Modeling and simulation of biogas production based on anaerobic digestion of energy crops and manure

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Preface

This book provides an introduction to the modelling method applied to anaerobic digestion (AD) to produce biogas from feedstock and is suitable for researchers, engineers, biogas operators and students interested in simulation and process optimization in the field of biotechnology. It can also serve as a reference of an alternative tractable model to predict and optimize the AD process from energy crops and livestock manure. In general, this work provides a good example of how modelling can be applied to simulate any combination of chemical and physicochemical processes with the goal to predict and establish the bases to control the process; this idea has eventually motivated me to write this thesis book.

Aside all subjects handled in paragraphs of the text, this publication focuses on two unified topics. One is related to anaerobic digestion models and the other concerns the optimization process to create a model. The book pretends to incorporate the most relevant information on the biogas process, such as benefits, models, challenges, substrates, optimization and future prospects. In the part of optimization, it presents the method to be developed to create a model.

While experimental data represent a fundamental component in the development of a model, the design of an experiment plays an important role to create a successful model in terms of operation conditions. Although simulations of a complex system as AD are thought experiments, the goal is not to study accurate representations of the process. Rather, the main purpose of a model is to broaden our understanding of general principles valid for the largest variety of sub-processes inside the system. This is a fascinating concept for bioprocess simulation and thus relevant to share with reader.

Biogas is an important topic for research since it is a renewable energy with huge prospects for the future worldwide. Statistics show that biogas installations are growing despite the challenges in Germany and Europe. No doubt it has incredible importance in the rest of the world; e.g. in China over 30 million households have biogas digesters converting wastes into clean-burning fuel; in one single year the number has risen to 900 households with digesters. However, there are also issues in the process operation that need to be solved. In recent years, biogas operators have been more concerned about how to obtain the optimum process without using the traditional “trial-error” method; sometimes it takes up to one and a half years to achieve the optimum. The work of this project aims to provide a contribution part in this respect, which makes it an interesting read.

The sheer volume of publications on the anaerobic digestion method makes the inclusion of every substantive concept in one single book quite impossible. However, this book does cover a range of topics which familiarity is essential to an understanding of how the AD method works. It also covers a few less essential topics, which are of special interest to the author, thereby presenting the topic from a more multidisciplinary point of view.

Danksagung

An dieser Stelle möchte ich meinen besonderen Dank nachstehenden Personen entgegen bringen, ohne deren Mithilfe die Anfertigung dieser Promotionsschrift niemals zustande gekommen wäre:

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Ich danke Herrn Dr. Stefan Junne für die hilfsbereite und wissenschaftliche Betreuung im Bereich von Biogas als Supervisor. Ich habe unsere Dialoge stets als Ermutigung und Motivation empfunden, vor allem aber seine konstruktive Kritik und die motivierenden Worte haben mir Kraft und Mut zur Anfertigung und Vollendung meiner Dissertation gegeben. Wegen seiner Unterstützung gebührt ihm hier meine voller und besonders herauszustellender Dank.

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Abstract

Despite all knowledge related to AD, the complexity of the process leads to the fact that there exists still a lack of knowledge how the process will behave at disturbances and flexible feedstock utilization. At biogas plants, sampling and monitoring is in most cases not sufficient to detect disturbances in the process at an early stage. This lack of knowledge does not allow for a demand-driven energy production and integration into local carbon cycles. Due to these reasons, research on monitoring and control of the process has been strongly intensified. Modelling is a method that can be used in AD to predict, quantify or simulate the process, when changes in operational parameters or substrates are applied to the process. It can also be a useful tool to recognize the key parameters that most affect the system. Although several models of anaerobic digestion have been developed, more suitable and efficient models are yet to be developed to simulate the system. Some complex AD models are capable to predict the system under certain conditions; however, a part of the process description is sometimes controversial or includes parameters that cannot be measured, especially under flexible feedstock operation. In this thesis, a reduced AD model called AM2 (or AMOCO) was formulated in order to accurately predict the dynamics of AD for crops and cattle manure. Firstly, the model was calibrated using sets of experimental data in a batch process, which was a mono-fermentation of maize silage. Subsequently, the concept was validated by experimental data where maize silage was digested and tested for twenty-eight days in a continuous pilot-scale biogas fermenter at discontinuous feedstock load. The model accurately predicted the dynamics of the CH_4 flow rate and the short-chain carboxylic acid concentration. Afterwards, the model calibration was performed using the ADM1 (Anaerobic digestion model No1) for grass silage and cattle manure. The calibrated models precisely predict the AD of the substrates for the flow rate of biogas and methane, the volumetric concentration dynamics of biomasses, shot-chain carboxylic acids, inorganic carbon, organic matter and pH values. Modelling of the process and an identifiability analysis of the model were conducted using MATLAB™. Moreover, the model was calibrated for the co-digestion of maize silage, grass silage and cattle manure in a flexible process, when using data from a large-scale biogas plant (BGP). Finally, the model was written in ASPEN Custom Modeler (ACM) V8 to perform an optimization of a co-digestion process by the test VOA/TA (Volatile Organic Acids/Total Alkalinity). The optimizer output presents better results in terms of energy production (an increment of 4.9 %) and process stability. The optimization of the process gives an option of a simulation in an integrated system within this platform.

Zusammenfassung

Trotz aller Kenntnisse im Bezug auf AD (Anaerobic Digestion) führt die Komplexität des Prozesses zu der Tatsache, dass es immer noch einen Mangel an Wissen darüber gibt, wie sich der Prozess bei Störungen und flexibler Rohstoffausnutzung verhalten wird. In Biogasanlagen reichen Probenahme und Überwachung in den meisten Fällen nicht aus, um Störungen im Prozess frühzeitig zu erkennen. Dieser Mangel an Wissen ermöglicht keine nachfragegesteuerte Energieerzeugung und Integration in lokale Kohlenstoffkreisläufe. Aus diesen Gründen wurde die Forschung zur Überwachung und Kontrolle des Prozesses intensiviert. Modellierung ist eine Methode, die in AD verwendet werden kann, um den Prozess vorherzusagen, zu quantifizieren oder zu simulieren, wenn Änderungen der Betriebsparameter oder Substrate auf den Prozess angewendet werden. Es kann auch ein nützliches Werkzeug sein, um die Schlüsselparameter zu erkennen, die das System am meisten beeinflussen. Obwohl mehrere Modelle der anaeroben Vergärung entwickelt wurden, müssen noch geeignetere und effizientere Modelle entwickelt werden, um das System zu simulieren. Einige komplexe AD-Modelle sind in der Lage, das System unter bestimmten Bedingungen vorherzusagen. Ein Teil der Prozessbeschreibung ist jedoch manchmal kontrovers oder enthält Parameter, die nicht gemessen werden können, insbesondere unter flexiblen Einsatzbedingungen. In dieser Arbeit wurde ein reduziertes AD-Modell namens AM2 (oder AMOCO) formuliert, um die Dynamik von AD für Nutzpflanzen und Rindergülle genau vorhersagen zu können. Zuerst wurde das Modell unter Verwendung von Versuchsdatensätzen in einem Chargenverfahren kalibriert, bei dem es sich um eine Monofermentation von Maissilage handelte. Anschließend wurde das Konzept durch experimentelle Daten validiert, bei denen Maissilage verdaut und achtundzwanzig Tage in einem kontinuierlichen Biogasfermenter im Pilotmaßstab bei diskontinuierlicher Substrat getestet wurde. Das Modell prognostizierte genau die Dynamik der CH4-Flussrate und der kurzkettigen Carbonsäurekonzentration. Anschließend wurde die Modellkalibrierung mit dem ADM1 (Anaerobes Verdauungsmodell Nr. 1) für Grassilage und Rindermist durchgeführt. Die kalibrierten Modelle sagen genau die AD der Substrate für die Durchflussrate von Biogas und Methan, die volumetrische Konzentrationsdynamik von Biomassen, Kugelkettencarbonsäuren, anorganischem Kohlenstoff, organischen Stoffen und pH-Werten voraus. Die Modellierung des Prozesses und eine Identifizierbarkeitsanalyse des Modells wurden mit MATLAB™ durchgeführt. Darüber hinaus wurde das Modell für den Co-Vergärung von Maissilage, Grassilage und Rindermist in einem flexiblen Prozess kalibriert, wenn Daten einer großen Biogasanlage (BGP) verwendet werden. Schließlich

wurde das Modell in ASPEN Custom Modeler (ACM) V8 geschrieben, um eine Optimierung eines Co-Digestion-Prozesses durch den Test FOSTAC durchzuführen. Die Optimierung des Prozesses zeigt bessere Ergebnisse im Bezug auf die Energieproduktion (ein Zuwachs von 4,9%) und die Prozessstabilität. Die Optimierung des Prozesses bietet die Möglichkeit einer Simulation in einem integrierten System innerhalb dieser Plattform.

List of original articles

The thesis includes mayor parts of the following papers, which are referred to in the text. Moreover, some unpublished information and data are presented.

Paper I (Conference paper)

Arzate, J. A., Bournazou, M. C., Kirstein, M., Neubauer, P., Junne, S., & Habermann, B. (2014). Modeling and parameter estimation of a biogas plant using maize silage in a two step model. *Engineering Optimization IV-Rodrigues et al. (Eds)*. Taylor & Francis Group, London ISBN 978-1-138-02725-1 (2014). 415-420.

https://www.taylorfrancis.com/books/9781315732107

Paper II (Conference paper)

Arzate, J. A., Ertem, F. C., Cruz Bournazou, M. N., Neubauer, P., & Junne, S. (2015). Life cyde assessment and modelling approaches for biogas production. *ETIKUM 2015*. ISBN: 978-1-315-73210-7 (eBook). 93-98.

http://www.dpm.ftn.uns.ac.rs/predmeti/Etikum/ETIKUM_2015_Proceedings_Online.pdf

Paper III (Published paper)

Arzate, J. A., Kirstein, M., Ertem, F. C., Kielhorn, E., Ramirez Malule, H., Neubauer, P., & Junne, S. (2017). Anaerobic Digestion Model (AM2) for the Description of Biogas Processes at Dynamic Feedstock Loading Rates. *Chemie Ingenieur Technik*, *89*(5), 686-695. DOI: 10.1002/cite.201600176 (2017) 686-695.

http://onlinelibrary.wiley.com/doi/10.1002/cite.201600176/full

The following manuscripts are in preparation.

Paper IV- Manuscript

Ertem, F. C., Arzate, J. A., Cruz-Bournazou, M. N., Neubauer, P., & Junne, S. Life cycle assessment and modeling approaches as a combined evaluation tool for control strategies for sustainable biogas production

Paper V – Manuscript

Arzate, J. A., Ertem, F. C., Cruz Bournazou, M. N., Neubauer, P., & Junne, S. Modeling of biogas production from energy crops and cattle manure through extended AM2 on ASPEN.

Paper VI – Manuscript

Ertem, F. C., Arzate, J. A., Cruz Bournazou, M. N., Neubauer, P., & Junne, S. Combination of life cycle assessment and modeling approaches as optimization tool for sustainable biogas production.

In all the manuscripts listed here I was responsible for the design and realization of the modelling, simulation and/or optimization work, interpretation of the results and did the main part of writing with respect to the same topic.

Contents

List of symbols

ADF	[%]	acid detergent fiber
ADL	[%]	acid detergent lignin
C	[mol C m^{-3}]	total inorganic carbon concentration
CA	[%]	crude ash
C_{aa}	[kmolC $kgCOD^{-1}$]	carbon content in amino acids
C_{ac}	[kmolC $kgCOD^{-1}$]	carbon content in acetate
C_{bac}	[kmolC $kgCOD^{-1}$]	carbon content in acetic acid
C_{bu}	[kmolC $kgCOD^{-1}$]	carbon content in butyrate
C_{ch}	[kmolC $kgCOD^{-1}$]	carbon content of component carbohydrates
C_{ch4}	[kmolC $kgCOD^{-1}$]	carbon content in methane gas
CF	[% DM]	crude fiber content of a substrate in dried form
C_{fa}	[kmolC $kgCOD^{-1}$]	carbon content of component fatty acids
cfch	[kgCOD $kgDM^{-1}$]	conversion parameter in COD for carbohydrates
cfi	[kgCOD $kgDM^{-1}$]	conversion parameter in COD for inert
cfli	[kgCOD $kgDM^{-1}$]	conversion parameter in COD for lipids
cfpr	[kgCOD $kgDM^{-1}$]	conversion parameter in COD for proteins
C_{in}	[mol C m^{-3}]	influent value for total inorganic carbon
CL	[% DM]	crude lipid content of a substrate in dried form
C_{li}	[kmolC $kgCOD^{-1}$]	carbon content of component lipids
COD	[kgCOD m^{-3}]	chemical oxygen demand
$COD_{total\text{-}th}$	[kgCOD d^{-1}]	total influent COD
CP	[% DM]	crude protein content of a substrate in dried form
C_{pr}	[kmolC $kgCOD^{-1}$]	carbon content of component proteins
C_{pro}	[kmolC $kgCOD^{-1}$]	carbon content of component propionate
C_{sI}	[kmolC $kgCOD^{-1}$]	carbon content of component soluble inert
C_{su}	[kmolC $kgCOD^{-1}$]	carbon content of component monosaccharides
C_{va}	[kmolC $kgCOD^{-1}$]	carbon content of component valerate
C_{xc}	[kmolC $kgCOD^{-1}$]	carbon content of component composites
C_{xI}	[kmolC $kgCOD^{-1}$]	carbon content of component particulate inert
D_{in}	[d^{-1}]	dilution rate
DM	[%]	dry matter
$f_{ac,aa}$	[kgCOD $kgCOD^{-1}$]	yield of acetate on amino acid
$f_{ac,su}$	[kgCOD $kgCOD^{-1}$]	yield of acetate on sugar
$f_{bu,aa}$	[kgCOD $kgCOD^{-1}$]	yield of butyrate on amino acid

$f_{bu,su}$	[kgCOD kgCOD^{-1}]	yield of butyrate on sugar
$f_{ch,xc}$	[kgCOD kgCOD^{-1}]	yield of carbohydrates on composites
$f_{fa,li}$	[kgCOD kgCOD^{-1}]	yield of chain long fatty acids on lipids
$f_{h2,aa}$	[kgCOD kgCOD^{-1}]	yield of hydrogen gas on amino acids
$f_{h2,su}$	[kgCOD kgCOD^{-1}]	yield of hydrogen gas on sugars
$f_{li,xc}$	[kgCOD kgCOD^{-1}]	yield of lipids on composites
FM	[kgFM d^{-1}]	fresh matter
$f_{pr,xc}$	[kgCOD kgCOD^{-1}]	yield of proteins on composites
$f_{pro,aa}$	[kgCOD kgCOD^{-1}]	yield of propionate on amino acids
$f_{pro,su}$	[kgCOD kgCOD^{-1}]	yield of propionate on sugars
$f_{sl,xc}$	[kgCOD kgCOD^{-1}]	yield of inert on composite
$f_{va,aa}$	[kgCOD kgCOD^{-1}]	yield of valerate on amino acids
$f_{xl,xc}$	[kgCOD kgCOD^{-1}]	yield of inert on composites
HRT	[d]	hydraulic retention time
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
$K_{a,ac}$	[kmol m^{-3}]	acid-base equilibrium coefficient for acetic acid
$k_{A,Bac}$	[m^3 kmol^{-1} d^{-1}]	acid-base kinetic parameter for acetate
$k_{A,Bbu}$	[m^3 kmol^{-1} d^{-1}]	acid-base kinetic parameter for butyrate
$k_{A,Bpro}$	[m^3 kmol^{-1} d^{-1}]	acid-base kinetic parameter for propionate
$K_{a,bu}$	[kmol m^{-3}]	acid-base equilibrium coefficient for butyric acid
$k_{A,Bva}$	[m^3 kmol^{-1} d^{-1}]	acid-base kinetic parameter for valerate
$K_{a,pro}$	[kmol m^{-3}]	acid-base equilibrium coefficient for propionic acid
$K_{a,va}$	[kmol m^{-3}]	acid-base equilibrium coefficient for valeric acid
k_{d1}	[d^{-1}]	decay rate of biomass *X1*
k_{d2}	[d^{-1}]	decay rate of biomass *X2*
$k_{dec,x1}$	[d^{-1}]	decay rate of acetogenic bacteria *X1*
$k_{dec,x2}$	[d^{-1}]	decay rate of methanogenic bacteria *X2*
$k_{dec,Xaa}$	[d^{-1}]	decay rate for amino acids degraders

$k_{dec,Xac}$	[d^{-1}]	decay rate for acetate degraders
$k_{dec,Xc4}$	[d^{-1}]	decay rate for valerate and butyrate degraders
$k_{dec,Xfa}$	[d^{-1}]	decay rate for fatty acids degraders
$k_{dec,Xh2}$	[d^{-1}]	decay rate for hydrogen degraders
$k_{dec,Xpro}$	[d^{-1}]	decay rate for propionate degraders
$k_{dec,Xsu}$	[d^{-1}]	decay rate for sugar degraders
k_{dis}	[d^{-1}]	parameter for disintegration process
K_H	[mol $atm^{-1}m^{-3}$]	Henry-coefficient
$k_{hyd,ch}$	[d^{-1}]	parameter for hydrolysis carbohydrates
$k_{hyd,li}$	[d^{-1}]	parameter for hydrolysis lipids
$k_{hyd,pr}$	[d^{-1}]	parameter for hydrolysis proteins
$K_{I,nh3}$	[kgCOD m^{-3}]	inhibition constant of ammonia
K_{I2}	[mol m^{-3}]	inhibition constant
$K_{Ih2,c4}$	[kgCOD m^{-3}]	hydrogen inhibition constant for valerate and butyrate degraders
$K_{Ih2,fa}$	[kgCOD m^{-3}]	hydrogen inhibition constant for LCFA degraders
$K_{Ih2,pro}$	[kgCOD m^{-3}]	hydrogen inhibition constant for propionate degraders
k_{La}	[d^{-1}]	volumetric gas-liquid mass transfer coefficient
$k_{m,aa}$	[kgCODS $kgCODX^{-1}$ d^{-1}]	maximum specific uptake rate for amino acids degraders
$k_{m,ac}$	[kgCODS $kgCODX^{-1}$ d^{-1}]	maximum specific uptake rate for acetate degraders
$k_{m,c4}$	[kgCODS $kgCODX^{-1}$ d^{-1}]	maximum specific uptake rate for valerate and butyrate degraders
$k_{m,fa}$	[kgCODS $kgCODX^{-1}$ d^{-1}]	maximum specific uptake rate for fatty acids degraders
$k_{m,h2}$	[kgCODS $kgCODX^{-1}$ d^{-1}]	maximum specific uptake rate for hydrogen gas
$k_{m,pro}$	[kgCODS $kgCODX^{-1}$ d^{-1}]	maximum specific uptake rate for propionate degraders
$k_{m,su}$	[kgCODS $kgCODX^{-1}$ d^{-1}]	maximum specific uptake rate for sugar degraders
k_P	[-]	factor related to the friction of the gas outlet
$K_{S,aa}$	[kgCODS m^{-3}]	half saturation constant for amino acid degraders
$K_{S,ac}$	[kgCODS m^{-3}]	half saturation constant for acetate degraders
$K_{S,c4}$	[kgCODS m^{-3}]	half saturation constant for valerate and butyrate degraders
$K_{S,fa}$	[kgCODS m^{-3}]	half saturation constant for LCFA degraders
$K_{S,h2}$	[kgCODS m^{-3}]	half saturation constant for hydrogen degraders
$K_{S,IN}$	[kgCODS m^{-3}]	half saturation constant for inorganic nitrogen
$K_{S,pro}$	[kgCODS m^{-3}]	half saturation constant of propionate degraders

$K_{S,su}$	[kgCODS m^{-3}]	half saturation constant for sugar degraders
K_{s1}	[kg m^{-3}]	half-saturation constant
K_{s2}	[mol m^{-3}]	half-saturation constant
N_{aa}	[kmolN $kgCOD^{-1}$]	nitrogen content in amino acids and proteins
N_{bac}	[mol kg^{-1}]	nitrogen content in the biomass
NDF	[%]	neutral detergent fiber
NfE	[%]	nitrogen-free extracts
N_I	[kmolN $kgCOD^{-1}$]	nitrogen content of component inorganic
N_{s1}	[mol kg^{-1}]	nitrogen content of substrate S1
N_{xc}	[kmolN $kgCOD^{-1}$]	nitrogen content of composites
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_c	[mol m^{-3} d^{-1}]	CO2 flow rate
q_m	[mol m^{-3} d^{-1}]	Methane flow rate
S1	[kgCOD m^{-3}]	organic substrate concentration
$S1_{in}$	[kgCOD m-3]	influent value for organic substrate
S2	[mol m^{-3}]	volatile fatty acids concentration
$S2_{in}$	[mol m-3]	influent value for volatile fatty acids
Saa	[kgCOD m^{-3}]	soluble component of amino acids
Sac	[mol m^{-3}]	soluble component of acetate
S_{an}	[mol m^{-3}]	anion concentration
Sbu	[mol m^{-3}]	soluble component of butyrate
S_{cat}	[mol m^{-3}]	cation concentration
Sfa	[kgCOD m^{-3}]	soluble component of total long chain fatty acids
Shco3	[mol m^{-3}]	soluble component of bicarbonate
Sic	[mol m^{-3}]	particulate component of inorganic carbon
S_{in}	[mol m^{-3}]	inorganic nitrogen
Spro	[mol m^{-3}]	particulate components of propionate
Ssu	[kgCOD m^{-3}]	particulate components of sugar
Sva	[mol m^{-3}]	particulate components of valerate
X1	[kgCOD m^{-3}]	Concentration of acidogenic bacteria
X2	[kgCOD m^{-3}]	Concentracion of methanogenic bacteria
Xaa	[kgCOD m^{-3}]	particulate component of amino acid degraders
Xac	[kgCOD m^{-3}]	particulate component of acetate degraders

Xc	[kgCOD m^{-3}]	particulate composite
Xc4	[kgCOD m^{-3}]	particulate component of valerate and butyrate degraders
Xch	[kgCOD m^{-3}]	particulate component of carbohydrates
Xch_{th}	[kgCOD d^{-1}]	influent particulate fraction of carbohydrates
Xfa	[kgCOD m^{-3}]	particulate component of LCFA degraders
Xh2	[kgCOD m^{-3}]	particulate component of hydrogen degraders
Xi	[kgCOD m^{-3}]	particulate fraction of inert
Xiin	[kgCOD m^{-3}]	concentration of particulate inert
Xi_{th}	[kgCOD d^{-1}]	influent particulate fraction of inert
Xli	[kgCOD m^{-3}]	particulate component of lipids
Xli_{th}	[kgCOD d^{-1}]	influent particulate fraction of lipids
Xpr	[kgCOD m^{-3}]	particulate component of proteins
Xpro	[kgCOD m^{-3}]	particulate component of propionate degraders
Xpr_{th}	[kgCOD d^{-1}]	influent particulate fraction of proteins
Xsu	[kgCOD m^{-3}]	particulate component of sugar degraders
Y_{aa}	kgCODX $kgCODS^{-1}$	yield of biomass on amino acids
Y_{ac}	[kgCODX $kgCODS^{-1}$]	yield of biomass on acetate
Y_{c4}	[kgCODX $kgCODS^{-1}$]	yield of biomass on valerate and butyrate
Y_{fa}	[kgCODX $kgCODS^{-1}$]	yield of biomass on LCFA
Y_{h2}	[kgCODX $kgCODS^{-1}$]	yield of biomass on hydrogen gas
Y_{pro}	[kgCODX $kgCODS^{-1}$]	yield of biomass on propionate
Y_{su}	[kgCODX $kgCODS^{-1}$]	yield of biomass on sugar
Z	[mol m^{-3}]	total alkalinity
Z_{in}	[mol m^{-3}]	influent value for alkalinity

Greek symbols

α	[-]	fraction of bacteria in the liquid phase
μ_1	[d^{-1}]	growth rate of acidogenic bacteria
μ_2	[d^{-1}]	growth rate of methanogenic bacteria

Sub- and Superscripts

in	Influent
max	Maximum
H	higher bound

L	lower bound

Abbreviations

AD	Anaerobic digestion
ADM1	Anaerobic digestion model No. 1
AM2	Anaerobic digestion model two steps
AS	Active Sludge
FIM	Fisher Information Matrix
HPLC	High-performance liquid chromatography
IWA	International Water Association
LCFA	Long chain fatty acid
VFA	Volatile fatty acid
WTP	Water Treatment Plant
WWT	Waste Water Treatment

Definitions

Acetogenesis	A process through which acetate is produced with help of anaerobic bacterias
Acidogenesis	A process where monomers are converted to shorter volatile fatty acids
COD	Chemical oxygen demand tells the amount of oxygen needed to decompose a specific amount of organic material. A high COD value corresponds to a high concentration of organic compounds in the materials, leading to a high gas exchange
Extra cellular	Outside the cells
Hydrolysis	Chemical process where a molecule is divided after water is added.
Intra cellular	Inside the cells
Methanogenesis	A biological reaction where acetates are converted into methane and carbon dioxide
Monod kinetics	Mathematical model for growth of microorganisms
Fermentation	A metabolic process that converts sugar to acids, gas and/or alcohol
Oxidation	Chemical reaction in which a substrate gives away one or more electrons
Reaction order	Determines rate of reaction
Arrhenius equation	Determines the reaction rates as a function of the temperature

I. Introduction

1.1. Biogas process

The perception on risks of using fossil fuels and rising energy prices have gained much interest for renewable energy in recent years. Biogas, a clean and renewable form of energy, is obtained from digestion of energy crops and wastes and can be harnessed as a source of sustainable energy. It can be produced from different sizes and designs of digesters, in an AD system. The process is a major focus and is carried out for the treatment of organic waste in which nearly all biodegradable material is digested via anaerobic bacteria. The biogas composition depends on the type of feedstock components and the operational conditions in the process. The main components of biogas are methane, CH_4 (the source of energy within the fuel) and carbon dioxide, CO_2. It may also contain small amounts of nitrogen or hydrogen. Biogas can be produced at hydraulic retention times (HRT) of 12-25 d. in mesophilic (35-45˚C) or thermophilic conditions (50-60˚C) (Horváth et al., 2016). Both types of processes normally require a supplementary source of heat to attain optimal digestion. This heat is mostly supplied by a combined heat and power (CHP) system, also known as cogeneration, which generates electricity and useful thermal energy for the process in a single, integrated system. As an efficient waste and wastewater treatment technology, AD has been mainly used at waste water treatment plants (WWTPs), where the stabilized sludge produced is used as a soil conditioner in agriculture. AD has also been extensively used for the treatment of agricultural and industrial wastes (Chen et al., 2008), converting it into a valuable resource, additionally solving a waste management problem.

1.2. Benefits of biogas

AD is a robust and efficient technological method that can reduce pollution from agricultural and industrial operations; meanwhile, it promises to diminish the processes' usage of burning fossil fuels. In terms of operational efficiency, AD can generate low sludge, requires a small amount of energy during the process and contains the potential for resource recovery. Compared to other processes, it has low operational costs, facilitates the reuse of the nutrients present in the original waste stream and can reach a pathogen-free effluent by additional treatment (Forbis-Stokes et al., 2016). Aside from an increasing recognition of the potential for environmental benefits of AD, the total biogas

produced offers carbon-neutral energy and mitigates greenhouse gas emissions (Chen et al., 2007). Indeed, there are more benefits of biogas that are worth mentioning; the most notable are described by sector in the following.

1.2.1 Agricultural benefits

Risk mitigation through energy sales. Energy sales have been continually placed under pressure in recent years. The causes have been mainly price-sensitive clients, more competition in the energy market and more detailed market regulations. At present, Biogas, as the same to hydroelectric power, is the only not fluctuating renewable energy that can supply electricity power able to relieve this pressure (Gomez, 2013).

Implementation of adequate nutrient management practices. Biogas digestate, a nutrient-rich residue remaining after anaerobic digestion of a biodegradable feedstock, can be used as a soil conditioner and/or organic fertilizer (Surendra et al., 2014). Application of digestate has been demonstrated to inhibit plant diseases and induction of resistance.

Support on local processing of agricultural production. The success of biogas can be assured when there is availability of seasonal substrates in the region. Hence, agricultural systems related to anaerobic digestion are found across many rural places, and have worked satisfactorily using different models according to various application purposes, such as biogas-poultry breeding-cropping, biogas-pig breeding-cropping, biogas-cattle breeding-vegetable growing (Wei et al., 2009).

Reduction of commercial fertilizer requirements. An improved fertilizer quality from AD digestate could reduce fertilizers' requirements, since it avoids the presence of chemicals in fertilizers that may be harmful to crop soils.

1.2.2 Economic benefit.

The green economy benefits of biogas are vast and include:

Local job creation in technical, manufacturing and construction/trades. BGP installations bring benefits for the whole supply chain, including farmers, agroindustry, providers and local community.

Economic development generating billions of dollars of investment in rural communities. The development and cost-efficient use of renewable energy technologies as biogas might bring the solution of fuel shortage in villages or rural areas, as well as improve living and health standards of their communities. It further provides job opportunities in spin-off small-scale companies (DaSilva, 2010).

Creation of useful by-products from wastes, which proceeds as a significant economic multiplier. The byproducts obtained from biogas production can be transformed into efficient biofertilizers and then used for fruit and plantation crops production, benefiting the environment by eliminating detrimental chemical compounds that might eventually be harmful to it (Börjesson and Berglund, 2007).

1.2.3 Energy benefits

As a source of renewable energy, biogas has unique characteristics and offers many energy end uses. Below the benefits of this concept:

Production of flexible power. The biogas output that can be adapted to energy demand by changing feeding regimes is what is increasingly required for balancing power to compensate power supply from fluctuating sources, such as solar or wind. Biogas production has the potential to generate electricity flexible on-demand (Hahn et al., 2014).

Management of intermittent renewable power supply through means of storage and flexible power. The unpredictability to generate the entire energy without fluctuation is a challenge in terms of balance of the demand and supply at all times (Østergaard, 2009), (Lund et al., 2012). An evident difficulty is observed between electricity demand profiles and electricity weather-dependent electricity supply profiles; such significant differences are registered all the time, as seen in Fig. 1 (Szarka et al., 2013). Biogas as a non-fluctuating renewable energy might ensure both the security of the continuous supply and stability of the grid.

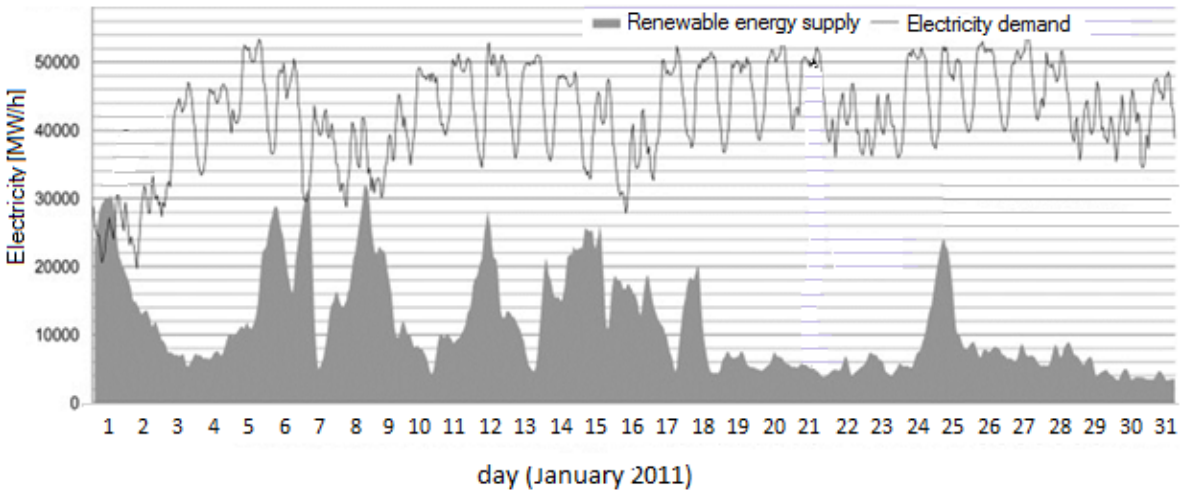

Figure 1. Daily profiles of renewable energy supply and electricity demand. Information provided by transmission network operator in Germany. Figure adapted from (Szarka et al., 2013).

Improvement/support of local infrastructure and power quality. Energy seen as an area of innovation is not only related to public policies, but also involves other actors e.g., industrial companies, researchers, innovative entrepreneurs, NGOs, etc. that can contribute significantly to developments in the energy sector (Borup et al., 2008). Hence, the generated energy innovation activities and initiatives promote the development of regional infrastructure, research and technology investment.

Upgrading to renewable natural gas (RNG) for injection into the natural gas grid. Biogas can be upgraded to biomethane by removing trace components which are the H_2S, moisture, and CO_2. Since production of such fuel typically exceeds immediate on-site demand, the biomethane must be stored for future use. To convert biogas into biomethane, two major processes are needed: a) a cleaning process to eliminate the trace components; b) an upgrading process to adjust the calorific value. The latter is usually carried out to accomplish the standards for use as vehicle fuel or for injects to the gas grid.

The use as transportation fuel or as a replacement of natural gas. The production and sale of biomethane as a transport fuel is financially competitive with liquid biofuels and fossil fuels. When being used in a Combined Heat and Power (CHP), it is also competitive (Patterson et al., 2011).

1.2.4 Environmental

The environmental benefits of biogas are complex.

Control weed seed germination, reducing herbicide use. The use of digested manure can result in crop yields equivalent to undigested manure or fertilizer at similar nitrogen rates, while simultaneously energy is produced. Anaerobic digestion might destroy weed seed viability under certain conditions, and germination times may be impacted (Allan et al., 2003).

Odor removal. Anaerobic digestion of manure is able to reduce smelling up to 80 %, the digestate does not smell so unpleasant and more like ammonia after treatment (Brebbia and Chon, 2012).

Capture and use of methane. Methane in biogas can be captured and used for electricity production or as a fuel, while avoiding greenhouse gas emissions 21 times worse than CO_2.

Conversion of high energy waste streams into fuel. Electricity generation from waste incineration, diverting them from landfill is another advantage of biogas. Thus, conversion of energy crops, livestock manure and empty fruit bunches offer a global alternative converting trash and biomass into usable energy (Sovacool and Mukherjee, 2011).

1.3. Scope of the project

Due to the steadily gained importance in anaerobic digestion processes, ways to enhance and further investigate the anaerobic digestion have been increased. Nowadays, the anaerobic digestion process to produce biogas has become a well-established energy technology, especially through the use of renewable biomass i.e. “energy crops or animal manure”. Factors affecting the process of a biogas plant are linked to feedstock issues related to disposition, digestibility, and pre-treatment needs. In terms of disposition, disturbances can be caused by the use of a broad variety of the feedstock quantity and quality which depends on the feedstock supplier. Obviously, it affects bacterial growth, and therefore, the biogas composition and methane yield. The hydrolysis and the content of methane in the biogas depend on the feedstock type, accumulation of intermediate products and the presence or generation of inhibitors. The study of this thesis focuses on the development of an anaerobic digestion model that is tractable and capable to predict the digestion

of the most used substrates in Germany, as well as to establish the bases of the process optimization.

In order to accomplish the goal of this thesis, this book is essentially based on four six (see Section Papers). Furthermore, supplementary data, computations and analyses (which have not been published yet) along the manuscript are also provided. The combination of published and new information is used to set the entire computational framework and to present an overall discussion and conclusion of the project.

2. Literature Review

2.1. Evolution of anaerobic digestion models – Generations

The evident benefits and clear potential of AD have marked an increasing interest in the research community to bring their resources and expertise to bear in the field. Research and development addressed to this aim have required interdisciplinary approaches, integrating concepts of biochemistry, modelling and process engineering. AD modelling has involved a significant scientific activity to better understand and visualize the process by referencing the existing and accepted knowledge or validated new concepts. Models to describe the anaerobic digestion process might be classified into generation through time. In 1969, the first approach of the AD which was created due to the necessity to simulate the stability of the system including prediction of disturbances and start-ups after a failed process. In general, the first AD models focused on the rate-limiting step and considered that the acetic acid degradation by bacteria was rate-limiting (Thorin et al., 2012). I herewith present a compilation of the most applied anaerobic digestion models over the time. The complexity of models for anaerobic digestion can be seen over the last 50 years in Fig. 2. In section 3.1 of paper IV, models of agricultural substrates for the production of biogas are given.

