the transport cause the highest GWP. The outcomes showed that macroalgae provided highly promising results by means of GHG emissions savings (Fig. 2).

3.1. Greenhouse gas balance

The combustion of biogas (biomethane) is climate neutral, assuming that methane is completely oxidized during biogas combustion. After biomass combustion, carbon dioxide is released back into the atmosphere with no net addition of carbon, as it is consumed during plant growth (photosynthesis) and converted back into biomass. GHG emissions are based on organic carbon depletion in the soil, diesel utilization, nitrous oxide emissions of the plant cultivation process, methane losses during digestion and the process energy input. Gross GHG emissions of the systems are for macroalgae 13.9 g CO_2-eq MJ^{-1} and 160 g CO_2-eq kg^{-1} feedstock, and for energy crops 28.9 g CO_2-eq MJ^{-1} and 140 g CO_2-eq kg^{-1} feedstock, respectively (Fig. 2a).

Naturally, the results of GHG emission savings depend on the type of feedstock. According to Fig. 2a, results suggest that the operation using energy crops has a GWP, which is 52% higher than that in the case of macroalgae. The GWP reductions were caused due to no agricultural activity within the macroalgae scenario. When macroalgae are co-digested with chicken manure, digestion (44%) and digestate storage (38%) contribute the highest to the GWP.

Various LCA studies have analyzed the environmental benefits and the deficiencies of biogas production from different feedstock (Börjesson and Berglund, 2007; Hartmann, 2006). The use of different data, functional units, allocation methods, system

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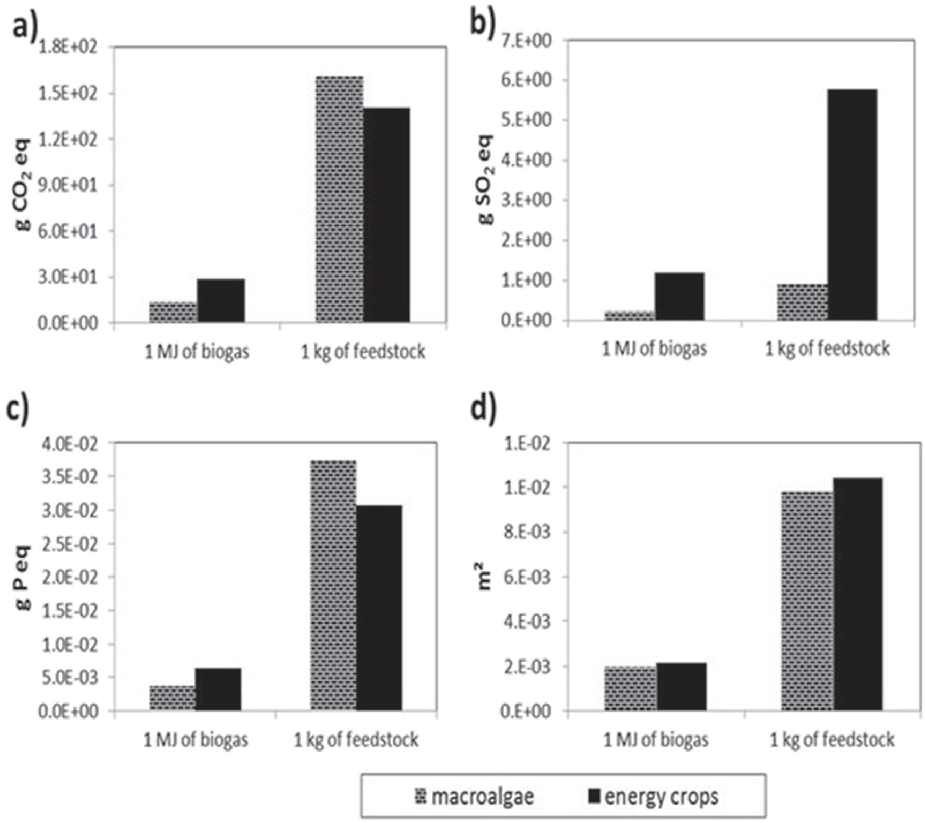

Fig. 2. The comparison of LCA results for energy production with macroalgae and energy crops based on a) global warming, b) acidification, c) eutrophication and d) land transformation. The results are given depending on FU's.

boundaries, impact methods and other assumptions impedes frank comparisons of LCA bioenergy studies (Cherubini and Strømman, 2011). In addition, uncertainties and the use of specific local parameters for indirect effects lead to a wide variability of results (Dressler et al., 2012).

(Poeschl et al., 2012a, b) investigated several digestion scenarios of different feedstock. They derived a GWP of mono-digestion of energy crops at small-scale biogas plants of 113.8, 163.86, 107.62 g CO_2-eq kg^{-1} feedstock for maize, wheat, and grass silage, respectively. They demonstrated that the largest environmental burdens are obtained by the use of energy crops as feedstock due to the higher fossil fuel consumption during the agricultural production.

Bachmaier et al. (2010) investigated the CO_2 emission of 10 biogas plants in Germany that emitted an average of 37.7 g CO_2-eq MJ^{-1}. The authors found out that the electricity production in the biogas plants avoids GHG emissions of 573–910 g CO_2-eq per kWh el. They conclude that a consistent estimate of the GHG emissions of electricity production from biogas can be realized only for individual plants, based on data over a period of at least 1 year. Furthermore, they have concluded that the validity of GHG balances should be improved by supplying reliable data on NO_x emissions from energy crop cultivation, methane leakage from biogas plants and emissions from unsealed digesters. Dressler et al. (2012) investigated the conversion of biogas produced from maize into electricity at several biogas plant within a life cycle assessment view and found out the GWP ranging between 16.1 and 50 g CO_2-eq MJ^{-1}. The authors identified the cultivation of maize as the most influential parameter for the GHG emissions. When the GHG emissions from biogas plants are considered, our study is in agreement with the results provided by other studies.

Not many LCA studies were conducted regarding to the utilization of macroalgae as feedstock for biogas plants. Alvarado-Morales et al. (2013) performed an LCA study for the biogas production from brown macroalgae. The authors showed that the highest GWP originates from macroalgae production. If the production was not considered, the GWP equals to 15 g CO_2-eq MJ^{-1}. In our study macroalgae were not digested alone, but instead co-digested with chicken manure. Low C to N ratio of macroalgae and a high sulphur content could be problematic for anaerobic digestion. Co-digestion with chicken manure (High in N content and low in S) will overcome these problems by increasing the C to N ratio to 21:1 and decreasing the S content to 0.72% (based on the operation of the plant described in this study, see also Section 2.2.2).

3.2. Emissions leading to acidification and eutrophication

Emissions that lead to acidification are on-site an include H_2S, NH_3, SO_2, and NOx emissions. In the current operation, the acidification potential is primarily caused by ammonia and secondly by

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nitrous oxide release during the application of digestate. Ammonia releases into the atmosphere are mainly caused due to the evaporation and strictly related to the season of the spreading due to differences in temperature. However, the system analyzing the co-digestion of macroalgae and chicken manure does not include any agricultural activities, since all the crop production are excluded from considerations. In this operation style, the highest AP resulted from SO_2 and NO_x emissions created during the collection of macroalgae, followed by Diesel combustion emissions from the transport of algae. This study determined the AP of the current operation system as 5.77. When the energy crops are replaced with macroalgae and co-digested with chicken manure, this potential decreases to 0.89 g SO_2-eq kg^{-1} feedstock (82% lower, Fig. 2b).

The eutrophication balance shows similar trends between the analyzed biogas production systems, as similar findings are reported by other studies (Bühle et al., 2011; Jury et al., 2010). This fact underlines the importance of obtaining feedstock for biogas production under sustainable conditions. Poeschl et al. (2012b) determined the eutrophication potentials of energy crops per kg feedstock as 0.01, 0.03, 0.09 g P-eq for maize, grass, wheat silage, respectively. This study determined the EP of the current operation style as 0.03 g P-eq kg^{-1} feedstock and the EP of the co-digestion of macroalgae and chicken manure as 0.037 g P-eq kg^{-1} feedstock (Fig. 2c).

For the current operation, the EP mainly depends on the phosphate content of digestate (applied P per ha during spreading) and the emissions from the main digester. Emissions of the main digester create the highest EP, when macroalgae are used. These emissions could have been avoided, if ammonia filters were applied (Deublein and Steinhauser, 2011).

3.3. Natural land transformation

When the FU per kg feedstock is considered, LTP was determined as 0.01 m^2 for energy crops and 0.0098 m^2 for macroalgae. LTP (Fig 2d) were mainly related to transport and agricultural crop production. When energy crops are substituted with macroalgae, the LTP is reduced by 2%, which is due to the unnecessity of agricultural production. If the biogas plant was located in a 50 km distance to the coastline, the LTP would be 0.009 m^2, at a distance of 150 km, it rises by 12%. Thus, the transport distance has a huge impact on the LTP.

4. Discussions

4.1. Limitations of the study

Although no sensitivity analysis was performed in this study, the chosen factors were based on practical considerations and thus are relevant as they can be substituted or changed in a real case. However, all chosen values, e.g. to model harvest, depend on many factors as the type of vehicle, fuel consumption, its capacity, etc., which cannot be varied for every plausible case. Analyzing the impacts of regional factors would be topic of further research, since this study has a limited scope. Another limitation lies in the restricted consideration of all possible pretreatment methods for macroalgae. However, as aforementioned pretreatment methods to be applied mainly depends on the vehicle chosen, The vehicle chosen in this study makes it sure that there is no sand accumulation in the harvested biomass. Only disadvantage of the vehicle is its long working hour requirements, since it moves quite slowly. Regarding any other inorganics or heavy metals, our study has already investigated the mechanical and electrolytic pretreatment. As described before, salinity could have been a problem, if the algae would have harvested from different regions or from another coastal line of another Sea except of Baltic Sea. This also requires further research regarding to impacts of region on the harvested biomass properties.

4.2. Limitations and benefits of biogas production with algal feedstock

Biogas is currently produced mainly from land-based crops. A constant utilization of these crops leads to a food versus energy argumentation. A feedstock is required, which is plentiful and carbohydrate-rich. The production of such a crop should not require the utilization of pesticides, herbicides, and a vast amount of fertilizer. Marine biomass could encounter these challenges, since it is an abundant, carbon neutral renewable resource with potential to diminish GHG emissions and the climate change impact.

However, a low interest in algal biomass as an alternative source of biodegradable organic matter applied in biogas production systems is mainly due to technological and technical difficulties in process operation due to a complex harvest of macroalgal biomass acquisition, high initial hydration of biomass, difficulties with its storage and high costs of its dehydration. Other main technology-related issues include the selection of an appropriate retention time, and methods of biomass conditioning and pretreatment (González-Fernández et al., 2011; Wu et al., 2010; Yuan et al., 2011). If the pretreatment is not conducted appropriately, macroalgae reduce or completely inhibit biogas formation (Bruhn et al., 2011; Chynoweth et al., 1993; Guo, 2007; Ras et al., 2011; Yen and Brune, 2007; Zeng et al., 2010). If the high protein content is not considered, it may lead to enhanced production of free ammonia and volatile fatty acids. They elicit toxic effects on methanogenesis. In addition, sodium ions in the algal biomass may inhibit the biogas production as well (Dębowski et al., 2013). The high sulphate concentration which is typical for green macroalgae can also lead to inhibition in the fermentation process as proven by Hilton and Archer (1988); Murphy et al. (2013).

In comparison to biomass crops, macroalgae comprise little cellulose, no lignin and a low C:N ratio (Wu et al., 2010). However, the C to N ratio of feedstock should range from 20:1 to 30:1 (Carver et al., 2011; Mata-Alvarez et al., 2000). The most accurate evaluation of the industrial potential of methane production from macroalgae was performed by Matsui et al. (2006) using a commercial scale 4-stage anaerobic digester, with a daily input between 0.2 and 1.0 tons of macroalgae at a retention time of 15–25 days. This resulted in an average production of 22 m^3 of methane per ton wet weight of brown macroalgae. However, recent advances suggest there is still potential for further optimizing biogas yields through co-digestion with a more nitrogenous substrate, for example chicken manure or maize silage. Mussgnug et al. (2010) tested the co-digestion of macroalgae with maize silage and concluded that this operation results in a higher yield of methane fermentation under the same technological conditions. Ertem (2011) demonstrated that under same mesophilic conditions with 10% inoculum addition, mono digestion of macro algae would result in lower biogas yields, compared to energy crops; 84.5 m^3t^{-1}VS for the mixture of brown&red algae, 578.9 m^3t^{-1}VS for sugar beet 107.9 m^3t^{-1}VS for straw, 461.6 m^3t^{-1}VS for maize.

Despite some limitations of algal biomass utilization for biogas production processes, the studies conducted so far enable acknowledging it as an alternative and prospective source of organic substrate. Macroalgae have many advantages over typical, higher energetic crops. The algae, especially the marine macroalgae contains high quantities of polysaccharides and lipid and arefree of sparingly-degradable lignocellulose compounds (Vergara-Fernández et al., 2008). The biomass of algae serves as a source of nitrogen and important microelements (cobalt, iron, nickel) for the

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appropriate growth of anaerobic microorganisms (Mata-Alvarez et al., 2000). Macroalgae grow by a higher rate than energy crops, whilst the feasibility of harvesting can make them a competitor on the feedstock market (Rittmann, 2008): According to Gao and McKinley (1994) uncultivated growth of brown and red algae is equivalent to 165–565 t ha^{-1} fresh weight per year, while this growth according to our values equals to 35, 6 and 67 t ha^{-1} fresh weight per year for maize, rye and grass, respectively.

5. Conclusions

The principal aim of this study was to assess the environmental load of macroalgae-based feedstock for the operation of a biogas process throughout the whole life cycle. Our results determine the affirmative impact of algae on the emission reductions: 52%, 83%, 41% and 8% lower global warming, acidification, eutrophication and land transformation potentials, respectively for 1 MJ of biogas production, moreover, 84% and 6% lower acidification and land transformation potentials for 1 ton of feedstock. However, based on the consideration aspect, the results could be debatable. Here one should answer a simple question: what should be considered as resulting in the lowest environmental damage: is it producing the highest possible amount of energy or using the lowest amount of feedstock?

When the aim is producing higher amounts of energy, substituting energy crops with macroalgal biomass is liable, because it helps to solve the dilemma between bioenergy and food production. On the other hand, when the amount of feedstock to be transported and fed into the digesters are the concern, it would be beneficial to analyze the whole system based on the FU of 1 kg feedstock: In this case, the energy crops could be more favorable to mitigate the negative environmental effects of biogas plants.

The outcomes indicate that sustainable energy production is achievable with the co-digestion of chicken manure (40%) and macroalgae (60%). The collection of the algal biomass from the costal lines for biogas production purposes would considerably reduce the total farmland effects caused by terrestrial crop production.

However, in order to produce bioenergy in the form of methane from macroalgae, it will be necessary to:

- Optimize the pre-treatment to improve the performance of a substrate for AD and to ensure that the digestate from the biogas production can be returned to the farmers and re-used as fertilizer.
- Overcome toxicity caused by high levels of phenols, heavy metals, sulfides, salts, and volatile acid compounds found in seaweeds, which can inhibit methanogenesis.
- Optimize harvesting procedures to minimize environmental impacts and overall costs.

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Abbreviations

AP	acidification potential
GWP	global warming potential
GHG	greenhouse gas
EP	eutrophication potential
FU	functional unit
LCA	life cycle assessment
LTP	land transformation potential
oTS	organic total solid
RE	renewable energy
TS	total solid

Appendices

Table A1
LCA characterization results inventory for energy crops based on two functional units: 1 MJ of biogas (FU1), 1 ton of feedstock (FU2).

Process units	GWP (kg CO_2eq)		AP (kg SO_2eq)		EP (kg Peq)		LTP (m^2)	
	FU1	FU2	FU1	FU2	FU1	FU2	FU1	FU2
Crop production[a]	2.64	1.28E+01	1.59E-02	7.72E-02	7.75E-04	3.76E-03	1.35E-03	6.56E-03
Storage[b]	9.96E-01	4.83	1.06E-02	5.14E-02	1.38E-04	6.68E-04	2.85E-05	1.38E-04
Transport[c]	1.30E+01	6.32E+01	9.20E-02	4.46E-01	4.07E-04	1.97E-03	6.26E-04	3.04E-03
Others[d]	1.22E+01	5.93E+01	1.07	5.20	5.02	2.43E-02	1.38E-04	6.71E-04

[a] Maize, rye and grass production.
[b] Storage of crops, manure and digestate.
[c] Transport of crops, manure and digestate.
[d] Fermentation, heat and electricity production from biogas and digestate spreading.

Table A2
LCA characterization results inventory for macroalgae based on two functional units: 1 MJ of biogas (FU1), 1 ton of feedstock (FU2).

Process units	GWP (kg CO_2eq)		AP (kg SO_2eq)		EP (kg Peq)		LTP (m^2)	
	FU1	FU2	FU1	FU2	FU1	FU2	FU1	FU2
Algae harvest[a]	2.10E+00	2.43E+01	7.62E-02	3.31E-01	1.15E-03	1.16E-02	6.11E-04	3.05E-03
Pretreatment[b]	1.32E+00	1.53E+01	1.27E-02	5.51E-02	6.95E-05	7.04E-04	2.03E-04	1.01E-03
Storage[c]	5.50E-01	6.37E+00	6.41E-03	2.79E-02	6.93E-05	7.03E-04	1.02E-05	5.08E-05
Transport[d]	7.77E+00	8.99E+01	1.08E-01	4.68E-01	6.63E-04	6.72E-03	1.00E-03	5.02E-03
Others[e]	2.16E+00	2.50E+01	3.03E-03	1.32E-02	1.75E-03	1.78E-02	1.38E-04	6.92E-04

[a] Harvesting of macroalgae from coastal line.
[b] Mechanical and electrolytic pretreatment of macroalgae.
[c] Transport of macroalgal biomass, manure and digestate.
[d] Transport of macroalgae, manure and digestate.
[e] Fermentation, heat and electricity production from biogas.

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Life cycle assessment of flexibly fed biogas processes for an improved demand-oriented biogas supply

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HIGHLIGHTS

- Comparison of baseload and demand driven biogas production within a LCA.
- Flexible production would require an investment in CHP costing 0.17 € kWh^{-1} el.
- 10–45% of GHG emissions could be saved by changes in feed management.
- 10% of the impacts on acidification and eutrophication potentials could be reduced.
- Demand based production would require 16% higher energy input.

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ABSTRACT

This paper analyses concepts to facilitate a demand oriented biogas supply at an agricultural biogas plant of a capacity of 500 kWh el, operated with the co-digestion of maize, grass, rye silage and chicken manure. In contrast to previous studies, environmental impacts of flexible and the traditional baseload operation are compared. Life Cycle Assessment (LCA) was performed to detect the environmental impacts of: (i) variety of feedstock co-digestion scenarios by substitution of maize and (ii) loading rate scenarios with a focus on flexible feedstock utilization.

Demand-driven biogas production is critical for an overall balanced power supply to the electrical grid. It results in lower amounts of emissions; feedstock loading rate scenarios resulted in 48%, 20%, 11% lower global warming (GWP), acidification (AP) and eutrophication potentials, and a 16% higher cumulative energy demand. Substitution of maize with biogenic-waste regarding to feedstock substitution scenarios could create 10% lower GWP and AP.

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1. Introduction

The economic situation and governmental support of renewable energy (RE) in Europe resulted in favorable conditions to establish biogas plants. Economic burdens of the biogas production are often compensated with a fixed income, depending on the plant size and the power fed into the electrical grid. Since biomass is available in a limited amount, the largest contributions to RE systems are originated in wind and solar power. Nevertheless, the high proportion of fluctuating RE present challenges, especially regarding the need to balance the energy to the electrical grid. By this aim, for the first time in 2012, the German RE law introduced new incentives for a flexible energy generation. Plant operators were allowed to select between a fixed feed-in tariff and a market premium on a monthly basis. Operators, who choose the market premium, are trading their power provision themselves. A management premium is paid to cover costs caused by the direct marketing. Operators who directly sell 100% of their produced electric power may claim the flexibility premium, if they can be configured as dispatchable during periods of a peak demand. Both, the market and flexibility premium promote investments into a demand-oriented energy generation (Hahn et al., 2014). Besides an even power supply, substrate flexibility allows an easier achievement of closed carbon cycles and concomitantly an increased sustainability, reduced transportation and feedstock storage costs and, in case the substrate is not produced in house, a greater independence on market prices.

