Doctoral Dissertation

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Anaerobic degradation of industrial carbon capture reclaimer MEA waste

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I would like to express my deepest love to my families: my father Wang Chengzhong, mother Wang Yalan, elder brother Wang Ming, my sister-in-law Zhang Qing and my uncle Wang Zhengan etc. Thanks for their encouragement, support and endless love. This achievement would be an honor shared by the whole family.

Shuai Wang
02.10. 2013
Porsgrunn, Norway

I would like to dedicate this thesis to our coming family member, my nephew, Wang Enzan, a blessed new life and hope. Wish the best for his life!

Let us under the love of God, welcome a new period!

Summary

Global warming and its impacts are serious and challenging international problems (Vitousek, 1994). Increasing fossil fuel consumption results in rising atmospheric greenhouse gas levels which enhances global warming (Vitousek, 1994). To limit the global temperature increase, protocols to reduce CO_2 emission worldwide promote CO_2 capture and storage (CCS) (IPCC, 2007). The most established CCS technology involves post-combustion CO_2 absorption using amine solvent and CO_2 desorption for storage (Rochelle, 2009). Life cycle assessment has shown that CCS can be a good solution to achieve a significant reduction in greenhouse gas emissions (Singh et al., 2011). There are, however, environmental trade-offs to consider, such as increased human and environmental toxicity potential due to solvent and the degradation products emissions (Singh et al., 2011). Chapter 1 gives a general introduction of the global warming and the proposed CCS technology.

The degradation products (amine waste) from CCS are recognized as hazardous waste (Council directive, 1991). It can pose threats to both humans and the environment, thus it is important to mitigate the threats in proper manners. Alternative waste treatment methods, including biological waste treatment, have been suggested for such waste (Abend et al., 1999). Anaerobic digestion (AD), that assimilates and degrades organics in a closed environment and produces renewable energy (CH_4), is the focus in this research. The degradation potential of monoethanolamine (MEA) waste (MEAw) is explored in Chapter 2. The amine solvent degradation in CCS processes, the products generated and their potential impacts are also summarized. Possible degradation pathways of the waste constituents of the specific MEA waste collected from an industrial CCS system are also introduced.

Researches of lab-scale AD of MEA waste with easily degradable co-digestion organics which resembles domestic wastewater are introduced in Chapter 3. Co-digestion feed provides minerals and easily accessible organics for organisms' development. A hybrid reactor system applying the concepts of a suspended sludge blanket and attached biofilm growth of the AD culture was employed with semi-continuous feeding. Mixed cultures from various sources were added initially to increase the diversity of AD culture. Experimental and theoretical analytical methods are also introduced in this chapter.

A slow culture adaptation to the MEA waste content that is resilient to degradation was observed. Degradation results presented in Chapter 4 show a stable and robust method to treat MEA waste. The main process limitation identified is that the methanogenesis AD step becomes inhibited when the feed contains less than ~ half co-substrate. Ammonia, as a product of MEA waste degradation, can be the main inhibition factor and caused the toxicity effects for aquatic species. MEA waste organics are degraded by AD to an extent that most of the toxicity to aquatic life is removed. The expanded anaerobic digestion model No.1 (ADM1) model successfully captured the trends of AD digester

performances and can be used as an effective tool to investigate and understand MEA waste degradation.

Successful anaerobic degradation of CCS MEA waste contributes directly to the deployment of CCS technology, by ensuring safe disposing of generated waste substances. Researches of co-digestion of MEA waste with easily degradable and accessible organics, such as domestic wastewater, can potentially reduce the cost of applying AD of MEA waste in full scale. Studying the AD capability and limitations for MEA waste treatment also expanded the knowledge associated with biological industrial waste treatment. Investigation of lab-scale AD of MEAw in terms of bioreactor efficiency, organisms' cultivation and inhibition preventions enhanced knowledge accumulation and can promote the development of CO_2 capture into a more efficient and environment friendly technology.

This study recognized the importance of co-digestion substrates and the positive effects of long sludge retention on waste assimilation and degradation. Further study on identification of the specific inhibitory chemicals in AD of MEA waste, the degradability of identified CCS MEA degradation products and promotion of lab scale to pilot scale tests can be interesting research topics.

Abbreviations

AD	Anaerobic digestion
ADM1	Anaerobic digestion model No.1
CCS	CO_2 capture and storage
COD	Chemical oxygen demand
FAN	Free ammonia nitrogen
GHG	Greenhouse gas
HEEDA	N-(2-hydroxyethyl) ethylenediamine
HEIA	N-(2-hydroxyethyl) imidazolidin-2-one
MEA	Monoethanolamine
MEAw	Reclaimer MEA waste
MEAwr	MEA waste COD ratio
OLR	Organic loading rate
OZD	Oxazolidin-2-one
PCA	Principal component analysis
TAN	Total ammonia nitrogen
UASB	Upflow anaerobic suspended blanket
VFA	Volatile fatty acid