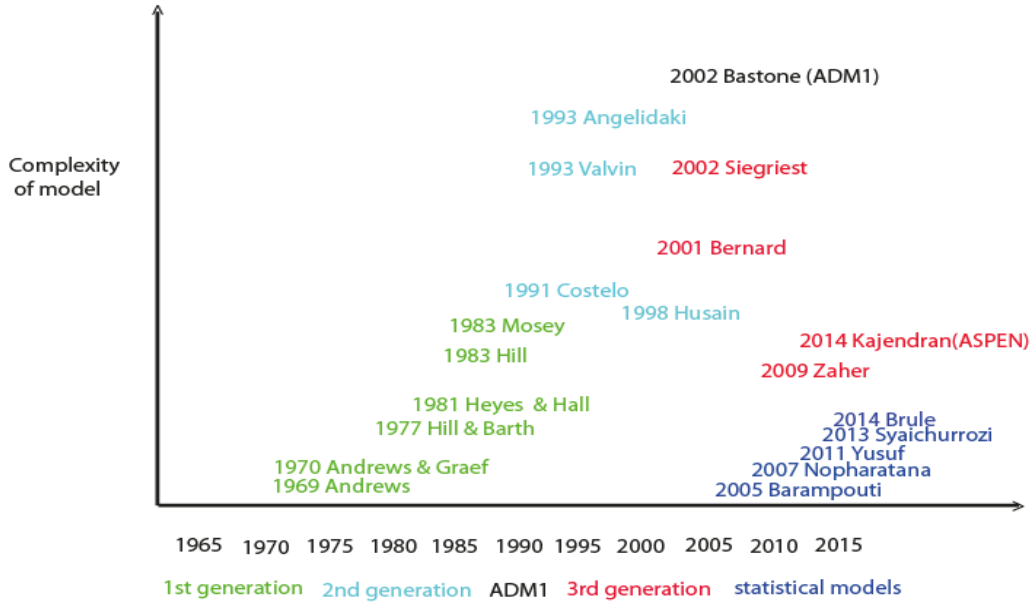

Figure 2. Evolution of AD models. Complexity over the last 50 years.

2.1.1. 1st generation (1969-1990)

Andrews, 1969 described the first anaerobic digestion model and from the concepts inside many others models were inspired. It assumes that a description of the rate-limiting step will also allow sufficient explanation of the entire process. The model characterizes the bacterial growth inhibition by Haldane expression, which can relate acid accumulation to process instability. The approach also considers the un-ionized acid as the growth-limiting substrate and inhibiting agent.

Andrews and Graef, 1970 developed a model to dynamically simulate the enzymatic hydrolysis process of the complex organic material, which is converted into soluble compounds. Subsequently, volatile fatty acids (VFA) are produced by acidogenic bacteria. The model incorporates interactions between volatile acids, pH, alkalinity, gas production rate, and gas composition. The substrate digestion is described with Haldane kinetics, taking into account that increasing substrate concentrations lead to an inhibition.

Hill and Barth, 1977 developed and validated a model for poultry waste and swine waste using experimental data. In general, it considers that the AD process is better described in three stages: solubilization of organics, acidogenesis and methanogenesis. The pH is determined using a carbonate equilibrium expression. In the fermentation process, two groups of bacteria and several mass balances were defined in detail, which are: concentration of volatile matter; concentration of soluble organics; concentration of volatile acids in the form of acetate; concentration of acidogens ("acidformers"); concentration of methanogens ("methane-formers"); concentration of dissolved CO_2 in liquid phase; partial pressure of CO_2 in the gas phase; concentration of NH_4^+ in the liquid phase; partial pressure of NH_3 in the gas phase; concentration of cations (other than ammonia and hydrogen).

Heyes and Hall, 1981 performed an AD model, in which the process is affected by hydrogen inhibition of acetogens and pH inhibition of methanogens. The unionized volatile fatty acids are not considered toxic. Hydrogen concentration could be a useful stability parameter.

Hill, 1983 developed a mathematical model of AD to simulate responses of biogas and methane for poultry, beef and dairy waste or swine waste. Two parameters are specified, which are the biodegradability constant and the acidity constant. A certain fraction of the fed volatile solid (VS) is assumed to be biodegradable. The hydrolysis step is not included. Model equations define four state

variables, which are: biodegradable volatile solids (BVS); volatile fatty acids (VFA) as acetate; acidogens concentration and methanogens concentration. Propionate and acetate are considered intermediates in digestion and thus regarded as stability indicators of digestion.

Mosey, 1983 indicated four bacterial groups as responsible for the anaerobic digestion of glucose to produce CH_4 and CO_2, where hydrogen-partial pressure is the regulatory of metabolism. See Tab. 1. The acetogenesis is considered a limiting step in the model.

Table 1. Bacterial groups present in AD model by Mosey, 1983

Involved bacteria in AD	Consumption	Component released
acid forming bacteria	glucose	mixture of acetate, propionate and butyrate
acetogenic bacteria	propionate and butyrate	Acetate
acetoclastic methane bacteria	Acetate	CO_2 , CH_4
hydrogen-utilising methane bacteria	CO_2	CH_4

2.1. 2nd generation (1991-2001)

In the nineties, complex models were formulated including mathematical expressions of inhibitions and interactions among various anaerobic bacteria groups.

Costello et al., 1991 related the physicochemical equations that describe the charge balance for each component species to the mass balance system of the anaerobic system. The new approach was able to calculate the pH of the system by the inhibition function of the anaerobic bacteria at any time (I_{pH}), as formulated in equation in Eq. 1. Moreover, the model was used to investigate the accumulation of lactic acid from glucose under specific process conditions.

$$I_{pH} = \left(\frac{pH - pH_H}{pH_H - pH_L} \right)^m \quad (1)$$

In where *pH*, pH_H and pH_L are the actual, upper and lower bound *pH* values, respectively; m is the inhibition coefficient, which can be modified to manipulate the shape of the inhibition curve.

Angelidaki et al., 1993 initially developed a model to investigate the effects of ammonia in manure digestion by performing experiments. The results clearly demonstrated that at a certain level of

ammonia concentration, the process is able to be stable after an initial adaptation period. However, as expected, there was a methane yield reduction and an increase in the VFA concentration. In 1999, a model based on the previous approach (Angelidaki et al., 1993) was performed in (Angelidaki et al., 1999) for degradation of oil wastes and manure. Co-digestion experiments and simulations were carried out for manure with glycerol triolate or manure with gelatin. The model included the hydrolysis of undissolved carbohydrates and undissolved proteins; it describes the bio-chemical reactions in greater detail. The substrate is characterized assuming an organic part (carbohydrates, proteins, lipids and their degradation intermediates) and an inorganic part (ammonia, phosphate, carbonate, hydrogen sulfide, anions and cations). The eight bacterial groups were defined for the entire metabolic process. During digestion, acidogenic bacteria convert soluble carbohydrates ($C_6H_{10}O_5$) into VFA and bacteria biomass. The glycerol triolate (GTO, $C_{57}H_{104}O_6$) was considered the most common lipid found in vegetable oils. In acidogenesis, GTO is converted into glycerol and oleate by acidogenic bacteria. The Michaelis pH function was adapted to affect the growth rate expressions depending on the severity of inhibition. The model was fitted to experimental data and solved to predict methane (L/L-reactor), acetate, propionate (g/L), GTO, oleate and pH values.

Vavilin et al., 1994 described the acidogenesis step in terms of biochemical reactions of the components involved. A comparative evaluation on digestion of swine waste, sewage sludge, cattle manure and cellulose concluded that the hydrolysis is the rate-determining step (Vavilin et al., 1996).

Husain, 1998 proposed a model that is based on chemical reactions. The death rates of acidogens and metanogens are VFA-based Monod functions instead of the maximum reaction rates as Hill did in (Hill, 1983). The state variables are the same as Hill's model declares.

2.1.3. 3rd generation (2001 - 2017)

Bernard et al., 2001 formulated a model under the assumption that biodegradation occurs in a two-steps process (acidogenesis and methanogenesis). Industrial wine distillery waste water was used as a feedstock. Alkalinity is included using an expression that defines the electrochemical equilibrium activity. The model was created for control strategies in which six states and thirteen parameters describe the AD process.

Siegrist et al., 2002 developed a model that is simpler and contains fewer input variables than ADM1. Valerate and butyrate are not considered state variables. The hydrolysis rate is defined by a

first-order reaction that depends on the concentration of particulate organic matter and includes a lumped constant. It determines the AD efficiency when ordinary municipal sewage sludge is used. Acetotrophic methanogenesis and propionate degradation are considered steps where AD process stabilization takes place. The model parameters were obtained carrying out a series of lab-scale experiments and the model was validated with full-scale experiments.

2.1.4. ADM1 (2002)

Bastone et al., 2002 described the anaerobic digestion as four subsequent steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis, which are linked in biochemical reactions. Disintegration of substrate components named the earlier process is associated with converting complex organic substrates into CH_4 and CO_2. Biochemical and physico-chemical processes concern liquid-gas processes (liquid-gas transfer) and liquid-liquid processes (ion association/dissociation). The solid-liquid processes are not included due to difficulties in describing them (Batstone et al., 2002). The ADM1 was formulated to be used with sludge waste from waste water treatment plants WWTP of anaerobic processes and might therefore not be as exact as other models that are developed for a specific task. The advantage of this is however that the model can be applied to a wide field of applications. Although the ADM1 is an advanced and well accepted approach for most AD applications, configuration is complex, so user is encouraged to work intensively when a new application is needed (Daels et al., 2009). The ADM1 model contains 19 biochemical kinetic reactions, 26 dynamic state concentration variables, 56 stoichiometric and kinetic parameters, 1 substrate degradation process and 6 specific biomass growth and decay processes. To understand the structure of the ADM1, the main equation of the processes involved in model are described in Fig. A-1. ADM1 describes cellular kinetics as substrate uptake, growth and decay. Substrate uptake for components uses the Monod equation, showed in Eq. 2.

$$vi = km\left(\frac{Si}{Si + K_s\ Xi}\right)Ii \qquad (2)$$

In where *vi* is the actual uptake, *km* is the maximum uptake rate, $\frac{Si}{Si + KsXi}$ is the substrate concentration factor, *Xi* is the biomass concentration and *Ii* is the inhibition factor.

The ADM1 model includes the degradation of complex solids in proteins, fats, carbohydrates and inert compounds. The degradation products are then hydrolyzed into amino acids, long chain acids

(LCFA), and sugars, respectively. Then LCFA, propionic acid, butyric acid and valeric acid are under anaerobic conditions, oxidized into acetate, carbon dioxide, and hydrogen (acetogenesis). Nonetheless, these intermediary reactions mechanism are hardly explained and understood in biogas production. The organic species and hydrogen, in this model, are expressed as COD, whereas inorganic nitrogen and inorganic carbon species are expressed through their molar concentrations. Finally, methane can be produced through 2 paths: the first one is based on acetate, whereas the second one is through the reduction of carbon dioxide by molecular hydrogen. The novel aspect, in comparison with other previously developed anaerobic digestion models as Angelidaki et al., 1999; Valvilin et al., 1994; and Siegrist et al., 2002 is the implementation of the disintegration state. The ADM1 model has been used and modified by several researchers to model anaerobic processes from different organic substrates incorporating a combination of manures and energy crops (Zhou et al., 2011). Studies have shown that Biogas yield and biogas composition depend strongly on the substrate used (Zhou et al., 2011). In most biogas processes the final input consists of a mixture of different materials.

Zaher et al., 2009 formulated a model for dairy waste, in which the AD process is defined in four steps: hydrolysis; acidogenesis; methanogenesis – hydrogenotrophic and acetotrophic. Model validation is performed using a real batch process data in a continuous mixing reactor. The state variables in the model are 15, which are the following: acidogens; acetotrophic methanogens; hydrogenotrophic methanogens; Bio-solids (particulate substrate); degradable substrate (as sugars); volatile fatty acids (as acetate); hydrogen; carbon dioxide; methane; bicarbonate; ammonium; phosphates; moisture (water); protons (H^+); cations.

AD on ASPEN; A: Rajendran et al., 2014 developed an AD model using ASPEN plus in steady state. It consists of 46 chemical reactions and includes an expression for inhibition, which depend on the pH values. The acidogenesis, acetogenesis and methanogenesis are solved using the reaction kinetics in thermophilic condition. As model inputs the volume of reactor (V), OLR, and HRT are needed. Validation was performed using a variety of lab and industrial data on anaerobic digestion. The kinetic constants of reactions were obtained from previous models, such as ADM1 and comprehensive models (Batstone and Keller, 2003); (Angelidaki et al., 1999). Sub-models are attached to the program in order to determine the kinetics of the processes. Each sub-model is written in FORTRAN to calculate the rate of reactions. The NRTL (Non-Random Two-Liquid model) is the thermodynamical property method used as it correlates and calculates mole fractions and

activity coefficients of compounds; it facilitates the setup of liquid and gas phase in reactor. Stoichiometric reactor was used to simulate hydrolysis and continuously stirred tank reactor (CSTR) was set for the other phases. ASPEN model provides an approximate prediction of methane and biogas produced in a wide variety of substrates; it was validated against industrial and research studies.

B: Arzate et al., 2015 (Paper II) adapted the model from (Rajendran et al., 2014) to digestion of energy crops such as grass, maize and clover silage in steady state. The study was carried out to an industrial BGP with a capacity of 500 kW. The model was able to simulate the operation with sufficient accuracy. The biogas process consisted of a main fermenter of 2000 m^3 and a secondary fermenter of 1500 m^3. Digesters were operated under 43 °C (mesophilic conditions) at a retention time of 115 days. In the process flowsheet, a stoichiometric reactor was simulated, in which thirteen reactions were placed for the hydrolysis phase. Carbohydrates, proteins and lipids are converted from the feedstock. The fractional conversion of each stoichiometric reaction is determined by the design specification tool included in ASPEN; the model calculates the output flow rates of all components. A Gibbs reactor unit is used, in which equilibrium reactions for water, ammonia, acetic acid, carbon dioxide, carbonic acid, hydrogen carbonate and sulphide hydrogen are applied to calculate the pH-value of the medium. Acidogenesis, acetogenesis and methanogenesis are simulated in a continuous stirred tank reactor. The model design in ASPEN includes some simulation units connected in line, which are shown in Fig. 3.

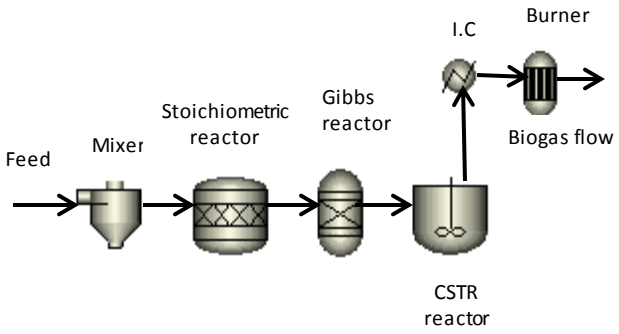

Figure 3. Simulation flow sheet of biogas process in ASPEN. (Figure taken from publication II- Arzate et al. (2015) in Methods - reprinted from ETIKUM 2015)

2.1.5. Statistical models

An empirical approach is used to study the biodegradability of organic material. Changes in the volatile solids influent and effluent concentration are observed using a first order rate equation,

which can quantify the corresponding biogas production for the digester and the first order kinetic. Some relevant works have been published as the following.

Barampouti et al., 2005 developed a dynamic model for biogas production from potato processing wastewater. An UASB reactor of 600 m^3 was used for the digestion with a mean hydraulic retention time of about 1 day. As a regression model residual analysis was applied. The parameters to be analyzed were: wastewater's flow rate; temperature; pH; total and soluble influent COD; soluble effluent COD; volatile fatty acids; alkalinity, and biogas production rate. The adequacy of the model was checked by χ2 test.

Nopharatana et al., 2007 *f*ormulated a mathematical model, although simplified, which describes the anaerobic digestion of MSW. The kinetics of hydrolysis is expressed by a Contois equation and of acidogenesis, acetoclastic and metanogenesis by Monod equations. The accumulative methane production from experimental data was fitted to the modified Gompertz equation and the model parameters were statistically estimated. The three model parameters were as follow: the methane production potential, (P) [l]; the maximum methane production rate, (Rm) [l d^{-1}] and the duration of lag phase, (λ) [d].

Yusuf and Ify, 2011 investigated the co-digestion of paper waste with cow dung and water hyacinth in five batch type reactors. The kinetic model was based on a mass balance approach improving for biogas to a fixed amount of cow dung. The maximum biogas yield was estimated by the model using a first order equation applied to four of the five digesters. The mathematical equation was solved by fitting the experimental biogas yield (yt), Eq. 3.

$$yt = \frac{(\exp(kt-1))}{\exp(kt)} \tag{3}$$

In where k_t is the first order parameter to solve the expression.

Syaichurrozi and Sumardiono, 2013 developed a model that is based on the modified Gompertz equation to predict biogas production potential (BPP) from vinassse. Model parameter fitting were performed by non-linear data regression system. Data were regressed to obtain the three parameters as follows: biogas production potential, A [mL/kg COD]; maximum biogas production rate, U [mL/kg COD. day], and minimum time to produce biogas, [day]. The objective to build the model was also to evaluate the relation COD/N on anaerobic digestion process. After optimization,

outcome shows that nitrogen is important for bacteria to build cell structures and in certain COD/N ratios the bacterial growth is affected.

Brulé et al., 2014 described a simplified exponential model for substrate utilization and methane production in batch anaerobic digestion. In order to set the methane production kinetics, the model assumes that hydrolysis step performs much slower than the methane production step. The Monod or the Michaelis– Menten equations were taken into consideration because under certain conditions saturation effects can be neglected and both models can be simplified to become first-order kinetics. Thus, the whole process was described to have the same order kinetics. The model was divided in two pools, in which particulate substrate was performed in two hydrolysis conversion velocities. Finally, the model was adjusted with a data-fitting method.

2.1.6. Artificial Neural Network (ANN) and Genetic Algorithm (GA) Models

The application of ANN and GA models has advantages over non-linear estimation approaches since they do not require prior knowledge regarding interconnections between variables. These tools are considered among the last ones for the solution of complex problems that cannot be solved by conventional solutions (Thorin et al., 2012). In biotechnology, ANN is considered as efficient alternative in the design of optimal production and optimal process operation conditions in fermentation (Kana et al., 2012). Neural network offers an alternative to traditional generic models for problem solving, especially when comprehensive knowledge of the metabolic pathways is limited (Curcio et al., 2014). Customized structure of the network architecture and the right amount of input data is all that required. Nevertheless, other important variables within the process for monitoring are difficult to predict as volatile fatty acids or inorganic carbon for the anaerobic digestion process. Sometimes there is lack of information about the mechanisms and kinetics of biological reactions of the process, in which ANN models could only predict part of the biological behavior of processes based on experimental data with high correlation coefficients, e.g. water treatment process. The use of these methods are also controversial, because of lack of scientific bases to handle the models. Some applications of ANN in modeling and simulating are in biological water and wastewater treatment in the presence of various microalgae, microalgae, bacteria, microbes, yeast, anaerobic sludge, aerated submerged membrane bioreactors and submerged biofilms (Khataee and Kasiri, 2011). In recent years ANN has been more applied and considered as a powerful tool to compete with conventional methods of measurement and data processing in the

biogas production processes (Levstek and Lakota, 2010). One of the most utilized ANN architecture is the multi-layered perceptron (MLP) that approximates non-linear relationships existing between multiple causal (input) process variables and the corresponding dependent (output) variables. After an ANN-based process model with good specific capability is constructed, its input space can be optimized appropriately to secure the optimal values of process variables (Kana et al., 2012). Applications of ANN on AD are shown in Tab. (A-2). ANN are described in section 3.1 of paper IV, in which models of (Kanat and Saral, 2009) and (Qdais et al., 2010) are explained.

2.1.7. Models for design

Modeling can be applied to a specific AD system, which might include a special bio-reactor design or the use of a new feedstock.

Vavilin et al., 2007 developed an AD model considering different non-uniform influent concentration distributions to analyze the effect of mixing intensity on the efficiency of continuous-flow anaerobic digestion. A previous model by (Vavilin and Angelidaki, 2005) was used to develop a new kinetic model. In general, hydrolytic microorganisms were considered using Contois kinetics for the hydrolysis and acidogenesis steps during degradation of municipal solid waste (MSW). In methanogenesis step, Monod kinetics was applied. Hydrolysis and methanogenesis were assumed to be inhibited by high volatile fatty acids (VFA) concentration. The mixing level reduction was depicted by increasing dimensionless Peclet number. High methanogenic biomass concentration is required for efficient anaerobic digestion of MSW to avoid possible inhibition due to high VFA concentration. An increment of organic loading during the startup of the CSTR digester can prevent a digester failure due to the accumulation of methanogenic biomass.

Beschkov et al., 2012 performed the prediction of biogas and other coumpunds as 2,3-butanediol, 3-propanediol, acetic acid, formic acid and lactic acid using an anaerobic multistage baffled reactor. The digestion of glycerol by the bacterium Klebsiella was modelled using eight differential equations. Methane is produced by two competitive ways either after acetic acid decarboxylation or by carbon dioxide reduction by hydrogen.

Muha et al., 2012 developed an AD model that is based on experiments in a two phase laboratory-scale digester under mesophilic conditions. The process design includes: reservoir; downstream fixed film anaerobic filter; two circulation systems; a biogas bag, and an automated gas analysis

system. The model incorporates expressions for biochemical reactions, process liquid transport, and the variation of microorganisms population living on the plastic tower packing. An inhibition factor MO_{max} is introduced in the model, which affects the growth of microorganisms when the plastic tower packing is overpopulated. After estimating the reaction parameters, the acetate outflow experimentally measured is in good agreement with that predicted by simulations.

2.1.8. Application of ADM1

The ADM1 model has been widely applied and validated in the literature with varying success. The research has been oriented to different applications, such as model reduction, study of a specific AD process, performance of a new substrate, and design of AD systems. In section 3.1 of paper IV, the ADM1 model and its applications are indicated for agro-waste (Galí et al., 2009); energy crops (Wolfsberger, 2008); co-digestion of organic waste with waste activated sludge (Derbal et al., 2009); olive pulp (Gavala et al., 2006); cattle manure (Schön, 2010) and grass silage (Koch et al., 2009). Some relevant studies are shown below.

Batstone* et al.,*2003 studied the degradation of n-butyrate, isobutyrate, n-valerate and isovalerate. The ADM1 was modified in order to include competitive uptake of isovalerate. An experiment setup was used in which a n-butyrate, iso-butyrate, n-valerate and isovalerate were fed into a thermophilic cattle manure digester. Parameters were optimized to describe n-butyrate, isovalerate, and n-valerate degradation, as well as a lumped set for all three substrates. The study was able to assess the assumptions in Batstone et al.(2002) with regard to n-butyrate, isobutyrate, and n-valerate degradation and the stoichiometry of isovalerate digestion in mixed-population systems. When mainy isovalerate is fed into the system, a modified model is needed to simulate the lag phase of the degradation reaction.

Parker, 2005 compared the ADM1 and experimental data for municipal sludge. He simulated several AD processes from literature. In most cases, overestimation of VFA was noticeable in reduced SRT reactors. Only a correct influent characterization, especially for ammonia and total Kjeldahl nitrogen (TKN) leads the right performance of pH buffering and inhibition functions.

Shang et al., 2005 predicted the steady-state of anaerobic digestion using the ADM1 for sewage sludges from waste water treatment plants.

Kalfas et al., 2006 calibrated the ADM1 for anaerobic digestion of olive pulp (a waste from the two-phase olive oil production). Data were collected from a CSTR-type digester process under mesophilic and thermophilic conditions. The parameter confidence region of key parameters were estimated. As key parameters of the digestion they applied the specific maximum uptake rate constants and the saturation constants for the volatile fatty acids degradation.

Rossen et al.,2006 reformulated the ADM1 model in order to computationally reduce the speed of solution applied to wastewater treatment process under the benchmark simulations in Matlab/ Simulink. Therefore they modified the model in view of the mass balances of carbon, nitrogen and solid inerts, acid-base equations, algebraic equations for pH and hydrogen gas, inhibition functions due to pH, and the constant in the flow gas equation.

Feng et al., 2006 used the ADM1 to simulate digestion of black water from vacuum toilets. Some scenarios were created to analyze different feeding frequencies and high NH_4^+ concentration.

Mu et al., 2008 aimed to simulate the anaerobic digestion process in high-rate reactors with relative high axial dispersion, such as in upflow anaerobic sludge bed (UASB) reactors. The model combines AMD1's kinetics of biomass growth and axial biomass dispersion mass balances. The one compartment model describes biomass distribution and meanwhile is compared with a two-compartment, sludge bed and liquid above the bed. Outcomes show similarities of both models.

Thamsiriroj and Murphy, 2011 developed a model for mono-digestion of grass silage in a 2-stage CSTR. An anaerobic digestion wet process with recirculation of liquor was designed in order to control VFA increase, solids content and pH. The model was calibrated to experimental data and methane production was estimated at 88% of maximum theoretical production. The first thirty days of simulation the model does not recognize variations of the process, after this period the model outputs were better fitted to experimental data.

Bollon et al., 2011 investigated the anaerobic digestion of municipal solid waste (MSW) in dry process under mesophilic conditions. ADM1 was simplified on microbial expressions and degradation pathways. The cellulose was considered as main particulate matter in MSW. The ADM1

reduction was written in 6 differential equations and 3 liquid-gas equilibrium equations for CH_4, H_2 and CO_2 which contain the output gas flow variable. The 5 acid-base equilibrium equations for OH^-, H^+, acetate, propionate and inorganic carbon (IC) were reduced to a single H^+ equation for pH calculation. The model is able to perform batch degradation of acetate and methane flow rate. The moisture content affects both the half-saturation constant (k_s) and for the lowest value of moisture content the maximum uptake rate ($qp_{max.}$).

Chen et al., 2016 implemented the ADM1 to simulate the biogas production from Hydrilla verticillata. Model simulation was carried out in AQUASIM 2.0 software. Sensitivity analysis was performed to indicate the most sensitive parameters to the biogas production which are: disintegration constant (kdis), hydrolysis constant of protein ($khyd_{\_pr}$), Monod maximum specific substrate uptake rate ($km_{\_aa}$, $km_{\_ac}$, $km_{\_h2}$) and half-saturation constants ($Ks_{\_aa}$, $Ks_{\_ac}$). Finally, the ADM1 well predicted biogas, methane concentration and inhibition effects during simulation.

However, as other complex models the application of ADM1 on control and process optimization is not widely performed. Research using ADM1 has been focused on reaction kinetics (Batstone et al., 2003).

2.2. Simulation programs for anaerobic digestion

AD model facilitates the understanding of the biological process by the formulation of the system, the validation of outcomes and the prediction of the system´s behavior (Donoso-Bravo et al., 2011). After an appropriate model is selected for application, a simulation program or a platform of choice can be implemented as a programing language. Some modelling packages have been used for AD modeling.

AQUASIM v 2.1b®, a computer program that was created for mathematical modeling and simulation of aquatic systems, incorporates techniques of simulation, parameter estimation and sensitivity analysis (Reichert, 1998). Some studies using AQUASIM v 2.1b® can be highlighted, including the following: The consumption of substrate and cell growth was adequately represented by a first-order kinetic model of degradation of dairy wastewater (Rosa et al., 2010); ADM1 was calibrated for opium alkaloid effluents from industrial wastewater (Dereli et al., 2010); ADM1 parameters were analyzed for the anaerobic digestion of blackwater with kitchen refuse (Feng et al., 2006).

MATLAB/Simulink®. Simulink is a model-based design environment to MATLAB™ for modeling and simulation of systems (Simulink and Natick, 1993). A number of publications have used this platform to simulate or modified AD models, some examples are as follows: ADM1 parameters were optimized to describe butyrate, isovalerate, and n-valerate degradation of digestion of cattle manure (Batstone et al., 2003); a reformulation of ADM1 to computationally reduce the speed of solution applied to wastewater treatment process (Rosen et al., 2006); in (Boubaker and Ridha, 2008), ADM1 model was modified and applied to simulate anaerobic co-digestion of olive mill wastewater (OMW) with olive mill solid waste (OMSW).

SIMBA®, a software for WWTP modelling, runs on the MATLAB®/SIMULINK® platform; It can be applied to a wide variety of engineering tasks and research. Some works on this platform are as follows: the analysis on water treatment systems and sewer network (Erbe et al., 2002); the application of AMD1 of sewage sludge under mesophilic conditions, in which a sensitivity analysis was included (Mendes et al., 2015).

Aspen plus is characterized by having an advance performance of chemical processes using best-in-class simulation software which includes database of pure component and phase equilibrium data for conventional chemicals, electrolytes, solids and polymers; Integrated solids, batch and custom processing unit modeling and online performance monitoring and real-time optimization. The software includes a subprogram called "ASPEN Custom Modeler" and can be used to write custom models, which are just suited for a specific structure and cannot be easily adapted to a different process. This option is quite useful when accuracy in the simulation of a number of simultaneous processes and variables are needed.

2.3 Substrates used in project

Maize silage, grass silage and cattle manure were the three substrates applied in the project since they are the most used for anaerobic digestion in Germany (Scheftelowitz et al., 2014). The AM2 model was initially developed considering maize silage as substrate, later the calibration of the model was performed for grass silage and cattle manure. The value of a substrate in the biogas process depends on its potential as a high yield energy crop and on the quality of the biogas produced, such as the achievable methane content. The most suitable energy crop for the production of biogas are those which are rich in degradable carbohydrates, lipids and proteins, and

poor in hemicelluloses and lignin, which address a low biodegradability (El Bassam, 1998). Hence, to find the optimal crop species for the process is of particular interest. The conditions and storage of biomass is also a necessary factor for the quality, using the substrate continuously as feedstock for biogas production. Biogas power generation from type of feedstock in Germany is depicted in Figure 4. Among different energy crops, maize silage and grass silage are considered to be the most promising biomass sources as they can produce high energy yield (KTBL, 2005). Hence, both substrates are attractive to be used in the anaerobic digestion process for biogas production. In Europe, Germany is the largest biogas producer and energy crops contribute about 52% of the total substrate input. Among energy crops, maize silage and grass silage take a share of 73% and 11%, respectively (Scheftelowitz et al., 2014). Similarly, energy generation from type of livestock manure is given in Fig. 5.

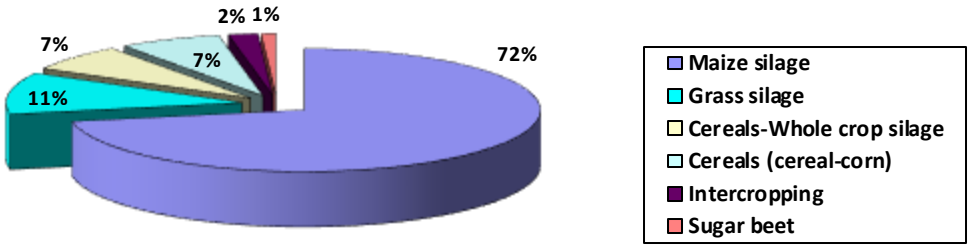

Figure 4. Energy-related substrate use in biogas plants installed in Germany, reference year in 2014 (German Biomass Research Center gGmbH (DBFZ) operator survey 2015). Adapted from (Scheftelowitz et al., 2014).

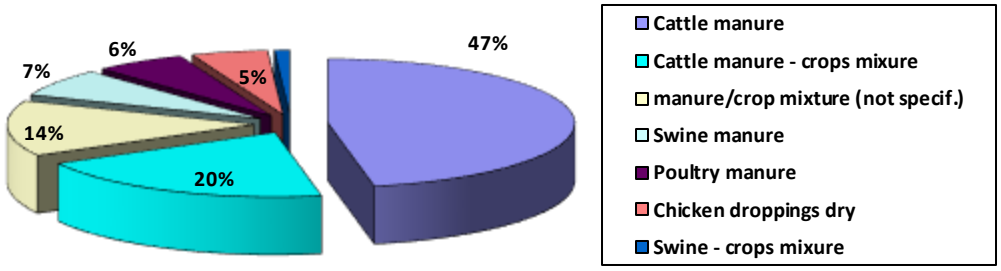

Figure 5. Energy-related manure use in biogas plants installed in Germany, reference year in 2014 (German Biomass Research Center gGmbH (DBFZ) operator survey 2015). Adapted from (Scheftelowitz et al., 2014).

2.4. Development of a model

The benefit to build a model is that can be better understood the system that is being developed. Advantages such as new product, process, configuration design, high quality product, profit increment, energy saving, cost and loss reduction, environmental damage mitigation, yield maximization and others come along by using models of product design, control, operation and optimization. In literature several approaches with a varied complexity are available to model a process. Kinetic models are capable of representing the complex biochemistry of the process. Black-box models (e.g., neuronal networks, genetic algorithms, etc.), first-principles models or hybrid models (which combine first-principles and empirical models) are some of them. The development of a suitable model in structure and concerning the quality of the parameters is a challenging for being accomplished. The distinct experimental data play a key role to either select an adequate model structure or to guarantee low uncertainty and not directly improve the process itself. In the model selection, plots of the data, process knowledge and assumptions about the process are used to determine the form of the model to be fit to the data. The process to develop a model is iterative until an apropiate model for the data has been developed. Moreover, during this procedure some steps will probably need to be repeated twice or even more times until a suitable model can be validated (van Riel, 2006). In other words, the model structure will be modified during the model building process, having new extensions added and others changed or removed. Consequently, parameter estimation has to be performed again as more data is collected, and different analyzes of the modified model may be carried out.

Purpose: The first step of modeling is to define the reason of the model. Most of the modeling purposes are related to understanding and predicting of process behavior by either internal (through genetic modifications), or external (changing various environmental factors) perturbations. The key questions for this step are: "Why do we need to build the model? What do we want to use the model for? Which variables or parameters should the model be able to explain?" (Almquist et al., 2014).

Network structure: The model network structure defines the metabolic pathway of linked reactions or components that are considered to be important for the modeling. It refers to elements of the process as compartments, concentrations of metabolites, enzymes and transcripts, and reactions (including their stoichiometric coefficients).

Parameter estimation: The value of parameters in the mathematic expressions, as well as the initial conditions and outputs have to be estimated. Parameter values can be obtained directly through experiments, from literature or by methods using sample data (usually times-to-failure or success data) of a selected distribution.

Validation: The model needs to be validated for quality and statistical testing. Thus, it should explain experimental data used for setting up the model and new sets of experimental data that was not used previously in the modeling process.

To start the process, the so-called model-based experimentation for model development can be applied, in which, the results of the experiments and the model are used to estimate parameters from a Design of Experiments (DoE). As a result, in an iterative process the most appropriate model is obtained. The iterative process for model development assumes the realization of experiments to obtain measurements (experimentation stage), the mathematical formulation of models to calculate the process states (Modeling stage), the estimation of parameters (Parameter estimation stage), and after (as required) design of new experiments (Optimal Experimental Design stage). This process is iterative and involves experimental techniques, mathematical modeling, model identification and optimal experimental design. The estimation of the model parameters is accomplished by minimizing the model error to available experimental data. The estimation and the model structure selection define the known model identification task. In Figure 6 two model-based experimentation iterative paths are shown. The inner iterative path (dashed-line circle) refers to the selection of the model structure among various model candidates. Similarly, the outer work cycle (solid-line circle) deals with the improvement of the parameter precision for a fixed model structure. Once the best model structure has been selected, it is allowed to pass from the inner to the outer level.

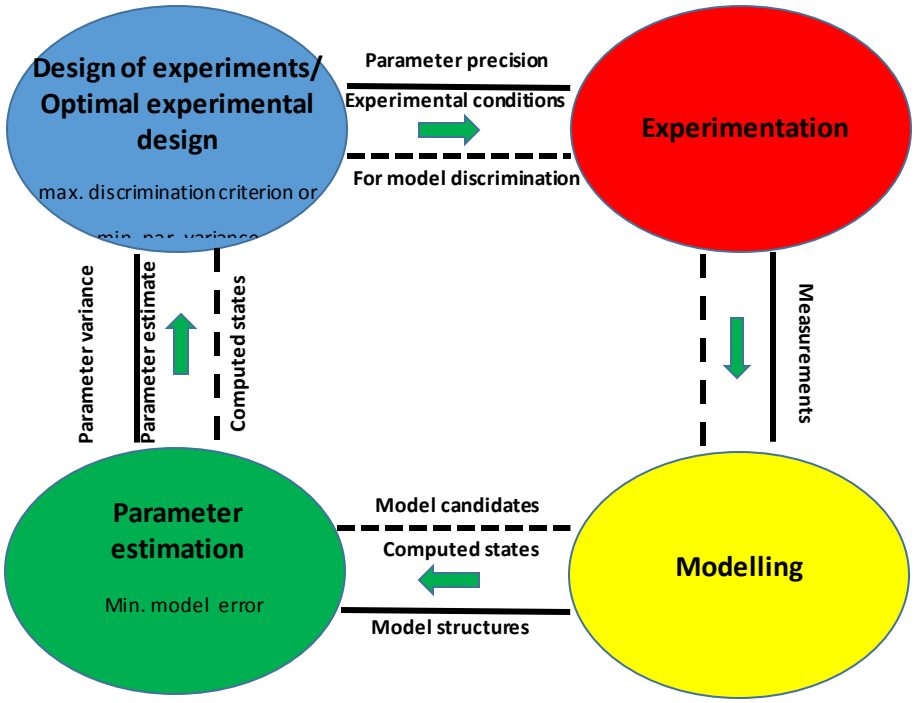

Figure 6. Iterative process of model-based experimentation for developing a model.