Biogas production is a widely applied technique. 14,563 biogas plants with a total installed capacity of 7857 MW el were operated in Europe in 2014. Currently, more than 8000 biogas plants with an installed capacity of 4 GW el are operated in Germany. In 2014,

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German biogas plants produced 27.58 TWh el with a baseload operation (Scheftelowitz et al., 2014). Depending on the requested long or short term balanced power supply, the yearly full load operation hours could be reduced up to 4000 h a^{-1} (Schmidt, 2015).

Flexible biogas supply is vital to balance the power generation and can basically be realized by biogas storage or flexible biogas production concepts. However, these concepts are still at an early stage of their technical implementation.

50–55% of EU biogas plants feedstock is originated from energy crops in spite of growing concern about using food to produce energy. In 2012, Germany used 2.5×10^6 ha of land for the growth of energy crops. Maize often results in highest yields, therefore it is a preferable feedstock for energy generation; thus, 90% of biogas plants in Germany run – at least partially - with maize as feedstock. The substitution of maize is widely encouraged due to manifold criticism about the intensified cultivation of it (Fuchsz and Kohlheb, 2015). For this reason, feedstock flexibility for biogas production will have greater interest in the near future to sustain energy production and (partially) reduce the amount of maize applied as feedstock.

Currently, only a few studies analyzed the feasibility and opportunities of a demand driven biogas production. (Linke et al., 2015) investigated the biogas production on demand from maize silage. Grim et al. (2015) and Liebetrau et al. (2015) assessed the technical necessities for flexible production. Mauky et al. (2015) evaluated different feeding strategies. Feedstock flexibility was analyzed by Di Corato and Moretto (2011) for the feasibility of revising the feedstock composition within economic circumstances. (Hahn et al., 2015) described the positive environmental impacts of flexible biogas production configurations. Currently, there is a lack of research comparing the demand driven and baseload biogas generation as the amount of data available for a flexible operation is still little. Due to the aforementioned challenges, this paper analyzes environmental impacts of the demand driven biogas plant operation, and its comparison to the baseload operation. The aim is to provide data about the environmental benefits a flexible operation might offer.

The studied biogas plant has a capacity of 500 kWh el and co-digests maize, grass, rye silage and chicken manure. Firstly, a variety of different feedstock co-digestion scenarios is assessed by substituting maize with sunflower, horse manure and biogenic waste, respectively. These analyses address the importance of "adjusted" feedstock utilization. Different from previous LCA studies, the changes in greenhouse gas (GHG) and energy balances for the whole production system in between one year is shown.

In a second step, the feedstock loading rate is altered. Here, the energy production/supply is adapted periodically and hourly. The alternation of the organic loading rate (OLR) is based on the biogas demand, which is driven by other fluctuating RE sources. The adaptations for hourly production are set depending on changes in the energy consumption/demand and spot market prices of a reference period. Although additional income could be gained by this way of operation, this study will not consider any economic analyses.

2. Methods

LCA is used to quantitatively assess the environmental performance of a process within a life cycle perspective. This means that all elementary process steps from feedstock acquisition/production until the electricity supply to the grid are considered. This study follows the ISO 14040-14044, which provides principles, framework, and methodological requirements for conducting LCA studies. The framework of LCA includes the definition of a goal and the scope, the inventory analysis, impact assessment and interpretation of results.

The area chosen for the case-study described here is Northeastern Germany. For this reason, all data of this study, including the chemical composition of the digestate, emission factors, the biogas plant's operational conditions, crop rotation, soil profiles, temperatures and climate conditions are chosen from the Federal German Office for Statistics (data sources are provided correspondingly).

The focused region is characterized by sandy or loamy soil. The amount of rainfall is approx. 20% lower compared to most other regions in Central Europe. The results of this study, due to the region-oriented quality of the assessment, may be considered for other geographical areas after an appropriate adaptation of data.

2.1. Energy production and feedstock utilization concepts

Biogas plants are traditionally operated with a continuous feed and constant feedstock composition. Energy is produced at a constant rate throughout the year. These plants are often designed for high efficiency, but may take weeks to achieve full operation. As a consequence, no response to peak/low demands of energy is feasible w/o increasing tremendously the risk of process failures. However, from a biotechnological point of view, the digestion can be influenced and regulated with an alternating feeding. In this way, biogas synthesis rates can be adjusted on demand such that the need for gas storage can be optimized w/o the need for extra installations.

2.2. Feedstock substitution and energy generation management

A mass balance approach was used to compute the feedstock compositions and energy fluxes within the system. Characterization of the substituted feedstock, the total solid (TS) to organic total solid (oTS) ratio and the biogas yields were determined based on data from Kuratorium für Technick und Bauwesen in der Landwirtschaft (KTBL) (2014) and FNR (2010). See Table 1 for an overview of the chemical composition of feedstock considered in this study.

Impacts of maize substitution with sunflowers in SC1 (SC: scenario), secondly with horse manure in SC2, and with biogenic waste in SC3 are analyzed, respectively. The amount of replaced feedstock is determined based on the biogas and biomass yields in the BS (baseload production, current operation with maize). Feedstock substitution scenarios are performed under the consideration of a 500 kWh energy production.

Table 3 lists the applied feedstock and their compositions. Amounts of the substituted feedstock were determined based on the biogas yields (Table 1) by aiming to keep generating 500 kWh el. Periodic energy demand changes are determined based on energy demand/ production from other renewable sources (Agora Energiewende, 2014). During the year, whenever the energy demand is high (186 days per year), all types of feedstock are co-digested to generate up to 750 kWh el. Whenever the required energy is low (179 days per year) and an electrical power between 150 and 350 kWh el is provided, only the co-digestion of grass silage and chicken manure is investigated. For an adaptation on a daily basis, a larger amount of energy is produced between 6 a.m. and 10 p.m. compared to the production between 10 p.m. and 6 a.m. Table 2 shows the combination of the estimated hourly production options based on a reasonable biogas storage capacity and feedstock loading rate management.

2.3. Life cycle assessment

The functional unit (FU) is a key element of LCA. FU is a measure of the function of the studied system and provides a reference, to

Table 1
Feedstock characteristics.

Feedstock	Maize silage	Rye silage	Grass silage	Sun flower	Poultry manure	Horse manure	Biogenic waste
TS* (% FM)	33	25	35	25	40	35	40
oTS* (% TS)	95	89	90	90	75	87	50
Biogas yield ($m^3\ t^{-1}$ FM*)	270	245	255	219	225	325	420
Methane content (%)	52	53	53	57	55	52	65
Methane yield ($m^3\ t^{-1}$ FM*)	140	130	135	125	124	169	273

* TS: Total Solid; oTS: organic Total Solid; FM: Fresh Matter.
Data obtained from Fachagentur für Nachwachsende Rohstoffe (FNR) (2010) and Kuratorium für Technick und Bauwesen in der Landwirtschaft (KTBL) (2014).

Table 2
Energy and biogas production scenarios for a demand driven energy production concept.

Production Scenario	Yearly energy demand (High) (kWh)				Yearly energy demand (Low) (kWh)			
	6 am–10 pm		10 pm–6 am		6 am–10 pm		10 pm–6 am	
	Biogas	Electrical energy	Biogas	Electrical energy	Biogas	Electrical energy	Biogas	Electrical energy
C1	500	650	500	350	350	350	150	150
C2	650	650	350	350	250	350	250	150
C3	750	750	150	150	250	350	250	150
C4	500	750	500	350	250	350	250	150
C5	650	650	350	350	350	350	150	150
C6	750	750	150	150	350	350	150	150

Table 3
Feeding rates of feedstock in the different scenarios and digestate properties.

	Maize*	Rye	Grass	Sunflower	Poultry manure	Horse manure	Biogenic waste
Feedstock amount (tons a^{-1})							
BS	2190	657	4380	–	912.5	–	–
SC1	–	657	4380	4509	912.5	–	–
SC2	–	657	4380	–	912.5	1814	–
SC3	–	657	4380	–	912.5	–	1123
Feedstock share (%)							
BS	27	8	54	0	11	0	0
SC1	0	6	42	43	9	0	0
SC2	0	8	56	0	12	23	0
SC3	0	9	62	0	13	0	16
Digestate Properties							
	Amount ($t\ a^{-1}$)	N content (% FM)		P content as P_2O_5 (% FM)		K content as K_2O (% FM)	
Feedstock substitution scenarios							
BS	6127	0.82		0.34		1.06	
SC1	8037	0.96		0.39		1.16	
SC2	6109	0.84		0.38		1.12	
SC3	5519	0.91		0.39		1.04	
*Feedstock loading rate scenarios***							
High	4153	0.98		0.41		1.33	
Low	1975	1.33		0.54		1.56	

* Created scenarios are based on the alteration of maize as feedstock due to the related challenges described in the text.
** Refers to periods of high and low energy demand.

which the inputs and outputs can be related. This enables a comparison of different systems. The collation in this study depends on a FU per kWh el.

The system boundaries determine, which unit processes to be included in the LCA study (ISO Standard, 2006). Fig. 1 illustrates the studied system, its boundaries and the included process steps: crop production/ acquisition, ensilage/ storage, anaerobic digestion, storage of residues and application of digestate for agricultural production, transport between multiple stages and lastly the biogas combustion; supply of generated electricity into the grid and heat utilization for temperature control at the fermenters and poultry housing. Concerning the animal farming, only the collection and storage of the biogenic residues for anaerobic digestion are considered, not the animal farming itself.

2.4. Life cycle inventory analysis

In life cycle inventory (LCI) analysis, the lists of resources, energy and emissions entering and leaving the life cycle are compiled. LCI comprises all stages dealing with data retrieval and management. Subsequently data are validated and related to the FU to allow the collation of results. The inventories of the feedstock scenarios include all process steps until electricity is fed to the grid. In this study, the operational data of the biogas plant for the period 2011–2012 was considered and additional literature data was applied whenever needed. Some material and energy fluxes of the biogas facility were automatically monitored on a continuous basis (e.g. weight of input substrate, gas volume and methane content of the biogas, electricity consumption and biogas production). Data

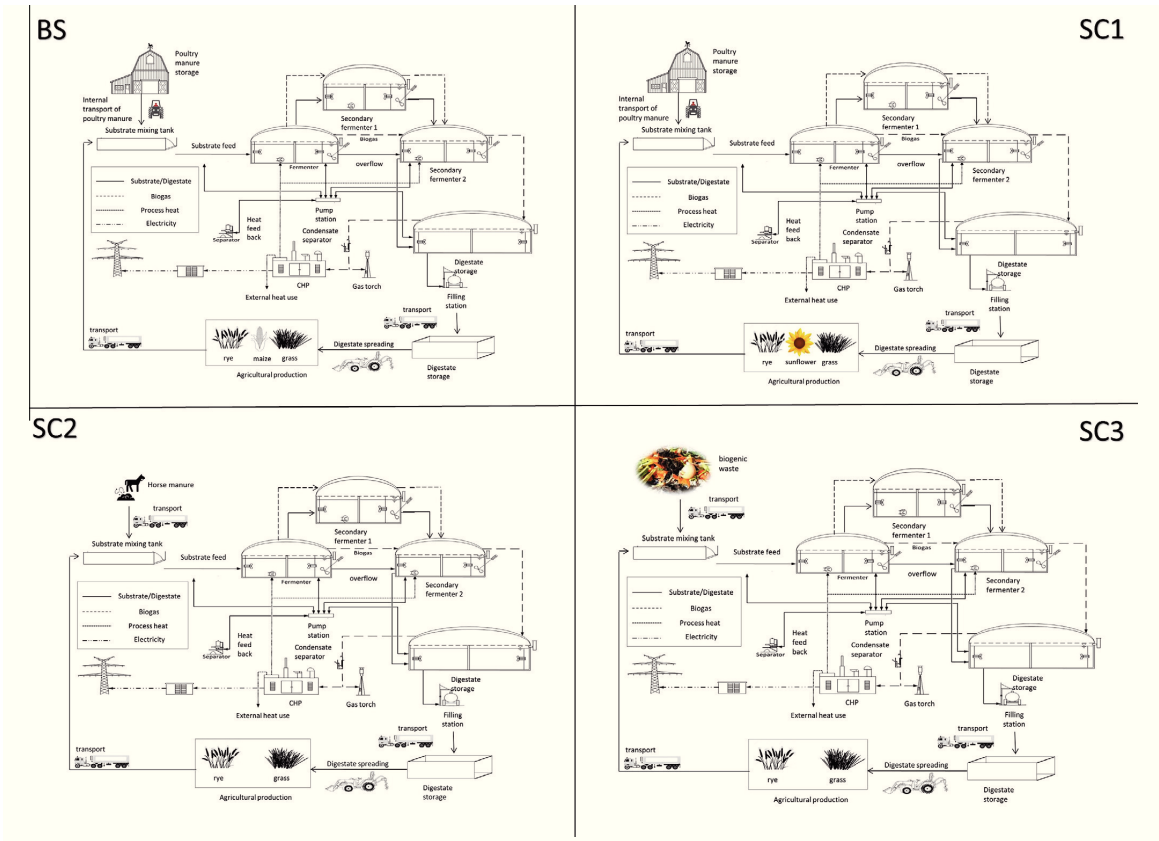

Fig. 1. System boundary for each scenario. Maize crop (baseload production) is substituted with sunflower (in scenario 1), horse manure (in scenario 2) and biogenic waste (in scenario 3). The scenarios are described in chapter 2.2. Arrows indicate material and energy flows. Common processes for all scenarios are indicated as straight lines and the substitution scenarios are indicated as dashed lines.

Table 4
Basic data of crop cultivation.

	Maize	Rye	Grass	Sunflower
Dates				
Sowing	1st of May	1st of October	1st of February	20th of March
Harvest	20th of September	20th of June	Harvest 1: 1st of April; arvest 2: 1st of July; Harvest 3: 1st of October	20th of September
Input (kg ha^{-1})				
Seed amount	28	110	40	13
Herbicide	3	3	1	
N fertilizer	166	130	38	50
P_2O_5 fertilizer	72.7	75	70	70
K_2O fertilizer	180	170	220	210

Cultivation data of maize, rye and grass are real data of the plant, while sunflower cultivation data were calculated based on data provided by Davoodi and Houshyar (2009).

related to the production of construction materials, the tractor, CHP unit, energy, fuels, fertilizers and pesticides were taken from the Ecoinvent 2.2 database (the Ecoinvent Centre, Switzerland).

2.5. Harvesting

Agricultural processes for crop production include the following steps: cultivation, chisel, harrow, sow, hoe and plough. Grass was harvested at two intervals of 60 days and finally one interval at 90 days, starting from February on. Maize and sunflower were harvested at the end of September and rye at the end of June. Table 4 provides an overview of the required input for the cultivation. Herbicide application was performed by field sprayer, fertilizing by a broadcaster and harrowing by a rotary harrow. Emissions from herbicide applications were calculated based on data from Lal (2004).

2.6. Storage

The 2.5 tons of manure daily produced from 14,500 broiler chicken were considered to be stored nearby the biogas plant.

Horse manure was stored at a pit with a 40 ton capacity (maximum of 8 days of storage). Biogenic waste was collected daily. Nitrogen emissions of the manure storage were estimated based on data and the methodology provided by Nicholson et al. (2004) and Baky (2013), respectively; 10% of the ammonium content of manure is considered to be released during the storage. Following the harvest period, crops were ensiled for 6 months. Emissions from ensilage were estimated based on data provided by the (Institut für regenerative Energietechnick Fachhochschule Nordhausen, 2013).

Digestate was considered to be stored at the plant or near the field. The storage of digestate resulted in emissions of CH_4, N_2O and NH_3. Emissions of CH_4 vary depending on the climatic conditions and the digestate nutrient composition. Biogas losses and emissions derived from the digestate storage were estimated according to data from De Vries et al. (2012).

2.7. Transportation

The transport distance between the arable land and the plant was set to 12 km. Energy crops were transferred by a tractor consuming 80 L h^{-1} Diesel fuel. Transport of digestate was accomplished by a truck of a capacity of 40 tons. Chicken housing was located at the plant, 40 m away from the manure storage. The manure was carried with a 250 kg capacity tractor to the storage daily. The Diesel fuel consumption was 40 L h^{-1}. Production of the vehicle and Diesel fuel were taken into account within the system boundary as well as combustion emissions. Biogenic waste was collected within a distance of 35 km to the biogas plant. Horse manure was picked up from a horse farm in a distance of 120 km and transported every 8th day with a truck.

2.8. Anaerobic digestion

Anaerobic digestion is the biodegradation of organic feedstock under anaerobic conditions by microbial organisms and leads to the formation of biogas and microbial biomass (Chen et al., 2008). The biogas plant consisted of a main digester (2000 m^3), a secondary digester (1000 m^3), a post digester (1500 m^3) and a digestate pool (3000 m^3), operated at 42 °C (mesophilic conditions). The hydraulic retention time (34 days in the main and the secondary digester, 102 days in the post digester) was sufficient to capture the produced methane and cut down the GHG emissions at the digestate pool. Methane leakage from fermenters was assumed as 1% of the total amount of biogas. Biogas was stored in a gasholder dome placed on top of the digesters, which had a total capacity of 520 m^3.

2.9. Biogas conversion

At the baseload production scenario, biogas was used in two CHPs of 350 and 150 kW to produce electricity and heat. For the demand-driven production, the maximum capacity was estimated to be increased by 150 and 250 kWh. Emissions occurring during the combustion of biogas were calculated based on data provided by Lansche and Müller (2012). Electricity used in the process was taken from the grid.

2.10. Digestate spreading

Digestate was used as fertilizer for arable land. The quantities of mineral fertilizer that were replaced by the digestate application were calculated on the basis of the digestate composition and fertilizer replacement values in each scenario. Additionally, the digestate properties were determined based on the decomposition rates of each feedstock (De Vries et al., 2012; Kuratorium für Technick und Bauwesen in der Landwirtschaft (KTBL), 2014). Digestate was spread by a splash plate method in the assumed case-study. Nitrogen-based emissions of the fertilizer were determined by factors provided by Brentrup et al. (2000), and phosphate emissions according to a previously published method (Rossier, 1998).

2.11. Life cycle impact assessment

The goal of life cycle impact assessment (LCIA) is to convert LCI results into indicator scores, which provide an estimation on the relative intensity on an environmental impact category (Goedkoop et al., 2009). A combination of impact categories was considered: GWP (global warming potential) in kg CO_2-eq, AP (acidification potential) in kg SO_2-eq, EP (eutrophication potential) in kg P-eq and the cumulative energy demand (CED) in kWh el. GWP represents a well-known problem and a conspicuous issue in the argument on energy production from biomass. AP accounts for acidification caused by SO_2 and NO_x emission. EP is related to an increase of chemical nutrients in an ecosystem leading to abnormal productivity. CED provides an evaluation of the energy efficiency. The analyzed system and possible production concepts were modeled in the Simapro 7.3.2. Software by using the Ecoinvent 2.2 database. Impact assessments were computed by using the ReCiPe midpoint v.1.06 and the CED v.1.08 method.

3. Results and discussion

3.1. Energy and GHG balance calculations for baseload production

As shown in Table 5, the digestate spreading contributes to the highest AP and EP due to high nitrate and phosphor emissions in the baseload production concept. Ammonia emissions from the rye fertilization were almost 50% higher compared to the ones from maize fertilization. The agricultural activities require a high amount of energy due to machinery activities for cultivation, fertilization, harvesting, etc. This amount equals to half of the total amount of the required energy for the current baseload production system. Among the energy crops, grass cultivation resulted in

Table 5
Overview of LCA results at different feedstock loading scenarios.