Contents

Chapter 1 Introduction

1.1 Global Warming and Greenhouse Gas Emission

Global warming as an environmental problem has aroused great attentions since late 1980s. It is considered to be the most serious and intense environmental issue that is challenging humans in our time (IPCC, 2011). A series of environmental impacts, such as polar ice cap recession, sea level rising, increasing frequency and intensity of extreme weather conditions (e.g. droughts) are accused to be caused by the global warming (IPCC, 2007). Release of greenhouse gases (GHG), CO_2, N_2O and CH_4 etc. from fossil fuel combustion, gas exploration and other human activities are blamed to be one of the main causes of global warming (IPCC, 2007). Research shows that a global temperature will increase by 1.1 to 6.4 °C in the 21st century if the current human activities proceed (Shao and Stangeland, 2009). Predicted consequence includes ecosystem collapses and the extinction of 15 to 40 percent of the world's animal species. However, due to demands for development and high quality living conditions in both developed and developing countries, energy requirements are intensified. The energy demand will mostly be fulfilled by the fossil fuel consumption in a predictable future (OECD, 2011). This trend will result in continued excessive emission and accumulation of GHG in the atmosphere, causing increasing concerns on the sustainability of human development.

Acute actions of avoiding such devastating effects, aiming to restrict global temperature increase by 2 °C or lower through constraints on CO_2 emission growth up to 2020 have been adapted as an international guiding principle (UNEP, 2010). Activities that counteract global warming, in agreements with curbing greenhouse gas emission by promoting renewable energy applications (e.g. solar, wind and biogas), implementing CO_2 capture and storage (CCS) etc. have been proposed and adapted in many countries (IPCC, 2011).

1.2 CO_2 Capture and Storage (CCS)

CO_2 is the main GHG generated in human activities of fossil fuel consumption. The control of CO_2 can potentially mitigate GHG effects. CO_2 scrubbing in natural gas processing by applying aqueous amine solvent is a mature technology for CO_2 capture (Rochelle, 2009). The complete CCS process involves capture, transport and storage of CO_2 (IPCC, 2005). Extensive research, testing and development on each of those subjects are ongoing with improvements steadily reported.

Alternative CO_2 capture processes are divided in groups of pre, post and oxygen combustion CO_2 capture depending on the different fuel combustion stages at which it is captured (MacDowell et al., 2010) (Fig. 1.1). The post-combustion CO_2 capture by employing alkanolamines solvents for CO_2

absorption is considered to be most compatible with existing infrastructure, suitable for retrofits as it is flexible in implementation as a downstream add on (Rochelle, 2009). It is therefore currently attracts attention for energy intensive industries such as power plants and cement factories. Globally, 25 of 45 running CO_2 capture projects implemented in power plants are employing post CO_2 capture technology (MIT).
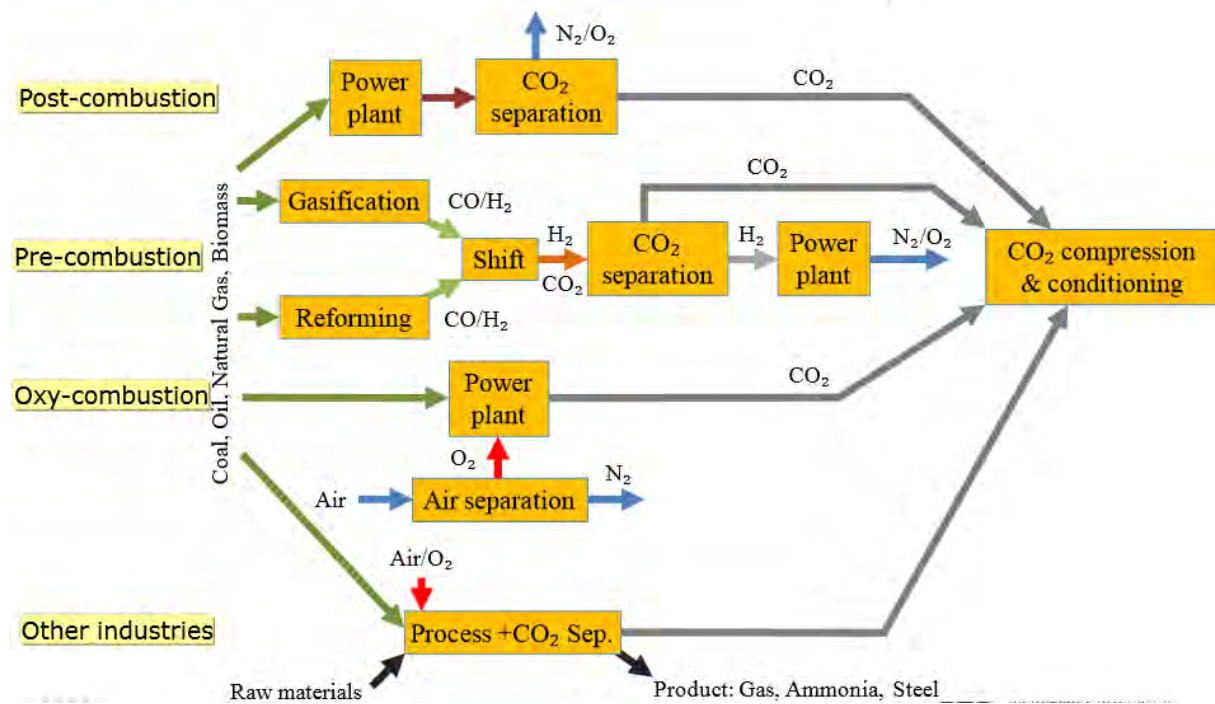
Fig. 1.1 CO_2 capture options in energy intencive industries (Mayuri, 2012)