Evidently, until having this fixed structure, a reliable estimation of parameters from the available data is performed. In both iterative processes the parameter estimation and optimal experimental design are required. Nevertheless, the optimal experimental design has different cost function (objective function). In this optimization the process model structure is a constraint and the degrees of freedom are the experimental conditions. For model structure selection, the optimal design is asked to maximize the difference of model predictions among the model candidates. This step is named model discrimination. For improving the precision of the parameters the experimental design deals with this process by reducing the parameter variance metric (e.g., parameter variance average or the largest parameter variance) of the respective model. Each level finishes when some stop criterion, for instance, on predictive quality/model fitting or parameter variance, is achieved. it is important to mention that in the model structure selection level the number of parameter vectors to be estimated depends on the number of model candidates, in which the level for improving parameter precision it is only one.

One of the interests of this thesis is to improve the understanding of the functionality of the outer cycle in Fig. 6 applied to a nonlinear anaerobic digestion model that in this case is the AM2 model additionally contemplating diagnosis and treatments of identifiability.

In summary, the following steps of the modeling part of the project can be denoted:

I. Process data from a lab scale experiment were collected, including online data generated from the on-monitoring as basis for improved modeling.

II. The data was used to adopt and improve the existing model AM2 and apply mechanism recognition methods for the identification of process disturbances

III. A process optimization for the digestion process was established and evaluated

3.0. Hypotheses and aim of the study

3.1. Research Hypotheses

1. The modelling of the anaerobic digestion model AM2 used for sludge from waste water is an adequate method to develop a reduced and tractable model for maize silage to predict methane and CO_2 with adequate precision.

2. The use of the modeling tool will facilitate the development of a dynamic anaerobic digestion model for energy crops and animal manure.

3. The new version of the AM2 model is able to predict biogas and state variables, such as biomass, volatile fatty acids, organic material, alkalinity, and inorganic carbon of the anaerobic digestion of energy crops, such as maize silage, grass silage and cattle manure.

4. In order to achieve a higher energy production, the use of an optimization tool applied to the AM2 model integrated into the platform Aspen Custom Modeler™ is an adequate method for the co-digestion of maize silage, grass silage and cattle manure.

5. The developed approach, called AM2 for energy crops and cattle manure, can be incorporated into the Aspen Custom Modeler™ to create simulations for a better analysis of biogas plant behavior and can facilitate the study of any other subject e.g. new substrate performance, changes in feedstock composition or LCA application.

3.2. Aim of the study

This study has three specific objectives:

I. Development and verification of the model

The extended version of AM2 that predicts the anaerobic digestion process comprises three steps: (1) hydrolysis; (2) acidogenesis; and (3) methanogenesis. A complex substrate is converted to

methane and carbon dioxide as final products of the AD process. Parameter estimation and sensitivity analysis is conducted. The model is calibrated for two energy crops (maize silage and grass silage) and for cattle manure. (see Section 5.1 "Modelling of AM2").

II. Validation of model

The extended AM2 model is validated against experimental data from a pilot scale reactor under different OLR's. Thus, the estimated methane production and VFA concentration are compared with the measured outputs.

III. AM2 in a simulation program

AM2 is coded in Aspen Custom Modeler (ACM), which is a simulation program to easily run dynamically customized models. The program can be used as a tool in biogas plants with which changes in the layout and new conditions in the process can be tested. Through simulations of the biogas process, along with stored process data the program can be used to gain a more stable process of production and, in the long term, obtain improved profit (see Section 5.7 Process optimization)

4. Materials and Methods

4.1. The AM2

The criteria to select the AD model to be applied for energy crops and manure for biogas producction were the following:

a) The model must be able to predict the AD process to produce biogas. Model outcome of biogas flow rate can be compared to real data at different loading capacities. Methane gas is required since it is directly related to substrate energy content.
b) The model should be easy to be adapted and to maintain the stability of the system including prediction of failures and start-ups after a failed process.
c) The model must be able to represent the dynamics of a mesophilic AD process.

4.1.1 Structure

The AM2 (or AMOCO) was selected to be the model for predicting the behavior of anaerobic digestion from agricultural energy crops and cattle manure for biogas production. The AM2 structure was built on the basis of the model of Andrews and Graef, 1970, thus after modification of the model structure became simpler and a second bacterial population, acidogenic bacteria, was introduced. In the acidogenesis of the influent substrate, the growth rate of bacteria is modeled using Monod expression. In the first step, the acidogenic bacteria (X1) consume the organic substrate (S1) and produce CO_2 and VFA (Bernard et al., 2001). The reaction rate of acidogenesis of substrate (r_1) is shown in Eq. 4 and the reaction is the following.

$$S1 \quad \rightarrow X1 + S2 + CO_2$$

$$r_1 = \mu_1 \, X1 \tag{4}$$

In the second step, namely methanogenesis, VFAs (S2) are further degraded by methanogens (X1) for the growth and the final production of CO_2 and CH_4. The inhibitory effects of VFAs is modeled using Haldane expression. The reaction rate of methanogenesis of VFA's (r_2) is shown in Eq. 5 and the reaction is the following.

$$S2 \rightarrow X2 + CO_2 + CH4$$

$$r_2 = \mu_2 \, X2 \tag{5}$$

As can be seen in the reaction, the biogas production rate and the growth rate of methanogens are both proportional to each other, where the inhibitory effects of VFA can affect the methane production. The basis for this equation is the assumption that the solubility of methane is very low. Thus the amount of dissolved methane is neglected and the produced methane goes directly out of the liquid. Simultaneously, the CO_2 release is determined from the acid base equilibrium and the gas solubility to the partial pressure of the component. In the model, alkalinity is included using an expression that defines the activity of electrochemical equilibrium, which facilitates the calculation of the amount of CO2 generated by the process. The AM2 model comprises six differential equations for calculating biomass, *X*; organic substrate, *S1*; alkalinity, *Z*; volatile fatty acids, *S2*; and inorganic carbon, C., Eqs 6-11; two expressions for acidogenic and methanogenic growth rate, μ_1 and μ_2, respectively Eqs. 12,13; and five algebraic equations to calculate the amount of methane and CO_2 production, qm and qc, Eqs. 14-18.

$$\frac{dX1}{dt} = (\mu_1 - \alpha D_{in})X1 \tag{6}$$

$$\frac{dX2}{dt} = (\mu_2 - \alpha D_{in})X2 \tag{7}$$

$$\frac{dS1}{dt} = D_{in} \, (S1_{in} - S1) - (k_1 \mu_1 X1) \tag{8}$$

$$\frac{dZ}{dt} = D_{in} \, (Z_{in} - Z) \tag{9}$$

$$\frac{dS2}{dt} = D_{in} \, (S2_{in} - S2) - k2 \, \mu_1 X_1 - k_3 \mu_2 X_2 \tag{10}$$

$$\frac{dC}{dt} = D_{in} \, (C_{in} - C) - qc \, + k_4 \, \mu_1 X_1 - k_5 \mu_2 X_2 \tag{11}$$

$$\mu_1 = \mu_{1\max} \frac{S1}{S1 + K_{s1}} \tag{12}$$

$$\mu_2 = \mu_{2\max} \frac{S2}{S2 + K_{s2} + (S2^2 / K_{I2})} \tag{13}$$

$$\phi = C + S2 - Z + KH\ P_T + \frac{k_6}{k_{LA}}\mu_2\ X2 \quad (14)$$

$$Pc = \frac{\phi - \sqrt{\phi^2 - 4KH\ P_T(C + S2 - Z)}}{2KH} \quad (15)$$

$$pH = -\log_{10}\left[k_b \frac{C - Z + S2}{Z - S2}\right] \quad (16)$$

$$qc = k_{LA}\left[C + S2 - Z - KH\ Pc\right] \quad (17)$$

$$qm = k_6\ \mu_2\ X2 \quad (18)$$

In where,

α = Fraction of bacteria in the liquid phase, [-]

D_{in} = dilution rate, [d^{-1}]

$S1_{in}$ = influent value for organic material, [g L^{-1}]

Z_{in} = influent value for alkalinity, [mol m^3]

C_{in} = influent value for inorganic carbon, [mol m^3]

P_T = Pressure inside the fermenter [atm]

KH = Henry-coefficient [mmol atm^{-1} L^{-1}]

μ_{1max} = Maximum acidogenic bacteria growth rate [d^{-1}]

μ_{2max} = Maximum methanogenic bacteria growth rate [d^{-1}]

K_{S1} = Half-saturation constant [g L^{-1}]

K_{S2} = Half-saturation constant [mmol L^{-1}]

K_{I2} = Inhibition constant [mmol L^{-1}]

k_1 = Yield-coefficient for substrate degradation [-]

k_2 = Yield-coefficient for VFA production [mmol g^{-1}]

k_3 = Yield-coefficient for VFA consumption [mmol g^{-1}]

k_4 = Yield-coefficient for CO_2 production [mmol g^{-1}]

k_5 = Yield-coefficient for CO_2 production [mmol g^{-1}]

k_6 = Yield-coefficient for CH_4 production [mmol g^{-1}]

K_{LA} = Liquid-gas transfer constant [d^{-1}]

It was assumed that lipids, carbohydrates, and proteins have similar hydrolysis and consumption rates, which can be considered as a realistic assumption as long as sufficient nutrients and other substrates are present. Hydrolysis and subsequent uptake of substrates are proposed as single steps that can be acceptable as long as the kinetic constants are adjusted to account for both processes.

4.1.2. Applications

In Ficara et al., 2012, AM2 performs well for waste activated sludge when compared to the ADM1. The model considers two bacterial populations, namely the acidogenic and methanogenic microorganisms. Some important modifications of the original model have been carried out, like a term for describing the alkalinity in terms of inorganic nitrogen (Ficara et al., 2012), or hydrolysis and growth decay (Della Bona et al., 2014). This model has also been applied to ultra-filtered cheese-whey in a lab scale equipment. However, some differences between an eight-day experimental data and the model response were detected, maybe for the lack of adaptation of bacteria (Della Bona et al., 2015). In the same study, a parameter identification of an acidification process using the modified AM2 was performed. Recently, Arzate et al., 2014 applied for the first time the AM2 model for dynamic simulation using maize silage as a substrate. In general, AM2 model fits well with biogas and methane flow rate on experimental data for maize silage but the model was not optimized for the state variables (Arzate et al., 2014). In (Mairet et al., 2011), the AM2 was adapted for anaerobic digestion of microalgae. However, the AM2 model should be modified to predict methane for the simulation of Chlorella vulgaris digestion. The model after caibration is able to fit COD, VFA and inorganic nitrogen concentrations to experimental data.

4.2 Experiment set

The experimental data for the research study was obtained from a lab scale digestion consisting of two continuously mixed reactors of a liquid volume of 50 L., as shown in Fig. 7. Maize silage was used as feedstock and the experiment lasted 36 days. Four or five days a week the feedstock was fed into the reactor once a day, and during the weekend, it was suspended (two or three days per week). In all feeds, the feeding time lasted 15 minutes and 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 on-line 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.

Figure. 7 Continuously stirred lab scale reactors for anaerobic digestion

4.3. Characterization of substrates

The substrate characterization as required for the ADM1 was carried out, which relies on the chemical oxygen demand (COD). A detailed characterization of the substrate was made for maize silage, grass silage and cattle manure, applying the described method in (Zhou et al., 2011), which is summarized below.

a) Chemical analysis of substrate: The composition of substrate was investigated in a chemical analysis lab. The analysis was carried out in terms of dry matter (DM) (see Tab. A-3), and the COD density was obtained from (Zhou et al., 2011).

b) Calculation of influent composition by the lumped variables. - A mass lumping was applied to the following variables according to AM2: organic substrate (*S1*) [kgCOD m^{-3}], volatile fatty acids (*S2)* [mol m^{-3}], acidogenic bacteria (*X1*) [kgCOD m^{-3}], methanogenic bacteria (*X2*) [kgCOD m^{-3}], alkalinity (*Z*) [mol m^{-3}] and inorganic carbon (*C*) [mol C m^{-3}]. Six equations were used to calculate the lumped variables to describe the feedstock, Eqs. 19-24 (Ficara et al., 2012).

$$S1 = Ssu + Saa + Sfa + Xc + Xch + Xpr + Xli \quad (19)$$

$$S2 = 1000 \times \left(\frac{Sva}{208} + \frac{Sbu}{160} + \frac{Spro}{112} + \frac{Sac}{64}\right) \quad (20)$$

$$X1 = \frac{Xsu + Xaa + Xfa + Xca + Xpro}{1.55} \quad (21)$$

$$X2 = \frac{Xac + Xh2}{1.55} \quad (22)$$

$$Z = 1000\left(\frac{Sva}{208} + \frac{Sbu}{160} + \frac{Spro}{112} + \frac{Sac}{64} + Shco3\right) \quad (23)$$

$$C = 1000\,x\,Sic \quad (24)$$

c) Calculation of particulate components. - The particulate component of carbohydrates (*Xch*), lipids (*Xli*) and proteins (*Xpr*) where determined from the values resulting from the laboratory analysis for maize silage, and the use of the corresponding equations in (Zhou et al., 2011). The nitrogen-free extracts (*NfE*) in dried form (% *DM*) are determined by Eq. 25. (Zhou et al., 2011).

$$NfE = ODM - CP - CL - CF \quad (25)$$

where *CP, CL* and *CF* are the crude protein, crude lipid and crude fiber content of a substrate in dried form, all in [%*DM*] (see Tab. A-3).

The total influent $COD_{total\text{-}th}$ is calculated by Eq. 30. The influent particulate fractions for proteins, (Xp_{th}); lipids, (Xli_{th}); carbohydrates (Xch_{th}) and inert (Xi_{th}) were calculated by Eq. 26-29.

$$Xpr_{th} = (FM\,DM\,cfpr)\,CP \quad (26)$$

$$Xli_{th} = (FM\,DM\,cfli)\,CL \quad (27)$$

$$Xch_{th} = (FM\,DM\,cfch)\left[(CF + NfE) - (ADL + (ADF - ADL)_{non-\deg}\right] \quad (28)$$

$$Xi_{th} = (FM\,DM\,cfi)\left[(ADL + (ADF - ADL)_{non-\deg}\right] \quad (29)$$

$$COD_{total-th} = Xch_{th} + Xpr_{th} + Xli_{th} + Xi_{th} \quad (30)$$

in which the influent particulate fractions depend on fresh matter, (FM) [$kg_{FM}\ d^{-1}$] and total solids, (DM) [%]; *cfpr, cfli, cfch and cfi* are the parameter of conversion of proteins, lipids, and inert, (see Tab. A-4); *ADL* and *ADF* are the acid detergent lignin and the acid detergent fiber [% of DM]. The term (C*F+Nfe*) of Eq. 28 represents the total content of carbohydrates, and (*ADF-ADL*) the inert part consisting of lignin and non-degradable cellulose. The particulate components *Xpr*, *Xli*, *Xch* and *Xi* were obtained dividing Eqs. 26-29 by the $COD_{total\text{-}th}$ and multiplying with the density.

The particulate components of *Ssu*, *Saa*, *Sfa*, *Sac* and *Si* for maize silage were obtained from (Wichern et al., 2008), (see Appendix Tab. A-5). Finally, the characterization of the substrate is shown in Tab. A-6. The influent composition used in the AM2 is summarized in Tab. A-7.

4.4. Software

All model codes and graphical interfaces were written in MATLAB R2013b (Mathworks Inc., Natick, MA). The ODE and DAE simulations were integrated using the SunDialsTB v.2.4.0 suite, OdeSol and Idas, respectively. Parameter estimation was performed using the Interior point based optimization program included in the TOMLAB optimization environment. ASPEN plus dynamics was used to simulate the model for energy crops and cattle manure. In order to optimize the process, the subprogram ASPEN Custom Modeler was applied which uses the SQP method.

4.5. Parameter estimation

Parameter estimation is a statistical process which uses sample information to accurately describe a system behavior. The prediction of the process by computational models is only accomplished from sample data. In bioprocess engineering, it is commonly used to estimate the model parameters of nonlinear algebraic or differential equations. The process for the calibration of AM2 is shown in Fig. 8, which includes the experimental data, the model input and the operating conditions.

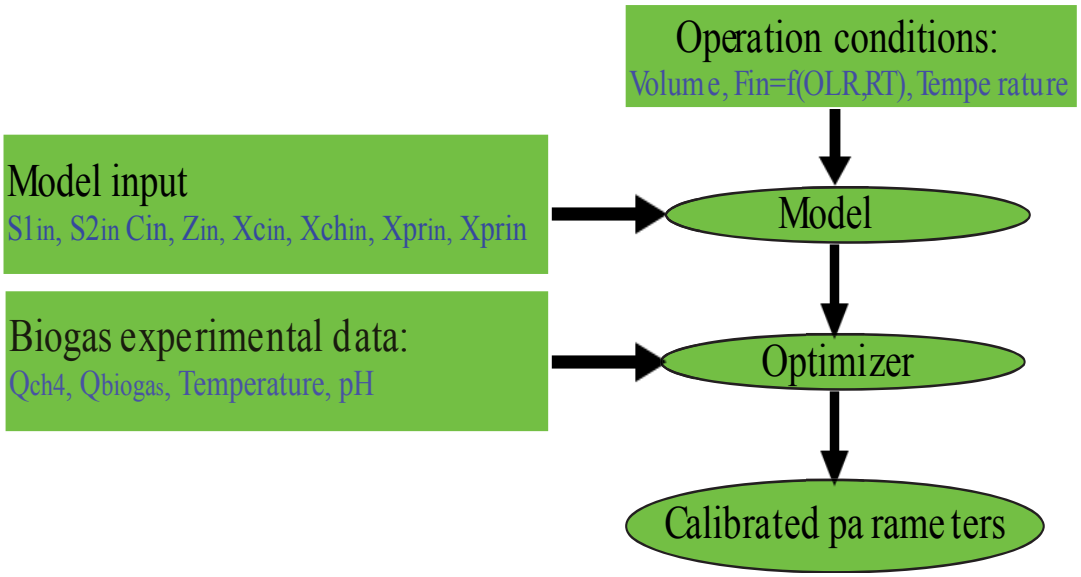

Figure 8. AM2 calibration process

The calibration methodology of parameters of the project was computationally efficient and suitable to obtain the satisfactory simulation of biogas and methane rate, as well as the state variables of AM2. The optimization was performed in the solver fmincon of MATLAB, in which the solution minimizes a constrained multivariable non-linear function**.** The objective function, represented by the symbol Φ, was comprised of the sum of the weighted squared deviations between the calculated and observed variables responses, Ycalc, Yobs, respectively. The difference between the calculated and observed values are referred to as a residual, and represented by the following equation:

$$r_i = (Ycalc - Yobs) \tag{31}$$

The objective function, Φ, is calculated using the following equation:

$$\Phi = r_i^2 \tag{32}$$

The parameter calibration for grass silage and cattle manure was performed using the ADM1 simulations as a reference model. The ADM1 simulations were carried out using the corresponding parameters for each feedstock published in (Wichern et al., 2008). The biogas process used in parameter calibration for both feedstocks was the same than the experiment carried out for maize silage, which consists of a 37 days of digestion in a pilot scale plant of 50-liter volume. Temperature and atmospheric pressure were considered 40ºC and 1 atm, respectively. Biogas, methane and CO_2 content in the gas phase and pH values were simulated by both models. The lumped variables for biomass, alkalinity, volatile fatty acids, inorganic carbon and organic substrate were simulated by ADM1 as well and used them to optimize the corresponding AM2 variables. In the process the reactor was fed once a day with a concentrated stock of substrate, and at weekend the feed was suspended. The retention time and organic loading rate (OLR) were 33.09 days and 3.58 g oTS $(L\,d)^{-1}$, respectively.

4.6. Optimization methods

The parameter calibration was performed by fmincon in MATLAB, which uses the optimization method Interior point algorithm. In the optimization process (Section 5.7), the program Aspen Custom Modeler uses the Sequential quadratic programming (SQP). These methods are described in some details in this part of the book.

4.6.1. Interior Point Algorithm

The interior-point approach to constrained minimization is to solve a sequence of approximate minimization problems. The original problem

$$\min_x f(x)\,,\ subject\ to\ h(x) = 0\ and\ g(x) \leq 0 \tag{33}$$

For each μ > 0, the approximate problem is

$$\min_{x,s} f_\mu(x,s) = \min_{x,s} f(x) - \mu \sum_i ln\,(Si), subject\ to\ h(x) and\ g(x) + s = 0 \tag{34}$$

There are as many slack variables (*Si*) as there are inequality constraints *g*. The (*Si*) are restricted to be positive to keep *ln (Si)* bounded. As μ decreases to zero, the minimum of f_μ should approach the minimum of f. The added logarithmic term is called a barrier function.

The approximate problem Eq. 33 is a sequence of equality constrained problems. These are easier to solve than the original inequality-constrained problem Eq. 34.

To solve the approximate problem, the algorithm uses one of two main types of steps at each iteration:

a) A direct step in (x, s). This step attempts to solve the Karush-Kuhn-Tucker (KKT) equations, Eqs. 35 and 36, for the approximate problem via a linear approximation. This is also called a Newton step.

$$\nabla x\ L(x,\lambda) = 0 \tag{35}$$

$$\lambda_{0g,i}\ g_i(x) = 0 \quad \forall i, \tag{36}$$

b) A CG (conjugate gradient) step, using a trust region.

By default, the algorithm first attempts to take a direct step. If it cannot, it attempts a CG step. One case where it does not take a direct step is when the approximate problem is not locally convex near the current iterate.

At each iteration the algorithm decreases a merit function, such as

$$f_{\mu}(x,s) + v \| (h(x), g(x) + s) \| = 0$$

The parameter may increase with iteration number in order to force the solution towards feasibility. If an attempted step does not decrease the merit function, the algorithm rejects the attempted step, and attempts a new step.

Direct Step

The following variables are used in defining the direct step:

• H denotes the Hessian of the Lagrangian of $f\mu$:

$$H = \nabla^2 f(x) + \sum_i \lambda i \, \nabla^2 gi(x) + \sum_j \lambda j \, \nabla^2 hj(x). \tag{37}$$

• *Jg* denotes the Jacobian of the constraint function *g*.

• *Jh* denotes the Jacobian of the constraint function *h*.

• *S* = diag (*s*).

• λ denotes the Lagrange multiplier vector associated with constraints *g*

• Λ = diag (λ).

• *y* denotes the Lagrange multiplier vector associated with *h*.

• *e* denotes the vector of ones the same size as *g*. Eq. 38 defines the direct step (Δx, Δs):

$$\begin{bmatrix} H & 0 & J_h^T & J_g^T \\ 0 & S\Lambda & 0 & -S \\ Jh & 0 & I & 0 \\ Jg & -S & 0 & I \end{bmatrix} \begin{bmatrix} \Delta x \\ \Delta s \\ -\Delta y \\ -\Delta\lambda \end{bmatrix} = \begin{bmatrix} \nabla f - J_h^T y - J_g^T \lambda \\ S\lambda - \mu e \\ h \\ g + s \end{bmatrix} \qquad \underline{o} \tag{38}$$

This equation comes directly from attempting to solve Eqs. 35 and 36 using a linearized Lagrangian.

Conjugate Gradient Step

The conjugate gradient approach to solving the approximate problem Eq. 33 is similar to other conjugate gradient calculations. In this case, the algorithm adjusts both x and s, keeping the slacks s positive. The approach is to minimize a quadratic approximation to the approximate problem in a trust region, subject to linearized constraints. Specifically, let R denote the radius of the trust region, and let other variables be defined as in "Direct Step". The algorithm obtains Lagrange multipliers by approximately solving the KKT equations.

$$\nabla xL = \nabla x f(x) + \sum_i \lambda i \nabla gi(x) + \sum_j yi \nabla hj(x) = 0$$

in the least-squares sense, subject to λ being positive. Then it takes a step (Δx, Δs) to approximately solve

$$\min_{\Delta x,\Delta s} \nabla f^T \Delta x + \frac{1}{2}\Delta x^T \nabla^2_{xx} L\Delta x + \mu e^T S^{-1}\Delta S + \frac{1}{2}\Delta S^T S^{-1}\Lambda\Delta s \quad (39)$$

subject to the linearized constraints

$$g(x) + J_g\Delta x + \Delta s = 0, \qquad h(x) + J_h\Delta x = 0 \quad (40)$$

To solve Eq. 40, the algorithm tries to minimize a norm of the linearized constraints inside a region with radius scaled by R. Then Eq. 39 is solved with the constraints being to match the residual from solving Eq. 40, staying within the trust region of radius R, and keepings strictly positive.

4.6.2. Sequential Quadratic Programming (SQP)

Sequential Quadratic Programming (SQP) represents the state of the art in nonlinear programming methods and is one of the most successful methods for the numerical solution of constrained nonlinear optimization problems. It relies on a profound theoretical foundation and provides powerful algorithmic tools for the solution of large-scale technologically relevant problems. The application of the SQP methodology is to nonlinear optimization problems (NLP) of the form

$$minimize \quad f(x) \quad (41)$$

$$over\ x \in \mathbb{R}^n$$

$$Subject\ to\ h(x)=0 \quad (42)$$

$$(x) \leq 0 \tag{43}$$

where $f: \mathbb{R}^n \to \mathbb{R}$ is the objective functional, the functions $h: \mathbb{R}^n \to \mathbb{R}^m$ and $g: \mathbb{R}^n \to \mathbb{R}^p$ describe the equality and inequality constraints.

The Eq. (41) -(43) contains as special cases linear and quadratic programming problems, when f is linear or quadratic and the constraint functions h and g are affine.

Sequential Quadratic Programming is an iterative procedure which models the NLP for a given iterate x^k, $k \in \mathbb{N}_0$, by a Quadratic Programming (QP), sub problem, solves that QP sub problem, and then uses the solution to construct a new iterate x^{k+1}. This construction is done in such a way that the sequence $(x^k)\, k \in \mathbb{N}_0$ converges to a local minimum x^* of the NLP (42)-(43) as $k \to \infty$. In this sense, the NLP resembles the Newton and quasi-Newton methods for the numerical solution of nonlinear algebraic systems of equations. However, the presence of constraints renders both the analysis and the implementation of SQP methods much more complicated.

Feasible set

The set of points that satisfy the equality and inequality constraints, i.e.,

$$F := \{ x \in \mathbb{R}^n \mid h(x) = 0 \, , g(x) \leq 0 \} \tag{44}$$

is called the feasible set of the Eq. (41) -(43). Its elements are referred to as feasible points.

A major advantage of SQP is that the iterates x^k need not to be feasible points, since the computation of feasible points in case of nonlinear constraint functions may be as difficult as the solution of the NLP itself.

Lagrangian functional associated with the NLP

The functional $\mathcal{L} : \mathbb{R}^{n \times m \times p} \to \mathbb{R}$ defined by means of

$$\mathcal{L}(x, \lambda, \mu) := f(x) + \lambda^T h(x) + \mu^T g(x) \tag{45}$$

is called the Lagrangian functional of the Eq. (41) -(43). The vectors $\lambda \in \mathbb{R}^m$ and $\mu \in \mathbb{R}^p_+$ are referred to as Lagrangian multipliers.

For a functional $f: lR^n \rightarrow lR$, it denotes by $\nabla f(x)$ the gradient of f at $x \in lR^n$, i.e.,

$$\nabla f(x) := \left(\frac{\partial f(x)}{dx1}, \frac{\partial f(x)}{dx2}, \ldots, \frac{\partial f(x)}{dxn}\right)^T$$

Moreover, $H f(x)$ is referred as the Hessian of f at $x \in lR^n$, i.e., the matrix of second partial derivatives as given by

$$\big(H f(x)\big)ij = \frac{\partial 2 f(x)}{dxidxj}, \quad 1 \leq \lambda, j \leq n.$$

For vector-valued functions $h: lR^n \rightarrow lR^m$ the symbol ∇ is also used for the Jacobian of h according to

$$\nabla h(x) := (\nabla h_1(x), \nabla h_2(x), \ldots, \nabla h_m(x)).$$

Throughout the following, it supposes that the functions $f, g,$ and h are three times continuously differentiable.

First order necessary optimality conditions

Let $x^* \in lR^n$ be a local minimum of the Eq. (41) -(43) and suppose there exist Lagrange multipliers $\lambda \in lR^m$ and $\mu^* \in lR^p_+$ such that

(A1) $\nabla \mathcal{L}(x^*, \lambda^*, \mu^*) = \nabla f(x^*) + \nabla h(x^*)\lambda^* + \nabla g(x^*)\mu^* = 0$

holds true. Then, (A1) is referred to as the first order necessary optimality or Karush-Kuhn-Tucker (KKT) conditions.

Critical points

A feasible point $x \in F$ that satisfies the first order necessary optimality conditions (A1) is called a critical point of the Eq. (41) -(43).

Second order sufficient optimality conditions

In addition to (A1) suppose that the following conditions are satisfied:

(A2) The columns of $G(x*)$ are linearly independent.

(A3) Strict complementary slackness holds at x^*.

(A4) The Hessian of the Lagrangian with respect to x is positive definite on the null space of $G(x^*)^T$, i.e.,

$d^T H \mathcal{L}^* d > 0$ *for all* $d \neq 0$ *such that* $G(x^*)^T d = 0$.

The conditions (A1) -(A4) are called the second order sufficient optimality conditions of the NLP (41)-(43). The second order sufficient optimality conditions guarantee that x^* is an isolated local minimum of the Eq. (41) -(43) and that the Lagrange multipliers λ^* and μ^* are uniquely determined. The convergence behavior of SQP methods will be measured by asymptotic convergence rates with respect to the Euclidean norm $\|\cdot\|$.

Convergence rates

Let $(x^k)_{k\in IN0}$ be a sequence of iterates converging to x^*. The sequence is said to convergence

• linearly, if there exist $0 < q < 1$ and $k_{max} \geq 0$ such that for all $k \geq k_{max}$

$\| x^{k+1} - x^* \| \leq q \| x^k - x^* \|$,

• superlinearly, if there exist a null sequence $(q_k)_{k\in IN0}$ of positive numbers and $k_{max} \geq 0$ such that for all $k \geq k_{max}$

$\| x^{k+1} - x^* \| \leq q_k \| x^k - x^* \|$,

• quadratically, if there exist $c > 0$ and $k_{max} \geq 0$ such that for all $k \geq kmax$

$\| x^{k+1} - x^* \| \leq c \| x^k - x^* \|^2$.

• R-linearly, if there exist $0 < q < 1$ such that

$$\frac{\text{Lim sup}}{k\to\infty} \quad \sqrt[k]{\|x^k - x^*\|} \leq \quad \sqrt[k]{q.}$$

4.7. Model validation

In a second pilot-scale experiment, the validation of the model was carried out under different operation condition. The new experiment consisted of two 15 L reactors fed with maize silage in which the biogas and methane production were measured daily and the pH value was registered

online. As in the first part of the study, the same procedure was performed to apply the AM2 model. The experiment lasted 20 days and the OLR was changed, as shown in Tab. 2.

Table 2. Experiment of digestion of maize silage in a 25 L. reactor

Time of digestion, [d]	OLR, [kg ODM m^{-3} d^{-1}]
10	3.17
3	4.22
4	5.27
3	6.33

The volatile fatty acids concentration in the culture solution was analyzed using an Agilent 1200 series HPLC system equipped with a refractive index detector (Agilent GmbH, Waldbronn, Germany) and a HyperRez XP column (Thermo Fisher Scientific Inc., Waltham, MA).

5. Results

5.1 Modelling of AM2

5.1.1. Development of extended version of AM2

Modeling and the incorporation of extensions to the original AM2 contributed to the development of a suitable approach. Extensions were taken from (Ficara et al., 2012) and some other were developed in (Arzate et al., 2017) (Paper III), which involve as well the use of specific parameters that represent chemical interactions and processes such as rate constants, and binding affinities to the digestion (see section 5.1.3). The model structure of the new approach incorporates the hydrolysis which in the previous model was only assumed. As a result, the model describes the digestion in three steps: hydrolysis; acetogenesis and methanogenesis. The anaerobic digestion begins with bacterial hydrolysis of the input materials. Insoluble organic polymers, such as carbohydrates, proteins, lipid, inert particles and inert soluble are broken down to soluble derivatives that become available for other bacteria. Acidogenic bacteria then convert the sugars, amino acids and long fatty acids into volatile fatty acids. Finally, methanogens convert these products to methane and carbon dioxide. The three stages of anaerobic digestion process of the new version of AM2 can be observed in Fig. 9.

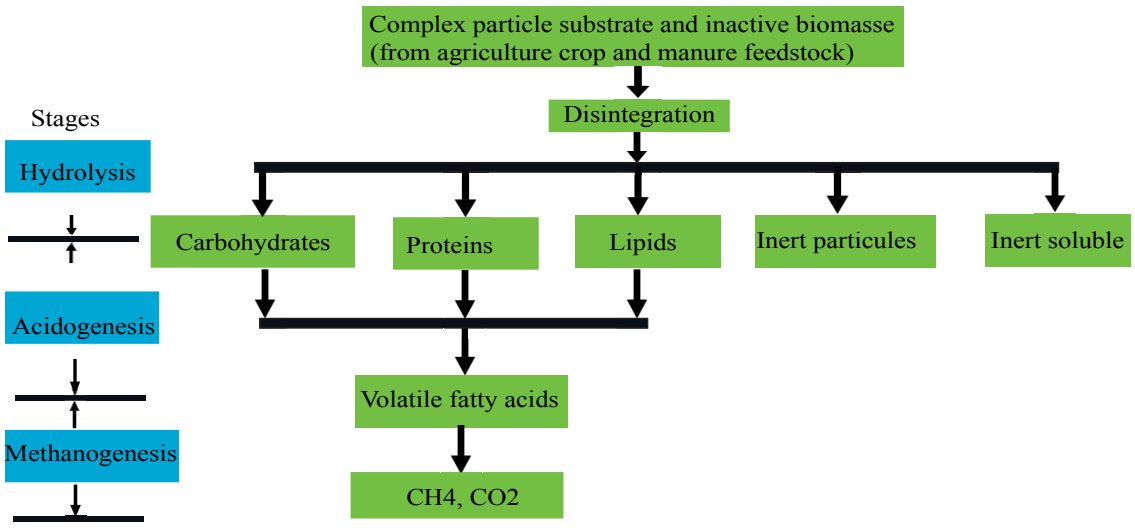

Figure 9. The anaerobic digestion model AM2 including biochemical processes. Three stages as a whole process: hydrolysis, acidogenesis and methanogenesis.

5.1.2. Comparison of AM2 vs. ADM1

In this thesis, the ADM1 was analyzed. The model is of great importance in anaerobic digestion modelling as discussed in section 2.1.4 and 2.1.8. However, due to its numerous parameters, its structural identifiability is questionable (Lauwers et al., 2015). This being understood, a fundamental question arises: Is the ADM1 able to estimate the parameters accurately under realistic conditions? Certainly, poorly specified models are normally nonidentifiable. If the number of unique model parameters exceeds the number of independent pieces of observed information, the model becomes not identifiable (Huang, 2005). Therefore, a sensitivity analysis of the ADM1 was performed for testing the robustness of the results of the model in the presence of uncertainty. The analysis was applied to the 80 ADM1 parameters of a digestion of sludge from a wastewater treatment plant. The details of the study and results are described in section 3.1 of paper III. Results from sensitivity analysis showed 6 insensitive parameters and 11 parameters exhibited a low to moderate degree of sensitivity. The rest of parameters were found sensitive. These results suggest a reduction of the ADM1 for the same application aiming for an increased identifiability, or the use of an alternative model.

After maize silage was characterized, the original AM2 was optimized to ADM1 and results were compared to both the ADM1 and the experimental data. Nevertheless, the optimization results do not completely fit the ADM1. A different profile for the acidogenic bacteria (X1) between the predicted and the ADM1 is depicted in Fig. S-1 (see supporting information Paper III); on the profile of methanogenic bacteria (X2) a higher concentration from the AM2 is evident when is compared to ADM1; the alkalinity (Z) profile for the AM2 is a line because the equation does not considerate description terms. The ADM1 simulation of organic matter (S1) shows higher values when compared to AM2 profiles, since the hydrolysis process in AM2 is not clearly defined. The simulation profile for volatile fatty acids (*S2*) and inorganic carbon (*C*) are similar when the two models are compared. The significant information from results were considered for the development of a new version of AM2 and the subsequent inclusion of extensions to improve the approach.

Once the new version of the AM2 was accomplished, the original and the new version of AM2 were compared with ADM1 and is given in Tab. 3.

Table 3. Comparative overview for the AM2 model (Bernard et al., 2001), the new version of AM2 (Arzate et al., 2017) and ADM1 (Batstone et al., 2002).