Process units	GWP (kg CO_2 eq)	AP (kg SO_2 eq)	EP (kg P eq)	CED (kWh)
Scenario 1 (substitution of maize with sunflower)				
Crop production	16.7 E−03	1.45 E−04	7.1E−06	13.9E−02
Storage	3.48E−03	4.7E−05	6.03E−07	8.6E−03
Transport	5.97E−02	4.2E−04	1.85E−06	4.37E−02
Others	5.11E−02	2.19E−03	1.44E−05	2.93E−02
Scenario 2 (Substitution of maize with horse manure)				
Crop production	6.53E−03	4.03E−05	2.02E−06	6.31E−02
Storage	3.54E−03	3.71E−04	4.51E−07	6.87E−03
Transport	4.80E−02	3.37E−04	1.82E−06	5.44E−02
Others	4.31E−02	3.85E−03	2.03E−05	2.93E−02
Scenario 3 (Substitution of maize with biogenic waste)				
Crop production	6.53E−03	4.03E−05	2.02E−06	6.31E−02
Storage	3.26E−03	1.95E−05	4.23E−07	6.35E−03
Transport	4.11E−02	2.90E−04	1.29E−06	3.16E−02
Others	4.25E−02	3.48E−03	1.95E−05	2.93E−02
Stable baseload production				
Crop production	9.52E−03	5.73E−05	2.79E−06	9.00E−02
Storage	3.59E−03	3.82E−05	4.95E−07	6.88E−03
Transport	4.70E−02	3.31E−04	1.47E−06	3.61E−02
Others	4.41E−02	3.86E−03	1.80E−05	2.93E−02
Demand driven production				
Crop production	1.99E−02	3.81E−04	7.59E−06	4.48E−02
Storage	3.47E−03	8.71E−05	2.32E−07	9.98E−03
Transport	9.02E−03	1.63E−04	4.86E−07	6.94E−02
Others	2.24E−02	2.84E−03	1.18E−05	5.11E−02

almost two times higher $CO_{2,fossil}$ compared to maize and rye cultivation. Fuel combustion emission of the transport was contributing the most to the GWP.

3.2. Baseload versus demand driven energy production

3.2.1. Alternating feedstock substitution scenarios

Fig. 2 illustrates the comparison of feedstock substitution scenarios under the selected impact categories. Every single process in all feedstock substitution scenarios and their individual impacts are shown. In all feedstock substitution scenarios, nitrate and phosphor emission from the application of digestate for agricultural production had the highest impact on AP and EP.

$CO_{2,fossil}$, N_2O and $CH_{4,biogenic}$ were the most significant components of emissions; gross GHG emissions of the scenarios ranged between 0.093 and 0.127 kg CO_2-eq per kWh el. The GHG emission was affected by the type of feedstock, and thus the nutrient content of the digestate, which was also reported by (Gerin et al., 2008) and (Plöchl et al., 2009). Furthermore, a significant GHG reduction is related to the utilization of CHP heat (3.6 g CO_2-eq) and the replacement of mineral fertilizers (2.8 g CO_2-eq). According to Fig. 2A, SC1 had the highest GWP; it was 23% higher in comparison to the baseload production (BS). Substitution of maize with sunflowers (SC1) resulted in an increase of the GWP by $0.24E^{-1}$ kg CO_2-eq. SC1 yielded a raise by 76%, 14% and 134% in $CO_{2,fossil}$, N_2O and $CH_{4,biogenic}$, respectively. This rise is the reason of a 1.4-fold higher energy demand of the cultivation of sunflowers compared to the cultivation of maize.

For SC2 and SC3, in which maize was substituted by horse manure and biogenic waste, respectively, the GWP dropped down by 3% and 10%, the N_2O emissions decreased by 66% and 70%. In contrast to our results, (Whiting and Azapagic, 2014) determined that the application of energy crops resulted in a lower GWP compared to waste. This was due to the consideration of industrial waste with a low content of biogenic residues, which leads to a low biogas yield. The GWP reductions in the scenarios compared to BS were caused due to the decline in energy crop cultivation. In all scenarios, fuel combustion emission generated during transport created the highest share of total GWP (45, 47, 48 and 44%, respectively). Approximately 35% of the GWP among all scenarios were mainly caused by N_2O emission of the digestate spreading.

Dressler et al. (2012) reported a GWP between 0.058 and 0.18 kg CO_2-eq kWh el at several biogas plants, which were operated with maize. Bachmaier et al. (2010) investigated the CO_2-emission of 10 biogas plants in Germany that emitted an average of 0.136 kg CO_2-eq per kWh el. The authors demonstrated that the electricity generation from biogas could prevent up to 910 g CO_2-eq per kWh el GHG emission compared to fossil fuel combustion. It was calculated that the replacement of maize with biogenic waste could save 9.6% of CO_2-eq, this value equals to 11% of CO_2-eq in the current study.

The AP and EP were caused mainly by the emission of the energy crop production, the CHP and the utilization of digestate as a fertilizer. Digestate spreading is the primary source of AP in all substitution scenarios (up to 90% in SC3), especially of NO_X, SO_2, NMVOC and N_2O. These high amounts are mainly related to the region-specific calculations of field emissions based on (Brentrup et al., 2000). Results suggest that the N content of the feedstock mixture and their biodegradation ratios affect the AP directly. Earlier studies (Dressler et al., 2012) determined the main AP contributor of biogas production as fertilization. Fig. 2B illustrates that SC1 and SC3 resulted in a decrease in the AP in comparison to the baseload operation. In these scenarios, N contents of the digestate were considerably high. However, spreading of digestate on a larger agricultural area resulted in lower amounts of N to be applied per ha. This caused lower NH_3 and NO_2 emissions from the fertilization. SC2 resulted in a 7.25% higher AP compared to the BS. This is caused by higher amounts of N emission originates from the digestate spreading due to the impacts of climatic conditions such as evaporation, rainfall, wind, etc.

The EP was mainly linked to the P content of digestate and emission of the digesters. Emissions are primarily caused by NH_3 and NO_x release from the digestate spreading. Substitution of maize resulted in a 5–8% increase of the EP (Fig. 2C), mainly as a result of increased leaching of NO_3 and P from digestate spreading, which also creates the highest share in EP ranging from 34% to 57%. Emissions from digesters create the second most important EPs of almost 25% in all scenarios.

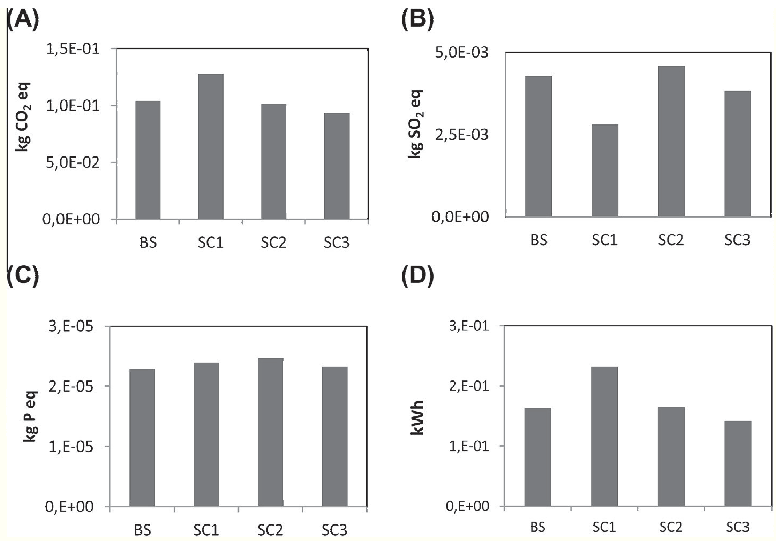

Fig. 2. LCA characterization of feedstock substitution scenarios. A. global warming potential, B. acidification potential, C. eutrophication potential, D. cumulative energy demand. Results are given per FU. BS: baseload production (stable biogas and energy production), SC: Scenario.

The results show that SC1 requires the highest CED (Fig. 2D). Compared to maize and due to a larger arable area required and lower biomass yields, machinery work for the cultivation and harvest of sunflower needs 1.5 times more energy. This situation elevated the CED required for the transport and storage of crops. Based on data of AGEE-Stat (BMWi, 2013), in 2013, 760.54 PJ of the primary energy demand in Germany was provided from biomass. 90% of the biogas was originated from maize plants (BMWi, 2013). If it was possible to replace the amount of maize used in biogas plants with biogenic waste, it would have been possible to gain extra 1122.6 PJ energy in Germany, because the biogas yield obtained would have been higher. This would increase the RE share in energy consumption from 10.4% (1436 PJ) to 13.15% (1877 PJ).

Previous studies, which analyzed the energy balances from a life-cycle perspective for biogas production (Berglund, 2006; Patterson et al., 2011; Poeschl et al., 2010) found similar trends regarding the impact of transport distances as exemplarily shown for horse manure in this study. Bacenetti et al. (2013) demonstrated the agricultural production and the feedstock transport as the two most energy demanding units of biogas production (>90% of total fossil energy demand). Based on the feedstock utilized, the CED of the system consumes between 13 and 40% of the generated energy.

3.3. Alternating feedstock loading rate scenarios

No LCA study is known to the authors that investigated different OLR at a biogas process. In our case-study, alteration in the feedstock loading rate resulted in a 36%, 23% and 10% reduction in $CO_{2,fossil}$, N_2O and $CH_{4,biogenic}$, respectively, compared to the baseload operation. Fig. 3 depicts the LCA characterization results at an alternating loading rate (co-digestion of maize, rye, grass silage and chicken manure for periods of a high energy demand and co-digestion of grass silage and chicken manure for periods of a low energy demand). The production concept 1 (C1) has the lowest environmental damage potential, C6 results in the highest GWP. When the periodic energy demand is higher (10 pm–6 am), 500 kWh el is generated in C1 (Table 2). The produced biogas is stored in the headspace of the digesters (capacity of 520 m^3) and the equivalent amount to generate 350 kWh el is transferred to the CHP. The equivalent of 150 kWh el of stored biogas is provided for the CHP between 6 am and 10 pm for a maximum energy supply of 650 kWh el. For this reason, concept C6 considers 3 CHPs (two of 150 kW and one of 350 kW power).

Concept C1 produces the lowest amount of biogas. C1, C2 and C5 require an investment for an additional 150 kW CHP, while C3, C4 and C6 require an investment for an additional CHP with a power of 250 kW. According to data from ASUE (ASUE Arbeitsgemeinschaft für sparsamen und umweltfreundlichen Energieverbrauch, 2011), CHP investment costs have to be calculated with approx. 750 € per kW power; consequently a CHP with a power of 250 kW is expected to cost 187,500 €, while a 150 kW CHP costs 112,500 €. Under consideration of the power, which is produced on top by CHPs in periods, during which a higher supply of energy is required (186 days), investments would equal to 0.17 € kWh^{-1} el. None of the analyzed production concepts demand a construction of an extra gas storage tank, because the required energy supply flexibility is limited to some hours (Mauky et al., 2015). However, daily storage would necessitate an investment in a 1350 m^3 volume tank, which costs around 40 € m^{-3} (costs were provided by a German manufacturer). When the yearly energy demand for biogas becomes lower, no biogas is stored neither during the day nor during the night at C1.

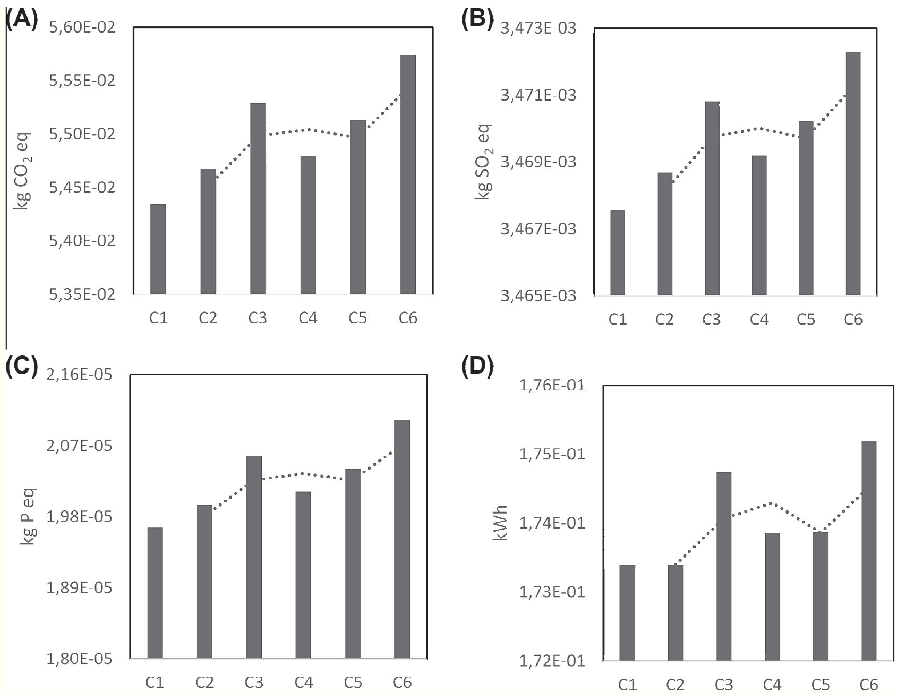

Fig. 3. LCA characterization of changes in feedstock loading rate. A. global warming potential, B. acidification potential, C. eutrophication potential, F. cumulative energy demand. The results are provided per FU. C: Concept.

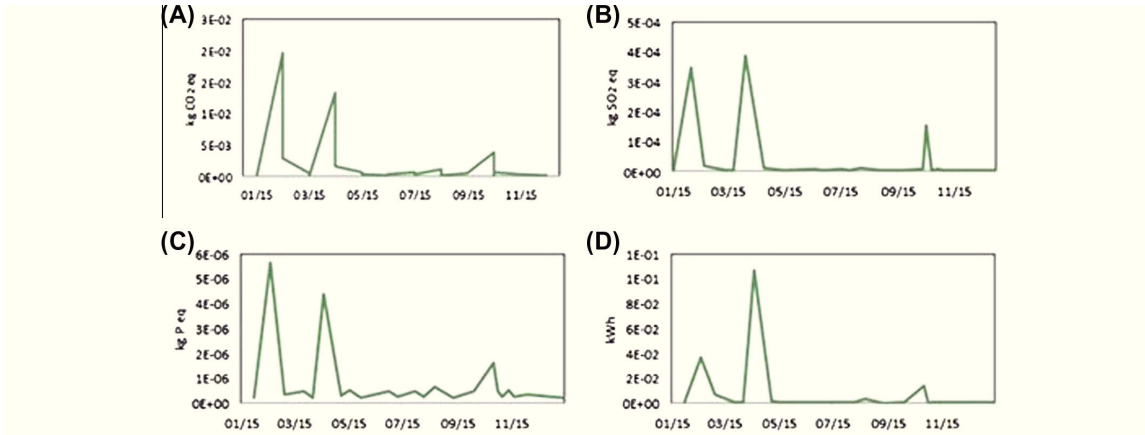

Fig. 4. Environmental impacts during a year based on changes in the feedstock loading rate. A. global warming potential, B. acidification potential, C. eutrophication potential, D. cumulative energy demand. Results are provided per FU.

350 kWh el are generated during the day and 150 kWh el during the night. A 34% of the flexibility is gained by biogas storage, while 17% is obtained by an adapted feeding regime.

Climate relevant gases are emitted into the atmosphere during biomass cultivation and biogas production. Gross GHG emissions of the configurations are between 0.0543 kg CO_2-eq and 0.0557 kg CO_2-eq per kWh el, which are based on Diesel consumption. Based on the variety of OLR, C1 resulted in a 3% lower GWP compared to C6 (Fig. 3A). At different feedstock loading concepts, agricultural production contributes the highest GWP (around 40%) followed by digestate spreading (almost 30%).

Fig. 4 illustrates the changes in emissions during a year. When the mean value of the OLR scenarios is compared to the baseload operation, a flexible production yields a 48% lower GWP (Fig. 4A). NH_3 emissions were lower, since the amount of biogas produced was also lower during a low energy demand. Moreover, the digestate consists of a lower nutrient content; therefore nitrogen emission from fertilization were also lower.

Emissions resulting from Diesel fuel combustion for biomass production and transport to the biogas plant as well as from electricity and heat consumption in order to operate the biogas plants are of minor importance for all configurations. AP and EP are primarily caused by ammonia and nitrous oxide emissions (80% share in total AP) during the fertilization due to evaporation.

Depending on the periodical and hourly energy production flexibility, C1 resulted in 1% and 7% lower AP and EP in comparison to C6 (Fig. 3B and C). 40% of EP is caused by Diesel fuel combustion emission from agricultural activities. When mean values are compared against the baseload production, it can be concluded that demand driven energy production provokes a 20 and 11% lower AP and EP.

The changes in AP and EP during a year are illustrated in Fig. 4B and C. The increases in AP have the same trend as the GWP, and are mainly associated with the agricultural cultivation and digestate spreading. The highest AP occurs in April; in turn the highest EP occurs in February as more phosphorous is released to water bodies due to higher amounts of rainfall and lower evaporation rates during this time.

Biogas plants, which are adapted to a flexible power generation, are characterized by an increased energy consumption (Hahn et al., 2015). C1 resulted in a 2% lower CED in comparison to C6 (Fig. 3D). Compared to the stationary baseload production, the demand driven energy production resulted in a 16% higher CED (Fig. 4D). Changes in feedstock composition and adaptations in electricity generation result in higher energy consumption at the fermenters and the CHP. Compared to a stable baseload production, the energy demand of transport and storage is 1.6-fold higher.

4. Conclusions

Modifications for flexible production would require an additional investment, mainly for a second CHP, which leads to an extra 0.17 € kWh^{-1} el in addition to 0.215 € kWh^{-1} el operational costs and optionally also for a biogas storage tank, which costs 40 € m^{-3} (40,000 € in total). The adapted feedstock and loading rate could save between 10% and 45% of GHG emissions, reduce 10% of impacts on AP and EP. However, it requires a 16% higher energy input. Certainly, further research should be performed also to analyze the effects on incomes of the operator and socio-economic benefits, which could be gained from flexible power generation in comparison to baseload production.

Acknowledgement

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III

Anaerobic Digestion Model (AM2) for the Description of Biogas Processes at Dynamic Feedstock Loading Rates

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Supporting Information available online

The anaerobic digestion of biomass is a complex, dynamic, and highly nonlinear process. Hence, a mathematical model that is capable of describing the complete operability region with sufficient accuracy cannot be identifiable even with the most advanced process monitoring technology. The complexity of the anaerobic digestion model no. 1 (ADM1) leads to the application of either parameter-reduced versions of the ADM1 or simpler models as, e.g., the anaerobic digestion model AM2. A comparative study for the simulation of biogas formation at dynamic feedstock loading using maize silage was performed with both models.

Keywords: Anaerobic digestion, Anaerobic digestion model, Biogas, Identifiability

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1 Introduction

Anaerobic digestion (AD) for biogas production is an attractive technology, which can contribute to the overall goal for the reduction of fossil fuel energy consumption. However, due to the complexity of the process, a better understanding and prediction of the system is required to take advantage of the full potential of biogas production. Moreover, AD can be operated with various feedstocks in a flexible manner in order to better integrate such systems in dynamic networks, like electricity grids and local carbon cycles, which are oriented to the seasonal availability of substrate [1].

Temporary process instabilities occur from alternating process conditions, however, a poor process performance can typically be solved by adjusting the feedstock load and composition [2], if the problem is diagnosed correctly and promptly. Several suitable models for the complex digestion process to produce biogas were described. The description of the physicochemical interactions among the various biological stages [3] with modifications of the Monod-type kinetic equations for the consideration of the inhibition of volatile fatty acids (VFA) on methanogenesis [4] was the original basis for many models. Approaches, which considered two bacterial groups, namely acid and methane producing microorganisms [5], and even those, which considered four populations, were applied [6]. The latter model type was inspiring for further developments based on four populations, predicting the change of VFA, pH-value, and biogas production [7, 8]. Other models considered that the limiting step can change under altered operation conditions [9] or occurs in hydrolysis of degradable suspended solids [10]. These models were easy to use, but they were unable to describe the process properly under transient conditions. Lyberatos et al. [11] showed that the limiting step of the AD process changes with variable operation conditions, which represents a real challenge in terms of modeling.

Substrate conversion is a central aspect in the modeling of the biogas process [12], especially under transient or generally dynamic conditions. The latter term is understood to describe a state, in which transient conditions are occurring frequently. There are four models, which include more detailed kinetics that consider this type of process mode [13 – 15], the International Water Association (IWA) AD

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model no. 1 – ADM1 [16] and its subsequent implementations [17], respectively.

The ADM1 was used for several applications, such as studies of biodegradability of wastes or substrates like olive mill wastewater [18], municipal solid with activated sludge wastes [19], agro-wastes as apple, pear, orange, rape, sunflower, pig manure, and glycerol wastes [20], and others like maize silage, grass, and cattle manure, which show reliable results [21]. The ADM1 was applied for state prediction from online measurements with pattern recognition. The modelled biogas process was predicted with an accuracy of 90 % [22]. Nevertheless, a high computational effort is involved when applying the ADM1.

2 Materials and Methods

2.1 Digestion Process

Data of lab scale digestion was obtained from two continuously mixed reactors of a liquid volume of 50 L. Maize silage was used as feedstock and the experiment lasted 36 days. Most of the time feedstock was added once daily, feeding was suspended during the weekend (two days per week). The temperature was held constant at 39 °C (mesophilic conditions). Biogas production, methane and CO_2 content in the gas phase, temperature, and the pH-value (7.0) were measured online every hour. The hydraulic retention time (HRT) and organic loading rate (OLR) were 33.09 days and 3.58 $kg_{ODM}m^{-3}d^{-1}$, respectively.

2.2 Model Validation

In a second experiment, two 15-L reactors fed with maize silage were investigated. The methane and CO_2 content were measured daily. The pH-value was measured online. The process was started with an OLR of 3.165 $kg_{ODM}m^{-3}d^{-1}$ for 10 days. After this period, the OLR was increased as follows: 4.22 $kg_{ODM}m^{-3}d^{-1}$ (three days), 5.27 $kg_{ODM}m^{-3}d^{-1}$ (four days), and 6.33$kg_{ODM}m^{-3}d^{-1}$ (three days). The experiment lasted throughout 20 days.

The concentration of VFAs in the culture broth was analyzed using an Agilent 1200 series HPLC system equipped with a refractive index detector (Agilent GmbH) and a HyperRez XP column (Thermo Fisher Scientific Inc.).

The substrate characterization as required for the ADM1 was applied also for the anaerobic digestion model AM2, which relies on the chemical oxygen demand (COD). In this work, a detailed characterization of the substrate was made for maize silage, applying the described method in [23], see supporting information.

2.3 Software

All models and graphical interfaces were written in Matlab R2013b (Mathworks Inc.). The ODE and DAE simulation were integrated using the SunDialsTB v.2.4.0 suite, OdeSol and Idas, respectively. Parameter estimations were computed using a Gauss-Newton based optimization program included in the TOMLAB optimization environment.

3 Results

3.1 The ADM1 – Evidence of Unidentifiability

Sensitivity analysis was conducted for all parameters to identify those that influence the predicted methane and biogas production rate at most. The study was performed for the 80 parameters of the ADM1 (Tab. S1 in the supporting information) as depicted in Fig. 1. The dilution rate for the feeding was 0.01 d^{-1} and the substrate was sludge, which was gained from waste water treatment plant (WTP) operated at mesophilic conditions. The process lasted 95 days and the values for the methane and CO_2 flow rate were taken every 0.01 d (14.3 min), which was the step size of simulation. Sensitivities with piecewise constant influent conditions were computed. The differential sensitivity analysis was performed keeping all parameters constant except the targeted parameter. This procedure was repeated for all parameters. The order of parameters in the program is shown in Tab. S1. The results of the sensitivity range of the parameters are depicted in Tab. 1. Parameters, which are not listed, were considered as sensitive. It can be seen that 6 parameters were insensitive and 11 parameters exhibited a lower to moderate degree of sensitivity. Sensitive parameters were found, which might cause variations in the output variables. Results indicate the requirement of parameter reduction of the ADM1 for the applied case with an increased identifiability, or alternative models are needed. If the AM2 is a suitable alternative remains to be evidenced in the following.

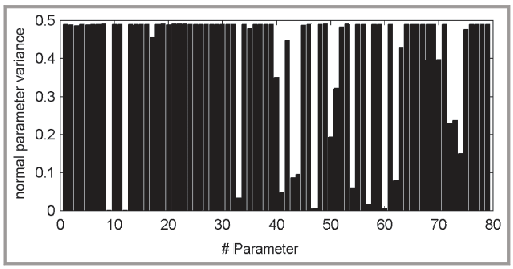

Figure 1. Sensitivity analyses of 80 parameters of the ADM1. Shown is the parameter variance of the sensitivity analysis. The normal distribution of variance is 0 – 0.5.

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Table 1. Identified parameters of the ADM1 – Sensitivity analysis.

	Insensitive parameters	Low to moderate sensitivity	Moderate sensitivity
1	C_{xc}	$f_{ac,aa}$	Y_{ac}
2	C_{pr}	Y_{h2}	$K_{S,aa}$
3	$k_{m,su}$	$k_{hyd,ch}$	$k_{m,fa}$
4	$k_{m,pro}$	$k_{hyd,pr}$	$k_{A,Bva}$
5	$k_{m,ac}$	$K_{I,nh3}$	$k_{A,Bbu}$
6	$K_{a,ac}$		$k_{A,Bpro}$

3.2 The AM2

In the AM2, only two bacterial populations are considered, namely the acidogenic and methanogenic microorganisms. The model performs well using sludge when compared to the ADM1 as reference model [24]. Modifications of the original model were implemented, like a term for describing the relation between inorganic nitrogen and alkalinity [24], hydrolysis and growth decay [25]. The model was applied once for the lab-scale description of cheese-way digestion. Although satisfying results were achieved to simulate the experimental data set, the fitting changed throughout the experimental period during 8 days, probably due to a biological adaptation of the microflora as suggested by the authors [25]. In the same study, a simulated data set was used to describe acidification with the AM2 for the purpose of proper parameter identification. So far, the simulation of data of a lab-scale biogas process fed with maize silage was performed once [26]. Therefore, the applicability of the AM2 to a close-to practice operated lab-scale biogas process is evaluated.

3.3 Comparison with ADM1 Model

The AM2 applied to the experimental data using maize silage as a substrate doesn't fit well when it is compared to the ADM1 simulation (see supporting information). A different profile for the amount of acidogenic bacteria (X_1) is shown between simulations with the AM2 and the ADM1. The methanogenic bacteria (X_2) profile results in a higher concentration when the AM2 is applied. Alkalinity (Z) for the AM2 is a horizontal straight line, due to lack of terms, which include the growth rates of bacteria in the differential equation. The organic substrate (S_1) is simulated to be higher in the AM2, in which the hydrolysis process is not clearly defined. The simulation profile for volatile fatty acids (S_2) and inorganic carbon (C) are similar when applying both models.

3.3.1 AM2 with Growth Decay

As described in [24], the AM2 was applied using maize silage as a substrate, the differential equations of biomasses and the alkalinity were modified from the original AM2 [27]. The differential equations for biomasses X_1 and X_2 include the term of the decay rate of biomasses X_1 and X_2, k_{d1}, k_{d2}, respectively, see Eqs. (1) and (2).

$$\frac{dX_1}{dt} = (\mu_1 - \alpha D_{in} - k_{d1})X_1 \tag{1}$$

$$\frac{dX_2}{dt} = (\mu_2 - \alpha D_{in} - k_{d2})X_2 \tag{2}$$

D_{in} is the dilution rate; α is the fraction of bacteria in the liquid phase; μ_1 and μ_2 are the growth rate of acidogenic and methanogenic bacteria respectively. Terms to consider the contribution of the nitrogen species were integrated in the differential equation describing the alkalinity in the AM2, Eq. (3).

$$\frac{dz}{dt} = D_{in}(Z_{in} - Z) + [(k_1 N_{S1} - N_{bac})\mu_1 X_1] - N_{bac}\mu_2 X_2 + (k_{d1} N_{bac}\mu_{1max} X_1) + (k_{d2} N_{bac}\mu_{2max} X_2) \tag{3}$$

Z_{in} is the influent value for alkalinity, N_{S1} describes the nitrogen content of the substrate and N_{bac} is the nitrogen content in the biomass.

3.3.2 Extended AM2

3.3.2.1 Extension for Growth Rates

Three new extensions to the AM2 model of Ficara, et al. [24] were added. The first extension describes the growth rate of acidogenic and methanogenic bacteria, Eqs. (4) and (5), including a term of the pH inhibition, under consideration of a lower bound of $pH_L = 5.0$ [28] and an upper bound of $pH_H = 8.5$ [16].

$$\mu_1 = \left(\mu_{1max}\frac{S_1}{S_1 + K_{S_1}}\right) - \left\{\mu_{1max}\frac{S_1}{S_1 + K_{S_1}}\exp\left[-3\left(\frac{pH - pH_H}{pH_H - pH_L}\right)^2\right]\right\} \tag{4}$$

$$\mu_2 = \left[\mu_{2max}\frac{S_2}{S_2 + K_{S_2} + \left(\frac{S_2^2}{K_{I_2}}\right)}\right] - \left\{\mu_{2max}\frac{S_2}{S_2 + K_{S_2} + \left(\frac{S_2^2}{K_{I_2}}\right)}\exp\left[-3\left(\frac{pH - pH_H}{pH_H - pH_L}\right)^2\right]\right\} \tag{5}$$

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3.3.2.2 Extension for Hydrolysis

Hydrolysis is a step in the degradation of a substrate, when composites (X_c), carbohydrates (X_{ch}), proteins (X_{pr}) and lipids (X_{li}) are broken into a smaller components. In this work, a description of the hydrolysis process was added to the AM2 from Ficara et al. [24], as in Eqs. (6) – (9).

$$\frac{dX_c}{dt} = -k_{dis}X_c + D_{in}\left(X_{c_{in}} - X_c\right) + k_{dec,X_1}X_1 + k_{dec,X_2}X_2 \quad (6)$$

$$\frac{dX_{ch}}{dt} = -k_{hyd,ch}X_{ch} + D_{in}\left(X_{ch_{in}} - X_{ch}\right) + f_{ch,X_c}k_{dis}X_c \quad (7)$$

$$\frac{dX_{pr}}{dt} = -k_{hyd,pr}X_{pr} + D_{in}\left(X_{pr_{in}} - X_{pr}\right) + f_{pr,X_c}k_{dis}X_c \quad (8)$$

$$\frac{dX_{li}}{dt} = -k_{hyd,li}X_{li} + D_{in}\left(X_{li_{in}} - X_{li}\right) + f_{li,X_c}k_{dis}X_c \quad (9)$$

k_{dis} is the first order parameter of the disintegration process from homogeneous particulates to carbohydrates, proteins, and lipids. The differential equation for organic substrate concentration, S_1, was modified including the hydrolysis process as described in Eq. (10)

$$\frac{dS_1}{dt} = D_{in}\left(S_{1,in} - S_1\right) - \left(k_1\mu_1X_1\right) + k_7\left(k_{dis}X_c - k_{dec,X_1}X_1 - k_{dec,X_2}X_2\right) + k_8\left[\begin{array}{l}\left(k_{hyd,ch}X_{ch} - f_{ch,X_c}k_{dis}X_c\right) + \left(k_{hyd,pr}X_{pr} - f_{pr,X_c}k_{dis}X_c\right) \\ +\left(k_{hyd,li}X_{li} - f_{li,X_c}k_{dis}\right)\end{array}\right] \quad (10)$$

k_7 and k_8 are the yield-coefficient of substrate disintegration and the yield-coefficient of carbohydrates, proteins, and lipids, respectively.

3.3.2.3 Extension for High Organic Loading Rates

Eq. (11) was incorporated into the AM2 from Ficara et al. [24] only when high organic loading rates up to 5.0 are present during the process.

$$R_{OLR} = \tanh\left[2.5\left(\frac{OLR_H - OLR}{OLR_H - OLR_L}\right)^2\right] \quad (11)$$

OLR_H and OLR_L are the high and low organic loading rates. This last equation was applied to the CO_2 and methane flow rate equations, q_c and q_m, respectively [mol m^{-3}d^{-1}]. Eq. (12) and (13).

$$q_C = K_{La}[C + S_2 - Z - (K_HP_C)]R_{OLR} \quad (12)$$

$$q_m = (k_6\mu_2X_2)R_{OLR} \quad (13)$$

3.3.3 Comparison Between the Extended AM2 vs the ADM1

The simulations of biogas and methane production and the state variables of the AM2 were compared between the model using the extension from Ficara et al. [24] and the ADM1. The simulations of the AM2 show a delay in the dynamics in comparison to the ADM1 (see supporting information). The acidogenic and methanogenic bacteria (X_1 and X_2) fit well to the ADM1 profiles. The comparison shows that both models simulate a similar tendency for the alkalinity (Z) due to extensions [24] accounting for the inorganic nitrogen of the organic substrate and of the biomasses. However, higher values of the organic substrate (S_1) are simulated in AM2 when compared to the ADM1 values due to the lack of a term describing hydrolysis in the original version of the AM2. VFA (S_2) and inorganic carbon content (C) simulations of both models have a similar profile.

3.3.4 Comparison of the Extended AM2 vs the ADM1

Measured values and simulation results of the extended AM2 for biogas and the methane production rate of the first experiment in a 50-L reactor, which was discontinuously fed with maize silage, are depicted in Figs. 2b and c. Model outputs for gas production and online data corresponded well. During the process, a decrease of the gas formation

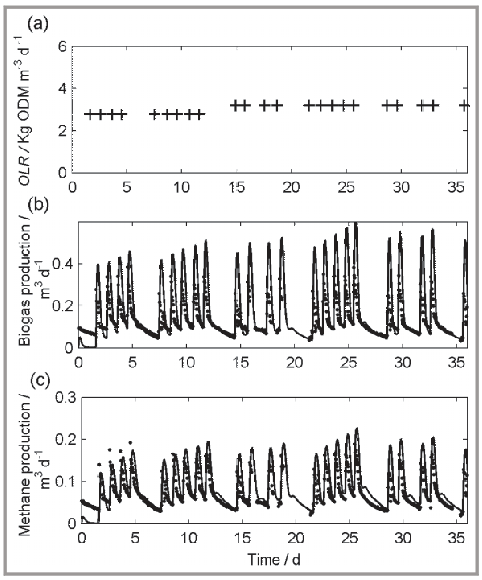

Figure 2. a) Organic loading rate (+) during a period of 36 days at alternating feedstock load in a 50-L scaled anaerobic digestion process. b) Biogas production: AM2 simulation (–), online experimental data (•), and c) Methane production: AM2 simulation (–), online experimental data (•).

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rate appeared due to reduced feeding, as it was the case after the 5th, 13th, 20th, 27th, and 34th day of operation. The period of time of each feeding into the reactor lasted 15 min. The organic loading rate is depicted in Fig. 2a. A comparison between biogas and methane production simulated with the ADM1 and AM2 is depicted in Figs. 3a – b. AM2 outputs for gas production and ADM1 values corresponded well.

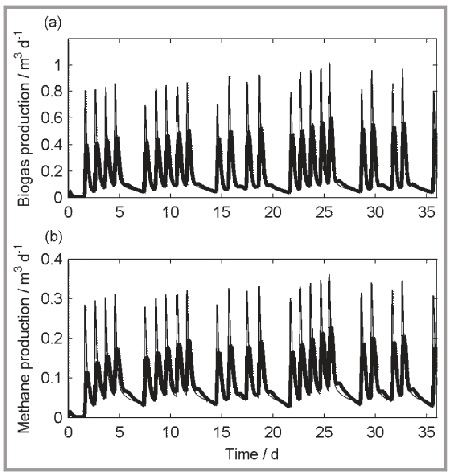

Figure 3. Comparison between the simulation of the modified AM2 (–) and ADM1 (–) for a period of 36 days at alternating feedstock load of a 50-L scaled anaerobic digestion process.

The output of variables of the modified AM2 simulation X_1, X_2, Z, S_1, S_2, and C are compared with the corresponding results of the ADM1 (see Figs. 4 and 5). The predictions of both models of the portion of acidogenic and methanogenic bacteria (X_1 and X_2) are very close to each other. The simulated profile of the organic substrate (S_1) depicts quite well the fluctuations caused by the discontinuous feeding into the reactor. The time course of the VFA concentration, alkalinity, and inorganic carbon content reflects this feeding profile as well. In these cases, the simulations of the two models are close to each other. The ADM1 simulates lower VFA concentrations due to a more diverse consumption of carbon and due to an increased number of conversion reactions. If this reflects a decreased overall prediction capability for the VFA content is further investigated during an acidification driven by an increased loading rate of the substrate in a follow-up experiment. The differences between experimental data and model simulation values for both, the biogas and the methane flow rate, were less than 7 %, which are acceptable for the process.

The simulation of the components of each variable from the ADM1 is shown in Fig. S5.

Key model parameters, which result in a satisfactory simulation of methane and biogas, are obtained through calibration, the initial values are taken from [27]. Output values are depicted in Tab. 2.

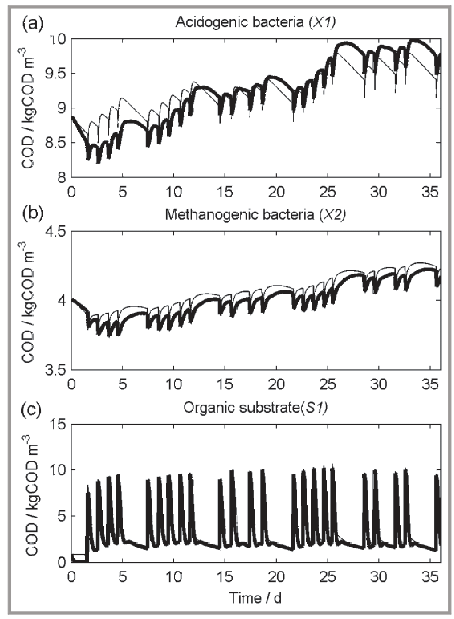

Figure 4. Comparison of main variables between the AM2 (–) and the ADM1 (–) of a 50-L reactor during a period of 36 days with changing influent conditions. a) Acidogenic bacteria; b) methanogenic bacteria, and c) organic substrate.

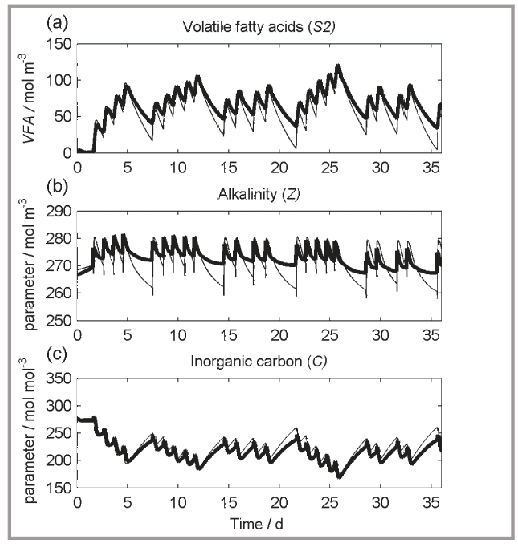

Figure 5. Comparison of main variables between the AM2 (–) and the ADM1 (–) obtained for a 50-L digestion process during a period of 36 days with changing feeding conditions. a) Volatile fatty acids, b) alkalinity, and c) inorganic carbon.

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Table 2. Calibrated parameters of AM2.

Parameter	Initial Values. Vinasses from the wine industry. [a]	Maize silage [b]
μ_{1max} [d^{-1}]	1.2	0.6
μ_{2max} [d^{-1}]	0.7	0.3
K_{s1} [$kg\,m^{-3}$]	7.1	3.5
K_{s2} [$mol\,m^{-3}$]	9.3	34.5
K_{I2} [$mol\,m^{-3}$]	256.0	998.2
k_{La} [d^{-1}]	19.8	22.0
k_1 [–]	42.1	25.5
k_2 [$mol\,kg^{-1}$]	116.5	309.7
k_3 [$mol\,kg^{-1}$]	268.0	1074.0
k_4 [$mol\,kg^{-1}$]	50.6	90.0
k_5 [$mol\,kg^{-1}$]	343.6	200.0
k_6 [$mol\,kg^{-1}$]	453.0	575.0
α [–]	0.5	1.0
Parameters of the extension [24]		
N_{s1} [$mol\,kg^{-1}$]	–	1×10^{-4}
N_{bac} [$mol\,kg^{-1}$]	–	11.0
k_{d1} [d^{-1}]	–	5.3 % μ_{1max}
k_{d2} [d^{-1}]	–	5.3 % μ_{2max}
Parameters of hydrolysis		
k_{dis}[d^{-1}]	–	0.5 [c]
$k_{hyd,ch}$ [d^{-1}]	–	10 [d]
$k_{hyd,pr}$ [d^{-1}]	–	10 [d]
$k_{hyd,li}$ [d^{-1}]	–	10 [d]
$k_{dec,x1}$ [d^{-1}]	–	–
$k_{dec,x2}$ [d^{-1}]	0.039	0.039
k_7 [–]	–	12.7
k_8 [–]	–	0.01
$f_{ch,xc}$ [$kg_{COD}kg^{-1}_{COD}$]	–	0.2 [c]
$f_{pr,xc}$ [$kg_{COD}kg^{-1}_{COD}$]	–	0.2 [c]
$f_{li,xc}$ [$kg_{COD}kg^{-1}_{COD}$]	–	0.3 [c]

[a] Obtained from [27], [b] including extension from [24] and the hydrolysis process, [c] obtained from [16], [d] obtained from [21].