Characteristic	AM2	New version AM2	ADM1
Model type	dynamic	dynamic, steady state	dynamic, steady state
Structure	single model	single model	single model
Adapted substrate	sludge from WWTP, microalge, Vinasses from the wine industry	maize silage, grass silage, cattle manure	various substrates
Growth kinetics	Monod, Haldane	Monod, Haldane	Modified Monod
Process reactions	2	3	19
Parameters:			
-stoichiometric	6	7	17
-kinetic	7	20	38
-physico-chemical	3	3	>8
State variables	6, COD based	10, COD based	24, COD based
Bacterial groups	2	2	6
Hydrolysis kinetics	None	first order	first order
Inhibition functions	None	1	4
Type of inhibition	NH_3, VFAs	NH_3, VFAs, pH	H_2, pH, NH_3, butyric acid
Products	CH_4, CO_2	CH_4, CO_2	CH_4, CO_2

5.1.3 Extensions for AM2

Once the original AM2 was not able to fit all the lumping variables of ADM1, the extensions described in Ficara et al., 2014 were included to the AM2 and the model was performed for maize silage. Subsequently, the output variables as biogas production, methane and state variables of AM2 were compared to ADM1. In general, the biogas production shows a delay in the dynamics after feedstock feeding compared to ADM1 (see supporting information in Paper III). Moreover, the model measures higher the organic substrate than observed in ADM1 due to the lack of explicit equations of hydrolysis. Despite this, the outcome variables of biomass, VFA, alkalinity and inorganic

carbon satisfy well to the ADM1 profiles (see supporting information Paper III). Relevant of results, is the correct accounting for inorganic nitrogen in the organic matter through the alkalinity.

5.1.3.1. Extension for biomass

The original AM2 (Bernard et al., 2001) has been recently applied to maize silage (Arzate et al., 2014) (see Paper I). In Arzate et al., 2014, the simulation of biogas and methane flow rates are adequately represented by the model when compared with experimental data. That was the basis to further investigating the model and achieving the optimization of the state variables. However, the model should be modified in order to perform accurate model predictions of states variables such as biomasses (x1, X2), organic substrate (S1), volatile fatty acids (S2), inorganic carbon (C), and alkalinity (Z). Thus, the incorporation of extensions to the basic structure of the model was carried out. The biomass extensions adapted to the AM2 are depicted as follow. The term of the decay rate of biomasses *X1* and *X2*, k_{d1}, k_{d2} respectively, was included to AM2 as can be seen in Eqs. 46-47 (Ficara et al., 2012).

$$\frac{dX1}{dt} = (\mu_1 - \alpha D_{in} - k_{d1})X1 \quad (46)$$

$$\frac{dX2}{dt} = (\mu_2 - \alpha D_{in} - k_{d2})X2 \quad (47)$$

The alkalinity balance was modified integrating the nitrogen content of the substrate, N_{s1} and the nitrogen content in the biomass, N_{bac}, as can be seen in Eq. 48.

$$\frac{dz}{dt} = D_{in}\ (Z_{in} - Z) + ([k_1\ N_{s1} - N_{bac}]\,\mu_1\ X1) - Nbac\ \mu_2\ X2 + (k_{d1}\ N_{bac}\ \mu_{1\max}\ X1)$$

$$+(k_{d2}\ N_{bac}\ \mu_{2\max}\ X2) \quad (48)$$

5.1.3.2. Extension for growth rate

In (Arzate et al., 2017), three more extensions were included into the AM2 in order to adjust the model for agricultural feedstock. The first extension was applied to the growth rate for acidogenic and methanogenic bacteria, Eq. 49 and 50, in which the inhibition term was also included as a function of *pH*, and when only low *pH* inhibition occurs below *pH* = 5.0 (Bornhöft et al., 2013). *pH*

and pH_H are the actual and the high *pH* values, respectively (Batstone et al., 2002), in which pH_H =8.5.

$$\mu_1 = \left(\mu_{1max}\frac{S1}{S1+K_{s1}}\right) - \left(\mu_{1max}\frac{S1}{S1+K_{s1}}\exp\left[-3\left(\frac{pH-pH_H}{pH_H-pH_L}\right)^2\right]\right) \quad (49)$$

$$\mu_2 = \left(\mu_{2max}\frac{S2}{S2+K_{s2}+(S2^2/K_{I2})}\right) - \left(\mu_{2max}\frac{S2}{S2+K_{s2}+(S2^2/K_{I2})}\exp\left[-3\left(\frac{pH-pH_H}{pH_H-pH_L}\right)^2\right]\right) \quad (50)$$

In where μ_{1max} is the maximum acidogenic bacteria growth rate, [d^{-1}]; μ_{2max} is the maximum methanogenic growth rate; S1 is the organic matter [kg COD m^{-3}]; S2 is the volatile fatty acid concentration, [mole m^{-3}]; K_{S1} is the half-saturation constant, [kg m^{-3}]; K_{S2} is the half-saturation constant, [mole m^{-3}]. The Eqs. 49 and 50 were applied for both energy crops maize silage and grass silage. In the model for cattle manure the equations of acidogenic and methanogenic bacteria growth rate were modified, as shown in Eqs. 12 and 51, respectively. The Eq. 12 is the same as original AM2. In Eq. 51, the exponent of S2 in the third term of denominator was changed from 2 to 1. Moreover, pH_H =8.3 and pH_L = 5.5 were considered.

$$\mu_2 = \left(\mu_{2max}\frac{S2}{S2+K_{s2}+(S2/K_{I2})}\right) - \left(\mu_{2max}\frac{S2}{S2+K_{s2}+(S2/K_{I2})}\exp\left[-4\left(\frac{pH-pH_H}{pH_H-pH_L}\right)^2\right]\right) \quad (51)$$

5.1.3.3. Extension for hydrolysis

The hydrolysis step was included into the AM2 (Arzate et al., 2017), in which degradable particulate organic substrate or composites, Xc are partially disintegrated into carbohydrates (*Xch*), proteins (*Xpr*) and lipids (*Xli*) and is described by Eq. 52. (Thamsiriroj and Murphy, 2011). The hydrolysis of *Xch*, *Xpr* and *Xli* are defined by Eqs. 53-55.

$$\frac{dXc}{dt} = -k_{dis}\ Xc + D_{in}\ (Xc_{in} - Xc) + k_{dec,x1}\ X1 + k_{dec,x2}\ X2 \quad (52)$$

$$\frac{dXch}{dt} = -k_{hyd,ch}\ \ Xch + D_{in}\ \ (Xch_{in} - Xch) + f_{ch,xc}\ k_{dis}\ Xc \quad (53)$$

$$\frac{dXpr}{dt} = -k_{hyd,pr}\ \ Xpr + D_{in}\ (Xpr_{in} - Xpr) + f_{pr,xc}\ k_{dis}\ Xc \quad (54)$$

$$\frac{dXli}{dt} = -k_{hyd,li}\ \ Xli + D_{in}\ (Xli_{in} - Xli) + f_{li,xc}\ k_{dis}\ Xc \tag{55}$$

In where k_{dis} is the parameter for disintegration process. The organic substrate concentration, *S1*, includes the terms related to hydrolysis, as shown in Eq. 56.

$$\frac{dS1}{dt} = D_{in}\ (S1_{in} - S1) - (k_1 \mu_1 X1) + k_7 (k_{dis}\ Xc - k_{dec,x1}\ X1 - k_{dec,x2}\ X2) + k_8 \{(k_{hyd,ch}\ Xch - f_{ch,xc}\ k_{dis}\ Xc)$$

$$+ (k_{hyd,pr}\ Xpr - f_{pr,xc}\ k_{dis}\ Xc) + (k_{hyd,li}\ Xli - f_{li,xc} k_{dis})\} \tag{56}$$

In where k_7 is the yield-coefficient of substrate disintegration and k_8 the yield-coefficient of hydrolysis of carbohydrates, proteins and lipids.

In (Ficara et al., 2012), the ADM1 and AM2 were compared against each other. Parameter estimation was performed to adapt AM2 further using the original values of the AM2 and a benchmark substrate. A new state variable accounting for the inorganic nitrogen was added. To keep the simple structure of 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 (Ficara et al., 2012). 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 (Ficara et al., 2012), while ADM1 defines alkalinity by Eq. 57, which involves the difference between cation (S_{cat}) and anion (S_{an}) concentrations in the solution and inorganic nitrogen. The alkalinity constituents in Eq. 57 are bicarbonates, VFA, hydroxide ions and free ammonia. Neglecting nitrogen affects the bicarbonate equilibrium, especially the amount of ammonium bicarbonate (NH_4HCO_3) (Ficara et al., 2012). Differences are noticed when predicted amount of methane is simulated. Results of the original AM2 (Ficara et al., 2012) 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.

$$Z = S_{cat} - S_{an} + S_{in} \tag{57}$$

5.2. Application of AM2 to substrates

5.2.1 maize silage

The organic loading rate during 37 days of digestion of maize silage in the 50-liter experiment is depicted in Fig. 10a. During digestion, several peaks corresponding to the gas formation rate appear due to short feeding time. The time period for each feeding to the reactor was 15 minutes. During the weekend the feeding was interrupted, as it can be seen after days 5, 13, 20, 27, and 34. The AM2 simulation and the experimental data of the biogas and methane production rate are shown in Figs. 10b and 10c, respectively. The outputs reveal that AM2 estimates the biogases production well (Arzate et al., 2017). The comparison between both models, AM2 and ADM1, is depicted in Fig. 11.

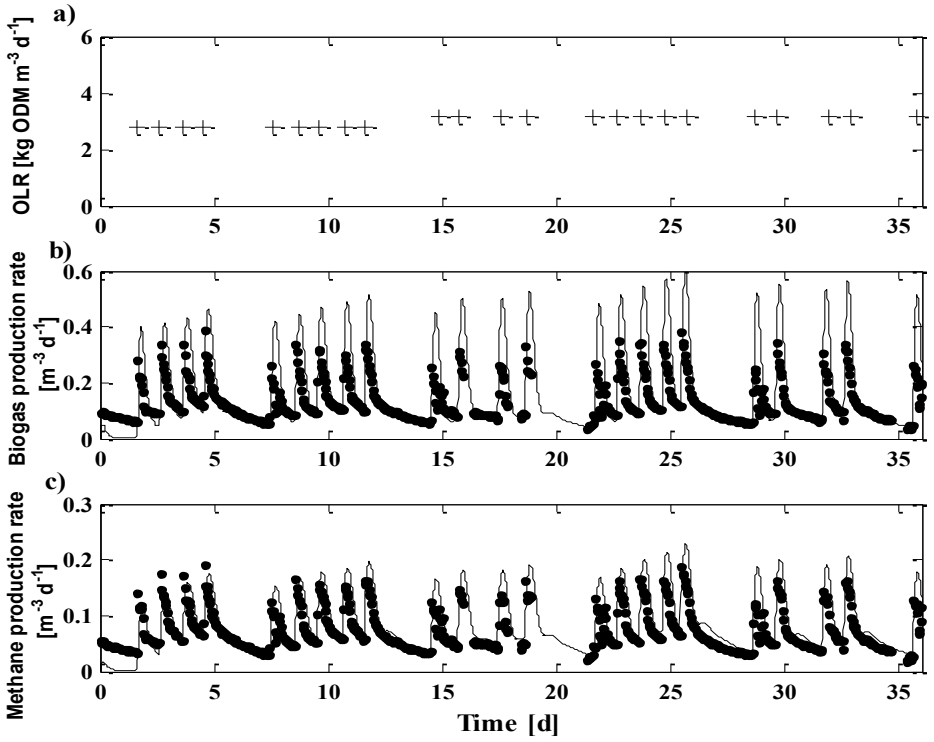

Figure 10. a) Organic loading rate (+) during a period of 36 days at alternating feedstock load in a 50-L scaled anaerobic digestion process. b) Biogas production: AM2 simulation (–), online experimental data (*), and c) Methane production: AM2 simulation (–), online experimental data (*). (Figure taken from publication III- Arzate et al. (2017) in Results - reprinted from Chemie Ingenieur Technik with permission from Wiley)

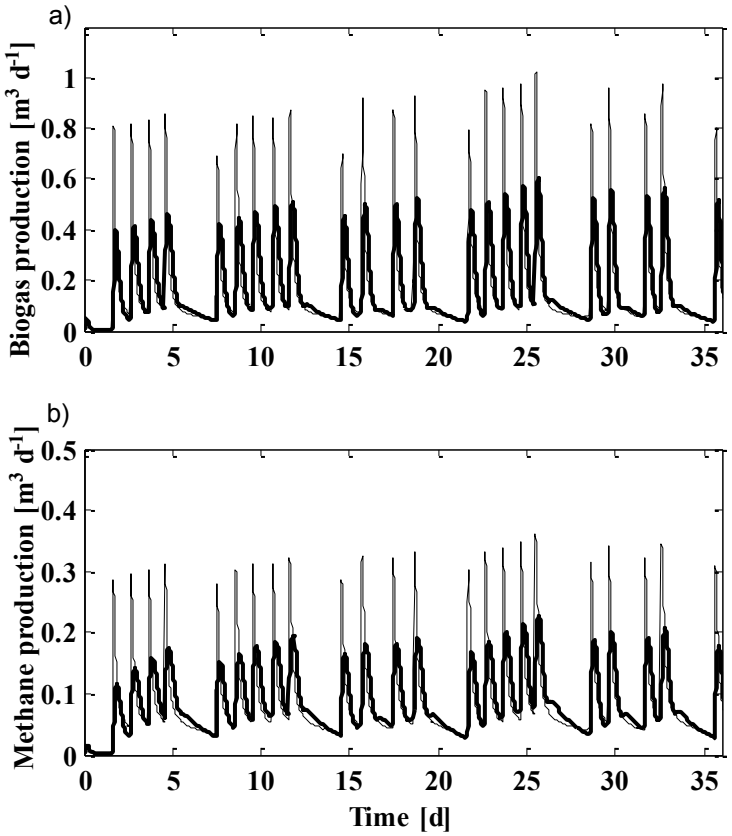

Figure 11. Comparison between the simulation of the modified AM2 (–) and ADM1 (–) for a period of 36 days at alternating feedstock load of a 50-L scaled anaerobic digestion process. (Figure taken from publication III- Arzate et al. (2017) in Results - reprinted from Chemie Ingenieur Technik with permission from Wiley)

The lumping variables of AM2, X1, X2, Z, S1, S2, and C are compared with the ADM1 and are shown in Fig. 12. The process fluctuations, such as the growth and decrease in biomass of methanogenic and acidogenic microorganisms, are adequately described by the AM2 model in relation to ADM1, (see Figs. 12a and 12b). The organic material also fits precisely to the process fluctuations due to short feeding times (see Fig. 12c). AM2 fits the alkalinity and the inorganic carbon content (see fig. 12e and 12f). In these cases, the results of the simulations of the two models are similar. In the case of volatile fatty acid concentrations, after the substrate is fed, ADM1 simulates lower values than AM2 due to higher carbon consumption, perhaps due to an increased number of conversion reactions (see Fig. 12d). The experimental data and model simulation for both the biogas and the methane production rate is less than 7 percent which is an acceptable approach. The simulation of the components of each lumping variable from the ADM1 is shown in Fig. 13.

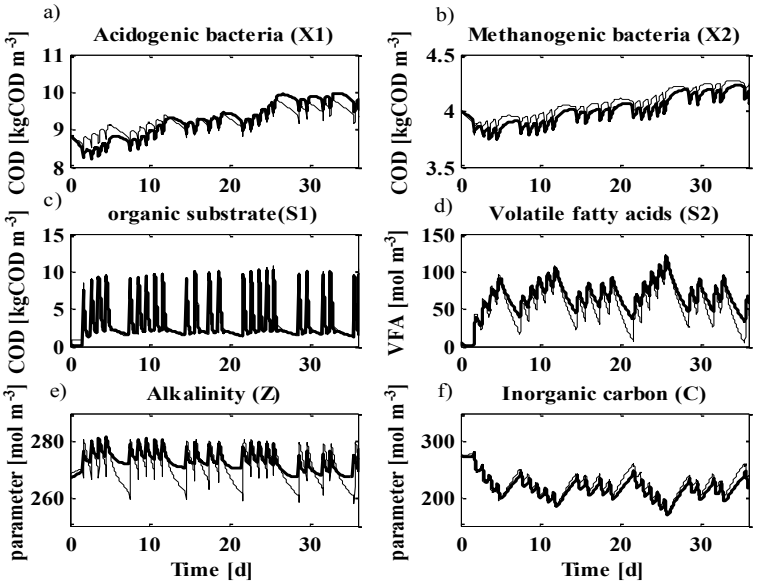

Figure 12. Comparison of lumping variables between the AM2 (**–**) and the ADM1 (–) obtained for a 50 L. digestion process during a period of 36 days with changing influent conditions. a) Acidogenic bacteria; b) methanogenic bacteria; c) organic substrate. d) Volatile fatty acids, e) alkalinity; and f) inorganic carbon. (Figure taken from publication III- Arzate et al. (2017) in Results - reprinted from Chemie Ingenieur Technik with permission from Wiley)

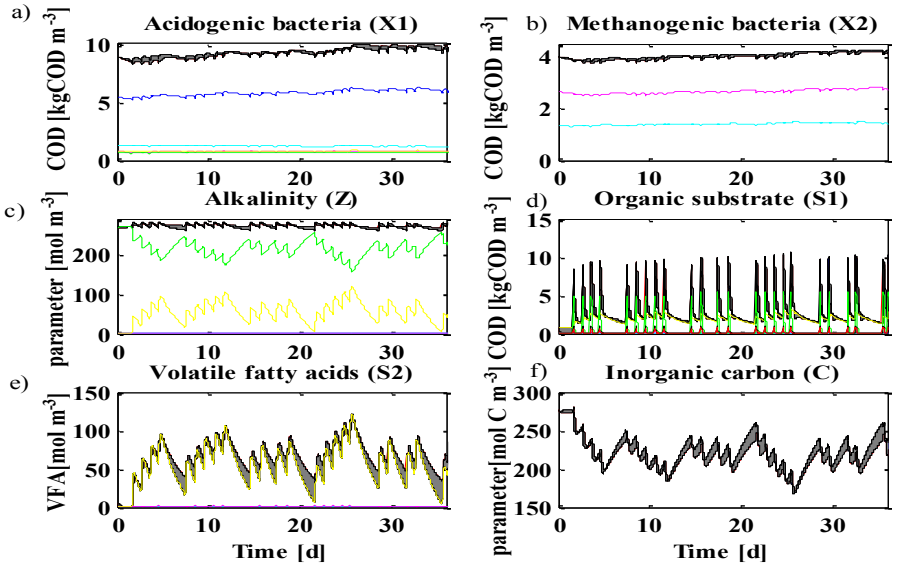

Figure 13. Difference between the AM2 and ADM1 models(▬) and composition in the ADM1 model variables: a) acidogenic bacteria: sugar degraders (-), amino acid degraders (-), LCFA (-), valerate and butyrate degraders (-), propionate degraders (-); b) methanogenic bacteria: acetate degraders (-), hydrogen degraders (-); c) alkalinity: bicarbonate ions (-), acetate ions (-), valerate ions (-), butyrate ions (-), propionate ions (-); d) organic substrate: composites (-), monosaccharides (-), amino acids (-), LCFA (-), carbohydrates (-); proteins(-), lipids (-); e) VFA: valerate (-); butyrate (-), propionate (-); acetate (-); f) inorganic carbon (-). (Figure taken from publication III- Arzate et al. (2017) in Appendix - reprinted from Chemie Ingenieur Technik with permission from Wiley)

5.2.2 Grass silage

The extended version of AM2 was also calibrated to the ADM1 in MATLAB™ 2015b for grass silage. ADM1 parameters were obtained from (Wichern et al., 2008). The same equations in the model were used as described in (Arzate et al., 2017). At the beginning, the ADM1 simulation was unstable, in which alkalinity and biogas flow production profiles presented inconsistencies. After reviewing literature, it was found that the parameter of the disintegration process, $k_{hyd}[day^{-1}]$, could be increased to a value of 0.266, as indicated in (Koch et al., 2009) (Lübken et al., 2010). After modification, both profiles showed adequate stability as is depicted in Figs. 14a and 14b. Thus, the initial parameter of k_{hyd} for parameter estimation the same value was proposed. Once the procedure was performed, a value of 0.5 was obtained. As operating parameters, the hydraulic retention time (HRT) and the organic loading rate (OLR) were considered 33.09 days and 3.58 kg ODM m^{-3} d^{-1} respectively. The output variables to be optimized were: biogas and methane production; acidogenic and methanogenic bacteria (X1, X2); alkalinity (Z); organic material (S1); volatile fatty acids (S2) and inorganic carbon (C). As optimization function fmincon of MATLAB™ was used. As can be clearly seen, the AM2 biogas and methane flow rate profiles coincide well with the output of the ADM1 model (Fig. 14). Similarly, the optimization results of AM2 to lumped ADM1 variables were adequate in all cases as shown in Fig. 15.

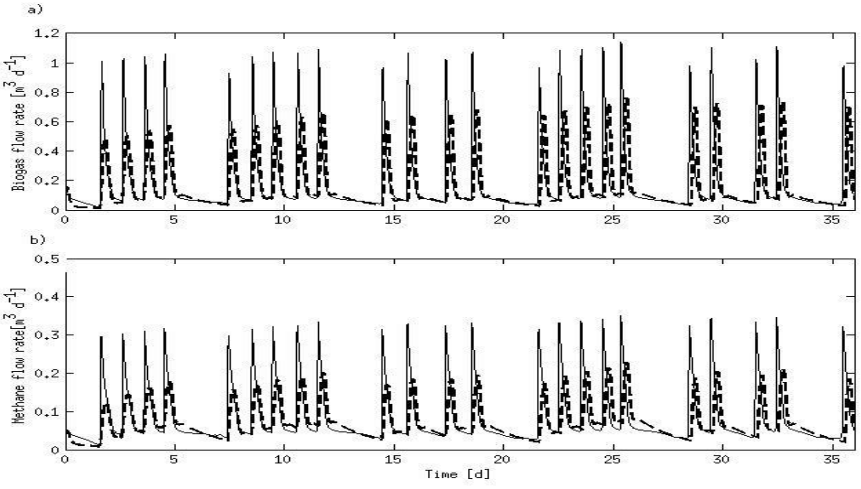

Figure 14: Comparison between the simulation of the extended AM2 (bold dash line) and ADM1 (straight line) for grass silage in a period of 36 days at alternating grass silage feed of a 50 L-scaled anaerobic digestion process. a) Biogas flow rate; b) Methane flow rate. (Figure taken from artide V. Results)

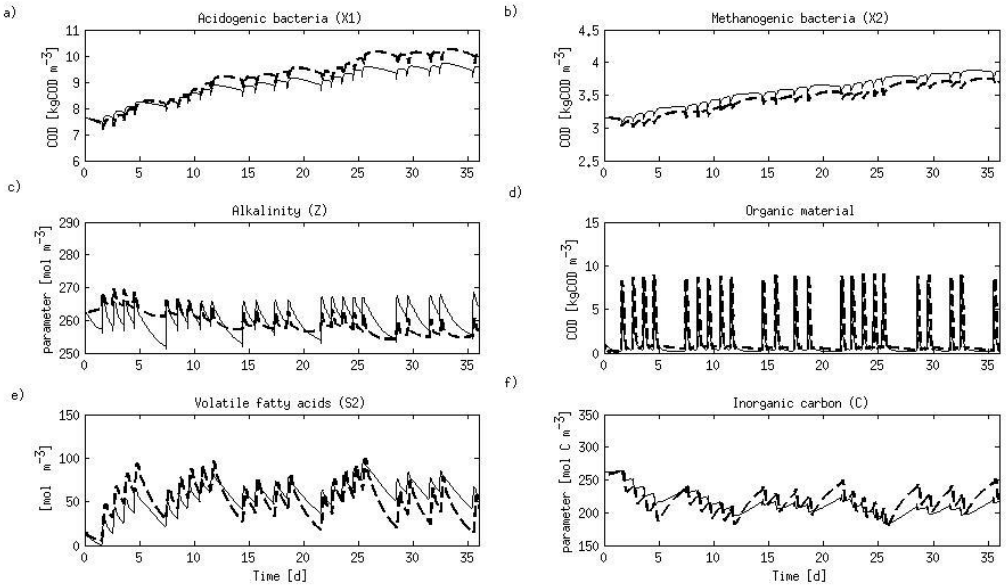

Figure 15. Comparison of lumped variables between the AM2 (bold dash line) and the ADM1 (straight line) for cow manure obtained for a 50 L digestion process during a period of 36 days at alternating cow manure feed. a) acidogenic bacteria; b) methanogenic bacteria; c) alkalinity; d) organic substrate; e) volatile fatty acids; f) inorganic carbon. (Figure taken from article V- Results)

5.2.3. Cattle manure

The parameter estimation of AM2 on ADM1 for cattle manure was carried out using the same procedure that was discussed for grass silage. The objective function of the optimization was to obtain the calibrated parameters in which the simulation outputs and model variables were as close as possible to ADM1 profiles of the process. The ADM1 parameters were obtained from (Wichern et al., 2008). To obtain the influent composition of individual organic fractions of the feedstock, the chemical composition of cattle manure was investigated and is given in Tab. A-3. The Influent composition of the substrate was calculated as indicated in (Arzate et al., 2017), the values are shown in Tab. A-7. The comparison of AM2 to ADM1 of biogas and methane flow rate and the six state variables of the model are given in Figs. 16 and 17, respectively. The AM2 outputs in all cases are in good agreement with ADM1.

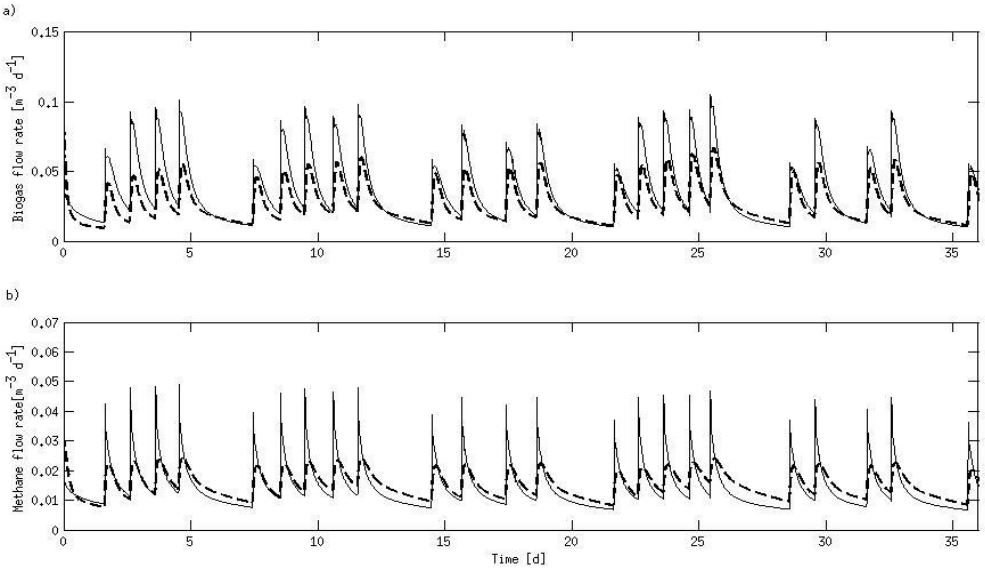

Figure 16: Comparison between the simulation of the extended AM2 (bold dash line) and ADM1 (straight line) for cow manure in a period of 36 days at alternating cattle manure feed of a 50 L-scaled anaerobic digestion process. a) Biogas flow rate; b) Methane flow rate. (Figure taken from article V- Results)

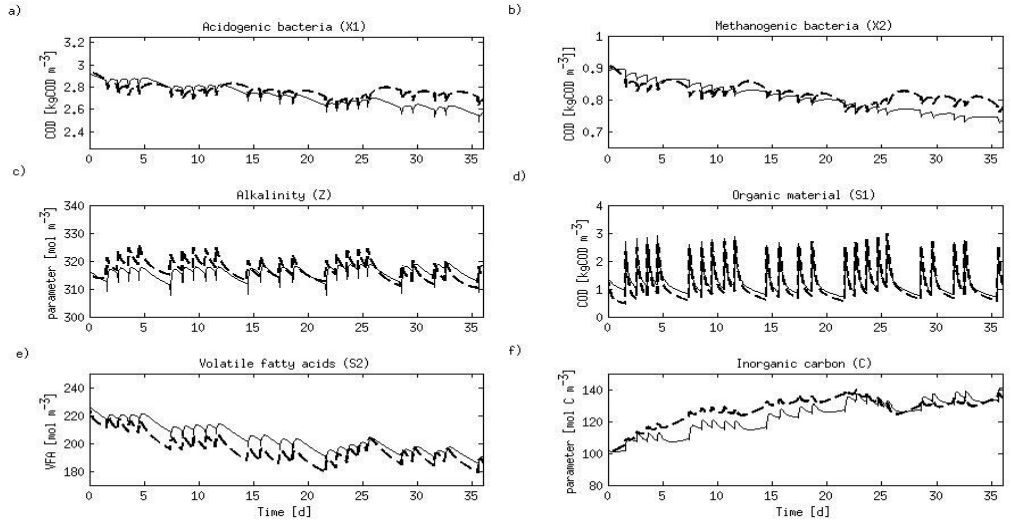

Figure 17. Comparison of lumped variables between the AM2 (bold dash line) and the ADM1 (straight line) for cow manure obtained for a 50 L digestion process during a period of 36 days at alternating cow manure feed. a) acidogenic bacteria; b) methanogenic bacteria; c) alkalinity; d) organic material; e) volatile fatty acids; f) inorganic carbon. (Figure taken from article V. Results)

In agriculture, manure is valued for adding nutrients, microbes, soil structure and the capacity for neutralizing soil pH. Cattle manure generally still conserves much of the nutrients the cow ingested in the manure, in despite of the fact that it's been through four stomachs. In some cases, the grass, feed and nutrients are simply converted, and just decompose easier for having been through the digestive system. In AD, the inclusion of crops in the feedstock can increase the methane production per digester volume above that produced from the digestion of the manure alone (Lehtomäki et al., 2007). During digestion, ammonia concentration can inhibit anaerobic digestion of cattle manure. A stable digestion could be maintained with ammonia concentrations at certain high levels after some time of operation. However, the methane is reduced and the concentration of volatile fatty acids increased as acetate (Angelidaki and Ahring, 1993). Moreover, ammonia toxicity on the acetate- and hydrogen-utilizing populations have proved a higher sensitivity of the aceticlastic compared to the hydrogenotrophic methanogens (Angelidaki and Ahring, 1993).

5.3 Parameter estimation

In the parameter estimation process, the input values for maize silage were taken from (Bernard et al., 2001) and the calibrated parameters for maize silage, grass silage and cattle manure are given in Tab. 4.

Tabla 4. AM2 calibrated parameters for maize, grass and cattle manure

Parameter	Unit	Maize silage	Grass silage	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	0.4
Half-saturation constant, K_{S1}	kg m^{-3}	3.5	1.3	9.0
Half-saturation constant, K_{S2}	mol m^{-3}	34.5	34.4	33.7
Inhibition constant, K_{I2}	mol m^{-3}	998.2	991.3	250.0
Volumetric gas-liquid mass transfer coefficient, kLa	d^{-1}	22.0	22.1	80.4
Yield of substrate degradation, k1	[-]	25.5	24.0	26.0
Yield of VFA generation, k2	mol kg^{-1}	309.7	220.7	226.6
Yield of VFA consumption, k3	mol kg^{-1}	1074.0	874.0	637.6
Yield of CO2 production, k4	mol kg^{-1}	90.0	90.0	34.9
Yield of CO2 production, k5	mol kg^{-1}	200.0	200.0	24.8
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}	$1X10^{-4}$	$1.9X10^{-2}$	$2.4X10^{-2}$
Nitrogen content in the biomass, Nbac	mol kg^{-1}	11.0	9.0	34.4
Decayrate of biomass X1 and X2, k_{d1} and k_{d2}	d^{-1}	5.3% μ1max 5.3% μ2max	4.4% μ1max 4.4% μ2max	7.9% μ1max 15.0% μ2max
Parameters , Hydrolysis process				
Disintegration, kdis	d^{-1}	0.5*	0.5	0.2
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 (Batstone et al., 2002)
** from (Wichern et al., 2008)

5.4. Sensitivity analysis

The sensitivity analysis was applied to 24 parameters of the extended version of AM2 to identify those that influence the model results. The defined order to analyze the parameters is shown in Fig. 18. As can be seen, the principal parameters that significantly affect the model results are the following: k_1, k_4, k_7, k_8, μ_{1max}, μ_{2max}, K_{s1}, K_{s2}, K_{I2}, k_{d1}, k_{d2}, $k_{hyd,ch}$, $k_{hyd,pro}$, $k_{hyd,li}$, $f_{ch,xc}$ $f_{pr,xc}$, $f_{li,xc}$. While parameters k_3, k_6, and $k_{dec,x1}$ retain lower degree of sensitivity. Finally, the parameters k_2, k_5, and k_{dis} have been presented as the most insensitive to the model (see Fig. 18). Among the most sensitive parameters, k_1 k_4, K_{s1}, K_{s2} *and* K_{I2} come from the original AM2 related to the substrate degradation, yield of CO_2, and half-saturation constants, respectively. They hold a substantial correlation to the

equations for organic substrate, volatile fatty acids and organic carbon in the model; the decay rates of biomass k_{d1} and k_{d2} are the key parameters of the extension to solve the alkalinity; 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, which present a strong correlation to the organic matter.

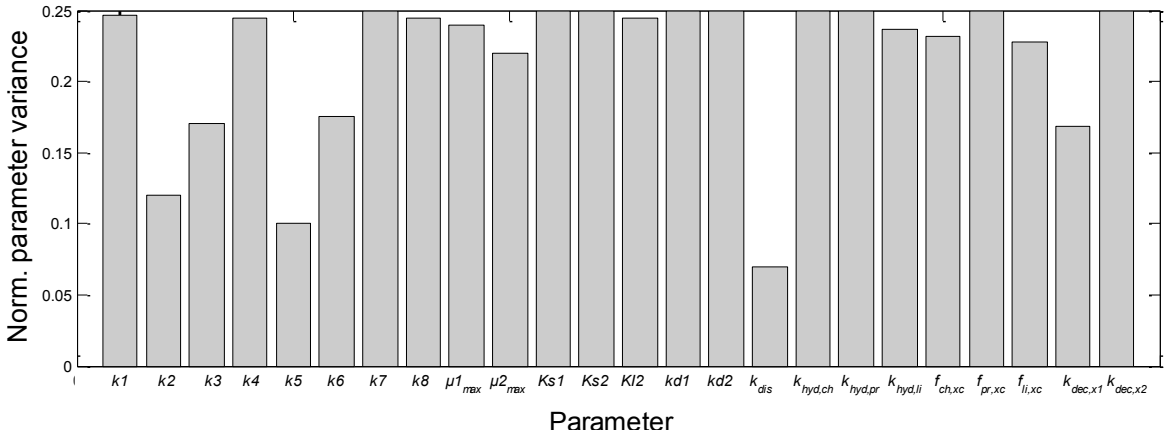

Figure 18. Sensitivity analysis to the 24 parameters of the extended AM2. Interval of normal parameter variance is 0 – 0.25. (Figure taken from publication III- Arzate et al. (2017) in Results - reprinted from Chemie Ingenieur Technik with permission from Wiley)

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, belong to a process that the model also describes. Therefore, ideally, all parameters should be considered in the parameter estimation. As a matter of fact, the AM2 is a reduced model in comparison with the ADM1 for the purpose of predicting the output variables of the AM2 as the biogas, methane and the lumping variables. Thus, 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.

5.5. Validation of AM2

In order to assess the extent to which AM2 mimics the anaerobic digestion, a validation study was carried out. The model outputs were compared to measured data of an anaerobic digestion process conducted in two 15-liter scale digesters operated at different OLRs. The model outputs for methane, CO_2 and volatile fatty acids were compared to experimental data. The simulation of methane production increased to a higher value due to the increase of the OLR. It can also be observed an adaptation phase from day 5 to day 11, and then sharply up to 0.024 $m^3\ d^{-1}$. later, methane level decreases to 0.018 $m^3\ d^{-1}$ near to the experiments 1 and 2 with values of 0.015 $m^3\ d^{-1}$ and 0.016 $m^3\ d^{-1}$ (see Fig. 19a). It can be noticed that the model predicted reasonably the dynamic behavior of the process with a slight delay to high values of organic loading rate. It can be noticed that the model's response to OLR changes is adequate in dynamic behavior with a slight delay to high values of organic loading rate.

The simulation of volatile fatty acids in comparison with experimental results of the two reactors is depicted in Fig. 19b. The increase of volatile fatty acids is due to excess of organic material at an OLR of 5.27 and 6.33 kg ODM $m^{-3}\ d^{-1}$. At the same time, the increase of the VFA concentration was predicted in close agreement with the experimental data, however, overestimated during initial phase.