The 24 parameters of the extended version of the AM2 that can exert an influence on model results, were subjected to a sensitivity analysis. The order of analyzed parameters was the same as indicated in Fig. 6. Simulation outcomes of the sensitivity analysis when applied to the AM2 show that parameters k_2, k_5, and k_{dis} are most insensitive, as can be seen in Fig. 6. The parameters k_3, k_6, and $k_{dec,x1}$, exhibit a low degree of sensitivity, all other parameters are considered as sensitive parameters. In general terms, the sensitivity analysis depicted six parameters with a low degree of sensitivity, but the ADM1 yielded twelve parameters of eighty, as shown in Fig. 1. Among the AM2 parameters, which are sensitive, are k_1, k_4, k_7, k_8, μ_{1max}, μ_{2max}, K_{s1}, K_{s2}, K_{I2}, k_{d1}, k_{d2}, $k_{hyd,ch}$, $k_{hyd,pro}$, $k_{hyd,li}$, $f_{ch,xc}$, $f_{pr,xc}$, $f_{li,xc}$, and $k_{dec,x2}$. The parameters k_1, k_4, K_{s1}, K_{s2}, and K_{I2} are from the original AM2 related to the substrate degradation, yield of CO_2, and half-saturation constants, respectively. They are markedly correlated to the equations for organic substrate, volatile fatty acids, and organic carbon in the model; k_{d1} and k_{d2} are both the decay rates of biomass, which are needed to obtain the real growth profiles of bacteria. k_8, $k_{hyd,ch}$, $k_{hyd,pro}$, $k_{hyd,li}$, $f_{ch,xc}$, $f_{pr,xc}$, $f_{li,xc}$, and $k_{dec,x2}$ are parameters for the hydrolysis process, however, they have strong significance for the prediction output.

Still, since sensitivity analysis and model comparison are valid only in a restricted vicinity of the parameter values, the results obtained have a local nature. In the study conducted by [24] the ADM1 and AM2 were compared against each other. Parameter estimation was performed to adapt the AM2 further using the original values of the AM2 and a benchmark substrate. A new state variable accounting for the inorganic nitrogen was added. For the sake of keeping the simple structure of the AM2, the reaction terms of the new state were directly incorporated into the total alkalinity state variable. Along with the new state variable, two new parameters were introduced. The first one describes the nitrogen content of the organic substrate and biomasses, the second one the nitrogen content in the biomass, taken up from or released into the environment [24]. At a steady state, both the original and the extended version of the AM2 predict the outcome of all parameters well, except the ones pertaining to the inorganic states. In the original AM2 inorganic nitrogen (S_{in}) is neglected [24], while ADM1 defines alkalinity by Eq. (14), which involves the difference between cation (S_{cat}) and anion (S_{an}) concentrations in the solution and inorganic nitrogen. The alkalinity constituents in Eq. (14) are bicarbonates, VFA, hydroxide ions, and free ammonia. Neglecting nitrogen affects the bicarbonate equilibrium, especially the amount of ammonium bicarbonate (NH_4HCO_3) [24]. Deviances arise in the predicted amount of methane. Results of the original AM2 [24] indicates that due to the absence of the description of free ammonia inhibition, the growth of methanogenic populations is increased. Therefore, the simulation of methane production is actually higher in the AM2.

$$Z = S_{cat} - S_{an} + S_{in} \tag{14}$$

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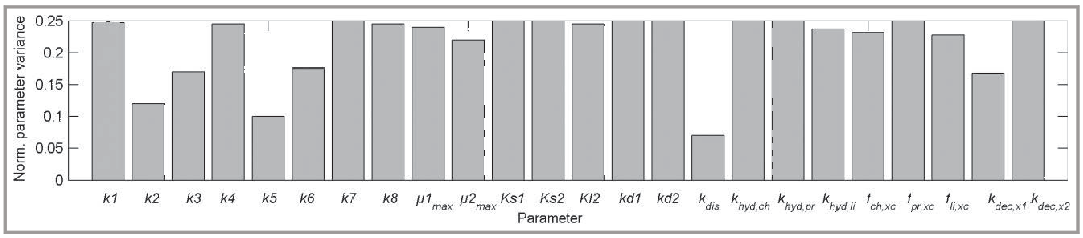

Figure 6. Sensitivity analysis to the 24 parameters of the extended AM2. Interval of normal parameter variance is 0 – 0.25.

3.4 Comparison with Original AM2

The AM2 is able to describe the experimental data of the biogas process using maize silage as a substrate, however, deviations from the real process appear in the biogas and methane rate production. The simulation made by the AM2 provides lower values than the experimental data after days 6, 13, and 28 when there is a two days period without feeding (see supporting information).

3.5 Experimental Study 2

In order to assess the quality of the optimized parameter set and their applicability in a biogas process, a validation study was performed. The model outputs were compared to measured data from an anaerobic digestion process conducted in two 15-L scale digesters operated at mesophilic conditions. The process was simulated applying the same implementation as described above without changing the previously optimized parameter set. The comparison of model outputs included experimental data for methane, CO_2, and volatile fatty acids. The OLR was increased in the following sequence during 20 days of the process: 3.16, 4.22, 5.27, and 6.33 $kg_{ODM}m^{-3}d^{-1}$. The methane production increased to a higher value after an initial adaptation phase, and then sharply decreased after the increase in OLR (Fig. 7a). It can be noticed that the model predicted reasonably the dynamic behavior of the process with a slight delay to high values of the organic loading rate.

The simulation of the amount of VFAs in comparison with experimental results of the two reactors is depicted in Fig. 7b. The amount of volatile fatty acids increased due to an excess of organic material at an OLR of 5.27 and 6.33 $kg_{ODM}m^{-3}d^{-1}$. Biogas production decreased under these conditions, which are known to be unfavorable for some methanogenic microorganisms. Particularly, the increase of the VFA concentration was predicted close to experimental data, although overestimated at the onset.

The standard procedure to increase model identifiability is to detect the parameters with a small sensitivity and high correlation and remove them from the parameter estimation problem. Nevertheless, the selection of these parameters, which are assumed to be highly correlated and of low sensitivity, is performed based on the Fisher Information Matrix (FIM), which is an approximation based on first order derivative information. This very rough approximation is only correct near the vicinity of the exact parameter values used to calculate the FIM. Therefore, ideally, all parameters should be considered in the parameter estimation. In order to take advantage of the information embedded in complex models, but allow its application in industrial plants without the need of improvement of the sensor system, methods to model reduction can be applied to tailor complex models to the needs of industrial processes. Representative examples are lumping [29, 30], sensitivity analysis [31], and time-scale analysis [32 – 34]. Beside many efforts, model reduction techniques still relay on process knowledge and experience in order to achieve the correct reduction of the model. In most cases, a combination of methods and

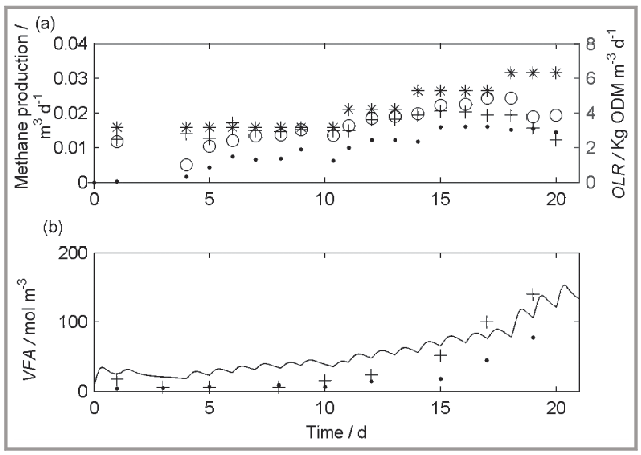

Figure 7. a) Extended AM2 simulation (o), experimental data of R1 (+) and R2 (•), and organic loading rate (*) during a period of 20 days of the acidification of anaerobic digestion processes conducted in two 15-L digestion processes. b) Simulation of volatile acid concentration (-) and experimental data of reactors R1 (+) and R2 (•).

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case studies is required to achieve the most suitable result. Some examples of the applicability of model reduction in biological processes are available in the literature [35] including its applications for advanced monitoring and optimization [36 – 38]. However, the complexity of the biogas process and the concomitant limitation in sufficient data limits practical application. Therefore, the AM2 with the extensions made as described in this study seems to be a good compromise for achieving reduced models for the description of AD for biogas production.

4 Conclusions

Advanced methods for optimization and control are required to allow for a dynamic operation of biogas plants while risks of a failed process is kept low. Nevertheless, in order to apply existing computer based methods, a robust and tractable model that is able to predict the dynamics of the process with sufficient accuracy is needed. Biogas processes are known for their complexity and limited installed monitoring capacities. Although many monitoring methods exist [39], their real application is restricted. Hence, existing models need to be adapted to fit the demands of large scale biogas production plants. In other words, models that are tractable and identifiable with the quality of information that is usually available from a biogas plant has to be used.

Nowadays, feed control of full-scale biogas plants is often performed by rules of thumb or simple calculation, although some attempts were made for optimal control of the feed rate at stable operation conditions, e.g., based on the ADM1 [40]. A first step towards a closed loop control is the availability of suitable models. In this study, the AM2 was evaluated for the application at dynamic process operation, caused by a fluctuating feedstock load. The calibration of the AM2 at a pilot-scale biogas plant was only feasible with a verification of the uncertainty in the model parameters, due to the nonlinearity of the biogas process. Very slow reactions occur when anaerobic microorganisms are fed in a dynamic real-time process, so the optimization using a complex and nonlinear process model seems to be a suitable approach. This is of special interest, when the loading rate is changed, e.g., for a better integration of biogas production and energy generation from it into smart systems. Then, a certain variation of the biogas synthesis rate is achieved by changing the feeding intervals, thus, creating a dynamic provision of biogas and energy. First attempts in this way have shown that this concept is suitable to gain a 9-fold variation in the biogas production if the process was fed every two days with dried distillers' grains in lab-scale bioreactors [41]. If more demanding conditions are used, e.g., a combination of rapidly and slowly digestible feedstock, any model-based approach might be useful to predict the feedstock load for various biogas production scenarios and for control purposes.

In this work, the AM2 was further compared to the ADM1 and it was shown that a tradeoff has to be made between model complexity and tractability in order to obtain reliable results:
(1) the ADM1, which is the most complex representation of the process including 36 states and more than 80 parameters.
(2) the AM2, which is a model developed for control purposes and is also tractable with only 6 states.

The ADM1 showed to be non-identifiable, if the data that is obtained in an usual biogas plant is considered. Taking this into consideration, the implementation of the AM2 in an adaptive framework should be preferred.

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Symbols used

ADF	[%]	acid detergent fiber
ADL	[%]	acid detergent lignin
CA	[%]	crude ash
C	$[kmol_C kg_{COD}^{-1}]$	carbon content
CF	$[\%_{DM}]$	crude fiber content of a substrate in dried form
cf	$[kg_{COD} kg_{DM}^{-1}]$	conversion parameter in COD
CL	$[\%_{DM}]$	crude lipid content of a substrate in dried form
COD	$[kg_{COD} m^{-3}]$	chemical oxygen demand
CP	$[\%_{DM}]$	crude protein content of a substrate in dried form
D_{in}	$[d^{-1}]$	dilution rate
DM	[%]	dry matter
f	$[kg_{COD} kg_{COD}^{-1}]$	yield
FM	$[kg_{FM} d^{-1}]$	fresh matter
HRT	[d]	hydraulic retention time
$k_{A,B}$	$[m^3 kmol^{-1} d^{-1}]$	acid-base kinetic parameter
k_{d1}	$[d^{-1}]$	decay rate of biomass *X1*
k_{d2}	$[d^{-1}]$	decay rate of biomass *X2*
k_{dec}	$[d^{-1}]$	decay rate
k_{dis}	$[d^{-1}]$	parameter for disintegration process
k_{hyd}	$[d^{-1}]$	parameter for hydrolysis
k_{La}	$[d^{-1}]$	volumetric gas-liquid mass transfer coefficient
k_m	$[kg_{CODS} kg_{CODX}^{-1} d^{-1}]$	maximum specific uptake rate
k_P	[-]	factor related to the friction of the gas outlet

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k_1	[–]	yield for substrate degradation
k_2	[mol kg^{-1}]	yield for VFA generation
k_3	[mol kg^{-1}]	yield for VFA consumption
k_4	[mol kg^{-1}]	yield for CO2 production
k_5	[mol kg^{-1}]	yield for CO2 production
k_6	[mol kg^{-1}]	yield for CH4 production
k_7	[–]	yield for substrate disintegration
k_8	[–]	yield for carbohydrates, proteins and lipids
K	[kg m^{-3}]	half-saturation constant
K_a	[kmol m^{-3}]	acid-base equilibrium coefficient
K_H	[mol atm^{-1}m^{-3}]	Henry-coefficient
K_{I2}	[mol m^{-3}]	inhibition constant
N	[mol kg^{-1}]	nitrogen content
NDF	[%]	neutral detergent fiber
NfE	[%]	nitrogen-free extracts
ODM	[%]	organic dry matter content
OLR	[$kg_{ODM}m^{-3}d^{-1}$]	organic loading rate
P_c	[atm]	CO_2 partial pressure inside the fermenter
q	[mol m^{-3}d^{-1}]	flow rate
S	[mol m^{-3}]	concentration
S_1	[$kg_{COD}m^{-3}$]	organic substrate concentration
S_2	[mol m^{-3}]	VFAs concentration
X_1	[$kg_{COD}m^{-3}$]	Concentration of acidogenic bacteria
X_2	[$kg_{COD}m^{-3}$]	Concentracion of methanogenic bacteria
X	[$kg_{COD}m^{-3}$]	particulate fraction
Y	[$kg_{CODX}kg_{CODS}^{-1}$]	yield of biomass
Z	[mol m^{-3}]	total alkalinity

Greek symbols

α	[–]	fraction of bacteria in the liquid phase
μ	[d^{-1}]	growth rate

Sub- and superscripts

aa	amino acid
ac	acetate
an	anion
bac	acetic acid
bu	butyrate
c	CO_2
cat	cation
ch	carbohydrates
ch_4	methane
fa	fatty acid
hco_3	hydrogen carbonate
h_2	hydrogen
H	higher bound
ic	inorganic carbon
in	influent
IN	inorganic nitrogen
li	lipids
L	lower bound
max	maximum
pr	proteins
pro	propionate
su	sugar
va	valerate
xc	composites

Abbreviations

AD	anaerobic digestion
ADM1	anaerobic digestion model no. 1
AM2	anaerobic digestion model
FIM	Fisher information matrix
IWA	International Water Association
VFA	volatile fatty acids
WTP	water treatment plant

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IV

Combination of life cycle assessment and modeling approaches as optimization tool for sustainable biogas production

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Abstract

Biogas production is applied in many regions of the world. However, full potential of the process for the conversion of multiple substrates is not fully explored in practice, as the process itself is equipped only poorly with monitoring and control devices. Recent attempts in research were made to combine engineering approaches with ecological and economical assessments to improve the efficiency and flexibility of biogas plant operation. Nevertheless, mathematical models are required that should describe the characteristic behavior of the process to find better or even “optimal” scenarios for biogas production. They should describe the main processes with sufficient accuracy at a low computational burden. Proper cost function is required to exploit advanced operation and control aiming a more sustainable energy production considering the complete life cycle of the process instead of a decision making. The quantification of the impact of each element in the system in a “cradle to grave” sense is required. To achieve this, life cycle assessment (LCA) need to be combined with a model-based approach to identify suitable operation points *in silico*. Then integration of simulation data into LCA studies allows the prediction of different production scenarios and a suitable choice of the scenario with the lowest environmental impact. This is highly relevant for processes that shall operate with complex cultures and multiple feedstock in the context of a bio-based economy. Therefore, this review summarizes the state-of-the-art of modelling and LCA in the area of biogas, which can achieve a simulation of biogas operation under sustainability constraints.

Keywords

Biogas; life cycle assessment; mathematical modeling; system optimization

7. Introduction

Biogas is an important part in the renewable energy (RE) sector [1, 2]. The European Union (EU) has a very ambitious target to mitigate greenhouse gas (GHG) emissions by the year 2020 and beyond. The plan "20-20-20" aims to reduce emissions of GHGs and primary energy consumption by 20% compared to the 1990s, and to increase the RE contribution to energy supply within the EU to 20% [3].

Currently, the installation of biogas plants in European countries is rising, although with a different speed. 17,376 biogas plants with an installed capacity of 8,728 MW el in total were operated in Europe in early 2016 [4]. Nowadays, there are almost 11,000 individually operated biogas plants in Germany with different varieties of plant architecture and operations. However, this independent and individual operation is clearly not leading to a maximum output, and non-optimal yields not to truly to sustainable processes. For these reasons, the efficiency, flexibility, predictability, and robustness of biogas production needs to be increased. This can be achieved if systems are better understood and controlled [5-7]. A proper objective function that minimizes the overall environmental impact of biotechnological biomass conversion needs to be combined with advanced design, optimization, and control strategies at plant and regional supply levels to achieve a higher level of sustainability.

Biomass is considered as one of the main RE sources expected to provide almost 10% of the energy demand in the near future [8]. 50-55% of EU biogas plants´ feedstock is originated from energy crops in spite of a growing concern about using arable land to produce energy instead of food.

Several studies have reported benefits in terms of the diminution of GHG emissions, air pollution, acidification, or eutrophication [9-14]. Nevertheless, the use of former forestry area as arable land for the production of renewable resources and concomitant impacts on biodiversity and carbon storage in the biosphere require a more diverse approach to evaluate biogas production, e.g. by a life cycle assessment (LCA) [15-18]. LCA scrutinizes numerous aspects related to the development of a product and its impacts throughout a product's life (i.e. cradle to grave) from the raw material production, processing, manufacturing, to the application and final disposal. It is widely recommended as a decision making tool to evaluate the real ecological footprint of a process [19]. The current waste management focusses on the biogas energy potential of residues and waste [15]. Nevertheless, there is a lack of knowledge of where to build a biogas plant, what size and how it should be operated in a stable manner while applying locally accessible feedstock in a flexible manor [20-22].

Due to the multiple species acting together during anaerobic digestion (AD), sensitive parameters vary between different plants and operations. The rather poor knowledge about the interrelations between the various organisms make changes in the operation crucial, e.g. at altered feedstock loading rates [23, 24].

Some of these drawbacks can be compensated, if a convenient mathematical model is applied that fairly describes the most relevant reactions [25]. Such a model, if properly validated, allows an accurate prediction of

nonlinear dynamics of the system. By this, it is possible to design and operate the plant in such a way that final objectives (e.g. the minimization of CO_2 equivalents) are achieved. In other words, the model shall predict the performance of biogas plants when different substrates or co-substrates are utilized under different loading rates [26].

By this, the integration of process modeling and LCA would allow a model predictive control of plants to produce biogas with the lowest negative impact on the environment, while keeping the profitability high. To approach this goal, this paper aims to summarize the existing LCA and modeling approaches in the area of biogas production, which are suitable to follow the described approach. The advantages of combining both approaches to bridge the gap between process control and a sustainable process conduction are depicted. Finally, the potential of how to combine LCA and process modeling is illustrated by successful examples from the area of waste-water treatment.

8. LCA Approaches for Biogas Production Processes

8.1. Definition of LCA

According to the ISO 14040 (Environmental management standard of principles and framework for LCA) [27] and 14044 standards (Environmental management standard of the specific requirements and guidelines for LCA) [28] , an LCA is performed in four independent steps as illustrated in Figure 1.

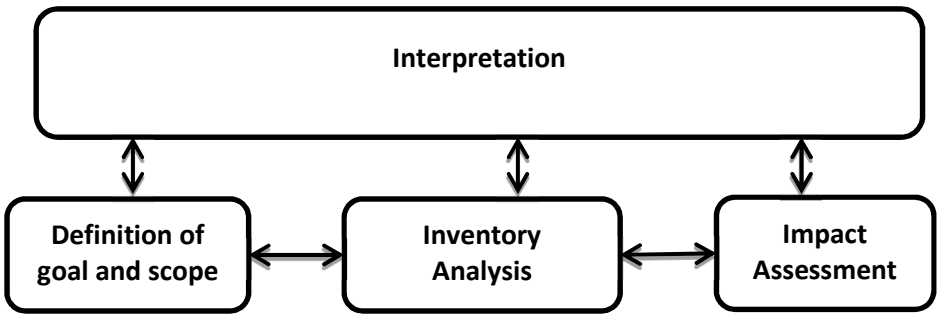

Figure 1. LCA framework based on ISO 14040:2006 Environmental management - LCA - Principles and framework [136].