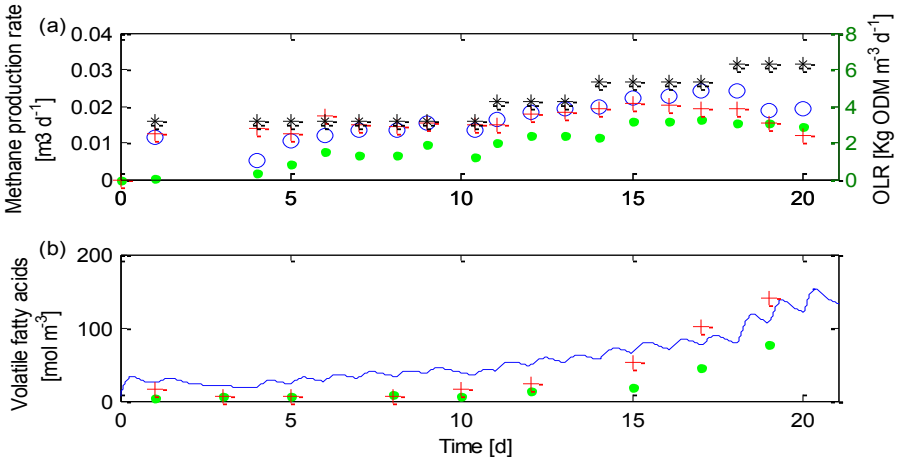

Figure 19: a) Extended AM2 simulation (o), experimental data of R1 (+) and R2 (•), and organic loading rate (*) over a period of 20 days of the acidification of anaerobic digestion processes conducted in two 15-liter digestion processes. b) Simulation of volatile acid concentration (-) and experimental data of reactors R1 (+) and R2 (•). (Figure taken from publication III- Arzate et al. (2017) in Results - reprinted from Chemie Ingenieur Technik with permission from Wiley)

5.6. Co-digestion process

The extended version of AM2 was performed on co-digestion and compared with data from a full-scale digester with a volume capacity of 1440 m^3. The co-digestion was composed of maize silage, grass silage and cattle manure in a continuous fed digestor. Biogas production was monitored on-line and the amount of each fed substrate into the digestor is shown in Tab. A-3 Paper V. The retention time was 76 days and the feedstock feed was carried out with different rates of loading. Dilution rate was changed almost every day due to a variable availability of feedstock in the region (North Germany). The influent feedstock composition was calculated and the calibration of AM2 was performed in three different programs considering as initial parameters the calibrated values of each feedstock. The results present the feasibility of the approach. After optimization, maize silage parameters taken as initial values showed the best-fit for codigestion. The AM2 model was able to predict reasonably well the dynamic results of biogas production amount. However, two AM2 parameters were modified to fit the co-digestion data. The parameters are the yield for VFA production (k2) and the yield for substrate disintegration (k7), the rest of model parameters had to be remained constant. The comparison between simulated results and biogas data is given in Fig. 20. The substrate loading rate and the composition were varied during the process as indicated in Tab. 5. The first 30 days of digestion, the three substrates were fed in a majority proportion of cattle manure. Subsequently, at days 31-37 of feed the grass silage was removed and changed by cattle manure, but the feed of maize silage was continued. During days 38-66, the cattle manure loading rate was increased without grass silage feed and maize silage was continuously fed. Finally, at days 67-74 only cattle manure was fed.

Table 5. Substrate loading rate of large scale BGP (volume capacity of 1440 m^3) and AM2 parameters K2 and K7 obtained after calibration.

Day	Loading rate (%)	k2	k7
1-30	maize silage(11.4-30.6); grass silage (13.6-46.9); cattle manure (39.5-55.8)	309.7	12.7
31-37	maize (37.7-40.7); grass silage (0); cattle manure (62.2-59.3)	329.6	17.8
38-66	maize (26.1-48.5) grass silage (0); cattle manure (48.6-73.8)	359.7	32.7
67 -74	only cattle manure (100)	329.6	17.8

The prediction of the calibrated mathematical model of co-digestion compared to the observed experimental data was 93.2 % for the volume of biogas, which is an acceptable agreement with on-line data.

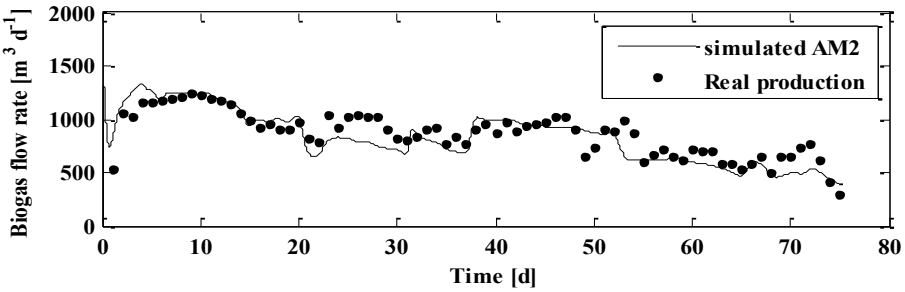

Figure 20: Extended AM2 simulation (-), real production data of bioreactor (•), over a period of 76 days of co-digestion process using maize, grass silage and cattle manure conducted in a 1414 m^3 reactor. (Figure taken from article V. Results)

5.7. Process optimization

The growing demand for efficient systems for the production of methane from biomass requires the developing of control strategies assuring the best performance and stability under a flexible operation. The biogas process is complex in which uncountable and relatively slow microbial reactions occur and still presents problems to be predicted and controlled it. In large-scale biogas plants the control of feeding to the digester is often done with a simple calculation after applying the trial and error method (Gaida et al., 2011). Although there have been also some attempts to determine the optimal operating conditions of the process using the ADM1 (Batstone et al., 2002), the model retains high rigidity and can only be applied with equal complex techniques. Therefore, the ADM1 seems to be too complex for its application with respect to the usual monitoring capabilities in biogas plants. An anaerobic digestion model can associate all the processes and reactions within the system through mathematical equations, variables and parameters to achieve a real process. The models include the relevant information of process to realistically describe the system; such as the characterization of substrates, effects of dilution, temperature or hydraulic behavior among others. The new AM2 developed in this thesis, was written in Aspen Custom Modeler (ACM), which is a simulation program to easily execute customized models. The objective of this program is that it can be used as a tool in BGP's and at the same time can be used to maintain the stability of the system.

The digestion of crops and manure have already been investigated with great interest. The efficiency increase of the process can be accomplished in different ways: (i) by optimization of the fermenting process, (ii) by cofermentation of animal slurry with energy crops or wastes or (iii) by fermentation of energy crops (Golkowska and Greger, 2010). The study of digestion of manure suggested the

importance of VOA control during the process (Angelidaki and Ahring, 1993). In the work, the effects of ammonia on digestion of manure were described. The results clearly demonstrated that at a certain level of ammonia concentration the process can be stable after an initial adaptation period. However, a reduction in methane yield was obtained with an increase of volatile organic acids (VOA) concentration. Thus, the parameter VOA/TA (Volatile Organic Acids / Total Alkalinity) better known as FOSTAC for its acronym in german (Flüchtige Organische Säuren Totals Anorganisches Carbonat), is a key parameter to control the digestion of raw material. This ratio represents the ability of the digester buffer capacity to resist a pH decrease due to the accumulation of VOA, which has been reported to be 0.3-0.4 for a stable digestion (Lili et al., 2011). Normally, several parameters are requested to analyze the process in BGP (pH, alkalinity, volatile organic acids, dry matter content and organic material and C/N ratio). Therefore, the quality of the measurement is expensive, consuming a lot of time. In contrast, FOSTAC method presents several advantages. The stability of the anaerobic degradation process can be promptly, easily and continuously determined. The result is a unique value depending on the ratio of the two parameters (Lili et al., 2011). Some other studies have been published in which the FOSTAC, the methane content (%) and the pH were used as parameters to control the stability of the digester; in digestion of chinese cabbage silage (CCS) (Kafle, 2009); with waste of chinese cabbage juice (CCJ) and swine manure (SM) (Kafle et al., 2012); it was investigated the co-digestion of a variable amount of fruits and vegetable residues (Scano et al., 2014) (Di Maria et al., 2014).

This study explores the anaerobic digestion process for biogas production in terms of process optimization. The AM2 simulation was conducted for co-digestion of maize, grass and cattle manure of a large scale BGP with a volume digester of 228 m^3 and 1000 tons of feed per year. It also provides an optimizer to stabilize the bioprocess by the test VFA/TA. The optimizer uses the AD model AM2 (Arzate et al., 2017) which was coded in ASPEN Custom Modeler V8 to simulate the anaerobic digestion. The program uses the optimization method Sequential Quadratic Programming (SQP) which is a highly effective tool for solving constrained optimization problems with smooth nonlinear functions in the objective and constraints. The important of the study is the process control through FOSTAC by optimizer using the feed loading as a decision variable. Thus, the maximum biogas and methane production and the recommended VFA/TA value of 0.3 for process stability were the objective functions.

The results show an optimized process including rate of feed of each component and methane production in comparison with the normal process. Optimized values of substrates feed, VFA/TA and methane production are given in Tab 5. The optimizer outputs present better results in terms of energy production (an increment of 4.9 %) and process stability. Furthermore, it confirms the higher energetic value of maize silage than manure and higher inhibition of the biogas process of manure due to higher amount of ammonia produced than maize.

Table 5. Process optimization results. Co digestion of maize silage, grass silage and cattle manure.

	maize silage ton d^{-1}	grass silage ton d^{-1}	cattle manure ton d^{-1}	VFA/TA, [-]	Methane production $m^3 d^{-1}$
Optimized process	1.2	0.8	0.8	0.19	265
Normal process	0.8	0.8	1.2	0.08	253

5.8. Combination of extended AM2 and environmental LCA approach

In this study a combination of a life cycle assessment (LCA) and a modelling approach for demand driven biogas production via a flexible feedstock management was carried out. 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, and the mechanistic model was implemented in a MATLAB™ environment. Base-load and flexible biogas production were performed by using the model approach. The LCA results were analized for production targets. This strategic combination of both LCA and modelling provides a solution aproach to identify rapidly operation points that are stable and feasible in terms of technical view from feedstock mixtures or loading scenarios. In paper VI, results, methods and conclusions are indicated.

Once the AM2 was adjusted based on the parameter calibration and validated based on biogas production data from a real biogas plant a series of simulations were performed. As LCA is habitually a non-dynamic methodology, an interface between dynamic modelling results and inventory flows in LCA was required, together with the conversion of specific inventory items. In order to be able to integrate the approaches, it was necessary to include the GHG formation processes for the biogas plants. Therefore, the calculations methodologies, which are commonly applied in Simapro software and the Ecoinvent database were used.

The model was performed to simulate the base load dependent biogas production from the co digestion of 1 t/h grass silage, 1 t/h maize silage and 1 t/h cow manure as illustrated in Fig. 2.b Paper VI. On the next step, a feed management approach was used to simulate the demand driven biogas production system as shown in Fig. 2.a Paper VI. After the parameter fitting, the model was able to successfully simulate the changes in the process. Results show that by feed management, the daily gas production rate can be modulated up to ±50% from the daily average gas production rate. By targeted reduction of the feeding quantity at the times where the energy demand is lower, the gas production was reduced even below 60 m^3 h^{-1}. The combination of AM2 and LCA approach can help the operation in terms of understanding operating limits and optimal maintenance schedules to maximize plant profitability, while operational risks are reduced.

6.0. Discussion

1) AM2 for maize silage

The anaerobic digestion model AM2, originally developed for sludge from wastewater, was adequately adapted to predict the biogas process for maize silage as feedstock (see Paper I). The new model is reduced and tractable in comparison to the complex ADM1 model, in which thirteen parameters were optimized of the AM2 model vs. ninety parameters of ADM1. The use of the reduced AM2 model offers important advantages over complex models as to take less time for characterization of the substrate, the calibration of the model and the optimization of the process are not a computational burden to obtain the outcome. The study in Paper I proposes the application of the AM2 two-step model which has a comparably simple structure requiring less experimental data than the ADM1. In Figure 2 of Paper I, experimental data and the model show the variation pattern of biogas and methane in form of fluctuations corresponding to the feed pulses of substrate, which was adequate because of data variability to the parameter estimation. It can provide more accurate predictions of fluctuations and operation start-ups during a normal process. The AM2 model was calibrated using the function nlinfit in MATLAB, the initial parameters were taken from the calibrated parameters of the original AM2 for raw industrial wine distillery wastewater. The experiment was implemented to investigate the biogas process under conditions of fluctuations within mesophilic conditions. The model was built from experimental data of lab scale digestion consisting of two continuously mixed reactors of a liquid volume of 50 l, and reactors were equipped with a mechanical mixer and fed manually including the monitoring system; the experiment lasted 80, and 92 days, respectively and the temperature was held at an average temperature of 38.7ºC for reactor 1, and 39.1ºC for reactor 2. Biogas production, methane and CO_2 content in the gas phase, temperature, and the pH-value (7.0) were measured on-line every hour. The organic loading rate (OLR) was changed six times for the second reactor as 2.39, 2.78,3.18, 3.58, 3.98 and 3.58 kg ODM m^{-3} d^{-1}, respectively. As can be seen in Paper I, the effects of changes in the organic loading rate (OLR) have shown potential for improving yields of methane in both anaerobic digesters (see Fig. 2b and 2e. Paper I). The stability of two reactors in a transient situation was adequately measured by the Indicator VFA/alkalinity ratio, which reflects the biokinetic state of the process. The VFA/alkalinity ratio values resulting from the model are between 0.1 and 0.6 at the two bioreactors (see section 3.4. Paper I).

2) Modeling as an adecuate tool

In this thesis, it was demonstrated that the incorporation of the term of the decay rate (k_{d1} and k_{d2}) to the biomass expression facilitate a better description of organic subrate, meanwhile, methane and biogas were fitted to experimental data. This approach defines the correct alkalinity balance integrating the nitrogen content of the substrate (Ns1) and the nitrogen content in the biomass (Nbac), as can be seen in Eq. 48. The extensions of Ficara et al., 2012 and three other developed extensions to the AM2 model were relevant for the adaptation of the model to the energy crops and cattle manure.

3) AM2 for grass silage and cattle manure

The process of biogas production is considered complex and involves simultaneous biochemical and physicochemical reactions catalyzed by a consortium of various bacteria. However, the AM2 model in its original form is not suitable to predict biogas, methane and fit the state variables of the anaerobic digestion of maize silage and should therefore be modified. Hence, in paper III and V, the AM2 model was adapted to simulate biogas and state variables for maize silage and grass silage and cattle manure, respectively. The new version of the AM2 model was formulated based on the AM2 model, anaerobic digestion concepts and on previous experience related with modelling and optimization tools. An important part of this study was to research most of the AD models to develop a tractable approach to mimic the digestion of a variety of energy crops and manure (see paper III). In this thesis, for the first time new extensions were incorporated into the AM2 model with respect to biomass and alkalinity, as described in Ficara et al., 2012. Furthermore, two new extensions were developed to achieve the best precision to the model for the bacterial growth rate and hydrolysis (see paper III). The extension related with alkalinity was described in terms of inorganic nitrogen; meanwhile, the biomasses were determined incorporating the term of the decay rate of biomasses *X1* and *X2*, k_{d1}, k_{d2} respectively (see section 5.1.3.1). The hydrolysis step in the AM2 model describes the process in which the bacteria hydrolyze the polymeric components (e.g., polysaccharides, proteins, and lipids) present in the feedstock and further ferment the resulting hydrolysis products to short chain fatty acids (SCFA). These intermediate products are ultimately converted to biogas (a mixture of CH_4 and CO_2) by archaeal methanogens. To obtain a more precise

estimation of AM2 parameters, the generation and consumption of VFA had to be measured during the dynamic simulation. Thus, the intermediate substrate (VFA) was dynamically calculated in (Arzate et al., 2017) (Paper III). Moreover, the input concentration of substrates was determined by applying the substrate characterization described in (Zhou et al., 2011) (see Section 4.3). Furthermore, the optimization of AM2 state variables to the lumped variables of ADM1 was applied (see Section 5.1). Hence, the procedure used to calibrate parameters allowed to obtain the state variables of AM2, which are X1, X2, S1, S2, C1 and Z (see Section 5.1). The calibration of the model for maize silage was accomplished by the use of experimental data to compare model predictions of biogas and methane. Moreover, the prediction of biogas and methane in the case of grass silage and cattle manure was performed using the simulated values from ADM1. In general, simulations and measured data show a good agreement in Figs 10, 13 and 15. The prediction capabilities of biogas and methane were ranging between 0.5 – 6.4 % as compared to the experimental data or ADM1 simulations (see Section 4.4).

Grass silage

The AM2 model was applied to maize silage, grass silage and cattle manure since they are the most used substrates for anaerobic digestion in Germany. The model was first developed for maize; however, its application for other substrates was demonstrated. In general, the calibration of the model was performed for grass silage and cattle manure. In literature, the biogas yield produced from AD of grass silage is 201.74 Nml biogas /g VS (Zhou et al., 2011). After the calibration of the ADM1 of digestion using grass silage in mesophilic conditions resulted a biogas yield of 194.3 Nml. CH4/g TS (Zhou et al., 2011) vs. 155.5 Nml CH4/g TS from AM2. On the other hand, biogas and methane were also compared with the data base of KTBL. The process was referred to a common digestion process of grass silage with 35%TM and 95% organic oTM and the percentage of methane produced in biogas was 52%; the biogas production was 289.6 ml CH4/g VS vs. 272.2 ml CH4/gVS from AM2, corresponding to a difference of 6 percent between both values, which reflects an acceptable fitting to the process. The biogas yield difference between the publication and the AM2 is caused by type and characteristics of the same substrate. In (Zhou et al., 2011), four grass species (cocksfoot, tall fescue, reed canary grass and timothy) were investigated to determine the specific methane yields. The specific methane yields of all grasses varied from 253 to 394 Nl CH4/kg volatile solids (VS) (Seppälä et al., 2009) (see section 5.2.2).

Cattle manure

In the new AM2 approach for cattle manure, the modification of equation for the acidogenic bacteria growth rate responds to the ammonia inhibition on acidogenic bacteria. The expression is the same as the Monod equation as is indicated in (Bernard et al., 2001). Evidently, the equation of the methanogenic bacteria growth rate was also affected by reducing the exponent of S2 in the third term of denominator (Arzate et al., 2017); these were the results of the modeling of the process, in which equations give the best fit of the bacterial growth rate. In literature, the biogas yield produced from cattle manure is 28.9 - 39.5 Nml biogas /g VS (Zhou et al., 2011). The simulation of the ADM1 of digestion of cattle manure in mesophilic conditions was 33.5 Nml. CH4/g TS (Zhou et al., 2011) vs. 25.5 Nml CH4/g TS from AM2. Biogas and methane were also compared with the data base of KTBL. The process was referred to a common digestion process of cattle manure with 10%TM and 80% organic oTM and the percentage of methane produced in biogas was 55%; the biogas production was 26.5 ml CH4/g VS vs. 25.0 ml CH4/gVS from AM2, corresponding to a difference of 6 percent between both values, which shows an acceptable difference to the process (see section 5.2.3).

4) Optimization of co-digestion process

A biogas production without fluctuations depends mainly on the digestion stability, which is influenced by the chemical composition of the feedstock. On the other hand, high variations in quantity and chemical content in organic waste influence the outcome of the process. Thus, effects on bacterial growth and on the overall performance of AD are noticed. Successful feedstock combinations require a method to predict the process outcome when new input waste material is added to the system. (see section 5.6)

With new insights into the FOSTAC performance of anaerobic digestion, better decisions for more efficient processes, operation support and troubleshooting can be made. This work gives the results of the functionality to the ASPEN Custom Modeler software, as well as optimization tool inside. This is the first time that a reduced model for agriculture substrates is coded in ACM to optimize the process. Moreover, this tool will enable operators to easily evaluate the process and take actions for better performance in real time (see section 5.7).

5) AM2 on Aspen plus

The simulation by using the new version of AM2 is not only helpful when predicting the process, it can also aid to avoid production failures or disturbances, whereby, along with optimization, it is possible to gain improved profitability as in the example of the optimization of the co-digestion process presented in the results. Aspen Plus is able to incorporate dynamic process modeling into a platform to create simulations for a better analysis of the process. In this project, once the new extended version of AM2 was written in ASPEN, the simulation and the optimization of the process were successfully performed due to the feasibility of the program to handle customized models. This is a clear example when benefits of a program use can facilitate to study any other subject; such as the study of LCA in manuscript VI. This is the first time that a reduced model as AM2 for codigestion of agriculture substrates and cattle manure is used for an LCA study.

7.0. Conclusions

-The construction of the extended anaerobic digestion model AM2 involved assumptions and wide research in scientific concepts to be adapted into the process. Throughout this proceeding, modifying parts of the system were sometimes needed to solve the experimental part as the modification growth rate equations of acidogenic and methanogenic bacteria and the incorporation of the hydrolysis equation into the system. In general terms, only by using modelling tools it was possible to predict the process. The development of a high-quality and validated model as the new AM2 model of anaerobic digestion is justified not only for the research trend to increase the knowledge about the process, but mainly for the economic and environmental benefits generated by model-based predictions of anaerobic digestion of agricultural substrates and livestock manure for biogas production, simulation, and optimization.

-Anaerobic digestion is a complex system and collects different behavior of bacteria in which a countless number of reactions occur and different consortia of microorganism coexist in the medium. The development of AM2 for energy crops and cattle manure involved the increase of equations, variables and parameters to associate with a view to attain a real simulation and to describe the process in a wide range of different scenarios. Relevant information was included into the model in order to realistically describe the system such as substrate characterization, which was calculated based on the Weender analyses. The procedure consists in the determination of the fractioning of the substrate into proteins, lipids and carbohydrates. Subsequently, the data was used to calculate the influent composition of each feedstock. This procedure is also followed when ADM1 is applied, nevertheless, this time using a reduced model as AM2.

-The application of an optimization method helped to develop an efficient dynamic operation of the biogas process using the ratio VFA/alkalinity (FOSTAC); thus, the risks of an inefficient process are reduced. In order to perform this method, a robust and manageable model such as AM2 was able to predict the dynamics of the process with adequate precision. In the digestion process, installations of sensors in the liquid phase in digesters are usually not sufficient for the fast detection of disturbances. Thus, the use of monitoring and control strategies is limited. Only robust, tractable and identifiable models as the new version of AM2 can be used to fit the demands of large-scale biogas production plants.

-In this thesis, the comparison between the AM2 and the ADM1, in terms of complexity and tractability to obtain reliable and quality results, was performed. While ADM1 is a complex and not user-friendly model including 36 states and more than 80 parameters, AM2 is a tractable model developed for control strategies with only six states. Structural identifiability of a model is a precondition for a successful parameter estimation (Lauwers et al., 2015). Furthermore, both models accurately simulate biogas, methane and state variables as X1, X2, S1, S2, C, Z and pH. Nevertheless, ADM1 is structurally unidentifiable if the data from a usual biogas plant is applied to the model. Taking this into consideration, the implementation of the AM2 in an adaptive framework should be preferred.

-The feed control of large-scale biogas plants is commonly carried out by operator experiences in the process. A first attempt towards a closed loop control is the availability of a suitable model. One objective of this study was to evaluate the performance of AM2 for the application at dynamic process operation when fluctuating feedstock load is present in the process. In terms of optimization and control of the process, the AM2 model has the appropriate structure to be used as a model for process optimization strategies.

8. Outlook

The AM2 is a tractable and flexible model to be adjusted according to operators' needs. It may be applied for new substrates, changes in operating conditions, different designs of digestions or even for the instruction and training of process operators.

The AM2 model may be used for a further investigation of the degradation of the substrates, instability cases (like organic overloading or variation of environmental conditions) and other configurations of biogas fermenters.

An anaerobic digestion approach such as the AM2 should be recognized not only as a mechanism exclusive to predict the process, but also as a future tool to show the economic, technical and environmental benefits it achieves. Moreover, an application of AD models means that single urban districts could be, in the future, self-supported in terms of electricity, heat, motor fuel and creation of useful by-products from wastes.

As mention in 1.2.1, the success of biogas can be only assured when there is availability of seasonal substrates in the region; in Mexico and in some vast regions of the american continent several types of Opuntia among a variety of 300 of them seem to be substrates with great potential for the production of energy through anaerobic digestion. In this case, the model AM2 offers an outstanding advantage for the investigation of the feedstock.

The development of biogas faces many challenges, in which power producers, technology providers, agricultural sectors, the food and beverage industry, waste industry, solution providers are all involved. In terms of process operation, the optimization of feed loading of feedstock to obtain the maximum methane production for a flexible process is a challenge; however, the use of the AM2 model within the platform Aspen Customer Modeler will facilitate the optimization process for any feedstock.

Appendix

Table A-1. ADM1 equations

Biochemical process rates (19 equations)	Eq.
$\rho 1 = kdis \cdot Xc$	1
$\rho 2 = khyd,ch \cdot Xch$	2
$\rho 3 = khyd,pr \cdot Xpr$	3
$\rho 4 = khyd,li \cdot Xli$	4
$\rho 5 = km,su \cdot \frac{Ssu}{KS,su + Ssu} \cdot Xsu \cdot I5$	5
$\rho 6 = km,aa \cdot \frac{Saa}{KS,aa + Saa} \cdot Xaa \cdot I6$	6
$\rho 7 = km,fa \cdot \frac{Sfa}{KS,fa + Sfa} \cdot Xfa \cdot I7$	7
$\rho 8 = km,c4 \cdot \frac{Sva}{KS,c4 + Sva} \cdot Xc4 \cdot \frac{Sva}{Sbu + Sva + 1e-6} \cdot I8$	8
$\rho 9 = km,c4 \cdot \frac{Sbu}{KS,c4 + Sbu} \cdot Xc4 \cdot \frac{sbu}{Sva + Sbu + 1e-6} \cdot I9$	9
$\rho 10 = km,pro \cdot \frac{Spro}{KS,pro + Spro} \cdot Xpro \cdot I10$	10
$\rho 11 = km,ac \cdot \frac{Sac}{KS,ac + Sac} \cdot Xac \cdot I11$	11
$\rho 12 = km,h2 \cdot \frac{Sh2}{KS,h2 + Sh2} \cdot Xh2 \cdot I12$	12
$\rho 13 = kdec,Xsu \cdot Xsu$	13
$\rho 14 = kdec,Xaa \cdot Xaa$	14
$\rho 15 = kdec,Xfa \cdot Xfa$	15
$\rho 16 = kdec,Xc4 \cdot Xc4$	16
Acid-base rates (6 equations)	
$\rho A,4 = kA,Bva(Sva-(Ka,va + SH+)-Ka,vaSva)$	21
$\rho A,5 = kA,Bbu(Sbu-(Ka,bu + SH+)-Ka,buSbu)$	22
$\rho A,6 = kA,Bpro(Spro-(Ka,pro + SH+)-Ka,proSpro)$	23
$\rho A,7 = kA,Bac(Sac-(Ka,ac + SH+)-Ka,acSac)$	24
$\rho A,10 = kA,Bco2(Shco3-(Ka,co2 + SH+)-Ka,co2SIC)$	25
$\rho A,11 = kA,BIN(Snh3(Ka,IN + SH+)-Ka,INSIN)$	26
Gas transfer rates (3 equations)	
$\rho T,8 = kLa(Sh2 - 16 \cdot KHH,h2pgas,h2)$	27
$\rho T,9 = kLa(Sch4 - 64 \cdot KHH,ch4pgas,ch4)$	28
$\rho T,10 = kLa(Sco2 - KHH,co2pgas,co2)$	29

ρTj = individual reaction rates

Table A-2 Applications of ANN on AD

Method	Feedstock/Process	Input	Output	Validation	Uncertainty	Reference
ANN, Multilayer, two hidden layers	organic waste /full-scale plant (60 tons/day), wet process	Temp., TS, VS, pH, 177 data points	methane producction	50 data points	R^2= 0.87	(Qdais et al., 2010)
fuzzy-logic, MIMO (multiple inputs and multiple outputs) + non linear regression analysis	molases waste water\pilot plant, 0.090 me, in up-flow anaerobic sludge blanket (UASB)UASB	OLR, TOD remola	biogas producction	40 data point	R2=0.98, r=0.97 for both biogas and CH4 R2=0.87, r=0.91 for biogas R2=0.89 r=0.92 for CH4	(Turkdogan-Aydınol and Yetilmezsoy, 2010)
ANN, multilayer, one hidden layer	molasses/lab. scale plant, 0.0075 m3, UASB, thermophilic	OLR, temp. influent alkalinity, pH, effluent VFA, alkalinity, 60 data point	biogas producction	60 data point	r=0.681 r=0.927 for 5 days moving average	(Kanat and Saral, 2009)
ANN, one hidden layer	te water/lab-scale, ATFBR, 0.0078 m3	OLR, pH	organic load removal rate, biogas production	30% of date	R2=0.999 R2=0.997	(Parthiban et al., 2007)

Table A-3 Chemical composition of maize silage, grass silage and cow manure

Component	Maize [%]	Grass Value [%]	Cattle manure Value [%]
Water	66.6 [a)]	62.6 [a)]	90.7 [b)]
Dry matter (*DM*)	33.4 [a)]	37.4 [a)]	9.3 [b)]
Organic dry matter (*ODM*)	81.7 [b)]	89.8 [b)]	81.7 [b)]
Crude ash (*CA*)	1.1 [a)]	3.1 [a)]	-
Crude protein (*CP*)	2.8 [a)]	4.0 [a)]	12.2 [b)]
Crude lipids (*CL*)	1.1 [a)]	0.97 [a)]	4.3 [b)]
Crude fiber (*CF*)	4.8 [a)]	8.8 [a)]	17.8 [b)]
Sugar as sucrose	3.1 [a)]	6.8 [a)]	-
Neutral detergent fiber (*aNDF*)	11.2 [a)]	17.9 [a)]	-
Acid detergent fiber (*ADF*)	5.7 [a)]	10.4 [a)]	-
Acid detergent lignin (*ADL*)	0.55 [a)]	0.97 [a)]	-

Table A-4. Parameter of conversion to COD values [a)]

Parameters	Value [kgCOD kgDM^{-1}]
Carbohydrates (*cfch*)	1.18
Proteins (*cfpr*)	1.53
Lipids (*cfli*)	2.86
Inerts (*cfi*)	1.38

[a)]

Table A-5 Parameters of soluble components in maize silage [a)]

Parameters	Value [% COD]
Inerts (S_i)	2.5
Monosaccharides (S_{su})	1.3
Total long chain acids (LCFA) (S_{fa})	0.0
Total acetate (S_{ac})	0.0
Amino acids (S_{aa})	0.0

[a](Wichern et al., 2008)

Table A-6 Quantitative characterization of the maize silage components

Component	Unit	Value
Ssu_{in}	kgCOD m^{-3}	0.00000
Saa_{in}	kgCOD m^{-3}	0.00000
Sfa_{in}	kgCOD m^{-3}	0.00000
Sva_{in}	mol m^{-3}	0.00000
Sbu_{in}	mol m^{-3}	0.00000
$Spro_{in}$	mol m^{-3}	0.00000
Sac_{in}	mol m^{-3}	4.76109
S_{ICin}	mol m^{-3}	0.00000
Xc_{in}	kgCOD m^{-3}	35.0483
Xch_{in}	kgCOD m^{-3}	185.4890
$pXpr_{in}$	kgCOD m^{-3}	37.44800
Xli_{in}	kgCOD m^{-3}	27.17700
Xi_{in}	kgCOD m^{-3}	67.15628

Table A-7. Influent composition of grass silage and cow manure for the AM2 simulation

Component	Unit	Maize silage value	Grass silage value	Cow manure value
$S1_{in}$	kgCOD m^{-3}	285.16	314.0	73.14
$S2_{in}$	mol m^{-3}	74.41	155.0	379.8
Z_{in}	mol m^{-3}	545.15	454.8	579.56
C_{in}	mol C m^{-3}	470.75	299.8	200.56
Xc_{in}	kgCOD m^{-3}	35.04	35.0	10.59
Xch_{in}	kgCOD m^{-3}	185.48	220.0	28.43
Xpr_{in}	kgCOD m^{-3}	37.44	47.69	9.31
Xli_{in}	kgCOD m^{-3}	27.17	11.69	6.13

CV

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Modeling and parameter estimation of a biogas plant using maize silage in a two step model

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ABSTRACT: The increasing demand for efficient systems for methane production from biomass has led to the deeper investigation of model predictive control strategies considering the yield and process stability under flexible operation. Most published work uses the complex ADM1 model as basis for the mechanistic description of the anaerobic digestion process. Unfortunately, the ADM1 has shown to be too complex for its application with respect to the usual monitoring capacities at biogas plants. Therefore, the present research proposes the application of the AMOCO two-step model which has a comparably simple structure requiring less experimental data. Results from a pilot-scale biogas reactor show the proper modeling of the pH value, methane and biogas production in two 50 liter reactors for 80, and 92 days, respectively. In total, thirteen parameters were optimized using Matlab 2013B and a non-linear regression toolbox that uses the Gauss-Newton method.

1 INTRODUCTION

In the European Union the leading countries concerning the installed biogas capacity are Germany, Denmark, Austria and Sweden. One of the main drivers behind this rapid expansion in the biogas field in Germany was the support by the government. These days many criticism came along with the utilization of corn and the land use in general. However, the production of energy from a clean and renewable source remains one key issue in near future. Therefore, the installed biogas production needs to be optimized in order to increase the efficiency and flexibility of the applied feedstock and integrate biogas production better into local carbon circles and face the problems discussed in science and public (Bachmaier et al., 2010).

Today, biogas production primarily results from energy crops (59%), animal residues (24%), wastewater (5%), municipal wastes (3%), harvest residues (3%), landscape (2%), industrial wastes (2%) and landfill (2%) (Weiland, 2010). In general, the anaerobic digestion (AD) is a complex biological process where myriad of microbial population are involved and some technological and operating difficulties due to the high sensitivity of the biological system exist. Instability of the process due to acidification is the main issue to be considered. Process control can improve such instability of the system by keeping the acid concentration within safety limits, while allowing sustainable and regular production of methane.

AD is a natural biological process when bacteria break down organic matter in environments with little or no oxygen (Molino et al., 2013). A number of models applied to this digestion have been developed to predict and control the process, from the first model which appeared in 1965 involving only some differential equations, subsequently, appeared more interesting models involving more complex biochemical processes, such as Siegrist et al., (2002), Vavilin & Lokshina (2006) and Angelidaki & Ahring (1999). It was until 2002, when a more structured model was presented, the ADM1 model (Bastone et al., 2002), which comprises dozens of series of linked reactions associated with converting complex organic substrates into CH_4 and CO_2 in biochemical and physico-chemical processes. In the year 2001 appeared the two step AMOCO model, which was developed within the framework of a European Economic Community project (AMOCO, FAIR program). This model was required for the design of monitoring and control of the anaerobic sludge digestion process. Simple models have considered biogas production using only the methanogenesis stage, because it was considered rate-limiting for solutes (Andrews 1969). The AMOCO model was a modification of the model from (Graef and Andrews, 1974) which included equations to describe the interaction between gas,

liquid and biological phases in a closed-flow reactor having a complete continuous mixed liquid region, the model also considered the formation of methane as a rate-limiting step in the conversion of the organic compounds to methane and carbon dioxide and proposed an inhibition expression for organism growth rate. The AMOCO model has a more suitable structure to represent the destabilization phase while introducing a second bacterial population. Moreover, it describes the gaseous flow rate in terms of chemical and biological species in detail. The model also incorporates a total alkalinity balance, which is defined as the sum of dissociated acids in the medium, the bacterial populations are divided into two groups of homogeneous characteristics, and the anaerobic digestion can be represented by a two stage process. In the first step (acidogenesis), the acidogenic bacteria (X_1) consume the organic substrate (S_1) and produce CO_2, and volatile fatty acids, VFA (S_2) .The population of methanogenic bacteria (X_2) uses, in a second stage, the volatile fatty acids as substrate for growth, and produce CO_2 and methane. The model assumes that the reactor behaves like a perfectly mixed tank and the biomass is uniformly distributed within the reactor (Bernard et al., 2001).

The scope of this work is to show the application of the AMOCO model using maize silage in two steps: (i)-for the application of the two step anaerobic digestion AMOCO model, and in order to test the ability of the dynamic behavior of reproducibility in a real system, the model was applied in the software Matlab 2013b for the simulation of a biogas process in two reactors of 50 Liters; (ii)- the optimization of 13 parameters using the Gauss Newton method to solve the non-linear least squares system.

2 MATERIALS AND METHODS

The model was applied to two 50 liter tank reactors completely stirred (circular of 0.6 m height and 0.45 m diameter) located at IASP laboratory of Humboldt University in Berlin. Biogas flow, methane content in the gas phase, temperature, volume and the pH-value were measured online. The process was operated at a defined hydraulic retention time (HRT) and organic loading rate (OLR) of substrate composed of maize silage as presented in Table 1. The experiment was carried out during 80 days in reactor 1 and 92 days in reactor 2. Reactors were equipped with mechanical mixer and fed manually including monitoring and control systems. The reactors were operated at mesophilic conditions at an average temperature of 38.7ºC for reactor 1 and 39.1ºC for reactor 2.

Table 1. Hydraulic retention time (HRT) and organic loading rate (OLR) for reactor 1 and 2

Reactor 1			
Time [d]	Hydraulic Retention Time,HRT [d]	Organic Loading Rate, OLR [g /(l*d)]	Concentration Maize Silage
0.63	37.65	2.39	1
4.5	36	2.78	1
18.6	34.48	3.18	1
40.6	33.09	3.58	1
80	33.09	3.58	1
Reactor 2			
Time [d]	Hydraulic Retention Time,HRT [d]	Organic Loading Rate, OLR [g /(l*d)]	Concentration Maize Silage
0.63	37.65	2.39	1
4.5	36	2.78	1
18.6	34.48	3.18	1
40.6	33.09	3.58	1
83.6	31.8	3.98	1
92	33.09	3.58	1

All along the anaerobic digestion process of the two reactors feeding pulses were carried out, the time period of each pulse lasted between 10 and 20 minutes and consisted of only solid substrate, the organic substrate concentration S_1 (g L^{-1}) and the feeding day is depicted in Figure 1 for both reactors.