Goal & Scope Definition:

The first step is to clarify the purpose and extent of the LCA. This entails formally determining the functional unit and system boundary. In a multifunctional process assessment, a variety of functional units can be used based on the application of the LCA. For this reason, every LCA study uses different functional units, which define the system or the processes [29].

System boundaries in LCAs have to be stated in multiple dimensions, including borders between the technological system and the surrounding

habitat [30]. Inventory analysis entails a list of all of the components of the product life cycle that fall within the defined system boundary [19]. Life cycle inventory assessment (LCIA) describes the specific flows for a system from and to nature. Inventory flows comprise inputs of water, energy and raw materials, and discharges to air, land and water. The required input and output data are collected for all activities within the system boundary, including the entire supply chain [29]. The data have to be connected to the functional unit that is described in the goal and scope definition. The result is a detailed description/visualization of all inputs and outputs in the form of the elementary flow to and from the environment for all distinct processes of the study.

There are four steps to the LCIA process, the first two are considered as mandatory, while the last two are optional: (i) classification, (ii) characterization, (iii) normalization, and (iv) weighting, respectively. Classification involves the assignment of specific environmental impacts to each component of the LCI. The impact assessment can be normalized by scaling the data by a reference factor, such as the region's per capita environmental burden. This helps to clarify the relative impact of a feedstock in a given context. The optional and final step of weighting is perhaps the most debated. Weighting entails multiplying the normalized results of each of the impact categories with a weighting factor that expresses the relative importance of the impact category. All weighted results have the same unit and can be added up to create one single score for the environmental impact of a product or scenario. It is a controversial step, since the selected weighting factors can influence the results and conclusions of an LCA [19, 31].

8.2. LCA for biogas production: state of the art

Although the use of a different functional units does not allow for a final conclusion, one can conclude that biogas production emissions mostly originate from: i) fertilization and digestate applications, and ii) diesel fuel consumption (for cultivation and for transportation) [7, 12, 13, 32-40]. Moreover, Tidåker et al., (2014) [41] determined that the acidification potential increased if nitrogen-based mineral fertilizer was replaced by digestate,. CH_4 and nitrous oxide emissions from digested slurry during storage or after field application represent another crucial issue [41]. Housing of digestate is a mean to reduce CH_4 release: Sommer et al., (2000) [42] determined that 38 % of the CH_4 emission of biogas production were released from uncovered digestate. Lansche and Müller, (2012) [43] [44] described that gas-tight digestate storage is recommended in order to reduce GHG emissions as other studies did [45][46]. Higher GHG emissions from digestate storage in comparison to emissions from field spreading were calculated by Capponi et al., (2012) [41] and Clemens and Huschka, (2001) [44] [47]. It seems that restraining CH_4 and N_2O emissions from digestate requires special care in the management of the anaerobic processes in general. Despite these issues, benefits of biogas production have been quantified, if diesel fuel generators were replaced [45]: Biogas contributes to a 58 % reduction of the global warming effect in this case. Furthermore, Ciotola et al., (2011) [46] [49]

indicated that the sustainability of electricity generation from biogas can be increased by maximizing engine conversion efficiencies, while minimizing the associated costs.

One important question is the scale of a sustainable biogas production. While large plants require a lot of logistic effort to supply the operation with sufficient amounts of feedstock, smaller plants rather rely on feedstock resources nearby the plant. The comparison of the energy efficiency of large-scale and small-scale biogas plants was performed by Wang and co-authors [50]. The results showed that large-scale plants provide a 78 - 96 % higher efficiency and a 126 - 173 times higher emission mitigation intensity, however, 66 - 74 % lower sustainability – what does this mean than that of the small-scale biogas plant. This finding is due to increased efforts of transportation and higher costs of equipment investment in AD and electricity production.

Whiting and Azapagic [47] demonstrated that LCA results are influenced by the type and source of feedstock, digestate storage and its application on arable land. In their study, the utilization of energy crops such as maize instead of waste reduced the GWP owing to higher biogas yields. The authors assumed a biogas yield of 145 Nm^3 /t feedstock. Lijó, González-García [48] examined the environmental consequences of feedstock selection for biogas production. Two biogas plants were assessed and compared from a life cycle perspective. Plant A was operated with energy crops (78%) and animal waste (22%), while Plant B was operated with energy crops (4%), food waste (29%) and animal manure (67%). The use of organic substrates with lower energy potential and high nutrient concentration like animal manure produced higher amounts of digestate, thus creating higher impacts on acidification and eutrophication categories. In this case, the comparison with alternative treatments of digestate is necessary to evaluate the benefits of biogas, and not the comparison with other feedstock sources.

Parameters that are required for the LCA of biogas production change among regions and corresponding values need to be used. As proven by Dressler, Loewen [32] and Ertem [49], local factors and regional parameters have a strong effect on LCA results. Therefore, it is necessary to consider e.g., transport distances, the agricultural area for biomass production and digestate spreading, and others, with the aim to perform a representative LCA study.

9. Model based process operation

A model is a poor mathematical representation of a physical system. Lack of accurate knowledge of the process to be modeled, insufficient measurement techniques and extensive computation time hinder an exact representation of the phenomena to be described [50]. Nevertheless, models are widely used in science and their contribution to a better understanding of engineering processes and their proper design, optimization and control is doubtless. In process engineering, the use of mathematical models has shown to be highly beneficial whenever properly developed, validated, and implemented [51].

Combined with powerful software and computational capacity, model-based tools are an important pillar in all engineering disciplines [52]. The work on mathematical modeling of the biogas production process is briefly reviewed, including data availability as well as first principle based methods.

Data-driven models do not consider the internal forces acting on the system, but they focus specifically on the interaction of large sets of data points. The most common methods are response surface methodology (RSM), principal component analysis (PCA), partial least squares (PLS), and lately machine learning tools (e.g. neural networks) [53]. This type of models can only be used within the boundaries of the experimental data set since there is no guarantee of its validity outside a defined space [54].

A first principle model is developed based on rational assumptions, while the consideration of physical laws, known physical interactions and mass balances in the systems material and energy flows lead to more sophisticated mechanistic and white-box models [55]. The parameter space of the models vary based on the process complexity and data availability [56, 57].

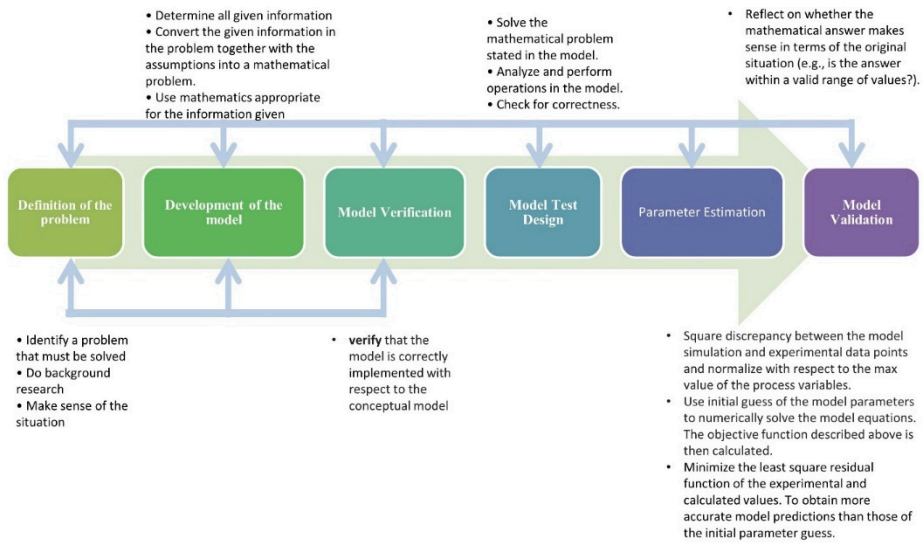

Figure 2. Steps of mathematical modeling of the bioprocesses

9.1. Model-based predictions of AD of agricultural substrates for biogas production

The main advantages of the existence of a model for a distinct biogas plant is its use for process optimization, production planning and early identification of process disturbances [58, 59], including the biotechnological conversions.

Deublein and Steinhauser [60] listed a number of operational disturbances, such as acidification, foaming, varying gas quality and odor, which can be prevented by an improved, model based, control system [61-65]. The anaerobic digestion model No. 1 (ADM1), developed by the International Water Association's Task Group in 2002 [66], is currently the most applied model. In this structured model, physico-chemical, chemical, and biological processes are included. The model focusses on the five major biogas production steps: disintegration, hydrolysis, acidogenesis, acetogenesis and methanogenesis. The biological processes are defined in multiple reactions. In summary, the model consists of 56 stoichiometric and kinetic parameters. The ADM1 was originally developed for sewage sludge processes [67], however, several research studies have adapted the model for other feedstock types like agricultural wastes [67] and energy crops like corn silage and grass silage [68]. Furthermore, co-digestion of organic waste with sewage sludge [69], olive pulp [70], and cattle manure, different organic materials, livestock manure and organic wastes [71] were investigated. These studies show that the ADM1 is able to simulate the process with different feedstock sources. In case of agricultural wastes, the feedstock was characterized and applied as feed input to the model. After the validation of the model with the mono-feedstock and co-feedstock scenarios in batch and continuous reactors, the model predicted the degradation of feedstock properly. Besides, Koch, Lübken [72] simulated the AD of grass silage by a modified ADM1 model with a separate compound of inert decay products and the integration with a hydrolysis function under consideration of nitrogen incorporation and release. The model was calibrated with the modified Nash–Sutcliffe model efficiency coefficient to assess the quality of the simulation. The model results showed a good agreement with the measured data. A modified ADM1, adjusted to a laboratory-scale digestion, which was operated with a feeding mixture of cow manure (30%) and corn silage (70%) was developed by Zhou, Löffler [73]. The impacts of the feeding mixtures on biogas composition and yield was adequately described with the model.

Mauky, Weinrich [74] developed a model predictive control to calculate feeding strategies in order to fulfill a demand-oriented gas utilization timetable. Full-scale experiments showed a high flexibility between days in a wide range of the average gas production and high process stability in reaction to pulse feeding. The study used a simplified ADM1 proposed in [89], in which the hydrolysis is considered as the rate-limiting process phase during the digestion of agricultural substrates and residues. The reduced model simulates the anaerobic digestion of carbohydrates, proteins, and lipids to biogas based on the superposition of first-order kinetics. Moreover, the kinetic parameters of ADM1 can be modified for a new substrate as described by Chen, Chen [75] in order to simulate the AD process in continuous digesters simply with the characterization of the substrate. The anaerobic digestion of municipal solid waste (MSW) was studied in a dry process under mesophilic conditions [76]. The ADM1 was simplified with respect to degradation pathways. It was reduced to six differential equations and three liquid-gas equilibrium equations for CH_4, H_2 and CO_2. Thamsiriroj, Nizami [77] used a series of mathematical models to

simulate the digestion process of grass silage. A model was built for a two-phase system, in which biogas was produced with an elevated CH_4 content of 71% v/v. The study concluded that longer retention times can maximize energy production per unit of feedstock and increase the CH_4 content in the biogas.

The AM2, also sometimes denoted as AMOCO [3], has proven to be accurate despite its reduced size. Hence, it should be the first choice in cases, in which model tractability is important. It was developed to support monitoring and control system design for AD processes, and not as a tool for the numerical simulation of the process behavior. The model considers two bacterial populations, which represent the acidogenic and methanogenic reactions. Ficara, Hassam [78] applied the AM2 to describe the anaerobic degradation of residual activated sludge and compared its applicability with the ADM1. Recently, Arzate, Kirstein [79] have adapted the AM2 to predict the digestion of maize silage at discontinuous feedstock loading rates. After fitting, outputs were compared to simulations of the ADM1, which showed the ability of the model to predict biogas, CH_4 and state variables. The relevance of the study is the achievement of a tractable model that simulates biogas production at dynamic feedstock loads.

Artificial neural network (ANN) models have been used extensively in biotechnological processes. Kanat and Saral [80] developed an ANN-based model to study biogas generation at a thermophilic digester depending on the influent and effluent total VFAs, OLR, alkalinity, pH value, and temperature of the reactor. A comparable study was also performed by Qdais, Hani [81]. Vavilin, Lokshina [82] simulated biogas production in an intensively mixed reactor. The authors observed that the average level and the general trend could be monitored, but the extreme points in biogas production were not reflected. The study considered how mixing intensity affects the efficiency of continuous-flow anaerobic digestion of MSW. Furthermore, Akbaşa, et al. [86] developed an optimization model of biogas production for sludge and used data from a wastewater treatment facility. The authors applied the multi-layer perceptron neural network and particle swarm optimization techniques. The study identified sensitive parameters of the treatment process that are shall be monitored as well.

9.2. Challenges of model implementation in practice

The frequency of many measurements is too low, the characterization of the feedstock is often not sufficient for a suitable data input for modeling. The measurement of organic content is not internationally standardized. Volatile solids (VS), total organic carbon (TOC) and chemical oxygen demand (COD) are basically three ways to measure the organic content. Lübken, Wichern [83] proposed that COD should be replaced by VS when feedstock like manure and energy crops are analyzed. COD is predominantly used in waste water treatment and for several other types of feedstock, VS is the most commonly used method of describing the organic content. A correlation between COD and VS was formulated to make it applicable to the ADM1 [74]. Other authors did similar

correlations of VS and COD [72, 84, 85] as well as correlating lipids, inerts, proteins and carbohydrates from kg TS to kg COD for its use in ADM1 [86, 87]. Beside conventional technologies, Weender analysis was performed using NIR to analyze the content of raw protein, lipids and raw fiber (carbohydrates) [88]. The analysis of the COD and TOC can be problematic with some types of substrate. Some are of a heterogeneous composition, which leads to a difficult determination of components and their contents.

Another issue, especially relevant for statistical models, is the time delay. For example, the gas production from one gram of substrate span over several days, which makes it complicated when it comes to allocation. However, there are many examples of data driven models for the prediction of gas production [81], in which a method for the calculation of the lumped elemental composition of the organic substrates is described. Additionally, the special distribution inside the reactor is important. Insufficient mixing and a high particulate content in the medium can cause significant heterogeneities in the fermenter, which have to be considered for a proper description of the process. Pre-treatment of substrates for biogas production, in this case, can improve mixing and prevent gradient formation to a certain extent, but this has not been addressed so far for biogas process modeling and further research is needed to investigate and quantify the benefits.

10. Combined LCA & Modeling approach

The combination of mechanistic models and LCA tools can bridge the gap between process control and environmental performance [89]. Such approaches are already being applied successfully at WWTP, however, the approach has not been applied for biogas plants yet. This section particularly aims to give an overview about how to apply combined LCA & modeling for biogas plants (Figure 3).

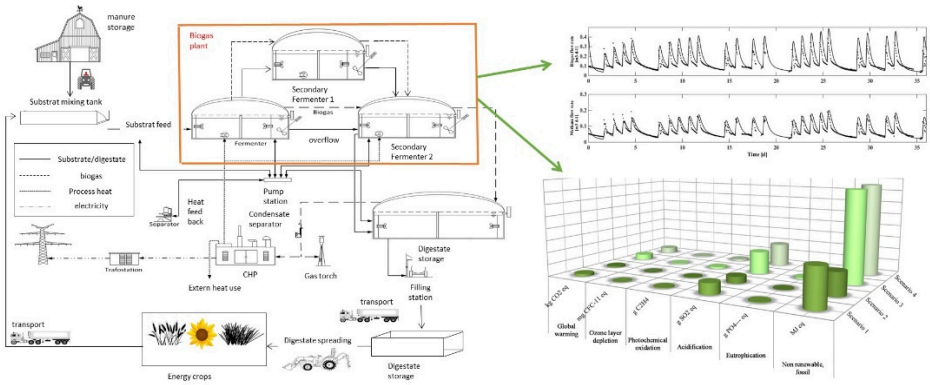

Figure 3. Combined application of LCA and modeling for control strategies at biogas plants

4.1. LCA & Modeling for WWTP

Model-based design and operation of WWTP has achieved important improvements in the past decades [90, 91]. Numerous LCA approaches have been published for different WWTP structures; developments were summarized by Corominas, Larsen [92] . Foley et al. (2010) used steady state simulation results gained with Biowin® for a methodical LCIA of ten scenarios in six WWTP designs. The results indicated that the amount of building materials and the chemical consumption were amplified when lower N and P concentrations were present in the effluent, as did energy consumption and GHG emissions in N-constraining effluent scenarios. Flores-Alsina, Arnell [93] applied dynamic simulations of an extended version of the Benchmark Simulation Model No.2 (BSM2), which is a developed model for plant-wide WWTP control strategy evaluation. It describes a pre-treatment process, an activated sludge process and sludge treatment processes [90]. In [81], the BSM2 was adapted to calculate the GHGs released on site, and the amounts of energy and chemicals created, with the goal of assessing control/operating strategies. The authors also presented the significance of considering both, water and sludge lines when analyzing GHG emissions, and described the considerable environmental impact of N_2O emission. Meneses, Concepción [94] presented a multi parameter decision study for WWTP operation strategies. The decision was based on the plant performance evaluation criteria described by the BSM2 scenario combined with LCA indicators. de Faria, Spérandio [95] developed an LCA- dynamic modeling (DM) framework by comparing five WWTP scenarios with a reference scenario. A Python™ interface was used to fit and convert simulation data. It was applied in Umberto to attain a comprehensive LCA assessment including the foreground and background processes.

4.2. LCA & Modeling for biogas plants

An operational integration of dynamic process modelling and comprehensive LCA were not accomplished so far. Such a combination requires adjusted

modeling and evaluation instruments, able to seize the effect of process parameters and dynamics in the impact calculation.

Simplified models based on emission factors tend to underestimate the GHG emissions [92]. Although simplified models (namely steady-state models) can be used to estimate the order of magnitude of GHG emissions from biogas plants, the dynamics of GHG formation cannot be captured. Dynamic modeling is recommended instead to provide more reliable GHG predictions paying particular attention on CH_4 formation dynamics and the control of the total GHG emissions from AD.

In order to adopt dynamic models that are characterized by a multitude of factors, it will be necessary to calibrate large amounts of data. Furthermore, full-scale models need to be applied to predict GHG emissions for different feedstock. Knowledge of the involved GHG production pathways must be expanded to create a suitable and comprehensive model framework that is able to reproduce all of the processes involved in N_2O, NH_3, CO_2 and CH_4 formation sufficiently. The modeling attempts described in this study are partly or fully able to provide such simulation, if adopted to the requirements of LCA. Future efforts should be dedicated to setting up mathematical software, tools and platforms for practical and feasible application during plant operation, in which both methodologies are combined in one graphical user interface.

11. Conclusions

Due to its flexibility and multi-functionality, the anaerobic digestion technology will play a relevant role in renewable energy production by transforming biomass streams into useful products, as a valuable contribution to close organic matter cycles. However, the flexibility of raw and residual feedstock utilization is also a demanding issue for a consistent sustainability assessment.

It is very important to note that LCAs always require interpretation, which in turn demands transparency and judgment itself. The data sources, assumptions, and all relevant information needs to be transparent to decision makers so that they can understand the full context of results. Deciding among design options is not as easy as just comparing LCIA outcomes, whether single- or multi-factor, weighted or not. Engineers will need to use them in context of other attributes they are trying to optimize, (e.g. cost, manufacturability and performance). In addition, there are other factors guiding process development decisions, including social impacts and acceptance, pricing, political agendas, and (local) regulations [96].

There is a need to develop and apply more intensively region-based LCA methods and overcome practical limitations for trying to develop and conduct such regionally contextualized LCA approaches, such as data availability, modeling capacities, and time constraints [97]. As LCA is traditionally a non-dynamic methodology, an interface between dynamic modeling results and inventory flows in LCA is required, together with the conversion of specific inventory items.

There is a further requirement to promote the development of common guidelines, which are specific for biogas production, in order to assess and communicate their environmental performance. Moreover, site-specific data shall be used to assess the most important sources of emissions at biogas plants, as they are deeply affected by climatic conditions and regional factors.