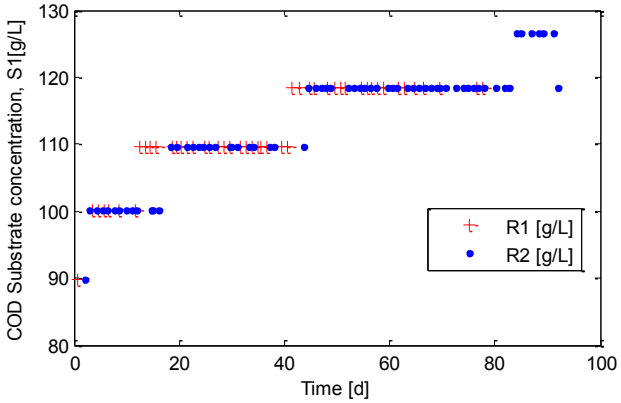


Figure 1. Organic substrate concentration and feeding time, each mark represents one dosage of substrate for reactor 1 and 2.

3 MATERIALS AND METHODS

In AD, several groups of bacteria and archea work in synergy to produce methane and carbon dioxide (Rajendran et al., 2014). Biogas is obtained through two important stages: at a first stage, acetogenic bacteria (acid formers) convert the substrate to simple organic acids, carbon dioxide and hydrogen.

The main acidic compounds produced are acetic acid (CH_3COOH), propionic acid (CH_3CH_2COOH), butyric acid ($CH_2CH_2CH_2COOH$), and ethanol (C_2H_5OH). A number of different microbes involved during acetogenesis, e.g. S*yntrophobacter wolinii*, propionate decomposer and S*ytrophomonas wolfei*, a butyrate decomposer. Other acid formers are *Clostridium* spp. *Petococcus anaerobius*, *Lactobacillus* and *Actinomyces* (Molino et al., 2012).

During the second stage, methane is produced by bacteria called methanogens, the process may occur in two ways: either by means of cleavage of acetic acid molecules to generate carbon dioxide and methane, or by reduction of carbon dioxide with hydrogen. Methanogenic bacteria include *Methanobacterium*, *Methanobacillus*, *Methanococcus* and *Methanosarcina*. Methanogens can also be divided into two groups, namely acetate, and H_2/CO_2 consumers, respectively. *Methanosarcina* spp. and *Methanothrix* spp. (also, *Methanosaeta*) are considered as acetate and H_2/CO_2 consumers (Molino et al., 2012).

3.1 *Biological reaction pathways*

The two biological reactions involved in the two-step process are the following:

-Acidogenesis step

$$k_1 S_1 \xrightarrow{r_1} X_1 + k_2 S_2 + k_4 CO_2 \quad (1)$$

-Methanization step

$$k_3 S_2 \xrightarrow{r_2} X_2 + k_5 CO_2 + k_6 CH_4 \quad (2)$$

where S_1= Organic substrate concentration, characterized by its COD (gL^{-1}); S_2 = Total concentration of VFA ($mmolL^{-1}$) composed of acetate, propionate and butyrate, basically behaves like pure acetate. μ_1 and μ_2 = Specific growth rates of acidogenesis and methanization respectively(d^{-1}).

3.2 . *Chemical species*

The Inorganic carbon mainly composed of dissolved CO_2, bicarbonate (B) and carbonate, which is considered negligible in comparison with bicarbonate at operation conditions of a pH-value between 6 and 8 and temperatures between 35 and 38 °C. Total concentration of VFA is composed of ions S^- (mainly acetate) and un-ionized SH (mainly acetic acid).

3.3. *Two step-model*

The mass balance model was published in the year 2001, variables were denoted using the vector $\xi=[X_1, X_2, Z, S_1, S_2, C]$, the model includes six ordinary differential equations.

$$-\frac{dX_1}{dt} = [\mu_1(\xi) - \alpha D]X_1 \quad (3)$$

$$-\frac{dX_2}{dt} = [\mu_2(\xi) - \alpha D]X_2 \quad (4)$$

$$-\frac{dZ}{dt} = D(Z_{in} - Z) \quad (5)$$

$$-\frac{dS_1}{dt} = D(S_{1in} - S_1) - k_1\mu_1(\xi)X_1 \quad (6)$$

$$-\frac{dS_2}{dt} = D(S_{2in} - S_2) - k_2\mu_1(\xi)X_1 - k_3\mu_2(\xi)X_2 \quad (7)$$

$$-\frac{dC}{dt} = D(C_{in} - C) - qc(\xi) + k_4\mu_1(\xi)X_1 + k_5\mu_2(\xi)X_2 \quad (8)$$

The kinetics for the growth of acidogenic bacteria μ1, and methanogenic bacteria μ2 are:

$$\mu_1(S_1) = \mu_{1\max}\frac{S_1}{S_1 + K_{S1}} \quad (9)$$

$$\mu_2(S_2) = \mu_{2\max}\frac{S_2}{S_2 + K_{S2} + \frac{S_2^2}{K_{I2}}} \quad (10)$$

$$q_c(\xi) = k_L a[C + S_2 - Z - K_H P_C(\xi)] \quad (11)$$

$$P_c(\xi) = \frac{\phi - \sqrt{\phi^2 - 4K_H P_T(C + S_2 - Z)}}{2K_H} \quad (12)$$

$$\varphi = C + S_2 - Z + K_H P_T + \frac{k_6}{k_L a}\mu_2(\xi)X_2 \quad (13)$$

$$q_M(\xi) = k_6\mu_2 X_2 \quad (14)$$

$$pH(\xi) = -\log_{10}(k_b\frac{C - Z + S_2}{Z - S_2}) \quad (15)$$

Values of amount of ammonia and volatile fatty acids for maize silage were obtained from Table 2 (Khan et al., 2012).

Table 2. Ensiling quality and fatty acid contents of maize silages (n=96 used in the experiment)

	Mean	SD	Minimum	Maximum
DM[#]	342	26.1	250	568
Ensiling quality*				
pH-value	3.84	0.135	3.9	4.4
NH3–N[e]	9.32	2.954	2.67	17.00
Fatty acids, g/kg DM				
Total fatty acids	19.98	3.305	12.37	35.25

*Predicted through near infrared reflection spectroscopy (NIRS) by Blgg, Oosterbeek, The Netherlands

[#]Fresh matter determined through freeze drying

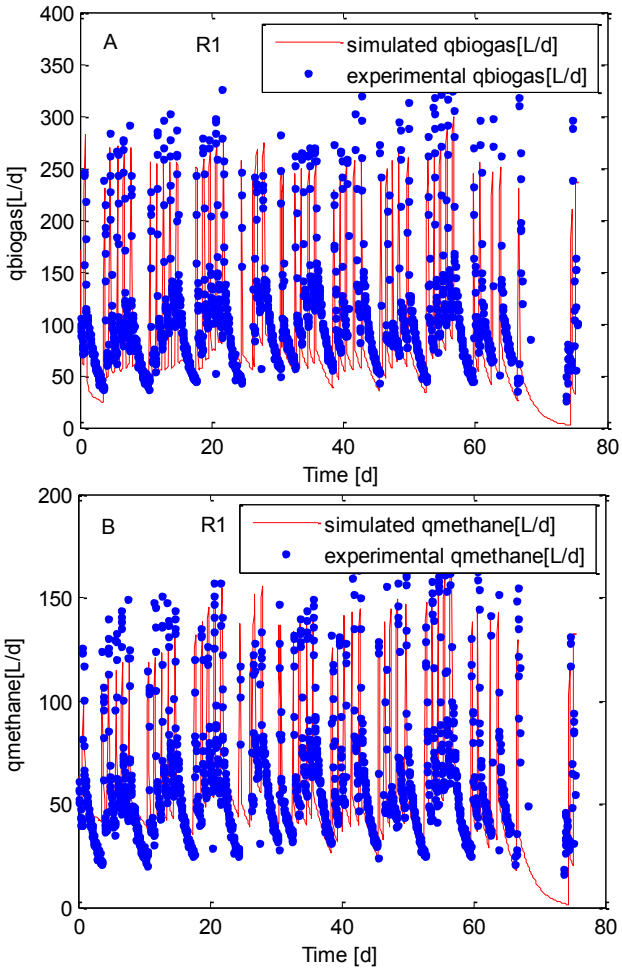
[e]Ammonia N g/100 g total

3.3 *Key indicators for digestors' stability*

Process upsets may result from temporal high load, deviations in the environment provided or the presence of toxic or inhibitory materials in the bioreactor influent (Grady et al., 1999). Usually proposed parameters for monitoring the stability of the process are: 1) pH value, 2) gas production rates and gas phase composition (methane and carbon dioxide), 3) gas phase hydrogen concentration, 4) volatile acids to alkalinity ratio, and 5) the acetate capacity number (ACN).The first four mentioned are commonly observed for detecting gradual changes during the process (Conklin et al., 2008; Switzenbaum et al., 1990). In general, values of the VFA/alkalinity ratio expressed in equivalents of the components are between 0.1 and 0.4 indicating favorably operation conditions without the risk of acidification. If the ratio exceeds 0.8, inhibition of methane production might occur and the process fails operation (Shoen et al., 2009). The VFA/alkalinity ratio values resulted from the model are between 0.1 and 0.6 at the two bioreactors.

4 RESULTS

In Figure 2, experimental data and model show the variation pattern of biogas and methane in form of fluctuations corresponding to the feed of substrate.



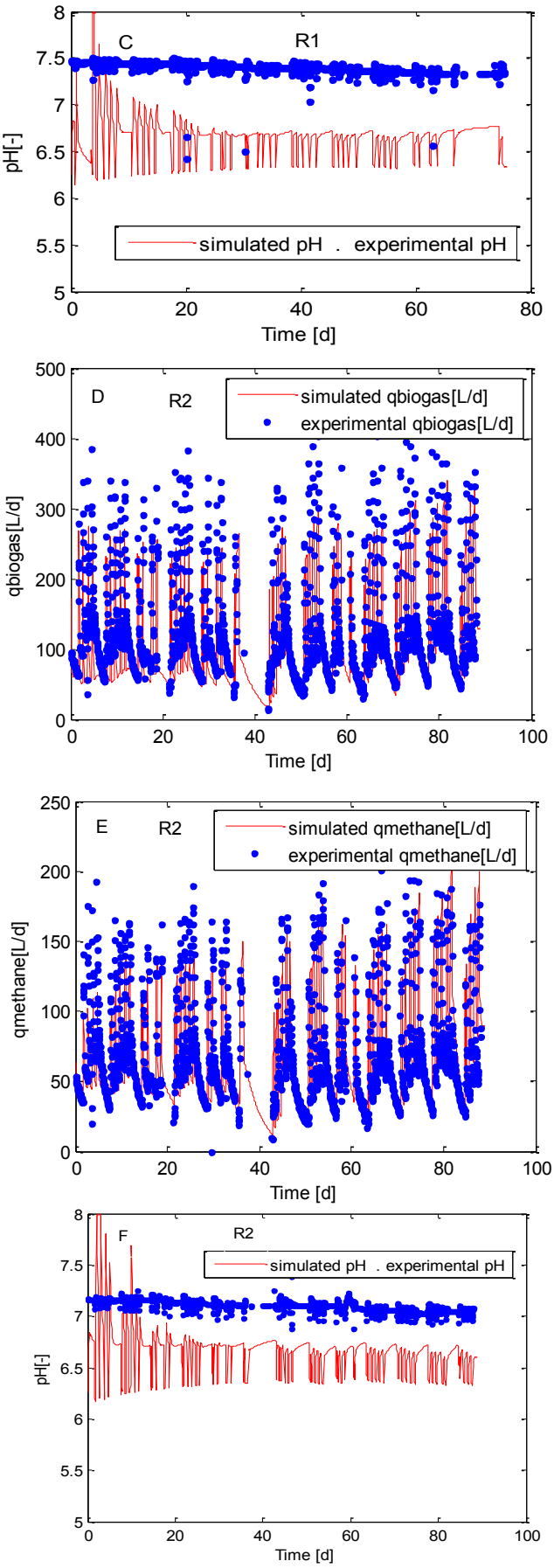


Figure 2. Experimental data and simulation results for reactor 1 and 2 applying maize silage as substrate. A. Biogas flow R1; B. Methane flow in the gas phase, R1; C. The pH values, R1 D. Biogas flow, R2; E. Methane flow in gas phase, R2; F. The pH values R2.

Calibration results of the application of the AMOCO model to the mono-fermentation of maize silage are shown in Table 3. The function nlinfit from MATLAB was used, the initial parameters were taken from a raw industrial wine distillery wastewater treatment plant (Bernard et al., 2001).

Table 3. Optimized and initial parameters

Parameter	Unit	Initial values	Maize Silage values
μ_{1max}, Maximum acidogenic bacteria growth rate	d^{-1}	1.2	4.2
μ_{2max}, Maximum methanogenic bacteria growth rate	d^{-1}	0.74	1.0
K_{S1}, Half-saturation constant	g^{-1}	7.1	469.1
K_{S2}, Half-saturation constant	$mmolL^{-1}$	9.28	150.2
K_{I2}, Inhibition constant	$mmolL^{-1}$	256	250
α, Fraction of bacteria in the liquid phase	[-]	0.5	0.2
k_{La}, Liquid-gas transfer constant	d^{-1}	19.8	19.8
k_1, Yield for substrate degradation	$mmolg^{-1}$	42.14	3.14
k_2, Yield for VFA production	$mmolg^{-1}$	116.5	155
k_3, Yield for VFA consumption	$mmolg^{-1}$	268	300
k_4 Yield for CO_2 production	$mmolg^{-1}$	50.6	80.6
k_5, Yield for CO_2 production	$mmolg^{-1}$	343.6	3.6
k_6, Yield for CH_4 production	$mmolg^{-1}$	453.0	350

4.1 *Optimization of parameters*

Optimization was carried out by using the Gauss Newton's method through the nlinfit function in Matlab. Initial parameters were used from the paper (Bernard et al, 2001), since so far no information of estimating parameters applied to an anaerobic process for biogas production using this two-step model operated with maize silage.

Parameters of the kinetic equations for the growth of acidogenic and methanogenic bacteria such as μ_1, μ_2, K_{S1} and K_{S2} were the most sensitive parameters showing high biogas and methane production variation, especially μ_1 has shown to have a high sensitivity for biogas production, especially in the early hours of modeling and during stabilization. The maximum growth rate for the methanogenic bacteria μ_2 exhibited low sensitivity to the process in comparison with μ_1. Already in the differential equations of the mass balances, the inorganic carbon concentration is affected by the variation on k_4, as it can be noticed in the values before and after optimization. This effect might be expected in the third term of equation 8 where parameter changes affect mainly the production of CO_2. The parameter k_6 has an effect only in methane production as deduced from equation 6, as it is the only equation affected. The variation shown by parameters k_1, k_2, and k_3 was not significant, values are similar before and after the estimation procedure. The constant k_5 did not show a significant effect on the production of CO_2, however k_4 has a relevant effect. Other parameters as k_{La}, α and K_{I2}, had no significant effects on the simulation results.

5 CONCLUSIONS

Anaerobic digestion is a complex process involving several groups of bacteria and substrates. With the progress in instrumentation and computer science, it is possible to measure online the main process variables, develop and apply mathematical models to fit the dynamic processes. The AMOCO model is definitely a model that is applicable for model-based process control.

The two-step mass balance model in mesophilic conditions was evaluated using experimental data from lab-scale biogas processes. The results show a properly calibrated model to the real system, which was validated through two reactors of the same volume. The AMOCO model was applied under dynamic conditions, which allowed the identification of all the parameters of the model.

The production of biogas and methane over 80 days of fermentation for reactor 1 and 92 days of reactor 2 under secure limits of acid concentration assured the system stability. Moreover, the pH value profile in both reactors were among the main indicators of suitable process conditions for the fermentation using maize silage as a substrate although the fluctuation is dependent on the buffer capacity of the media.

Experiments were conducted covering various scenarios in operating conditions such as hydraulic retention time (HRT) and organic loading rate (OLR) in order to validate the model applied in two reactors of the same capacity.

The AMOCO model is easy to simulate and incorporates all important processes of anaerobic digestion. Hence, it is advisable to use and prevent stiffness that may occur in handling complicated mathematical systems like for example the ADM1 model.

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NOMENCLATURE

C, C_{in} total inorganic carbon concentration($mmolL^{-1}$)
D dilution rate (d^{-1})
HRT hydraulic retention time, [d]
OLR organic loading rate, [g / (L*d)]
d/dt time derivative
k_1 yield for substrate degradation
k_2 yield for VFA production ($mmolg^{-1}$)
k_3 yield for VFA consumption ($mmolg^{-1}$)
k_4 yield for CO_2 production ($mmolg^{-1}$)
k_5 yield for CO_2 production ($mmolg^{-1}$)
k_6 yield for CH_4 production ($mmolg^{-1}$)
K_H Henry´s constant (mmol/L per atm)
k_La liquid-gas transfer constant (d^{-1})
K_{I2} inhibition constant ($mmolL^{-1}$)
K_{S1} half-saturation constant (gL^{-1})
K_{S2} half-saturation constant ($mmolL^{-1}$)
Pc CO_2 partial pressure (atm)
P_T total pressure (atm)
q_c carbon dioxide flow rate (mmol/L per d)
r reaction rates (d^{-1})
r_1 reaction rate acidogenesis step (d^{-1})
r_2 reaction rate methanogenic step (d^{-1})
S_1, S_{1in} organic substrate concentration (gL^{-1})
S_2, S_{2in} volatile fatty acids concentration ($mmolL^{-1}$)
X_1 concentration of acidogenic bacteria (gL^{-1})
X_2 concentration of methanogenic bacteria (gL^{-1})
Z, Z_{in} total alkalinity ($mmolL^{-1}$)
α fraction of bacteria in the liquid phase
μ_1 specific growth rate of acidogenic bacteria (d^{-1})
μ_{1max} maximum acidogenic bacteria growth rate(d^{-1})
μ_2 specific growth rate of methanogenic bacteria (d^{-1})
μ_{2max} maximum methanogenic bacteria growth rate (d^{-1})

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LIFE CYCLE ASSESSMENT AND MODELING APPROACHES FOR BIOGAS PRODUCTION

Abstract: *Biogas production as a complex biological process requires tailored solutions to achieve a real sustainable operation. In this regard, better control, monitoring and optimization strategies are required. If the objective is the optimal design and operation of a biogas production while reducing the GHG, it is useful to combine LCA and mathematical modelling approaches. Thus, this study evaluates the biogas production in an industrial plant located in Irland. The plant operates with the co-digestion of grass, maize and clover silage and produces 500 kW energy. LCA was performed by using Simapro software to determine the environmental impacts of the operation. The mathematical modelling was realized by ASPEN, which enables a process description based on stoichiometric biochemical networks.*
Key words: *Case study, mathematical modeling, Life cycle assessment, biogas production, ASPEN*

1. INTRODUCTION

Biogas production plays a remarkable role to reach European Union´s goal, which is enhancing the renewable energy ratio to 20 % and to cut the greenhouse gas (GHG) emissions by 20% until 2020 [2].

Nonetheless, biogas production is a complex process and many challenges still should be unraveled to attain a maximum of sustainability during operation. In this regard, improved control, monitoring and optimization strategies are necessary. Though, if the objective of the biogas production is the reduction of GHG, the impacts of each component and procedure should be quantified. To achieve this, life cycle assessment (LCA) need to be performed. From scientific concepts including experimental trials to the application of statistical methods using experimental data records, several modelling approaches for describing the anaerobic digestion (AD) have been developed. In 2014, a novel model applied to AD, which is using ASPEN was published [3]. The model included several reactions considering four phases in the metabolic process. The hydrolysis phase was related to the conversion of reactants from macromolecules to short-chain compounds. Acidogenic, acetogenic, and methanogenic phases were described by kinetic equations depending on temperature, pH-value, compound concentrations and inhibitory effects. The kinetic constants of the reactions were obtained from previous models like the anaerobic digestion model 1 (ADM1) and others [4, 5]. The modelling approach used in the current paper uses a model based on ASPEN [6]. Moreover, this paper examines the accurateness of the combination of process modelling and LCA for biogas production for the aim of GHG emission reductions.

However, such a method requires accurate data of operation. To be independent of data availability to foresee scenarios for improved operation, the development and application of suitable mathematical models is required [7]. They should be able to simulate the operation with sufficient accuracy and limited computational effort. Data of these simulation studies are integrable to LCA studies. Such an approach permits the forecast of different production scenarios and a seemly choice of the one with fewer GHG emissions [8].

2. METHODS

2.1. Life cycle assessment

LCA is a method that is utilized to quantitatively assess the environmental benefits of all process steps. In this study, the stages from feedstock production to electricity generation were considered. The standard ISO 14040:2006, which provides the fundamental basis for LCA procedures was pursued [9].

Due to data availability, the scope of the assessment is the southwest region of Ireland [10, 11].

2.1.1. System boundary

Fig. 1 shows the examined system, its boundary and involved processes:

- crop production
- ensilage and storage
- manure storage
- anaerobic digestion

- storage of digestate and its spreading
- electricity and heat generation from biogas
- transport between several process steps.

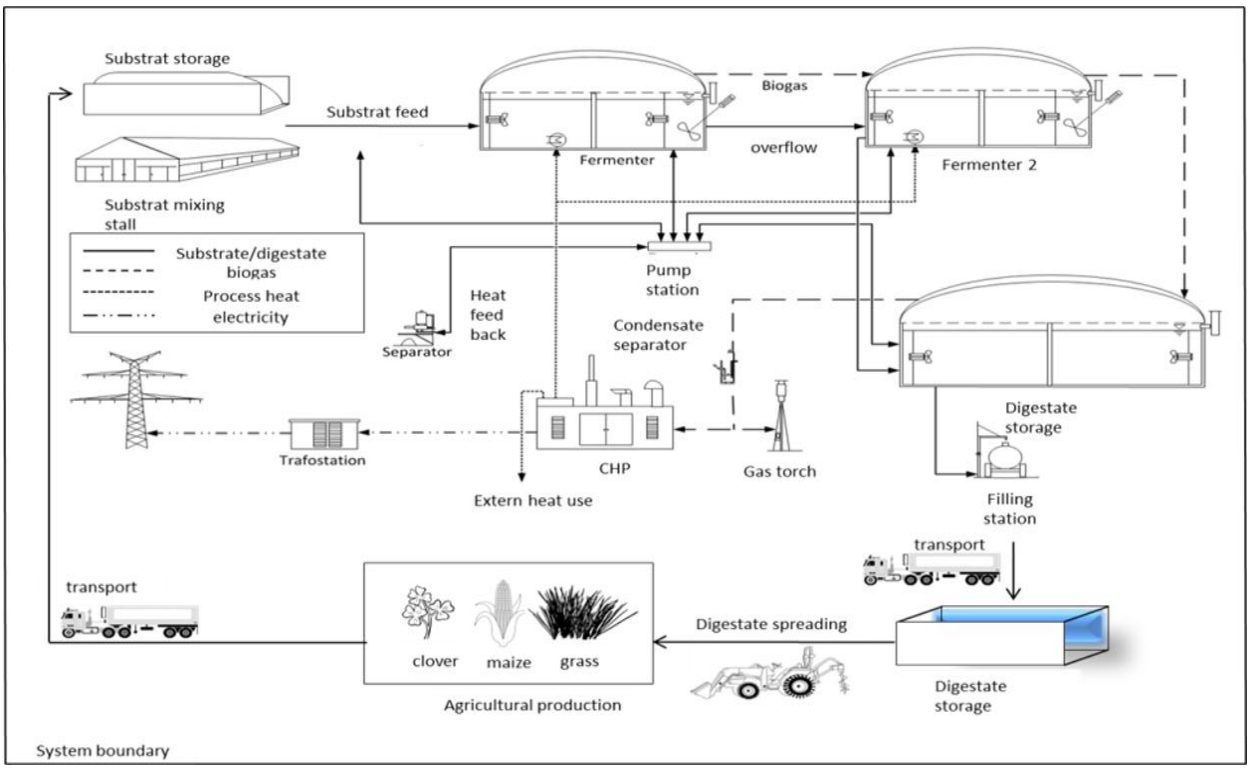

Fig. 1. System boundary. Images for ArcClip were used to adapt from KTBL [1].

Poultry manure was not considered, since it is considered as product from another process. Four different scenarios are created, where GHG emission changes are determined for each of the codigestion ratios. Substrate amounts for each scenario are provided in Table 1.

Feedstock	Maize	Clover	Grass
TS (% FM)	35	30	35
oTS (% TS)	95	90	90
Gas yield ($m^3 t^{-1}$ FM)	189	156	216,1
Methane content (%)	52	55	53
Real Situation ($t a^{-1}$)	5940	1374	2181
Scenario 1 ($t a^{-1}$)	5000	2894	2000
Scenario 2 ($t a^{-1}$)	4000	4279	2000
Scenario 3 ($t a^{-1}$)	3000	5664	2000
Scenario 4 ($t a^{-1}$)	2000	7049	2000

Table 1. Characteristics of the feedstock [1, 12]. TS: Total Solid, oTS: organic Total Solid, FM: Fresh

2.1.2. Life cycle inventory analysis

The yearly operational data for the biogas plant was used and literature data was complimented whenever required. The production of construction materials, tractor, cogeneration unit were taken from the database of Ecoinvent 2.2 (the Ecoinvent Centre, Switzerland) [13].

2.1.3. Determination of feedstock amounts and compositions

The functional unit (FU) is a measure of the function of the studied system. It provides a reference, to which the input and the output can be related. This enables a comparison of different systems. The collation in this study was performed depending on the functional unit (1 ton of feedstock). Characterization of the feedstock, the total solid (TS) to organic total solid (oTS) ratio and the biogas yield was determined based on data from KTBL, 2014, and FNR, 2010. See Table 1 for an overview for the chemical compositions and gas yields of the feedstock.

2.1.4. Agricultural feedstock

Yearly, 5940 tons maize on 144 ha, 1374tons clover on 44 ha and 2181 tons grass were cultivated on 112 ha agricultural area. Agricultural processes for crop production were cultivation, chisel, harrow, sow, hoe and plough Harvesting was done once in a year for maize and rye, three times for grass and two times for cup plant.

Table 2 provides an overview of the required input for the cultivation. Following the harvest period, crops were ensiled for 6 months.

Emissions from ensilage were estimated based on data provided by the University of Applied Sciences Nordhausen (2013) (www.fh-nordhausen.de).

	Maize	Clover	Grass
Dates			
Sowing	End of April	1-10 July	1-10 July
Harvest	End of October	20-30 September	20-30 September
Input (kg ha^{-1})			
Seed amount	28	7.5	22
N fertilizer	140	82	37.5
P_2O_5 fertilizer	50	22	70
K_2O fertilizer	225	97	220

Table 2. Basic data for the cultivation of the crops (Cultivation data of crops are real data of the plant).

After ensilage, the crops were carried to the biogas plant. The transport distance between the agricultural area and the biogas plant was 5 km. Transport was done by a tractor with a trailer consuming 45 L h^{-1} of Diesel fuel.

2.1.5. Anaerobic digestion

The biogas plant consisted of a main fermenter (2000 m³) and a secondary fermenter (1500 m³) and a storage tank for the digestate of a volume of 2000 m³. Digesters were operated under 43 °C (mesophilic conditions) at a retention time of 115 days. Methane emissions from fermenters were assumed as a 1% share of total biogas produced [15]. Electricity used in the process was taken from the grid and heat was supplied from the biogas combustion.

2.1.6. Anaerobic digestion

The biogas plant consisted of a main fermenter (2000 m³) and a secondary fermenter (1500 m³) and a storage tank for the digestate of a volume of 2000 m³. Digesters were operated under 43 °C (mesophilic conditions) at a retention time of 115 days. Methane emissions from fermenters were assumed as a 1% share of total biogas produced [15]. Electricity used in the process was taken from the grid and heat was supplied from the biogas combustion.

2.1.7. Biogas utilization

The produced biogas is used in a 500 kW capacity combined heat and power plant (CHP) for the production of electricity and heat. 35% of the produced heat was used for the fermenters, 65% was sold. Emissions occurring during the combustion of biogas at the CHP were taken from Lansche and Müller (2012).

2.1.8. Digestate

Digestate was stored at the plant or at the agricultural area. The storage of digestate resulted in emissions of CH_4, N_2O and NH_3, which were estimated based on data from De Vries et al. (2012), Jülich (2008), and Lukehurst et al. (2010). Transport of digestate between the biogas plant and the agricultural area was accomplished by a 40 ton truck.

Digestate was spread on the fields. The quantities of fertilizers that were replaced by the digestate were calculated on the basis of the digestate composition and fertilizer replacement values. Furthermore, digestate compositions were determined based on the decomposition rates of the substrates and available organic nitrogen [1, 17].

The field emissions such as ammonia, nitrous oxide, nitrogen, nitrate and phosphate, were calculated. Nitrogen-based emissions were determined by factors provided by Brentrup et al. (2000). Phosphate emissions into water were calculated according to the method of Rosier (1998).

2.1.9. Life cycle impact assessment

All emissions and resources used were included in the assessment and categorized with respect to the global warming potential (GWP) in kg CO_2-eq. The scenarios were simulated with the Simapro 7.3.2. [21] by using the Ecoinvent 2.2 database. The impact assessment was computed by using the ReCiPe midpoint v.1.06 method. To enable the comparison of feedstock, environmental impacts were calculated based on FU.

2.2. Description of the ASPEN model

The model includes four biochemical phases of anaerobic digestion, described through interconnected chemical reactions and degradation of some intermediates by bacteria. The digestion process starts with the hydrolysis of substrate. Insoluble organic polymers, such as carbohydrates, proteins and lipids, are broken down into sugars, amino acids and fatty acids, and become available for other bacteria. Acidogenic bacteria convert these compounds into carbon dioxide, hydrogen, ammonia, and short chain fatty acids (e.g. acetic acid, propionic acid, butyric acid, valeric acid). In the acetogenic phase, bacteria convert these resulting organic acids into acetic acid, along with additional ammonia, hydrogen, and carbon dioxide. Finally, methanogenic

microorganisms convert these products to methane and carbon dioxide.

2.2.1. Model equations

The model includes different simulation units connected in series, which are shown in fig. 2. A stoichiometric reactor is simulated, where thirteen reactions are applied for the hydrolysis phase. Carbohydrates, proteins and lipids are converted from the feedstock [3]. The fractional conversion of each stoichiometric reaction is determined by the design specification tool included in ASPEN; the model calculates the output flow rates of all components. A Gibbs reactor unit is used, where equilibrium reactions for water, ammonia, acetic acid, carbon dioxide, carbonic acid, hydrogen carbonate and sulphide hydrogen are applied to calculate the pH-value of the medium. Acidogenesis, acetogenesis and methanogenesis are simulated in a continuous stirred tank reactor. Chemical reactions, kinetic equations and kinetic parameters are taken from published models [4, 5]. Composition of maize silage [22, 26], grass silage [23, 24] and clover [25, 27] were obtained from literature.

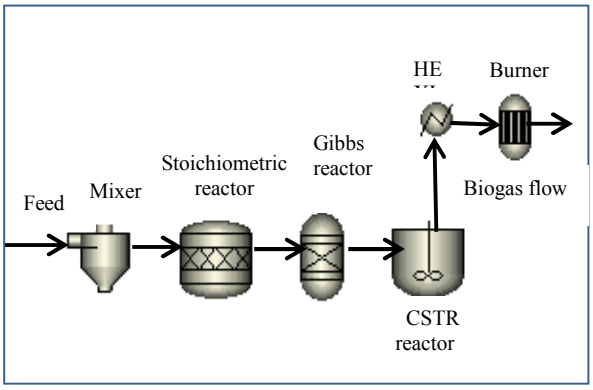

Fig. 2. Simulation flow sheet of biogas process in ASPEN.

3. RESULTS

3.1. LCA Results

Fig. 3 illustrates the comparison of LCA characterization results for different scenarios. The results show that it is possible to reduce GHG emissions just by optimizing the co-digestion ratios and produce still the same amount of energy. For the real situation, it is seen that emissions are mainly resulted from the digestate transport (36%), followed by agricultural activities of maize (21%). All scenarios resulted in lower emissions due to relatively low maize production except of scenario 1. Scenario 1 resulted in a 2.35 g CO_2 eq higher GWP, that was caused by the reason of (110% more) almost doubled clover production against only 16% less maize production.

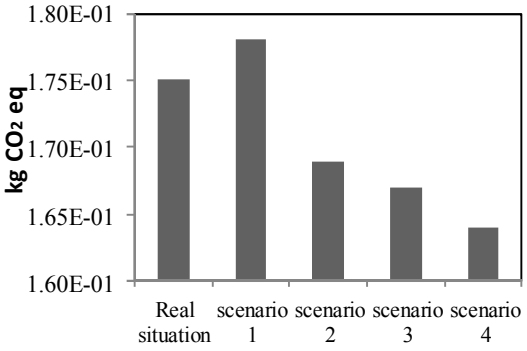

Fig. 3. Comparison of global warming potentials (kg CO_2 eq) of different scenarios. The results are given per FU.

3.2. Simulation results

A comparison of the biogas flow rate between the ASPEN simulation and the KTBL values for each substrate (maize silage, clover and grass silage) and co-digested mixture is shown in Table 3. A close approximation in biogas production of -3% to values of KTBL is achieved, when all substrates are co-digested. The prediction of power capacity and the comparison to KTBL values for each substrate and co-digested mixture is depicted in Table 4. The efficiency considered for the CHP was 47.5% % [1] (KTBL, 2014).

Substrate	Feed flow t a^{-1}	Biogas production		
		KTBL*	ASPEN	Difference
		m^3h^{-1}	m^3h^{-1}	%
Maize	5940	150	147	-2
Clover	1374	25	25	0
Grass	2181	50	47	-6
All substrates**	9495	225	219	-3

Table 3. Simulation and comparison of results to KTBL values of the biogas flow rate for each co-substrate and co-digested mixture.
*KTBL, 2014
** Maize, clover and grass silage are co-digested

The portion of methane in biogas is predicted to 54% (difference to the KTBL value: -2.0 %), when all substrates are co-digested. The composition of the biogas is estimated when co-digestion occurs (beside methane) to: CO_2 – 43 %, H_2O – 3.6 %, H_2S – 0.4 %, H_2 – 175 ppm, NH_3 – 9 ppm.

The prediction of power capacity based on the ASPEN model is acceptable with a difference of -5% between the simulation and the KTBL values, when digestion involves all substrates.

Substrate	Feed flow t a^{-1}	Power capacity		
		KTBL*	ASPEN	Difference
		kW	kW	%
Maize	5940	361	349	-3
Clover	1374	64	56	-13
Grass	2181	118	109	-8
All substrates**	9495	543	514	-5

Table 4. Simulation and comparison of results to KTBL values of power capacity for each co-substrate and co-digested mixture
*KTBL, 2014
** Maize, clover and grass silage are co-digested

3.3. LCA and modelling

The results show that modelling can predict the real behaviour of biogas production systems and helps to increase the GHG emission reduction potential of the plants. Therefore, process modelling can be an influential instrument to optimize the processes.

The simulations can be applied for various scenarios of the LCA studies, predicting the environmental impact of feedstock changes. The prediction of biogas flow and power capacity of scenario 4, which has the lowest emissions of the study, is shown in Table 5.

Substrate	Feed flow t a^{-1}	Simulation	
		Biogas flow m^{3}h^{-1}	Power capacity kW
Maize	2000	53	116
Clover	7049	134	278
Grass	2000	46	99
All substrates*	11049	232	493

Table 5. Simulation of the biogas flow rate and power capacity of scenario 4 for each co-substrate and co-digested mixture.
* Maize, clover and grass silage are co-digested

4. CONCLUSIONS

The decision concerning the most suitable production of biogas entirely depends on the view of which environmental impacts are considered to be of the highest importance for biomass supply. In this paper, a close approximation to values of simulation and real power capacity was achieved. Thus, the performance of a biogas plant basically represented by chemical conversion is efficiently simulated by the ASPEN model. Once the system optimization with modelling is done, negative impacts of biogas plants on the environment could be diminished and even positive impacts would be increased.

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

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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.

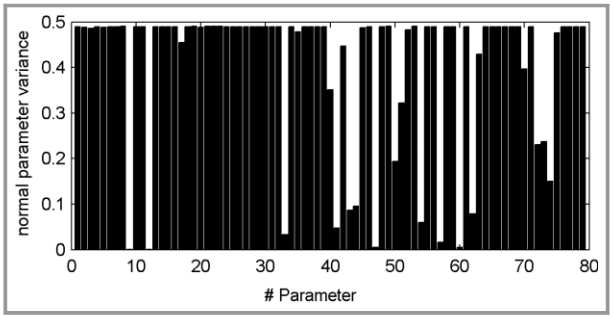

Figure 1. Sensitivity analyses of 80 parameters of the ADM1. Shown is the parameter variance of the sensitivity analysis. The normal distribution of variance is 0 – 0.5.

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].