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V

Combination of extended AM2 and environmental LCA approach: assessment of a demand driven biogas production via feedstock management

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Abstract

Renewable technologies shall contribute to a reduction of greenhouse gas (GHG) emissions during energy generation and provision. Unfortunately, large amount of unpredictable renewable energy (RE) causes several challenges. Among them is the requirement to balance an alternating energy demand with the weather-dependent energy provision of several RE sources. Energy from biomass, in particular biogas plants (BGP), can buffer such fluctuations to a certain extent, if the biogas production can be adopted.

This study aims to combine a life cycle assessment (LCA) and modelling approach for demand oriented biogas generation through a flexible feedstock control. An extended version of the AM2 model was applied to predict the biogas production under dynamic feedstock loading scenarios. LCA was performed based on SimaPro 7.2 software and Ecoinvent® v2.1 database, while the mechanistic model was implemented in a Matlab® environment. Baseload and flexible biogas production were simulated by using the model approach. Later, the LCA outcomes were compared for both production concepts. Integration of LCA and modelling provides a suitable way to identify rapidly operation points that are stable and feasible in view of technical criteria, and which are sustainable, too, if several options of feedstock mixtures or loading scenarios can be chosen. Depending on the fluctuating energy demand scenarios, flexible production resulted in 35% lower GWP, 19% lower AP and 13% lower EP in comparison to a baseload production.

Keywords— Biogas production; AM2; LCA; modelling; flexibility; feedstock management

1. Introduction

The governmental support of renewable energy (RE) in many European countries brought about positive conditions to expand the quantity of biogas plants. In Europe 14,563 biogas plants that account to a total installed capacity of 7,857 MW el were under operation in 2014. Nowadays there are about 10,000 individually operated biogas plants in Germany with different varieties of plant architectures and operations. Optimization strategies to increase profitability and operational stability include the optimization of the feedstock pre-treatment for flexible substrate utilization and improved control for a flexible production, e.g. to counteract fluctuating energy provision of other renewable energy sources. A suitable control strategy can support the goal to minimize the environmental impact of energy production from biomass.

Although there is a growing apprehension regarding the utilization of food to generate energy, still energy crops create a proportion of 50-55% of EU biogas plants´ feedstock. The exploitation of maize every so often gives the highest yields and steady production, consequently it is amongst the most chosen feedstock for energy generation. 90% of biogas plants in Germany use at least partially maize as feedstock for their operation (e.V, 2014).

Wind and solar power create the largest proportions in RE systems in Central Europe resulting in great challenges for a stable energy supply due to their fluctuating characteristics. This is the motivation behind why the German legislative presented new incentives for a flexible energy generation right off the bat in 2012. Operators were permitted to choose between a settled feed-in tariff and a market premium on a month to month premise. Operators, who pick the market premium, are exchanging their power provision by themselves. A management premium is paid to take care of the expenses caused by this direct marketing. With the end goal to claim the flexibility premium, operators are relied upon to directly trade the total generated electric power they produced, this additionally implies the plant can be composed as dispatchable during the times of a high energy demand. These both premiums (market and flexibility) underwrite any conceivable ventures for a flexible energy generation (Hahn et al., 2014). Additionally, adaptability of feedstock helps to close the carbon cycles, improve the sustainability, diminish transportation and feedstock stockpiling costs, and in conclusion if the feedstock is not generated in house, a more freedom on market prices can be accomplished.

It is important to assess locally available biomass, which can be used efficiently as a source for RE production and within a sustainable waste management. The utilization of biogenic residues is gaining more interest as part of such a waste management (Lupp et al., 2014); nevertheless, there is a knowledge gap of the localization, size and operation with regional feedstock (Franco et al., 2015; Mol, 2014; Willeghems & Buysse, 2016).

Recent scientific findings described that the appealing prices linked to energy crop production accelerate the transition of pastures and forests into cropland on a worldwide scale, with a subsequent loss of biodiversity and carbon storage in the biosphere (Lupp et al., 2014). This could cause to cumulative quantities of GHGs, which are released into the atmosphere (Fargione et al., 2008; Johansson & Azar, 2007; Searchinger et al., 2008). Therefore, it is crucial to evaluate a biogas plant operation in a life cycle assessment (LCA) framework

to evaluate the real and global environmental outcomes. LCA scrutinizes numerous aspects related to the production effect throughout a product's life (i.e. cradle to grave) from raw material income, processing, manufacturing, use and final disposal from an environmental point of view. It is widely recommended as a decision making tool to evaluate the real footprint of a process (Baumann & Tillman, 2004).

Anaerobic digestion (AD) is a dynamic multi-stage process involving a wide microbial population structured in several groups of microorganisms whose composition and dynamics are not understood or measurable. Therefore, a number of challenges must be faced, such as its instability, slow reaction rates compared to aerobic processes, long hydraulic retention time (HRT) requirements (20 - 30 days) (Navia et al., 2002), critical components as sulfide, ammonia or metal salts (Duarte A, 1982), sensitivity to fluctuating loads, and its complex operation (Hwang et al., 1997; Lin, 1997). The energy content of the gas may also vary and is dependent on the nature of the substrate. These problems could be reduced through suitable monitoring strategies (Colussi I., 2012). Further, a mathematical model, which is able to describe the process, can be used for simulation of flexible feedstock loading scenarios, when different substrates or co-substrates ratios are applied (Arzate et al., 2017).

The ADM1 is the most commonly used model for anaerobic digestion modelling, although it has a complex structure. It contains a vast amount of parameters that can hardly be determined (Razaviarani & Buchanan, 2015). The extended AM2 is a model, which contains a lot less parameters. The model structure involves two main groups of microorganisms, which are described as acid-forming bacteria and methanogenic bacteria. It was proven to be a suitable model for the prediction of gas production, biomass, organic matter, short chain carboxylic acids, inorganic carbon and alkalinity (Arzate et al., 2017).

This study applies the extended anaerobic digestion model AM2 as a simulation platform for biogas production scenarios. A chosen scenario processes maize silage, grass silage and cow manure. In this study, the model was applied with the end goal to simulate a demand driven energy production for a 500 kW el biogas plant. Scenarios were created dependent on the adjustments in power generation and consumption from Agorameter (Energiewende, 2017) and spot market prices of a reference period based on the feed management.

The plant operation and energy production scenarios were analyzed and compared from an LCA point of view. The present work includes the assessment of emission outcomes at transient conditions of a biogas process. Under the consideration of 2 different energy production scenarios, required costs of the investments and feedstock, changes in the gas storage and energy production efficiencies, and potential incentives provided by the German Renewable Energy law (EEG) were calculated.

The coupled approach of simulation and LCA aims to identify the most suitable feedstock utilization and can be used as a decision-making tool.

2. Materials and methods

2.1. Feedstock supply scenario

Maize silage (1 t/h), grass silage (1 t/h) and cow manure (1 t/h) were selected for the simulated scenario (baseload stage). The parameter fit of a mono-digestion process for grass silage and cow manure was performed using the extended AM2 as described in Arzate et al. (2017).

2.2. Biogas plant

The examined plant has an electrical power capacity of 500 kW. In baseload production, the plant comprised of a primary digester (1,400 m^3 with 524 m^3 of gas storage), and 2 secondary digesters (2 × 2,851 m^3 with each 942 m^3). These were run at 37 °C (mesophilic conditions). The hydraulic retention time was 87 days. The production process is illustrated in Figure 1.

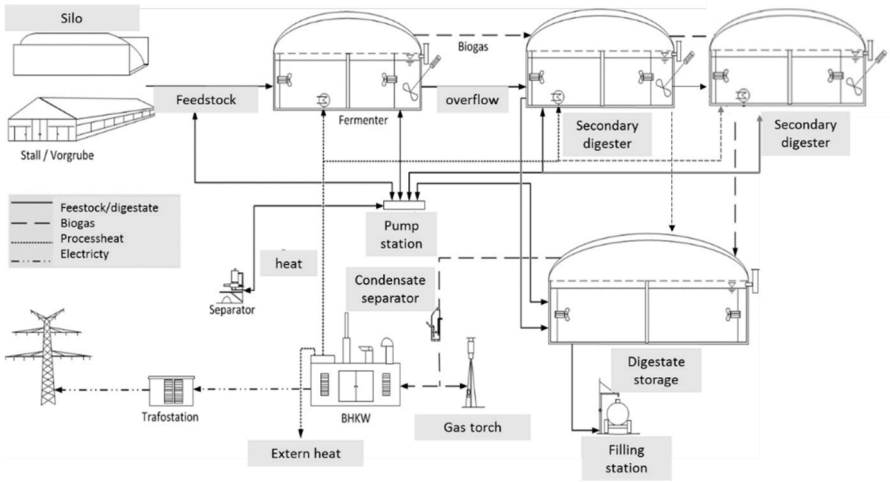

Figure 4. Biogas production process of the plant.

2.2.1. Demand driven biogas production and scenarios

The energy generation/supply is adjusted hourly dependent on changes in the energy consumption/demand and spot market prices of a reference period by the feedstock management. Time periods between 5 am and 10 am as well as 5 pm and 10 pm were selected as time periods of a high electricity demand based on Agorameter (Energiewende, 2017).

Extra revenue could be earned by this way of operation, however, venture of either an external gas storage or CHP is needed. In order to be able to produce more electricity in case the energy demand is higher, a 160 kW el power CHP unit was installed additionally, so that both CHP can supply energy in parallel. Production scenarios are illustrated in Table 1.

Table 2. Demand driven production scenarios

	Scenario 1				Scenario 2				Scenario 3				Scenario 4				Scenario 5			
Days	Day 1				Day 2				Day 3				Day 4				day 5			
Time Period	05:00-10:00	10:00-17:00	17:00-22:00	22:00-05:00	05:00-10:00	10:00-17:00	17:00-22:00	22:00-05:00	05:00-10:00	10:00-17:00	17:00-22:00	22:00-05:00	05:00-10:00	10:00-17:00	17:00-22:00	22:00-05:00	05:00-10:00	10:00-17:00	17:00-22:00	22:00-05:00
Feedstock tons/h																				
cow manure	1	1	1	1	1.2	0.86	1.2	0.86	0	0.86	2.4	0.86	0	1.14	1.6	1.14	1	1	1	1
Maize sil.	2	0.57	2	0	2.4	0.14	2	0	4.8	0	0	0	2.4	0.43	1.2	0.43	4	0.57	0	0
Grass sil.	2	0.29	2	0.29	2.4	0	2	0.14	0	0.29	4	0.29	2.4	0	2.4	0	0	0	4	0.57
proportion (%)																				
cow manure	20.00	53.85	20.00	77.78	20.00	85.71	23.08	85.71	0.00	75.00	37.50	75.00	0.00	72.73	30.77	72.73	20.00	63.64	20.00	63.64
Maize	40.00	30.77	40.00	0.00	40.00	14.29	38.46	0.00	100.00	0.00	0.00	0.00	50.00	27.27	23.08	27.27	80.00	36.36	0.00	0.00
Grass	40.00	15.38	40.00	22.22	40.00	0.00	38.46	14.29	0.00	25.00	62.50	25.00	50.00	0.00	46.15	0.00	0.00	0.00	80.00	36.36

2.3. Extended AM2 model

As published in Arzate et al. (2017), the extended AM2 includes some additional equations about hydrolysis and biochemical conversion than a previously published version (Bernard et al., 2001).

2.4 Life cycle assessment

LCA is deployed to quantitatively calculate the environmental performance of a process. This implies that all basic process stages are considered starting from feedstock acquisition/production until the point when the electricity power is fed into the grid. This study pursues the ISO 14040-14044, which gives standards, structure, and methodological for leading LCA studies. The outline of LCA incorporates the description of a goal and the scope, the inventory analysis, impact assessment and interpretation of results.

Northeastern Germany was chosen as area for the case-study. The Federal German Office for Statistics gave all the pertinent information in regards to the chemical features of the digestate, associated emission factors, the biogas plant's working settings, crop rotation, soil characteristics, temperatures and climate conditions (data sources are given correspondingly).

The studied area is described by sandy or loamy soil. The amount of precipitation is approx. 20% lower contrasted with most other regions in Central Europe. Since the valuation was region oriented, the results of this study might be additionally utilized for other geographical locations simply after an adjustment of the deployed data.

The functional unit (FU) is a key component of LCA. FU is a proportion of the capacity of the examined system and gives a reference, to which the inputs and outputs can be connected. This empowers a correlation of various systems. The collation in this study is based on a FU per kWh el. The system boundaries determine, which unit processes have to be incorporated in the LCA study (ISO Standard, 2006). The system boundaries comprised: crop production, ensilage/ storage, anaerobic digestion, storing of residues and spreading of digestate for agricultural, transport between production stages, the biogas combustion, supply of electricity into the grid and heat usage as temperature regulator at the fermenters and animal housing are as depicted in Ertem et al. (2016a).

2.4.1 Life cycle inventory analysis

The resources, energy and emissions entering and leaving the life cycle are accumulated in a life cycle inventory (LCI) analysis. LCI involves all stages managing data retrieval and management. Accordingly, data are validated and related to the FU to permit the organization of outcomes. The inventories of the feedstock include all process stages up to the conveyance of electricity into the grid. Details are described in Ertem et al. (2016b) and Ertem et al. (2016a).

2.4.2. Conversion of LCA data for modelling

LCA parameters were calculated by Simapro software and the Ecoinvent database. The parameters for any type of feedstock and for the industrial biogas plant and process used in the LCA are shown in Tab. [A-1]. The LCA parameters for maize silage, grass silage and cow manure are provided in Tab. [A-2].

The equations necessary to obtain total emission for climate change impacts, $CC_{total\_substrate}$, [kg CO2 eq. per kWh electricity produced], the acidification potential, $AP_{total\_substrate}$, [kg CO2 eq. per kWh electricity produced] and the eutrophication potential, $EP_{total\ substrate}$, [kg CO2 eq. per kWh electricity produced] of the whole production system were based on the ReCiPe midpoint v.1.06 methodology. The equations to obtain the emission of CO_2 equivalents, $EqCO_2$ [kg CO_2 eq. day^{-1}] are provided in the appendix.

2.5. Combination of AM2 and LCA

AM2 model and the built-in LCA approach were integrated into a Matlab 2015b framework. The AM2 model code used on Matlab and the parameters used in the model are depicted in the appendices.

3. Results & Discussion

Model parameters were firstly calibrated and validated for the baseload scenario with data from a real biogas plant. The developed simulation was able to quantify the effect of process parameters and dynamics for the impact calculation.

Since LCA is regularly a non-dynamic methodology, an crossing point between dynamic modelling outcomes and inventory flows together with the conversion of definite inventory in LCA was necessary. In order to be able to integrate the approaches, it was necessary to include the GHG formation processes for the biogas plants. Consequently, the calculation practices, which are normally applied in the Simapro software and the Ecoinvent database were used. Particular attention was paid on CH_4 forming dynamics while neglecting side product formation to achieve a suitable suggestion of the total GHG emissions from AD w/o making the approach too complex.

The model was used to simulate the baseload dependent biogas production from the co-digestion as illustrated in figure 2.b. On the next step, a feed management approach was used to simulate the demand-driven biogas production system as shown in figure 2.a. The model was able to successfully simulate the alterations within the process after the parameter fit. Outcomes demonstrate that the daily gas generation can be controlled up to ±50% from the day-to-day gas generation proportion thanks to the feeding management. The gas production was diminished straight under 60 $m^3\ h^{-1}$ by a tailor-made decrease of the feeding amount during the low energy demand periods. Outcomes also indicate the impacts of demand based feedstock feeding on the gas generation frequency, consequently the flexibility of the entire process. The simulated process was able to respond to the feeding alterations within few minutes with a significant hurdle in the gas generation frequency.

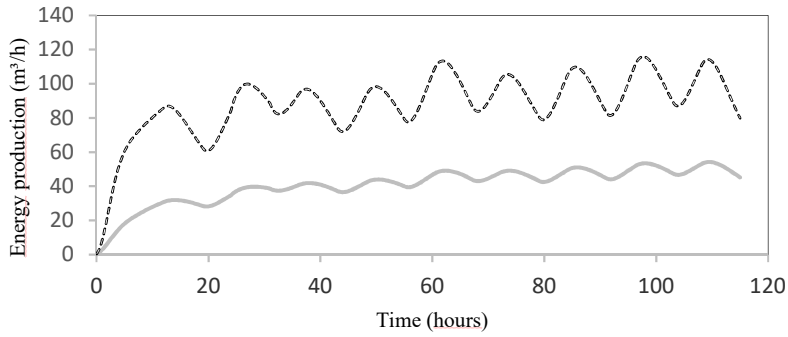

Figure 5. Comparison of methane (grey straight line) and biogas (black dashed line) production at a a) flexible feeding management and b) baseload scenario.

Based on the model, the volatile constituents in the feedstock were firstly digested; CO_2 was discharged because of the hydrolytic activity. A considerable growth in the gas generation was detected within an hour. After each feeding the CH_4 concentration descended below 50% and the CO_2 quantity increased, while the hydrolytic and acidogenic activity stayed high, process was stabilized always again.

The peak in the estimated gas generation rate seen in the first 30 min of the feeding of all feedstock mixtures is high most likely due to the amount of volatile acids in the ensiled feedstock and the volume of fast degradable ingredients. This behavior is well comprehended within the model. Figure 3 illustrates the cumulative biogas productions for 2 production concepts. It can be seen that flexible production increases the production efficiency by 6% by means of the total biogas production.

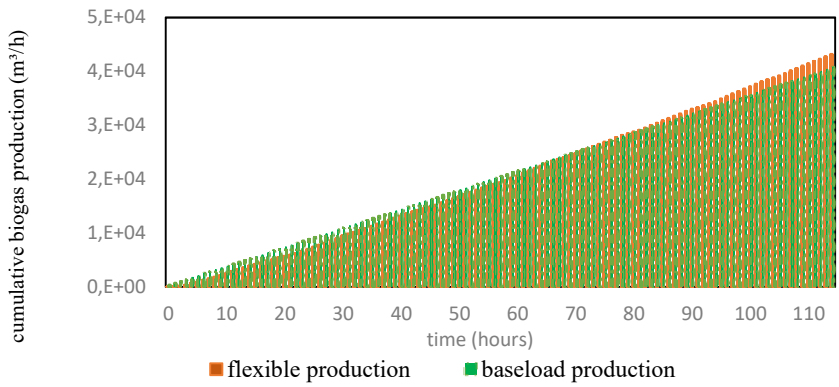

Figure 6. Comparison of cumulative biogas production at flexible (orange) and stable production (green).

Kinetic constants in the model are similar for grass silage and maize silage digestion. At a real biogas plant, however, this behavior might show differences

due to long fibers, a changed rheological behavior and mixing times, which were not considered in this approach. Due to varying consortia and feedstock qualities, a very close approximation of the real case is difficult anyway. In large-scale biogas plants the generated gas is directed into in bulky storages for several hours. As a result, diverse gas qualities are dispensed together to achieve lower disparities in the gas quality. Figure 3 shows the cumulative biogas production and Figure 4 illustrates the changes in the biogas volume retained in the gas storages (524m³ Fermenter + (2 × 942) m³ Secondary Fermenter and Digestate Storage). Modifications for flexible production would require an additional investment, mainly for a second CHP with 160 kW el (160,000 € investment cost), which leads to additional costs of 0.215 € kWh^{-1} el. Figure 4b illustrates the time periods, during which biogas was combusted through the CHPs.

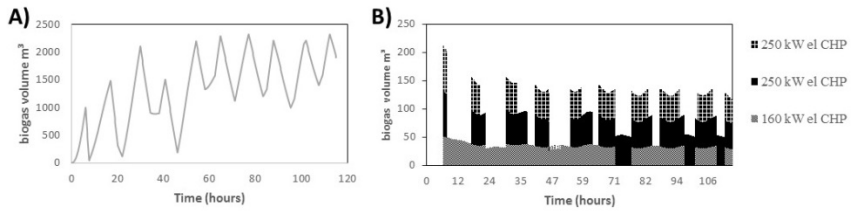

Figure 7. Changes in the volume of the biogas per hour a) retained at the gas storages b) biogas combustion at CHP´s: 250 kW el (dashed squares), 250 kW el (black squares) and 160 kW el (grey squares).