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

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

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)

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

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

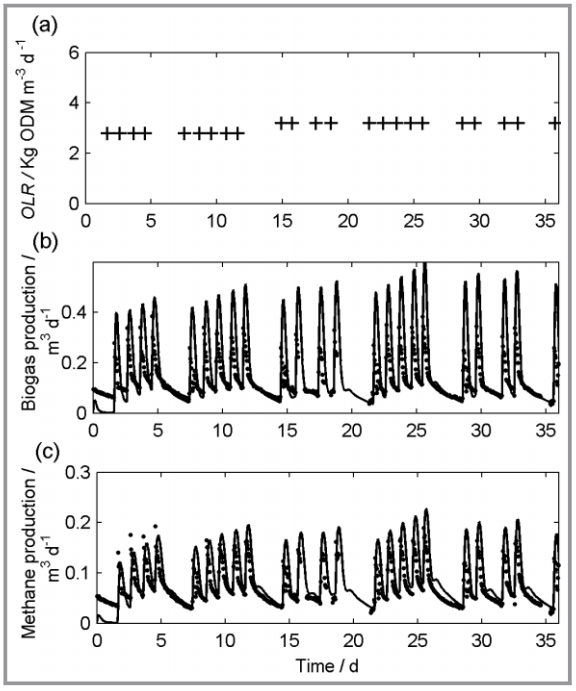

Figure 2. a) Organic loading rate (+) during a period of 36 days at alternating feedstock load in a 50-L scaled anaerobic digestion process. b) Biogas production: AM2 simulation (–), online experimental data (•), and c) Methane production: AM2 simulation (–), online experimental data (•).

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.

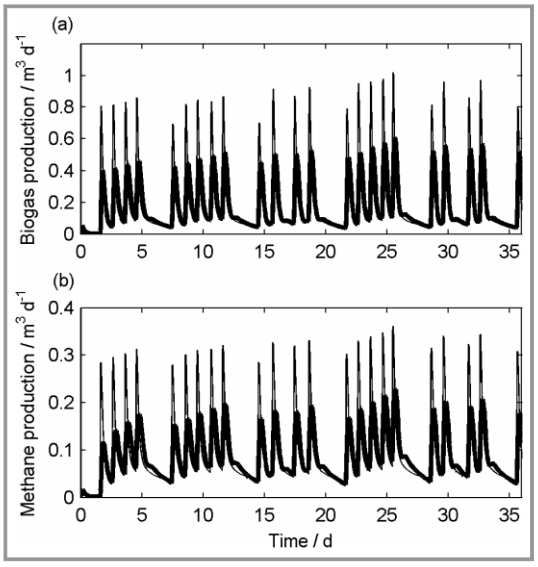

Figure 3. Comparison between the simulation of the modified AM2 (–) and ADM1 (–) for a period of 36 days at alternating feedstock load of a 50-L scaled anaerobic digestion process.

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.

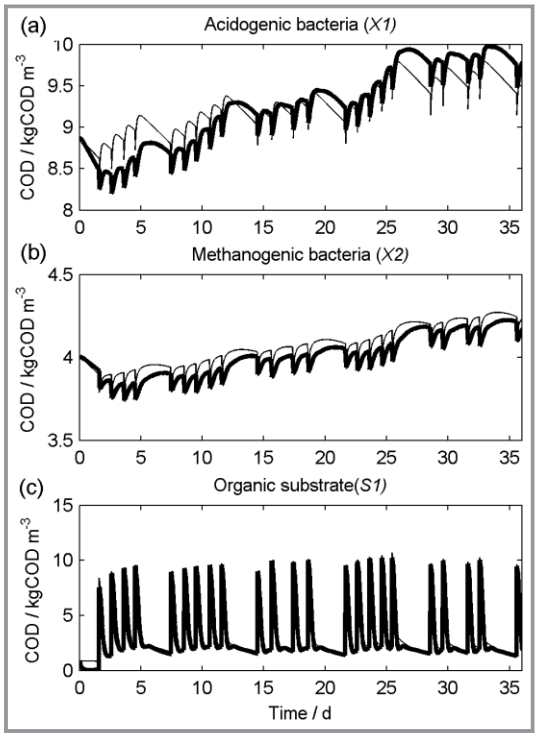

Figure 4. Comparison of main variables between the AM2 (–) and the ADM1 (–) of a 50-L reactor during a period of 36 days with changing influent conditions. a) Acidogenic bacteria; b) methanogenic bacteria, and c) organic substrate.

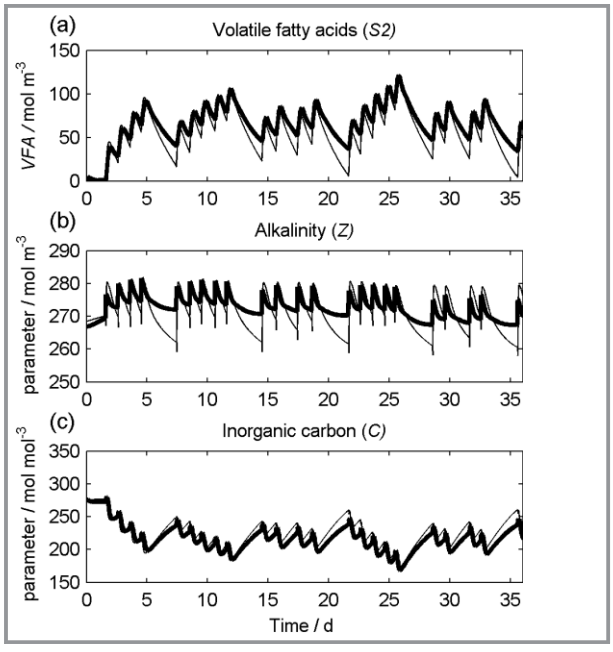

Figure 5. Comparison of main variables between the AM2 (–) and the ADM1 (–) obtained for a 50-L digestion process during a period of 36 days with changing feeding conditions. a) Volatile fatty acids, b) alkalinity, and c) inorganic carbon.

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
$f_{ch,xc}$ [$kg_{COD}kg_{COD}^{-1}$]	–	0.2 [c]
$f_{pr,xc}$ [$kg_{COD}kg_{COD}^{-1}$]	–	0.2 [c]
$f_{li,xc}$ [$kg_{COD}kg_{COD}^{-1}$]	–	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.

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

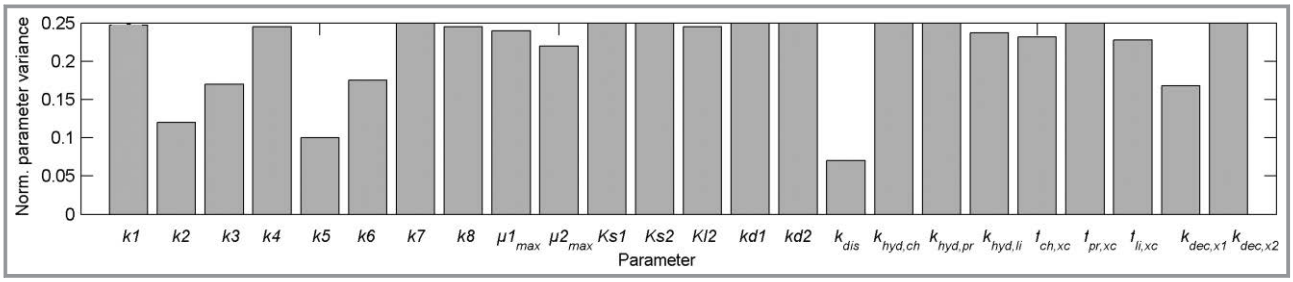

Figure 6. Sensitivity analysis to the 24 parameters of the extended AM2. Interval of normal parameter variance is 0 – 0.25.

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

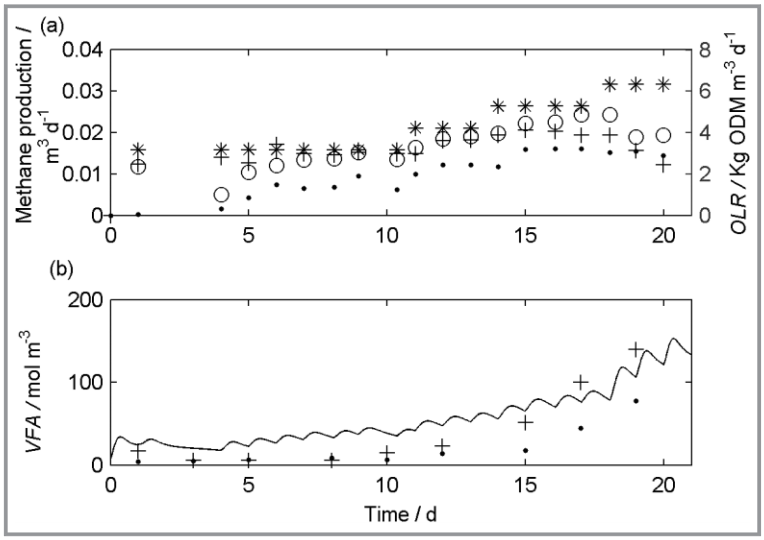

Figure 7. a) Extended AM2 simulation (o), experimental data of R1 (+) and R2 (•), and organic loading rate (*) during a period of 20 days of the acidification of anaerobic digestion processes conducted in two 15-L digestion processes. b) Simulation of volatile acid concentration (-) and experimental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

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

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$^{-1}_{CODS}$]	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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Paper IV- (Manuscript in preparation)

Ertem, F. C., Arzate, J. A., Cruz-Bournazou, M. N., Neubauer, P., & Junne, S. Life cycle assessment and modeling approaches as a combined evaluation tool for control strategies for sustainable biogas production-Review.

Life cycle assessment and modeling approaches as a combined evaluation tool for control strategies for sustainable biogas production-Review.

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

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Abstract

Biogas production is widely applied in many regions of the world. However, the full potential of the process for the conversion of multiple substrates is hardly explored in practice, as the process itself is often equipped only poorly with monitoring devices and process control. Nevertheless, several recent attempts in research have been made to combine engineering approaches as well as ecological and economical assessments to improve the efficiency and flexibility of biogas plant operation. First, mathematical models are required that are tractable and describe the characteristic behavior of the process to find better or even "optimal" scenarios for biogas production. They should be able to describe the main processes with sufficient accuracy, while they keep a low computational burden. Secondly, a proper cost function is required to exploit advanced operation and control policies aiming a more sustainable energy production.

If the objective of a biogas production network is the reduction of greenhouse gases, the quantification of the impact of each element in the system in a "cradle to grave" sense is required. In order to achieve this, life cycle assessment (LCA) studies need to be combined with a model-based approach to identify suitable operation points. The integration of simulation data into LCA studies allows the prediction of different production scenarios and a suitable choice of the one with the most favorable environmental impact despite the complexity and varying behavior of the system. This is, beyond bio-based energy production, 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 formerly conducted LCA and modeling studies in the biogas production field, emphasizes some

important issues and good modeling practices, and discusses the potentials of a combination of them.

Keywords

Biogas; life cycle assessment; mathematical modeling, system optimization

1. 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. The plan "20-20-20" aims to reduce emissions of GHGs and primary energy consumption by 20% compared to the 1990, and 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 velocity. 17,376 biogas plants with a total installed capacity of 8,728 MW el 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 optimal yields not to the most sustainable strategy. For these reasons, the efficiency, flexibility, predictability, and robustness of biogas production needs to increase. This can only be achieved if we understand the system better and are able to detect and prevent disturbances promptly [5-7]. To do so, 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.

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 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 forests 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] [16-18]. 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 the raw material production, processing, manufacturing, use and final disposal. It is widely recommended as a decision making tool to evaluate the real ecological footprint of a process [19].

The current sustainable waste management focusses on the biogas energy potential of residues and waste [15]. 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 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]. Furthermore, the laminar flow and restricted power input leads to gradients in the liquid phase, which represents a challenge for a suitable monitoring of the liquid phase. A convenient mathematical model that fairly describes the most relevant reactions can support a proper plant control [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 manner 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].

Therefore, 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. To approach this goal, this paper summarizes the existing LCA and modeling approaches in the area of biogas production. Later, it depicts the advantages of combining both approaches to bridge the gap between process control and a sustainable performance. Finally, the potential of how to combine LCA and process modeling is illustrated by successful examples from the area of waste-water treatment is described.

2. LCA Approaches for Biogas Production Processes

2.1 Definition of LCA

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

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 could 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 [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 creating a list of all of the components of the products 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 input and output data required 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 of which are considered mandatory, while the last two are optional; classification, characterization, normalization and weighting. Classification involves assigning specific environmental impacts to each component of the LCI. Sometimes, the impact assessment is 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. 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. 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. 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. It is a controversial step, since the selected weighting factors can influence the results and conclusions of an LCA [19, 31].

2.1. LCA for biogas production: state of the art

Although the use of a different functional unit in each studies does not allow for a comparison or a conclusion, one can emphasize from the former LCA studies [7, 12, 13, 32-40] that biogas production emissions mostly originate from: i) fertilization and digestate applications and ii) diesel fuel consumption (for cultivation and for transportation). Moreover, Tidåker et al., (2014) [41] determined that if N mineral fertilizer was replaced by digestate, the acidification potential increased, either. Methane and nitrous oxide emissions from the digested slurry during storage or after field application represent another crucial issue [41]. Covering slurry surface is a basic measure to curb methane release: Sommer et al., (2000) [42] [42] [42] [42] determined that 38 % of CH_4 emission of biogas production were released from an uncovered slurry surface. The last finding indicates the need for stricter measurements for handling of post-digestion slurries. However, AD enhances the production of CH_4, which is removed from the system instead of a slow release to the atmosphere [43].

System efficiency is another important point in LCA. Lansche and Müller, (2012) [44] indicated that in order to ascend the diminution of GHG, gas-tight digestate storage is recommended. Liebetrau et al. (2010) [45] stated that the most important methane emissions come from open digestate tanks. Poeschl et al., (2012) [46] stated the recovery of residual biogas from the digestate storage areas as the key determinant of the performance of digestate processing and handling.

Higher GHG emission outcomes from slurry storage in comparison to emissions from field spreading were detected by Capponi et al., (2012) [41] and Clemens and Huschka, (2001) [47]. Moreover, the collection of CH_4 through an appropriate cover of digestate may contribute to further energy production. It seems that restraining CH_4 and N_2O emissions from digestate requires special care in the management of the anaerobic processes.

Despite these issues, the benefits of biogas production have been quantified if diesel fuel generators were replaced [48]: Biogas contributes to a 58 % reduction of the global warming effect with in comparison to the diesel fuel. Furthermore, Ciotola et al., (2011) [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 biogas production. While large plants require a lot of logistic effort to supply the operation with enough of feedstock, smaller plants require usually only feedstock from sources nearby the plant. The comparison of the energy efficiency of a large-scale biogas plants and small-scale biogas plants was performed by Wang et al., (2013) [51]. The results showed that large-scale plants provide 77.9 - 95.6 % higher efficiency and 125.7 - 172.7 times higher emission mitigation intensity, however, 66.0 - 74.4 % lower sustainability than that of the small-scale biogas project. This finding is due to increased efforts of transportation and higher costs of equipment investment in AD and electricity production.

Wang, Li [51] assessed a process-based LCA of biogas production from straw to figure out which sub-process owed the most damage or benefit. GWPs of the whole process were 254 kg of CO_2-eq for 20 years, 281 kg CO_2-eq for 100 years and 312 kg CO_2-eq for 500 years. This indicated that impact on GHG emission would be strengthened with time, which was because of larger amount of CH_4 produced that has a stronger effect on GHGs.

Whiting and Azapagic [52] demonstrated that LCA results are influenced by the type and source of feedstock, digestate storage and its application on land. In their study, using energy crops such as maize instead of waste reduced the GWP owing to higher biogas yields. Lijó, González-García [53] tried to identify the environmental consequences of the feedstock selection for biogas. Two real biogas plants were assessed and compared from a life cycle perspective. Plant A performed the co-digestion of energy crops (78%) and animal waste (22%) while Plant B consumed energy crops (4%), food waste (29%) and animal waste (67%). According to the results, electricity production from biogas implied lower impacts in climate change than the existing electric mix. Maize silage and food waste were identified as an interesting source of bioenergy. The use of organic substrates with lower energy potential and high nutrients concentration such as animal manure produced higher amounts of digestate, producing impacts in acidification and eutrophication categories. These results indicate that economic incentives should include further requirements on feedstock type to promote the use of different types of wastes and to prevent the use of energy crops that may compete with other uses.

CO_2 footprint largely depends on regional parameters that are required for the LCA of biogas. These parameters change among regions and always parameters for the relevant region needs to be employed. As proved by Dressler, Loewen [32] and Ertem [54] local factors and regional parameters have a strong effect in LCA results. Therefore, it is necessary to consider regional parameters (e.g., transport distances, agricultural area for biomass production and digestate spreading, competition for cereal silage between biogas production and livestock activity) with the aim of performing a representative LCA study. Only if regional variations are considered, the results of environmental indexes will be representative, as the results could vary from one region to another.

3. Model based process operation

In process engineering, the use of mathematical models has shown to be highly beneficial whenever properly developed, validated, and implemented. Combined with powerful

software and exploiting modern computational capacity, model-based tools are an important pillar in all engineering disciplines. Developed tools can be applied regardless of the field and nature of the systems once a proper model that described the process under study has been developed. Hence, the work on mathematical modeling of the biogas production process is briefly reviewed, including data availability as well as first principle based methods.

Among applications for AD, statistical, first principle, mechanistic, or white box models are applied. Statistical models are created by mathematical equations that define how the diverse parameters and variables are stochastically correlated to each other. The models have no relation to the physical laws so disparities outside normal parameters will be controlled in the same method as all parameters. 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 the space that has been fitted to [55] (ref: Empirical Model-Building and Response Surfaces, GP Box).

A first principle model is developed by physical laws and known physical interactions and mass balances between the different parameters and variables [56]. The complexity of the model varies based on how well the process is known and the quality of data that is at hand [57, 58]. Additionally, computational burden and tractability in general should be considered when developing, tailoring or selecting the structure and parameters of a model [59]. The advantages of white box models include the possibility to make scale-up predictions and find new and more efficient design, operation, and control strategies [60].

3.1. 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, including the biotechnological conversions. Deublein and Steinhauser [61] listed a number of operational disturbances, such as acidification, foaming, varying gas quality and odor, which could be prevented by an improved, model based, control system[62, 63][64][65][66]. The anaerobic digestion model No. 1 (ADM1), developed by the International Water Association's Task Group in 2002 [67], is currently the most applied model. In this structured model, physico-chemical, chemical, and biological processes are included in a biochemical kinetic matrix. The model focusses on the five major steps: disintegration, hydrolysis, acidogenesis, acetogenesis and methanogenesis. The biological processes are defined in 19 reactions which involve 24 components. In summary the model consists of 56 stoichiometric and kinetic parameters and for physico-chemical processes additional processes and parameters are defined.

The ADM1 was originally developed for sewage sludge processes [68]. However, several research studies have adapted the model for other feedstock types like agro wastes [68] and energy crops as corn silage and grass silage [69]. Furthermore, co-digestion of organic waste with sewage sludge [70], olive pulp [71], and cattle manure, different organic materials, livestock manure and , manure and organic wastes [72] were investigated. These studies show that the ADM1 is well able to handle different feedstock. In case of agro-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 agro-wastes properly. Besides, Koch,

Lübken [73] simulated the AD of grass silage by a modified ADM1 model with a separate compound of inert decay products and the integration with a solid-influenced hydrolysis function reflecting nitrogen incorporation and release. The model was calibrated by using the modified Nash–Sutcliffe coefficient to assess the quality of the simulation. The model results indicate a good agreement with the measured data. A modified ADM1, adjusted on a laboratory digester with a weight feeding mix of 30% of cow manure and 70% of corn silage, was developed by Zhou, Löffler [74]. The model was applied as a decision-supporting instrument for the AD of agricultural feedstock. The impacts of the feeding mixtures on biogas composition and yield provide the adequate prediction of the model, and in general agreement with literature reports.

Some authors conducted batch experiments to obtain experimental data for model modification. However, continuous AD processes are usually required to gain conditions that are suitable to reflect the real case as described by Mauky, Weinrich [75]. The authors 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 intraday flexibility 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 [76] to simulate the AD process in continuous digesters simply by characterization of the substrate and parameter calibration, which will help to predict the reaction process and prevent the failure of the AD process in advance. The anaerobic digestion of municipal solid waste (MSW) was studied in a dry process under mesophilic conditions [77]. ADM1 was simplified on microbial expression and degradation pathways. The cellulose was assumed as main particulate matter in MSW. The ADM1 was reduced to six differential equations and three liquid-gas equilibrium equations for CH_4, H_2 and CO_2, which contain the output gas flow variable. The five acid-base equilibrium equations for OH^-, H^+, acetate, propionate and inorganic carbon were reduced to a single H^+ equation for the calculation of the pH. The model is able to predict the batch degradation of acetate and methane flow rate. The moisture content affects both, the half-saturation constant (k_s) and for the lowest value of moisture content the maximum uptake rate ($qp_{max.}$). Thamsiriroj, Nizami [78] used a series of mathematical models to simulate the digestion process of grass silage in a two-phase digestion system. A model was performed for a two-phase system which generates a biogas with elevated methane content (71%) as compared to a wet continuous system (52%). The study concluded that longer retention times maximise energy production per unit feedstock and increase methane content in the biogas.

In the literature, several AD models are described, which are less complex compared to ADM1, because they reflect either a simple process or a particular feedstock. Among them, the AM2, also sometimes referred as AMOCO, is to mention [3]. It was developed to support monitoring and control system design for AD process not just as an instrument for numerical simulation of the process behavior. The model considers two bacterial populations, which represent the acidogenic and methanogenic reactions. Ficara, Hassam [79] applied the AM2 to describe the anaerobic degradation of residual activated sludge and compared its

applicability with the ADM1. The AM2 was able to well predict steady state values of biomasses and methane production rates, while being less efficient in foreseeing the inorganic carbon species and pH values. Recently Arzate, Kirstein [80] have adapted the AM2 to predict the digestion of maize silage. The outputs of the simulation were compared with experimental data and with the ADM1, showing the ability of the model to predict biogas, methane and state variables. The relevance of the study is the development of a tractable model based feedstock to produce biogas.

Artificial neural network (ANN) models have been used extensively in biotechnological processes. Kanat and Saral [81] developed an ANN-based model to study biogas generation at a thermophilic digester depending on the influent and effluent total VFAs, OLR, alkalinity, pH, and temperature of the reactor. A comparable study was also performed by Qdais, Hani [82], in which an ANN-based model was developed to optimize methane production using TVS, TS, pH, and temperature. Vavilin Vavilin, Lokshina [83] modeled biogas production from a batch and completely mixed reactor. The authors observed that the average level and the general trend could be monitored, but the extreme points in biogas production could not be reflected. The study includes how the mixing intensity affects the efficiency of continuous-flow anaerobic digestion of municipal solid waste (MSW). Akbaşa, et al., 2015 [86] developed an optimization model of biogas production for sludge and used data from a wastewater treatment facility. The model uses the multi-layer perceptron (MLP) neural network and particle swarm optimization (PSO) techniques. The maximization of methane percentage, biogas production and biogas quality were the objective functions. The rate of digestion increases by temperature and the optimum temperature was found between 34.3 and 37.3ºC. The input variables in the model were the following: sludge loading rate (SLR), temperature (T), pH, total solid (TS), total volatile solid (TVS), volatile fatty acid (VFA), alkalinity (ALK), sludge retention time (SRT) and organic loading rate (OLR). The study reveals the characteristics in the treatment process that should be monitored.

Matheri et al., 2016 [87] investigated the co-digestion of cow dung and grass clippings. The study consisted of a Lab experiment in which data from a 10-liter batch anaerobic digester at mesophilic temperature of 37ºC and pH of 6.9 were used for modified Gompertz model. The substrate characterization of grass clippings and cow dung was performed by elemental analysis of Carbon (C), Hydrogen (H), Nitrogen (N) and Sulphur (S). The authors proposed a C/N ratio value for the co-digestion (19.08), which is higher that digestion of cow dung (17.7). In the model, the kinetics constants of A (ml/g COD), μ (ml/g COD. day), λ (day) were calculated and the coefficient of determination (R2) of 0.996.

AD processes of crop straws combined with a pretreatment prior to the main AD process are also investigated, digestion condition involves co-digestion with other organic matter in mesophilic and single batch-digester. Gu, Y. et al 2014 [88] investigated rice straw combined with digested dairy manure including pretreatment of screened 8-mesh sieve. The digestion achieved the highest biogas production in comparison when is combined with digested swine manure (SM), digested chicken manure (CM), digested municipal sludge (MS), anaerobic granular sludge (AGS) and paper mill sludge (PS). The result indicated that digested dairy manure was more suitable than sludge.

3.2. Challenges of model implementation in practice

The data being collected today in the biogas industry works well to get a rough estimate of the energy content of the substrate, but is not extensive enough for most of the models available. The frequency of the measurements is too low for any type of on line monitoring, the characterization of the feedstock is often not sufficient. One of the main parameters used in AD process and modeling to characterize the substrate is inconsistently used internationally/regionally, and that is the measurement of organic content. VS, total organic carbon (TOC) and chemical oxygen demand (COD) are basically three ways of measuring the organic content. Lübken, Wichern [84] proposed that COD should be replaced by VS when analyzing substrates as manure and energy crops. COD is predominantly used in waste water treatment and for other types of substrate as manure, VS is the most commonly used method of describing organic content. A correlation between COD and VS was formulated in this work to make it compatible with ADM1 [74]. Other authors did similar correlations from VS to COD [73, 85, 86] as well as correlating lipids, inerts, proteins and carbohydrates from kg TS to kg COD for its use in ADM1 [87, 88]. Weender analysis was performed using near infrared spectroscopy (NIR) to analyze the content of raw protein, lipids and raw fiber (carbohydrates) [89]. The analysis of the COD and TOC can be problematic with some types of substrate. Some are of a heterogeneous composition, which leads to issues to gain representative results of contents.Kleerebezem and Van Loosdrecht [85] modeling approach to simplify the input for ADM1 for practical use.

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, as in [82], in which also describes a simple method for calculation of the lumped elemental composition of the organic substrates in the wastewater..

The issue of gradient formation need to be considered if data of the liquid phase is gained. Most model simulations for continuously stirred tank reactor are assuming that mixing is suitable to achieve a gradient-free reactor. 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 modelling.

4. Combined LCA & Modeling approach

The combination of mechanistic models for evaluating control strategies with LCA tools can bridge the gap between process control and environmental performance [90]. Such approaches are already being applied successfully at wastewater treatment plants (WWTP) as described in section 3.1. However, the approach has not been applied for biogas plants yet. Therefore, this section particularly aims to give an overview about how to apply combined LCA & modeling for the biogas plants (Figure 3).

4.1. LCA & Modeling for WWTP

Model-based design and operation of WWTP has achieved important improvements in the past decades [91, 92]. Numerous LCA approaches have been published for different WWTP structures and the current developments were clarified by Corominas, Larsen [93] . Foley et

al. (2010) used steady state simulation outcomes gained with Biowin® for a methodical assessment of the life cycle inventories of ten scenarios in 6 WWTP designs. The outcomes indicated that the amount of building materials and the chemical consumption were amplified when lower N and P concentrations were enacted in the effluent, as did energy consumption and GHG emissions in N-constraining effluent scenarios. Flores-Alsina, Arnell [94] applied dynamic simulations of an extended version of Benchmark Simulation Model No.2 (BSM2), which is a developed model for plant-wide WWTP control strategy evaluation and consists of 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 indicated the considerable environmental impact of N_2O emission. Meneses, Concepción [95] presented a multi parameter decision study for WWTP operation strategies. Decision was based on the plant performance evaluation criteria described by the BSM2 scenario combined with LCA indicators. de Faria, Spérandio [96] have developed LCA- dynamic modelling (DM) framework by comparing five WWTP scenarios with a reference scenario. Dynamic simulations were performed in BioWin® to get an accurate assessment of the dynamic behavior and performance of plants under agitation. LCA calculations were done in Umberto® using the Ecoinvent database. A Python™ interface was used to fit in and convert simulation data and to present them into Umberto® to attain a comprehensive LCA assessment including foreground and background processes.

4.2. LCA & Modeling for biogas plants

An operational integration of dynamic process modelling and complete LCA were not projected until now. Such combination requires adjusted modelling and evaluation instruments, able to seize the effect of process parameters and dynamics in the impact calculation results.

Simplified models based on emission factors can provide local results. However, they tend to underestimate the GHG emissions [93]. 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 using steady-state modelling. Dynamic modelling is recommended to provide more reliable GHG prediction. Particular attention must be paid on CH_4 formation dynamics in order to achieve an improved control of the total GHG emissions from AD.

To adopt dynamic models that are characterized by a multitude of factors, it will be necessary to calibrate large amount of data. Furthermore, full-scale mathematical model experiments should be performed to establish clear kinetics and formation mechanisms of GHG for different feedstock types. Knowledge of the involved GHG production pathways must be expanded to create a suitable and comprehensive model that is able to reproduce all of the processes involved in N_2O, NH_3, CO_2 and CH_4 formation. Future efforts should be dedicated to setting up mathematical software and tools/platforms for practical and feasible application during plant operation. Further, efforts on the model calibrations should be performed in order to establish a specific procedure for calibrating such complex and often over-parameterized models.

5. Conclusions

It is very important to note that LCAs are never the "real" answer. They require interpretation, which in turn requires 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 the 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 use them in context of other attributes they are trying to optimize, including e.g. cost, manufacturability and performance. In addition, there are other factors guiding product development decisions not covered by LCAs, including social impacts and acceptance, pricing, political agendas, and regulations [97].

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. Such limitations could be a shortcoming for their application, as they are more comprehensive than classic LCA approach [98].

In order to be able to combine LCA and modelling approaches, it will further be necessary to include the GHG formation processes for biogas plants, which would make mathematical models more complex. As LCA is traditionally a non-dynamic methodology, an interface between dynamic modelling results and inventory flows in LCA is required, together with the conversion of specific inventory items.

Environmental LCA evaluations are increasingly relevant for marketing strategies, managing supply chains, and politic decision-making. A higher level of transparency and a harmonization of the preparation of biogas LCAs are needed to improve the comparability of LCA study results. There is a need to promote the development of common guidelines specific for biogas systems to assess and communicate their environmental performance. Moreover, site-specific data should be used to assess the most important sources of emissions at the biogas plants, as they are deeply affected by climatic conditions and regional factors. LCA should be applied as a site selection tool for newly planned biogas plants.

Thanks to its flexibility and multi-functionality, the anaerobic digestion technology will play a relevant role in renewable energy production by transforming several biomass streams into useful products, contributing to closing of organic matter cycles. However, this multifunctional feature is also a demanding issue for a consistent sustainability assessment of biogas systems.

From an aspect of sustainability, modelling of anaerobic digestion has evolved drastically: starting from very simplified models that consider digestion as a fermentation process from sugars, to the advanced and extended models.

However, future model development should focus on user-specific conditions, i.e. other data sets, the biological aspect of modelling: mathematically relating the performance of a digestion to microbial diversity and activity. The developed models should certainly be further modified with more user specific application dependent modifications, with additional emphasis on the digestate properties. The estimation methodology should mature:

including full substrate characterization and resolving identifiability issues. Furthermore, new advances on the characterization of microbial community composition will pave the way to integrate these aspects in mathematical modeling.

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Figure Legends

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

Figure 2. Steps of mathematical modeling of the bioprocesses

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

Figures

Figure 1

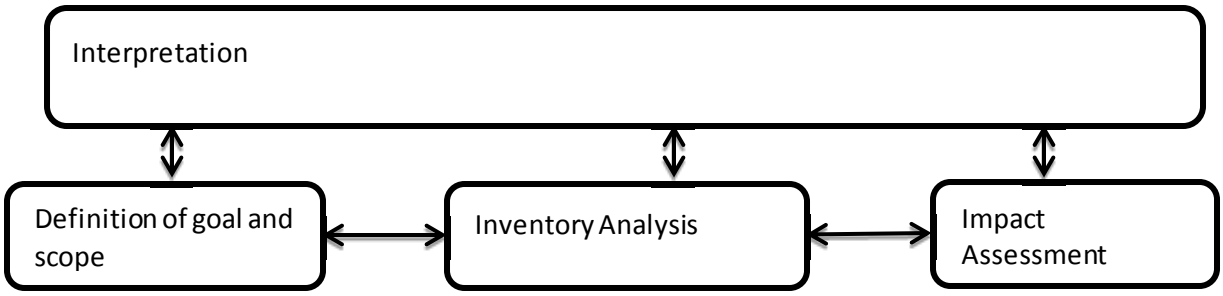


Figure 2

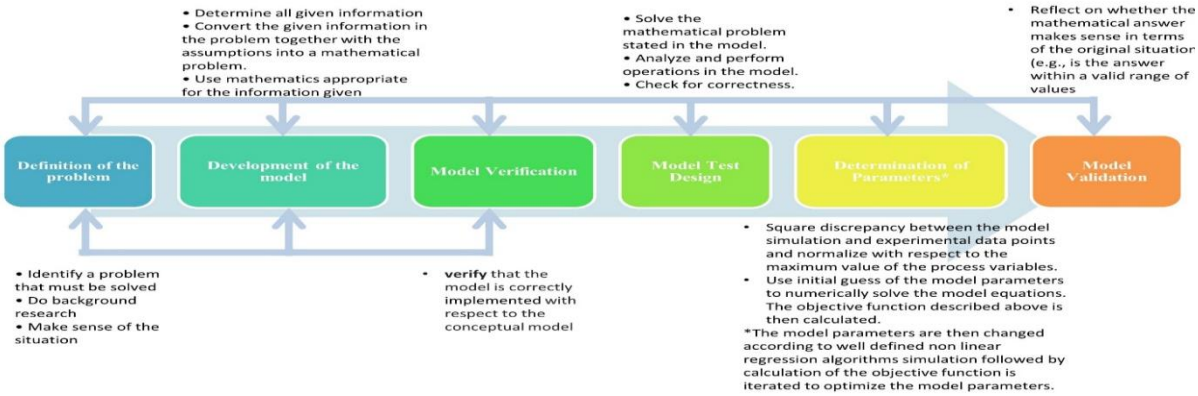
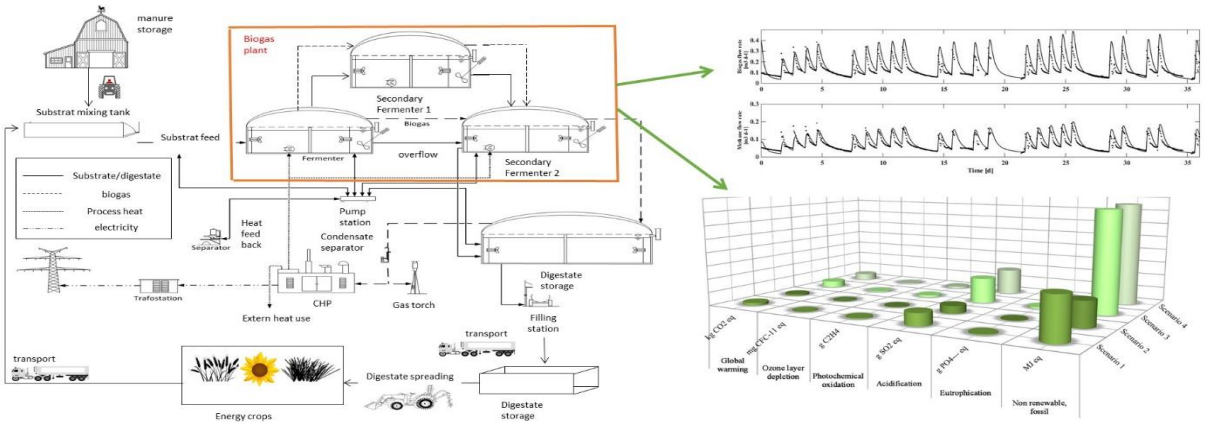


Figure 3



Paper V- (Manuscript in preparation)

Arzate, J. A., Ertem, F. C., Cruz Bournazou, M. N., Neubauer, P., & Junne, S. Modeling of biogas production from energy crops and cattle maure through extended AM2 on ASPEN.

Modeling of biogas production from energy crops and cow manure through extended AM2 on ASPEN.

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Keywords— AM2 model, modelling, anaerobic digestion, ASPEN

Abstract

Currently, renewable biomass has become a well-established energy resource worldwide. Among them, anaerobic digestion of biomass can contribute to replace fossil fuels. However, an operation of a biogas plant (BGP) is not a simple procedure; if alternating feedstock is used or the quality of it changes during season. Process stability might be increased by the application of models for the prediction, monitoring and control of digestion.

The objective of this study was to apply the extended version of the anaerobic digestion model, AM2, to grass silage and cow manure, which are common feedstock for biogas production. The biogas, methane and the state variables of the model were optimized for each feedstock based on the anaerobic digestion model 1, ADM1. Once the model was calibrated for both feedstock, maize silage was included in the study to simulate a co-digestion process of a size up of 1414 m^3. Parameter calibration were performed in MATLAB and on Aspen Custom Modeler V8 in order to quickly simulate steady-state or dynamic conditions. In future, the program can be integrated into a larger system, including i.e., a substrate pretreatment or optimal control approaches.