Figure 5 depicts the LCA results based on the feeding management approach (co-digestion of maize, grass silage and cow manure). Climate relevant gases are emitted into the atmosphere during biomass cultivation and biogas production. The average gross GHG emissions of the feedstock mixtures is 0.0093 kg CO_2-eq per kWh el. When the amount of manure is decreased, GWP from digesters decreases accordingly. A low biogas potential of manure (in comparison to energy crops) results in higher amounts of manure to be fed into the digesters in order to produce the same amounts of biogas (if biogas yields for each substrate are considered as follows: maize silage 216.1 m³/ t FM, cow manure 30.4 m³/ t FM, grass silage 189 m³/ t FM).

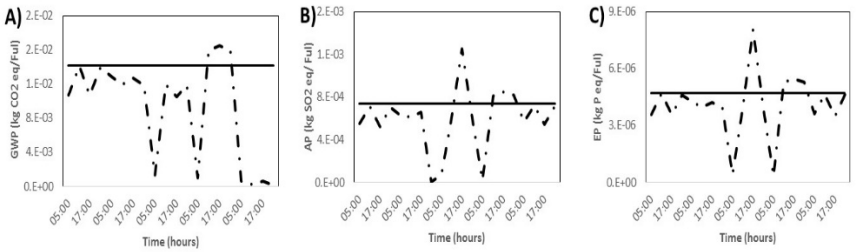

Figure 8. Environmental impacts caused by flexible feed management (dashed-dotted line) vs. baseload production (straight line), a) global warming potential, b) acidification potential, c) eutrophication potential. FU is 1 kWh el produced.

According to the Ecoinvent database, the emissions resulting from Diesel fuel combustion for biomass production and transport to the biogas plant as well as from electricity and heat consumption in order to operate the biogas plants are of minor importance for both energy production concepts.

NH_3 emissions from anaerobic digestion were lower during time periods of reduced production as it is assumed that the emission is directly coupled to the biogas production and combustion. AP and EP are primarily caused by ammonia and nitrous oxide emissions (80% share in total AP) during the fertilization due to evaporation. For the manure, a high share of emissions are resulted during the manure storage. It was assumed that the storage process results in a release of 10% of the ammonium content to the atmosphere (Ertem et al., 2016b).

Depending on the hourly alternating energy production, flexible production resulted in 35% lower GWP, 19% lower AP and 13% lower EP in comparison to baseload production. It can be concluded that a demand-driven energy production provokes lower emission. The complex substrate including its heterogeneous nature and fractions of the organic pool with different biodegradability characteristics and a separate pool for inert materials remain to be considered in the model. Knowledge of the involved GHG production pathways must be expanded to improve the model so that it will enable the simulation of all processes that are involved in N_2O, NH_3, CO_2 and CH_4 formation.

Biogas plants can have an economic benefit in times of low demand, if they can reduce the feed-in energy into the grid for several hours, as depicted in Table 2. Despite of an investment of 160,000 € in an additional 160 kW CHP unit for flexible production, incentives provided through EEG can help to earn additional 300,000 € per year to the plant operators. In this study, it was possible to increase the biogas production efficiency by 6% with a flexible production approach. This saved 5,000 € of feedstock costs per year. Thus, in total, an economic production is feasible.

Table 2. Summary of potential incomes and expenses for biogas production under different loading scenarios

	Demand driven production	Baseload production
Total power [kW el]	660	500
CHP investment [€]	160,000	-
Feedstock costs [€] 35€/t maize 31€/t grass	573,342	578,160
Biogas production [m³/5d]	43,202.3	40,833.33
Production Efficiency	1.06	1
Flex premium 160kW CHP*	15,000	-
Markt premium*	295,177.66	-

*calculated based on the DBFZ incentives calculator tool (DBFZ, 2016)

4. Conclusions

The consideration of LCA at transient state operations is difficult, as a dynamic process cannot provide data, which is required for a static method. If steady states are necessary, a long time is needed before measurements provide sufficient data within the anaerobic digestion. In these cases, the integration of the AM2 and LCA approach can provide a suitable solution. A model can help predicting the biogas production process. When it is combined with LCA, it can help to increase biogas production efficiency, because it allows to simulate feedstock mixtures, e.g. from local resources. Moreover, the model can help to determine the best possible substrate mix under consideration of emissions within the whole system. Consideration of LCA and modelling together provides an additional criterion to define optimal operation points at biogas plants and also allows for a faster, *in silico* environmental evaluation.

Sometimes, operators are faced with a decision that requires trade-offs. For example, what if they run the plant longer between turnarounds or when the substrate is limited? A difficult decision has to be made. The combination of AM2 and LCA approach can help operator better understand operating limits and optimal maintenance schedules to maximize plant profitability, while operational risks are reduced.

Future efforts should be dedicated to setting up mathematical software and tools/platforms for practical and feasible application for plant operators. In parallel to an improved on-line instrumentation and extended sampling campaigns for GHG emission monitoring, standardized analytical protocols have to be developed how to reduce GHG emissions practically in biogas plants.

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Compliance with Ethical Standards

Conflict of Interest. The authors declare that there is no conflict of interest.

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Appendices

Appendix 1. parameters for the model

Table A1. AM2 calibrated parameters for maize, grass and cow manure

Parameter	Unit	Maize silage	Grass silage	Cow manure
Maximum acidogenic bacteria growth rate, μ1max	d^{-1}	0.6	0.7	0.7
Maximum methanogenic bacteria growth rate, μ2max	d^{-1}	0.3	0.4	0.5
Half-saturation constant, KS1	kg m^{-3}	3.5	1.3	9.0
Half-saturation constant, KS2	mol m^{-3}	34.5	34.4	20.0
Inhibition constant, KI2	mol m^{-3}	998.2	991.3	250.1
Volumetric gas-liquid mass transfer coefficient, kLa	d^{-1}	22.0	22.1	80.8
Yield of substrate degradation, k1	[-]	25.5	24.0	26.0
Yield of VFA generation, k2	mol kg^{-1}	309.7	220.7	265.8
Yield of VFA consumption, k3	mol kg^{-1}	1074.0	874.0	622.8
Yield of CO2 production, k4	mol kg^{-1}	90.0	90.0	36.0
Yield of CO2 production, k5	mol kg^{-1}	200.0	200.0	24.9
Yield of CH4 production, k6	mol kg^{-1}	575.0	488.2	155.0
Fraction of bacteria in the liquid phase α,	[-]	1.0	1.0	1.0
Parameters of Ficara's extension				
Nitrogen content of substrate, Ns1	mol kg^{-1}	$1X10^{-4}$	$1.9X10^{-2}$	$3.1X10^{-2}$
Nitrogen content in the biomass, Nbac	mol kg^{-1}	11.0	9.0	33.9
Decayrate of biomass X1 and X2, kd_1 and kd_2	d^{-1}	5.3% μ1max 5.3% μ2max	4.4% μ1max 4.4% μ2max	8.4% μ1max 20.9% μ2max
Parameters , Hydrolysis process				
Disintegration, kdis	d^{-1}	0.50*	0.50	0.21
Hydrolysis carbohydrates, khyd_ch	d^{-1}	10**	10**	10
Hydrolysis proteins, khyd_pr	d^{-1}	10**	10**	10
Hydrolysis lipids, khyd_li	d^{-1}	10**	10**	10
Decay rate of biomass X1 and X2, kdec_x1 and kdec_x2	d^{-1}	0.032	0.033	0.032
Yield-coefficient of substrate disintegration, k7	[-]	12.7	12.7	25.0
Yield-coefficient of carbohydrates, k8	[-]	0.01	0.01	0.01
Yield-coefficient of proteins, k9	[-]	0.01	0.03	0.01
Yield-coefficient of lipids, k10	[-]	0.01	0.01	0.01

* from (Bastone, 2002)
** from (Wichern, 2008)

Table A-2 Chemical composition of grass silage and cow manure

Component	Grass Value [%]	Cow manure Value [%]
Water	62.6 [a)]	90.7 [b)]
Dry matter (DM)	37.4 [a)]	9.3 [b)]
Organic dry matter (ODM)	89.8 [b)]	81.7 [b)]
Crude ash (CA)	3.1 [a)]	-
Crude protein (CP)	4.0 [a)]	12.2 [b)]
Crude lipids (CL)	0.97 [a)]	4.3 [b)]
Crude fiber (CF)	8.8 [a)]	17.8 [b)]
Sugar as sucrose	6.8 [a)]	-
Neutral detergent fiber (aNDF)	17.9 [a)]	-
Acid detergent fiber (ADF)	10.4 [a)]	-
Acid detergent lignin (ADL)	0.97 [a)]	-

[a)] Laboratory analysis report Nr. F2570 for Maize Silage. Abteilung Futtermittel. Universität Hohenheim, Germany
[b)] Values obtained from [Zhou, H,et al, 2011]

Table A-3. Influent composition of grass silage and cow manure for the AM2 simulation

Component	Unit	Grass silage value	Cow manure value
$S1_{in}$	kgCOD m^{-3}	314.0	73.14
$S2_{in}$	mol m^{-3}	155.0	379.8
Z_{in}	mol m^{-3}	454.8	579.56
C_{in}	mol C m^{-3}	299.8	200.56
Xc_{in}	kgCOD m^{-3}	35.0	10.59
Xch_{in}	kgCOD m^{-3}	220.0	28.43
Xpr_{in}	kgCOD m^{-3}	47.69	9.31
Xli_{in}	kgCOD m^{-3}	11.69	6.13

Appendix 2. Extended AM2 Model for anaerobic digestion

```
Model AM2_Anaerobic_D
// Anaerobic digestion model, created on ASPEN modeler V8.0 - aspenONE
// State variables
  YX1 as Conc_mass;   //biomass concentration (acidogenic baceria)[g/L]
  YX2 as Conc_mass;   //biomass concentration (methanogenic bacteria) [g/L]
  YZ  as Conc_mole;   //total alkalinity [mmol/L]
  YS1 as Conc_mass;   //organic substrate  concentration[g/L]
  YS2 as Conc_mole;   //VFA (volatil fatty acids)[g/L]
  YC as Conc_mole;    //inorganic carbon concentration [mmol/L]
  YXc as Conc_mole;   //composites concentration [g COD /L]
  YXch as Conc_mole;  //Carbohydrates concentration [g COD /L]
  YXpr as Conc_mole;  //proteins concentration [g COD /L]
  YXli as Conc_mole;  //lipids concentration [g COD /L]
  YQM1 as Conc_mole;  // acidogenic bacteria growth rate [1/d]
  YQM2 as  Conc_mole; //methanogenic bacteria growth rate [1/d]
  YQC as Conc_mole;   // carbon dioxide concentration
  YQCO2 as Flow_vol;  // carbon dioxide gas [m3 d-1]
  YQCH4 as Flow_vol;  // methane flow rate [m3 d-1]
  YQBiogas as Flow_vol; // biogas flow [m3 d-1]
  V as Volume;        // liquid volume [l]
  Fin as Flow_vol;    // substrate flow rate [m3/d]
  Zin as Conc_mole;   // total alkalinity [mmol/L]
  S2in as Conc_mole;  // VFA (volatil fatty acids)[g/L]
  S1in as Conc_mass;  // organic substrate  concentration[g/L]
  Cin as Conc_mole;   // inorganic carbon concentration [mmol/L]
  Xcin as Conc_mole;  //Carbohydrates concentration [g COD /L]
  Xchin as Conc_mole; //Carbohydrates concentration [g COD /L]
  Xprin as Conc_mole; //proteins concentration [g COD /L]
  Xliin as Conc_mole; //lipids concentration [g COD /L]
  PT  as Pressure;    //Pressure inside the fermenter [atm]
  KH  as Constant;    //Henry-coefficient [mmol/atm*L]
  Fi  as Constant;    // Substituent of mass ballance
  YQH as press_diff;  // Substituent for calculating the CO2 partial pressure
  YQF as press_diff;  // Substituent for calculating the CO2 partial pressure
  YQPc as press_diff; // Substituent for calculating the gass partial pressure
  YQPH as press_diff; // H value for pH equation
  YQP as press_diff;  // difference of pH values
  YQR as press_diff;  // ratio of pH values
  YQRatio as press_diff;// complete ratio equation
  YQRexp as press_diff;// Exponential of ratio equation

  //AM2 Parameters;
  MMAX_1 as Constant; // Maximum acidogenic bacteria growth rate [1/d]
  MMAX_2 as Constant; // Maximum methanogenic bacteria growth rate [1/d]
  KS1    as Constant; // Half-saturation constant [g COD/L]
  KS2    as Constant; // Half-saturation constant [mmol/L]
  KSI    as Constant; // Inhibition constant [mmol/L]
  K1 as Constant;     // Yield-coefficient for substrate degradation [mmol/g]
  K2 as Constant;     // Yield-coefficient for VFA production [mmol/g]
  K3 as Constant;     // Yield-coefficient for VFA consumption [mmol/g]
  K4 as Constant;     // Yield-coefficient for CO2 production [mmol/g]
  K5 as Constant;     // Yield-coefficient for CO2 production [mmol/g]
```

```
  K6 as Constant;     // Yield-coefficient for CH4 production [mmol/g]
  K7 as Constant;     // Yield-coefficient for braking down of substrate degradation-
hydrolysis
  K8 as Constant;     // Yield-coefficient for braking down of carbohydrates [mmol/g]
  K9 as Constant;     // Yield-coefficient for braking down of proteins [mmol/g]
  K10 as Constant;    // Yield-coefficient for braking down of lypids[mmol/g]
  NS1  as Constant;   // Nitrogen content of substrate
  Nbac as constant;   // Nitrogen content  in the biomass
  KLa  as constant;   // Liquid-gas transfer constant [1/d]
  Kb  as Constant;    // Equilibrium constant [mol/L]
  kd1 as Constant;    // Parameter of extension, Ficara, 2014
  kd2 as Constant;    // Parameter of extension, Ficara,2014
 Khyd as Constant;    // Disintegration parameter
 Fdec1 as Constant;   // parameter related to the X1 - hidrolysis
 Fdec2 as Constant;   // parameter related to the X2 - hidrolysis
 Kch as Constant;     // parameter related to the Xch - hidrolysis
 Kf1 as Constant;     // parameter related to the Xch and Xc - hidrolysis
 Kpr as Constant;     // parameter related to the Xpr - hidrolysis
 Kf2 as Constant;     // parameter related to the Xpr and Xc - hidrolysis
 Kli as Constant;     // parameter related to the Xli - hidrolysis
 Kf3 as Constant;     // parameter related to the Xli and Xc - hidrolysis
//%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
/*
*/
//Model inputs
  Zin  = 545.15  // total alkalinity [mmol/L]
  S2in = 74.41;  // VFA (volatil fatty acids)[g/L]
  S1in = 285;    // organic substrate  concentration[g/L]
  Cin  = 470.75; // inorganic carbon concentration [mmol/L]
  Xcin = 35.04;  // composites concentration [g COD /L]
  Xchin= 185.48; // Carbohydrates concentration [g COD /L]
  Xprin= 37.44;  // proteins concentration [g COD /L]
  Xliin= 27.17;  // lipids concentration [g COD /L]
// Parameter values
  MMAX_1 = 0.59;   // Maximum acidogenic bacteria groth rate [1/d]
  MMAX_2 = 0.29;   // Maximum methanogenic bacteria groth rate [1/d]
  KS1    = 3.5;    // Half-saturation constant [g/L]
  KS2    = 34.49;  // Half-saturation constant [mmol/L]
  KSI    = 998.22; // Inhibition constant [mmol/L]
  K1     = 25.5;   // Yield-coefficient for substrate degradation [mmol/g]
  K2     = 309.71; // Yield-coefficient for VFA production [mmol/g]
  K3     = 1074.0; // Yield-coefficient for VFA consumption [mmol/g]
  K4     = 90;     // Yield-coefficient for CO2 production [mmol/g]
  K5     = 200.00; // Yield-coefficient for CO2 production [mmol/g]
  K6     = 575.00; // Yield-coefficient for CH4 production [mmol/g]
  K7     = 12.69;  // Yield-coefficient for braking down of substrate degradation-hydrolysis
  K8     = 0.01;   // Yield-coefficient for braking down of carbohydrates [mmol/g]
  K9     = 0.01;   // Yield-coefficient for braking down of proteins [mmol/g]
  K10    = 0.01;   // Yield-coefficient for braking down of lypids[mmol/g]
  NS1    = 0.0001; // Nitrogen content of substrate
  Nbac   = 11;     // Nitrogen content  in the biomass
  KLa    = 22.01;  // Liquid-gas transfer constant [1/d]
  kd1    =0.0529;  // Parameter of extension, Ficara, 2014
```

```
  kd2    =0.0529;  // Parameter of extension, Ficara,2014
  Kb     = 6.5e-7; // Equilibrium constant [mol/L]
  Khyd   =0.5;     // Disintegration parameter
  Fdec1  =0.032;   // parameter related to the X1 - hidrolysis
  Fdec2  =0.032;   // parameter related to the X2 - hidrolysis
  Kch    = 10;     // parameter related to the Xch - hidrolysis
  Kf1    = 0.2;    // parameter related to the Xch and Xc - hidrolysis
  Kpr    = 10;     // parameter related to the Xpr - hidrolysis
  Kf2    = 0.2;    // parameter related to the Xpr and Xc - hidrolysis
  Kli    = 10;     // parameter related to the Xli - hidrolysis
  Kf3    = 0.3;    // parameter related to the Xli and Xc - hidrolysis
//%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
//Equations
PressureDifferenceQH:  YQH = Kb*((YC + YZ + YS2)/(YZ - YS2));
PressureDifferenceQPH:  YQPH = -log10(YQH);
PressureDifferenceQP:  YQP = (YQPH);
PressureDifferenceQR:  YQR = (YQP-8.5)/(8.5-5.0);
PressureDifferenceQRatio:  YQRatio = (-3*YQR*YQR);
PressureDifferenceQRexp:  YQRexp = exp(YQRatio);
MolFractionQM1:  YQM1=MMAX_1*YS1*(1-YQRexp)/(YS1 + KS1);
MolFractionQM2:  YQM2=MMAX_2*YS2*(1-YQRexp)/(YS2 + KS2 + (YS2*YS2/KS1
));
ReactionRateX1: $YX1=(YQM1 - (Fin/V)-kd1*MMAX_1)*YX1;
ReactionRateX2: $YX2=(YQM2 - (Fin/V)-kd2*MMAX_2)*YX2;
ReactionRateZ: $YZ= ((Fin/V)*(Zin - YZ)) + ((K1*NS1-Nbac)*YQM1*YX1)-
Nbac*YQM2*YX2 + (kd1*MMAX_1*Nbac*MMAX_1*YX1) +
(kd2*MMAX_2*Nbac*MMAX_2*YX2);
ReactionRateS1: $YS1= ((Fin/V)*(S1in - YS1))-(K1*YQM1*YX1)+K7*(Khyd*YXc-
Fdec1*YX1 - Fdec2*YX2)+K8*(Kch*YXch-Kf1*Khyd*YXc)+ K9*(Kpr*YXpr-
Kf2*Khyd*YXc) + K10*(Kli*YXli-Kf3*Khyd*YXc);
ReactionRateS2: $YS2= ((Fin/V)*(S2in - YS2)) + K2*YQM1*YX1 - K3*YQM2*YX2;
ReactionRateC: $YC= ((Fin/V)*( Cin - YC))- YQC + K4*YQM1*YX1 +
K5*YQM2*YX2;
ReactionRateXc: $YXc= -Khyd*YXc + ((Fin/V)*( Xcin - YXc)) + Fdec1*YX1 +
Fdec2*YX2;
ReactionRateXch: $YXch= -Kch*YXch + ((Fin/V)*( Xchin - YXch)) + Kf1*Khyd*YXc;
ReactionRateXpr: $YXpr= -Kpr*YXpr + ((Fin/V)*( Xprin - YXpr)) + Kf2*Khyd*YXc;
ReactionRateXli: $YXli= -Kli*YXli + ((Fin/V)*( Xliin - YXli)) + Kf3*Khyd*YXc;
PressureDifferenceQF:  YQF = YC + YS2 - YZ + (KH*PT) + ((K6/KLa)*(YQM2*YX2));
PressureDifferenceQPc:  YQPc = (YQF - ((YQF^2 - (4*KH*PT*(YC + YS2 -
YZ))))^(0.5))/(2*KH);
MolFractionQC:  YQC = KLa*(YC + YS2 - YZ-(KH*YQPc));
VolumetricFlowQCO2:  YQCO2 = YQC*22.4*V/1000;
VolumetricFlowQCH4: YQCH4 = K6*YQM2*YX2*22.4*V/1000;
VolumetricFlowQBiogas: YQBiogas = YQCO2 + YQCH4;
End
```