1. Introduction

The microbial diversity of anaerobic digestion is a large delicate process, where several microbial species have different optimed operating conditions. The stability of the system might be altered by several process parameters such as acidity of the medium, feedstock components, trace elements, pre-treatment, etc (Appels, L., et al., 2008). In the last decades, anaerobic digestion models were developed to describe the biological process treatment and biogas production plants; some particular cases, within models were applied to consider conditions, in which different operational parameters were applied, like changes in feedstock composition, biodegradability and operational conditions (Ficara, et al., 2012). The anaerobic digestion no 1 ADM1, is recognized as a reference model for such studies (Hassam, et al, 2015) . Furthermore, it has proven to be reliable for the application to full scale agricultural BGP (Gaide, 2011). However, the ADM1 contains a large number of parameters and requires a full substrate characterization (Razaviarani, V., 2015). The extended AM2, a reduced model, has lower number of parameters; it requires the substrate characterization in terms of particulate organic matter. The model structure involves two main groups of microorganisms, (i) The acid-forming bacteria, and (ii) methanogenic microbes; it is a suitable model for

prediction of methane, biomass, organic matter, fatty acids, inorganic carbon and alkalinity (Arzate, JA, et al 2017).

AD models have been widely applied to the investigation of substrates or to be incorporated into the design of BGP's, process optimization, assessment of process performance and real time process control. Some simulation programs or platforms of choice have been used for mathematical modeling and/or simulation of the anaerobic system which can help the operator understand and visualize the process as SIMBA under MATLAB/SIMULINK (Lübken, M., 2007); AQUASIM v 2.1b® (Reichert, P. 1998) (Rosa, M. A., 2010) (Dereli, R. K. 2010) (Feng, Y., 2006); Aspen plus (Kajendran K, 2014) (Arzate, 2015). The latter includes a tool program called Aspen Custom Modeler (ACM), which can be used to easily develop and use custom models. The models in this platform can be built into complete simulation flowsheet to visualize better the whole process. In this way, it opens the possibility to carry out studies on feedstock, or performance and alternative processes in AD.

This study was conducted to investigate the application of the AM2 in connection with ASPEN Custom Modeler as a simulation platform. Firstly, the AM2 model was fitted to each feedstock in comparison with a validated ADM1 simulation from literature. Maize silage, grass silage and cow manure were applied as feedstock. Once model parameters were estimated, the model was applied for a co-digestion process. Predictions were compared to a large-scale BGP of 500 kWe power, located in Germany. To develop the model, parameters had to be recalibrated to handle different feed ratios of feedstock and produce the least difference between real data and values of model prediction.

2. Materials and methods

Substrates

As feedstock for biogas simulations, maize silage, grass silage and cow manure were applied, since they represent the energy crops and the type of manure used the most in Germany (Scheftelowitz, M., 2014). The characterization of substrates was performed as described in Koch et al. (2010), which is based on the measured data of Weender analyses. The important of the procedure is the fractioning of the substrate into proteins, lipids and carbohydrates. Basic data for substrate characterization is shown in Tab. A1, which presents the chemical composition of substrate. The data was used to calculate the amount of each component of the model input as described by the method in Koch et al. (2010). The calculated Influent composition of each feedstock are given in Tab A-2. Parameter calibration of mono-digestion processes with either grass silage or cow manure was performed using the extended AM2 as described in Arzate et al (2017). The parameters for maize silage were taken from the same literature source (Arzate, JA., 2017). AM2 was also performed on co-digestion process of maize silage, grass silage and cow manure as feedstock.

Extended AM2 model

The extended version of AM2 describes the digestion of maize silage in three steps (Arzate. J. A., 2017), it was developed from a previous two-step model [Bernard, O, et al., 2002]. In the new version, the feedstock is characterized and the enzymatic hydrolysis is recognized as step-limiting in the overall conversion of organic material to biogas. As previously

published in (Arzate. J. A., 2017), the extended AM2 describes in more detail the various pathways involved in anaerobic digestion than the previous AM2 (Bernard, O, et al., 2002); the pathways intermediate include the interactions, which occur during degradation of fatty acids. Furthermore, the model includes fatty acid inhibition of the acetoclatic methanogenesis and inhibition of the hydrolytic steps by the total VFA concentration.

Parameter calibration

The ADM1 was used as a reference model for parameter calibration. The AM2 parameters for grass silage and cow manure were adapted to these values. The ADM1 parameters for substrates were obtained by [Wichern, M., 2008]. The biogas process data were taken from a previously publication [Arzate, JA., et al. 2017]. It consists of an experiment in a pilot scale plant of 50 liter volume, and the simulation lasted for 37 days. The temperature was constantly controlled at 40ºC, biogas, methane and CO_2 content in the gas phase and pH values were simulated by both models. The lumped variables for biomass, alkalinity, volatile fatty acids (VFA), inorganic carbon (C) and organic matter were determined by ADM1 and used to optimize the corresponding AM2 variables. The reactor was fed once a day with a concentrated stock of substrate; the feed was suspended during the weekend. The retention time and organic loading rate (OLR) were 33.09 days and 3,58 g oTS $(L\ d)^{-1}$, respectively.

For calibration of the model for grass silage digestion, all equations of AM2 were applied. However, a modification in equations of acidogenic and methanogenic bacteria growth rate were considered for cow manure, μ_1 and μ_2, respectively, $[d^{-1}]$, as shown in Eqs. (1+2). The Monod equation for the growth of acidogenic bacteria improved curve-fitting for biogas profile from the previous equation considered for energy crops. Thus, Eq. (1) has the same form as the original AM2 (Bernard, O., 2002). For growth of methanogenic bacteria, Haldane's equation has been found the best equation that fits the profile of methane production. In this case, it was considerate the exponent on inhibitory substrate of the third term in 1 instead of 2. If the inhibition constant K_{I2} is very large, the model reduces to the Monod model as can be seen in Eq. (2).

$$\mu_1 = \left(\mu_{1\max} \frac{S1}{S1 + K_{s1}} \right) \tag{1}$$

$$\mu_2 = \left(\mu_{2\max} \frac{S2}{S2 + K_{s2} + (S2/K_{I2})} \right) - \left(\mu_{2\max} \frac{S2}{S2 + K_{s2} + (S2/K_{I2})} \exp\left[-4 \left(\frac{pH - pH_H}{pH_H - pH_L} \right)^2 \right] \right) \tag{2}$$

where

$\mu_{1\max}$ = maximum acidogenic bacteria growth rate, $[d^{-1}]$

$\mu_{2\max}$ = maximum methanogenic growth rate, $[d^{-1}]$

$S1$ = organic matter [kg COD m^{-3}]

$S2$ = volatile fatty acid concentration, [mole m^{-3}];

K_{S1} = half-saturation constant, [kg m^{-3}];

K_{S2} = half-saturation constant, [mole m^{-3}].

K_{I2} = inhibition constant, [mole m^{-3}]

pH_i = pH value; if i = L = low pH value and if i = H = high pH value {Batstone, 2002 #20}, where pH_H = 8.3 and pH_L = 5.5 were determined during optimization.

Once the AM2 was fitted to ADM1, the AM2 model was written in ASPEN Custom Modeler program, which is depicted in Appendix. Finally, results were compared to data of KTBL, Kuratorium für Technik und Bauwesen in der Landwirtschaft (KTBL, 2015).

AM2 to a co-digestion process

The extended AM2 was applied to a co-digestion process of a BGP of 500 kW power. Biogas production was compared with AM2 simulations during 76 days of digestion. As feedstock, maize silage, grass silage and cow manure were used in different ratios, all of them are pumped into the digester, mixed by agitators. The fermenter had a volume capacity of 1414 m^3 and the substrate loading rate is given in Tab 3.

3. Results

Calibration of AM2 for grass silage

The extended version of AM2 was fitted to the ADM1 for grass silage. Most of ADM1 parameters were obtained from [Wichern, M., 2008], only the disintegration process parameter, k_{hyd} [day^{-1}] was taken from a more recent investigation [Wichern, M., 2009] [Lübken, M., 2010], which suggested that it may be taken as 0.266. As operational conditions, the hydraulic retention time (HRT) and the organic loading rate (OLR) were considered as 33.09 days and 3.58 kg ODM m^{-3} d^{-1} respectively. ADM1 simulations of biogas and methane production and the lumped variables of biomasses (X1, X2); alkalinity (Z); organic material (S1); volatile fatty acids (S2) and inorganic carbon are given Figs. (1+2). In parameter calibration of AM2, the initial values of parameters were considered the parameters of maize silage, which are given in Tab. 1 (Arzate, 2017). The parameters for the hydrolysis of carbohydrates, proteins and lipids: khyd_ch, khyd_pr and khyd_li, respectively, were considered those reported for grass in (Wichern, 2008); The rest of the parameters were determined by the calibration process, which are shown in Tab. 2. Biogas and methane production and the lumped variables: X1, X2, Z, S1, S2 and C were optimized using the fmincon function in the optimization toolbox of MATLAB. Simulation profiles of biogas and methane flow rates are presented along with satisfactory results in Fig. 1. The comparison between lumped variables of AM2 and ADM1 was satisfactory in all cases and is given in Fig. 2.

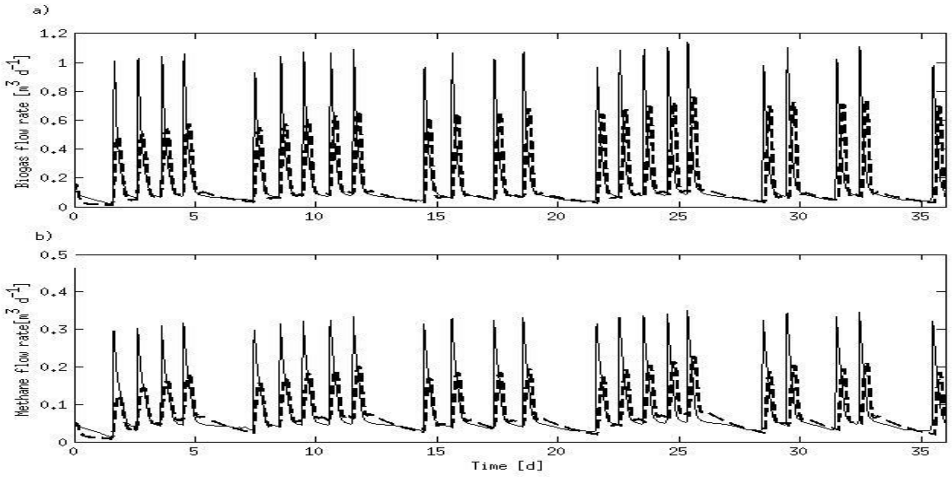

Figure 1: Comparison between the simulation of the extended AM2 (bold dash line) and ADM1 (straight line) for grass silage in a period of 36 days at alternating grass silage feed of a 50 L-scaled anaerobic digestion process. a) Biogas flow rate; b) Methane flow rate.

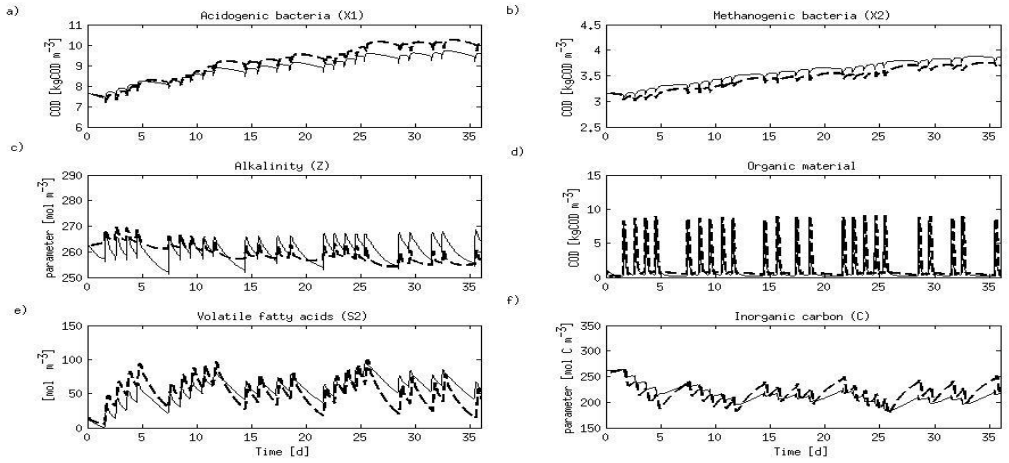

Figure 2. Comparison of lumped variables between the AM2 (bold dash line) and the ADM1 (straight line) for grass silage obtained for a 50 L digestion process during a period of 36 days at alternating grass silage feed. a) acidogenic bacteria; b) methanogenic bacteria; c) alkalinity; d) organic material; e) volatile fatty acids; f) inorganic carbon.

Cow manure

The AM2 for cow manure was fitted to ADM1. The aim of the parameter calibration was to obtain the simulation outputs as close as possible to the real operation. All ADM1 parameters for the substrate were obtained from (Wichern, 2008). Initial values of the AM2 parameters were considered the parameters of maize silage, which are given in Tab. 1. All parameters of AM2 were determined by the calibration process with the same program as the used for grass silage. The comparison of AM2 to ADM1 of biogas and methane flow rate are given in Fig.

3. The lumped variables of the models are shown in Fig. 4. The AM2 outputs were in good agreement with ADM1.The calibrated parameters for the cow manure are depicted in Tab.1. The modification of equation for acidogenic bacteria growth rate responds to the higher amount of acids in the digestor, caused by the cow manure as feedstock. The expression is the same than the Monod equation, as that reported in (Bernard, O, 2001). Moreover, in the equation of methanogenic bacteria growth rate, the increased VFA in the medium maintains the same expression as that published in (Arzate, 2017). It facilitates the growth of methanogenic bacteria, by reducing the exponent of S2 in the third term of denominator.

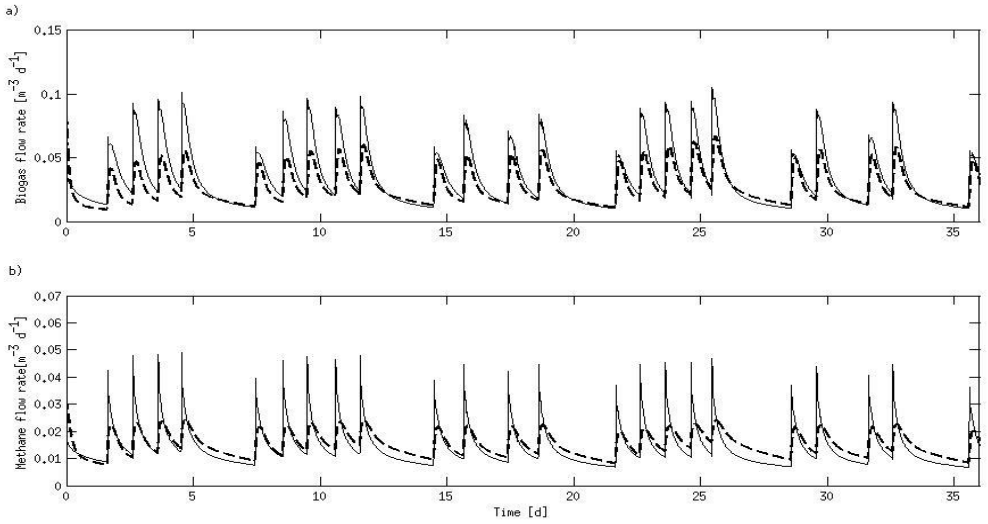

Figure 3: Comparison between the simulation of the extended AM2 (bold dash line) and ADM1 (straight line) for cow manure in a period of 36 days at alternating cow manure feed of a 50 L-scaled anaerobic digestion process. a) Biogas flow rate; b) Methane flow rate.

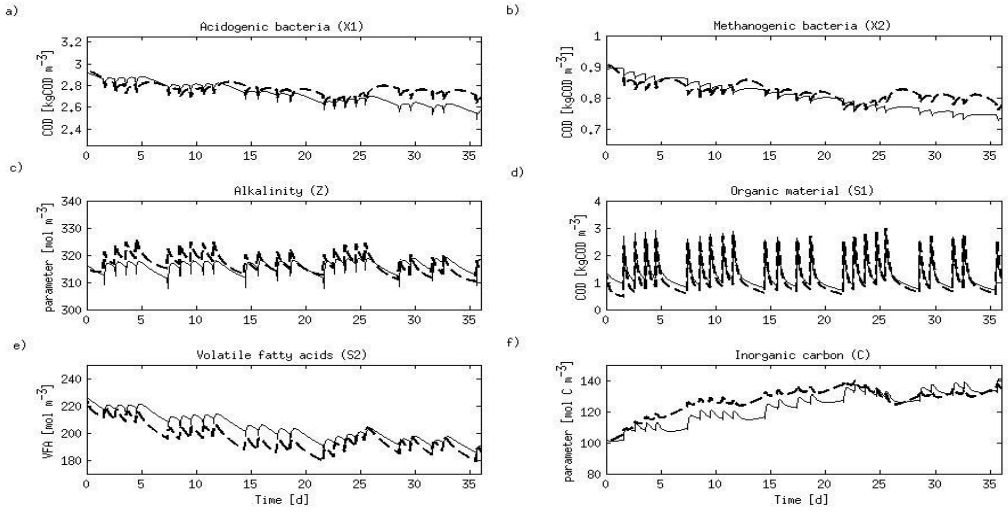

Figure 4. Comparison of lumped variables between the AM2 (bold dash line) and the ADM1 (straight line) for cow manure obtained for a 50 L digestion process during a period of 36

days at alternating cow manure feed. a) acidogenic bacteria; b) methanogenic bacteria; c) alkalinity; d) organic material; e) volatile fatty acids; f) inorganic carbon.

Tabla 1. 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)

AM2 on co-digestion process

The extended AM2 was investigated in a co-digestion process using data from a full-scale BGP with a volume capacity of 1440 m^3. The biogas production was reported on-line; the amount of each feedstock used is shown in Tab. A-3. The feedstock used in the process was fed into the reactor during 76 days in different loading ratios. Dilution rate was changed almost every day due to substrate disposition in the region. The influent composition was calculated as in (Arzate, 2017) and is shown in Tab. A-4. The calibration of AM2 was performed considering as initial parameters the calibrated parameters of each feedstock. In parameter calibration of the co-digestion, the maize silage parameters as initial parameters showed the best-fit for the co-digestion. The AM2 model is able to predict reasonably well the dynamic results of biogas production amount, in which two AM2 parameters were

modified to fit the co-digestion data. The parameters are the yield for VFA production (k2) and the yield for substrate disintegration (k7), the rest of model parameters had to remain constant. The comparison between simulated results and biogas data is given in Fig. 5. The parameters k2 and k7 were adjusted by fitting the simulation results to the observed experimental data; the variation of these parameters and the amount of fed substrate during the process is indicated in Tab. 2. The first 30 days of digestion, the three substrates were fed in a majority proportion of maize silage. Subsequently, at days 31-37, grass silage was no longer fed and only maize silage and cow manure are fed in a proportion of 47.7% to 62.2% of maize silage. The feed at days 38-66, the cow manure loading rate was increased without grass silage feed and maize silage was continuously fed. Finally, at days 67-74 only maize silage was fed.

Table 2. Amount of substrate fed to a digester with a capacity of 1440 m3 related with AM2 parameters k2 and k7 from simulation.

Day	amount of substrate fed	k2	k7
1-30	maize silage (min. 39.5%-max. 55.8%) ; grass silage (min. 0- max. 46.9 %); cattle manure (min. 11.4 %- max. 31.6 %)	309.7	12.7
31-37	maize (min. 47.7 %- max. 62.2 %); grass silage (0); cattle manure (min. 37.7%- max. 52.3 %)	329.6	17.8
38-66	maize (min. 48.5 % – max. 73.7%) grass silage (0); cattle manure (48.6 % -51.3 %)	359.7	32.7
67 -74	Only maize silage was fed (100%)	329.6	17.8

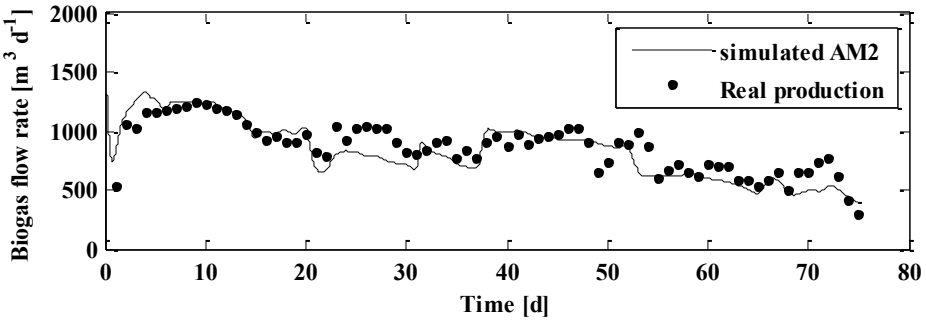

Figure 5: Extended AM2 simulation (-), real production data of bioreactor (•), over a period of 76 days of co-digestion process using maize, grass silage and cow manure conducted in a 1414 m^3 reactor.

Discussion

The results demonstrate that the response of digesters exposed to variations in OLR including different substrates depends on influent concentration of organic substrate ($S1_{in}$) and volatile fatty acids ($S2_{in}$). As can be seen in Figure 5, in the first 30 days of digestion the highest biogas production occurs due to a higher amount of organic substrate concentration in the influent, on day 31 this value decreases and the amount of biogas decreases as well. At the same time, the volatile fatty concentration in the influent increases from day 31 to 51, since the increase of manure in the system. After day 52, the concentration of volatile acids in the influent decreases together with higher organic concentration in the influent similar to some

days of the first 30 days, however the biogas production did not recover. From day 67 the minimum amount of VFA in the influent is recorded but at the same time the minimum amount of methane registered during the process.

AD process stability is linked to the quality of the feedstock material entered in the system. Fluctuations of the OLR will affect the microbial community in terms of methane production. Understanding how to manipulate the AD microbial communities to cope with more mixed feedstock is the only way to grow and maintain a successful process.

Parameters K2 and K7 had be adjusted when adverse conditions occur in OLR changes. As on day 31, where the grass silage did not feed more to the system, which considerably affects biogas production. Similarly, on day 67 when manure is not fed anymore, so the parameters had to be adjusted.

The results also established links between the microbial composition and OLR changes. Studies of the microbial communities have indicated that the change in OLR induces changes in the microbial community structure, abundance and dynamics and that decreases in biogas might be linked to decrease in both bacterial and archaeal biomass (De Vrieze, 2013).

Conclusions

AM2 considers complex feed compositions inside of feedstock as carohydrates, proteins, lipids, particulate inerts, and in a second step volatile fatty acids production. Parameter calibration of grass silage and cow manure ensured a proper model implementation without numerical inconsistencies. The use of AM2 offers new insights into the prediction of the biogas process for any other feedstock.

Uncertain parameters are commonly found in models for biotechnology, in which the number of outcomes, which can be measured are only few. An estimation of a large number of parameters as from the ADM1 is complicated. A large set of experimental data is required, thus the results may exhibit inconsistencies. Therefore, a decrease of parameters in the model is recommended or simply the use of reduced models are preferred.

Biogas production is a key parameter for indicating total process performance, but can not exhibit stress conditions of the process. VFA can be used as a warning indicator of the balance of the system. The extended version of AM2 can be used to estimate dynamics of VFA production, thus the biogas formation can be used to adjust the feedstock mixture to the needs by the operator.

Nonlineality of anaerobic digestion process makes monitoring and optimal control to be a challenge; reduced models as the AM2 will facilitate the application of programs to simulate the whole process including ASPEN Custom Modeler. The reduced AM2 which considers prediction of the main variables of the process appears as a model well-suited for monitoring and control to support stability and robustness of flexibility feed digestion process.

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Appendix

Table A-1 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 {Löffler, 2012 #43}

Table A-2. 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

Table A-3. Substrate loading rate to a digester of 1414 m^3

day	fed substrate [m^3 d^{-1}]			day	fed substrate [m^3 d^{-1}]		
	maize silage	grass silage	cow manure		maize silage	grass silage	cow manure
1	3.279	3.279	0.000	38	1.683	0.000	1.399
2	3.279	3.891	1.115	39	1.683	0.000	1.399
3	3.563	3.235	0.874	40	1.749	0.000	1.366
4	3.563	3.235	0.874	41	1.781	0.000	1.683
5	3.224	2.732	0.787	42	1.683	0.000	1.224
6	3.071	2.022	1.344	43	1.508	0.000	1.421
7	3.421	2.317	1.311	44	1.552	0.000	1.639
8	3.071	2.514	1.377	45	1.552	0.000	1.639
9	3.432	2.197	1.388	46	1.552	0.000	1.639
10	3.279	2.284	1.322	47	1.590	0.000	1.464

11	3.508	2.120	1.366	48	1.590	0.000	1.464
12	3.388	1.858	1.344	49	1.424	0.000	1.341
13	3.639	1.421	1.301	50	1.424	0.000	1.341
14	3.399	1.246	2.087	51	1.424	0.000	1.341
15	3.443	0.000	1.333	52	1.749	0.000	1.093
16	2.896	1.497	1.246	53	1.967	0.000	0.940
17	2.842	1.410	1.443	54	1.967	0.000	0.940
18	2.896	1.683	1.519	55	1.858	0.000	0.820
19	2.612	1.552	1.410	56	1.967	0.000	0.874
20	2.934	1.844	1.557	57	1.858	0.000	0.874
21	0.978	0.615	0.519	58	2.077	0.000	1.060
22	2.678	0.000	0.000	59	1.825	0.000	0.874
23	2.678	1.268	1.388	60	1.749	0.000	0.667
24	2.601	1.311	1.421	61	1.770	0.000	0.645
25	2.525	1.137	1.322	62	1.694	0.000	0.601
26	2.601	0.721	1.344	63	1.530	0.000	0.546
27	2.678	0.754	1.443	64	1.311	0.000	0.546
28	2.339	0.721	1.344	65	1.169	0.000	0.546
29	2.421	0.590	1.328	66	0.973	0.000	0.546
30	2.421	0.590	1.328	67	0.776	0.000	0.000
31	2.612	0.000	1.585	68	0.448	0.000	0.000
32	2.361	0.000	1.443	69	1.148	0.000	0.000
33	2.197	0.000	1.355	70	1.137	0.000	0.000
34	2.197	0.000	1.355	71	0.907	0.000	0.000
35	1.672	0.000	1.836	72	1.519	0.000	0.000
36	1.858	0.000	1.273	73	0.645	0.000	0.000
37	1.858	0.000	1.273	74	0.623	0.000	0.000

Extended AM2 Model for anaerobic digestion in ACM

```
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
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Paper VI – (Manuscript in preparation)

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

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Abstract
Renewable technologies shall contribute to a reduction of greenhouse gas (GHG) emissions during energy generation and provision. Nevertheless, high proportions of fluctuating renewable energy (RE) leads to a number of 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.

The objective of this study is to combine a life cycle assessment (LCA) and modelling approach for demand driven biogas production via a flexible feedstock management. 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. Base-load 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

3.Introduction
The economic situation and governmental support of renewable energy (RE) in Europe resulted in favorable conditions to establish biogas plants. 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. Nowadays 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 clearlynot leading to a maximum output, and optimal yields not necessarily to the most sustainable strategy. For these reasons, it is required to optimize the current biogas production processes with a proper

objective function to design a control strategy that indeed minimizes the environmental impact of energy production from biomass.

Biomass resources are considered as one of the main RE sources and 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 concern about using food to produce energy. Maize often results in the highest yields, therefore it is a preferable feedstock for energy generation, meaning that 90% of biogas plants in Germany run – at least partially - with maize as feedstock (e.V, 2014).

The largest contributions to RE systems are originated from wind and solar power in Central Europe. Nevertheless, the high proportion of fluctuating RE lead to challenges. The weather-dependent energy generation needs to be balanced. By this aim, for the first time in 2012, the German RE law introduced new incentives for a flexible energy generation. 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.

In line with the above-mentioned fact, it is important to assess locally available biomass, which can be used more efficiently as a source for RE production and a better waste management. With a focus of sustainable waste management, the biogas energy potential of residues and waste represent the current focus of interest (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 with locally accessible feedstock (Franco et al., 2015; Mol, 2014; Willeghems & Buysse, 2016).

Recent scientific findings described 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 (Fargione et al., 2008; Johansson & Azar, 2007; Searchinger et al., 2008). Therefore, it is crucial to evaluate biogas production plants operation 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 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 shock 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 (Edwards & Hamson, 2001).
The ADM1 is the most commonly used model for anaerobic digestion modelling, although it has a complex structure. It contains a large number of parameters for calibration and a full substrate characterization is required (Razaviarani & Buchanan, 2015). The extended AM2 is a reduced model, which was recently published; it requires the substrate characterization in terms of particulate organic matter. 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 (Arzate et al., 2017) based on Matlab as a simulation platform. The template process co-digests the maize silage, grass silage and cow manure. In a previous study from Arzate et al, 2018, AM2 simulations were compared with results obtained with the ADM1. So that this study aims to create the LCA approach in dynamic state and place into the AM2 for each feedstock based on estimated model parameters. The model was applied for a co-digestion process of an agricultural biogas plant of 500 kW el power. In this study, the previously validated model was applied in order to simulate a demand driven energy production for a 500 kW el biogas plant. Scenarios were created based on the changes in power generation and consumption from Agorameter (Energiewende, 2017) and spot market prices of a reference period by mainly 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, the LCA parameters and their interaction on AM2 model. The simulation program constitutes a development to reduce the impact of feedstock utilization and can be used as a decision-making tool. After having reviewed the basic principles and techniques of the anaerobic digestion process, modelling concepts were assessed to delineate the dominant LCA parameters. Later, 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, possible incentives provided by German Renewable Energy law (EEG) were calculated.

4.Materials and methods

2.1. Feedstock

Maize silage, grass silage and cow manure were selected for simulations on biogas process. 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 studied biogas plant has an electrical power capacity of 500 kW. Maize silage (1 t/h), grass silage (1 t/h) and cow manure (1 t/h) is digested. Under baseload production mode, the plant consisted of a main digester (1,400 m^3 with 524 m^3 of gas storage), and 2 secondary digestors (2 × 2,851 m^3 with each 942 m^3). All were operated at 37 °C (mesophilic conditions). The hydraulic retention time was 87 days. The energy production is illustrated in Figure 1.

2.2.1. Demand driven biogas production and scenarios

The energy production/supply is adapted hourly based on changes in the energy consumption/demand and spot market prices of a reference period by feed management. Time periods between 5 am and10 am as well as 5 pm and 10 pm were selected as high electricity producing times based on Agorameter (Energiewende, 2017).

Additional income could be gained by this way of operation, however, investment of either an external gas storage or CHP becomes necessary. In order to be able to produce more electricity at a time, in which the energy demand is higher, additional 160 kW el power CHP unit was installed, so that both CHP can work together. Production scenarios are illustrated in the Table 1.

2.3. Extended AM2 model

As published in Arzate et al. (2017), the extended AM2 includes some more equations about hydrolysis and biochemical conversion than previously published versions (Bernard et al., 2001). The model includes short-chain carboxylic inhibition of the acetoclatic methanogenesis and hydrolytic steps.

2.4 Life cycle assessment

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 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 the data.

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 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 have to be included in the LCA study (ISO Standard, 2006). The studied system boundaries included: crop production/ acquisition, ensilage/ storage, anaerobic digestion, storage of residues and application of digestate for agricultural production, transport between multiple stages, the biogas combustion, supply of generated electricity into the grid and heat utilization for temperature control at the fermenters and animal housing Ertem et al. (2016a).

2.4.1 Life cycle inventory analysis

In a life cycle inventory (LCI) analysis, the lists of resources, energy and emissions entering and leaving the life cycle are compiled. LCI comprises of 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 up to the provision of electricity to 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 with the Ecoinvent database. All parameters were calculated for region in Northeastern Germany. The parameters for any type of feedstock and for industrial scale biogas plant used in 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], acidification potential, $AP_{total\_substrate}$, [kg CO2 eq. per kWh

electricity produced] and eutrophication potential, $EP_{total\_substrate}$, [kg CO2 eq. per kWh electricity produced] of the whole production system were based on 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 given in 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 is depicted in Appendix.

3. Results & Discussion

An operational integration of dynamic process modelling and an LCA is not yet common. For such a combination, the developed model was first adjusted based on the parameter calibration. Then the simulation was validated based on biogas production data from a real biogas plant. The developed simulation is able to quantify the effect of process parameters and dynamics in the impact calculation results. Some magnification complexities and restrictions involved were related to the fact that, biogas plants are constantly subjected to dynamic aspects which should be taken into account to realize relative robustness in operational conditions in any situation, ensuring stability and the correct simulation of the plant.

As LCA is habitually a non-dynamic methodology, an interface between dynamic modelling results and inventory flows in LCA was required, together with the conversion of specific inventory items. In order to be able to integrate the approaches, it was necessary to include the GHG formation processes for the biogas plants. Therefore, the calculations methodologies, which are commonly applied in Simapro software and the Ecoinvent database were used. Particular attention was paid on CH_4 forming dynamics to achieve better control of the total GHG emissions from AD w/o making the model for complex.

The model was used to simulate the base load dependent biogas production from the co digestion of 1 t/h grass silage, 1 t/h maize silage and 1 t/h cow manure 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. After the parameter fit, the model was able to successfully simulate the changes in the process. Results show that by feed management, the daily gas production rate can be modulated up to ±50% from the daily average gas production rate. By targeted reduction of the feeding quantity at the times where the energy demand is lower, the gas production was reduced even below 60 $m^3\ h^{-1}$. Results show the effects of flexible substrate feeding on the gas production rate, and thus the flexibility of the process itself. The simulated process is reacting to the feeding changes within several minutes with a significant jump in the gas production rate. According to the model, the volatile components in the substrate are initially degraded; CO_2 is released due to the prevalence of hydrolytic activity. A considerable increase in the gas production rate can be observed within an hour. After each feeding event, the CH_4 concentration drops below 50% and the CO_2 proportion rises up, while the hydrolytic and acidogenic activity is high. However, the anaerobic system reacts, buffers the disturbance and gains stability again.

In the model, grass silage shows a similar behavior as maize silage regarding kinetic constants [28]. However, at a real biogas plant, this behavior might show differences. Explanations for that different behavior could be found in the rheology and fermenter dimensions as well as in the general process conditions in practice. Due to varying consortia and feedstock qualities, reproducibility might be limited anyway.

In the first 30 min time during the feeding of all substrate mixes, a peak in the measured biogas production rate can be observed. This can probably be explained by the proportion of volatile acids in the respective ensiled substrates and the content of fast degradable components. This behavior

is well comprehended within the model. Figure 3 illustrates the cumulative biogas productions for 2 production concepts. From the figure, one can see that flexible production increases the production efficiency 6% by means of total biogas produced.
In conventional full-scale plants, the gas is collected in large gas storages for several hours. Thus, different gas qualities are mixed, leading to lower variations in the gas quality. Figure 3 shows 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 an extra 0.215 € kWh^{-1} el operational costs. Figure 4.b. illustrates the times where biogas was combusted through CHPs.
Figure 5 depicts the LCA results based on the feed 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 used in the substrate mix is decreased, GWP from digesters is decreasing accordingly. A low biogas potential of manure compared to energy crops results in higher amounts of manure to be fed into the digesters in order to produce the same amounts of biogas; (biogas yields for each substrate; maize silage 216.1 m³/ t FM, cow manure 30.4 m³/ t FM, grass silage 189 m³/ t FM).
According to Ecoinvent database 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.
During low energy production times, NH_3 emissions resulting from anaerobic digestion at the digesters were also lower, since the amount of biogas produced was also lower. 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 is 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 energy production flexibility, 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 outcomes.
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.
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.

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 long time is needed before measurements within the anaerobic digestion provide useful data. In these cases, the integration of the AM2 and LCA approach can provide a suitable solution.

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.

To adopt more detailed dynamic process-based models that are characterized by a multitude of factors, it will be necessary to calibrate large amount of data. Furthermore, full-scale mathematical model experiments should be performed to establish apropiate kinetics and formation mechanisms of GHG for different feedstock types. Knowledge of the involved GHG production pathways must be expanded to create a suitable and comprehensive model that is able to reproduce all of the processes involved in N_2O, NH_3, CO_2 and CH_4 formation. Future efforts should be dedicated to setting up mathematical software and tools/platforms for practical and feasible application for plant operators. Further, efforts on the model calibrations should be performed in order to establish a specific procedure for calibrating such complex and often over-parameterized models. The environmental trade-off is now recognized, and further studies and modelling development will enable process optimization for GHG emissions for multiple cases. Thus, an increase in the quantity and quality of measured data for GHG emissions from biogas plants will be available, which supports accuracy of LCAs. Although improved on-line instrumentation and extended sampling campaigns for GHG emission monitoring will be required, standardized analytical protocols must be set up, and operators and plant managers must be educated on how to monitor/control/reduce GHG emissions from biogas plants; in summary, the tools, which are there now, have to be applied in practice.

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Erklärung

Ich erkläre hiermit, dass ich die vorliegende Dissertation selbst verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel verwendet habe.

Berlin, 2017 Juan Antonio Arzate Salgado