The study in this dissertation is focusing on waste from post CO_2 capture CCS technology with amine solution used as the capture solvent. The waste studied was collected from CO_2 capture technology that consists of CO_2 absorption in absorber and desorption in stripper such as shown in Fig. 1.2. The process is designed to be added downstream to existing combustion facilities. The flue gas from fossil fuel combustion flows through the capture unit. CO_2 rich flue gas is first absorbed by alkaline amine solvents (e.g. monoethanoamine, MEA) in the absorber. The CO_2 rich solvents are regenerated in the stripper by driving off CO_2. A stream of the stripper bottom solution is normally directed to reboiler, where the solvents are recovered at a relatively higher temperature. The regenerated solvents (lean solution, Fig. 1.2) are repeatedly used in the capture process with the driven off CO_2 collected and compressed for transportation and storage. Such CO_2 can be utilized for food industry and other purposes (Shao and Stangeland, 2009).
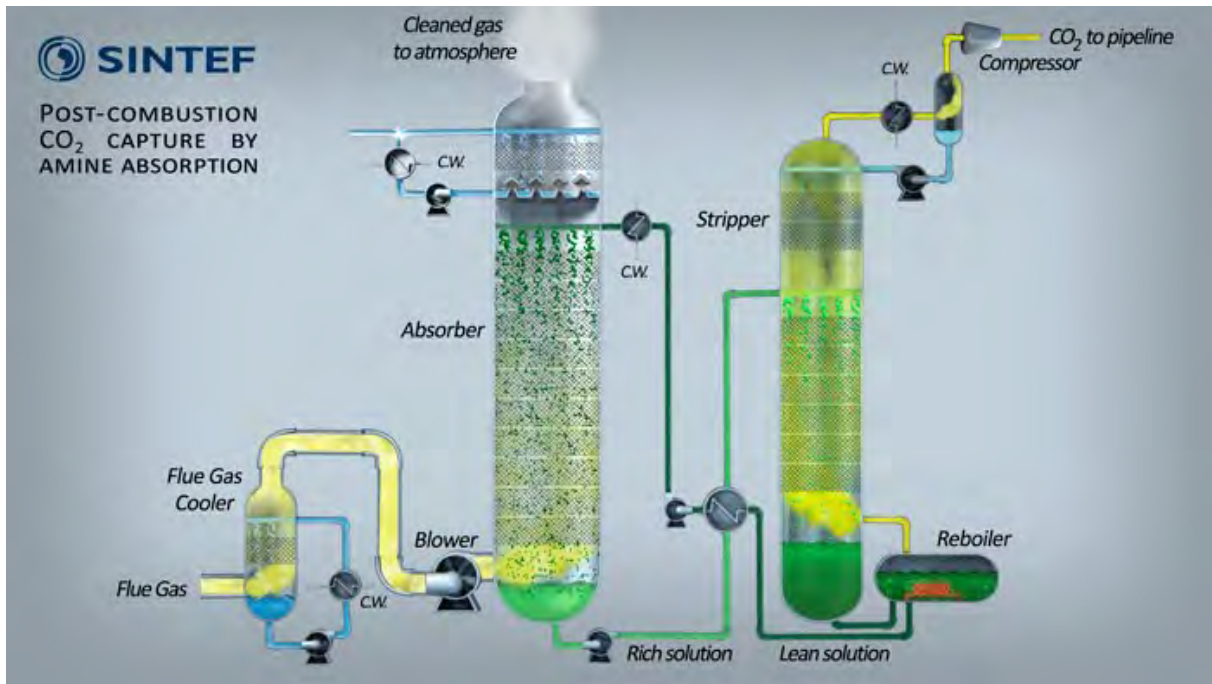
Fig. 1.2 Sketch of post carbon capture process (Sintef, 2010)

1.3 MEA Solvent Degradation

Amine solvents are normally used in the post CO_2 capture processes for CO_2 absorption (Rochelle, 2009). The commonly used amines are monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA) (Thitakamol et al., 2007). MEA is the most used solvent due to its comparably low price and properties of high water solubility, high absorption capacity and fast kinetic at low CO_2 partial pressure (Islam et al., 2011). While one of the problems associated with CCS using amine solvent is irreversible solvent degradation in reactions with impurities in the flue gas (Thitakamol et al., 2007). A typical flue gas from a coal fired power plant contains 70 - 75% N_2, 10 - 15% CO_2, 8 - 10% H_2O and 3 - 4% O_2 (Bhown and Freeman, 2011) and some trace amounts of SOx and NOx are also detected in such flue gases (Fostas et al., 2011). Some of those chemicals are potentially reactive with amine solvents which can facilitate amine degradation in CCS process (Strazisar et al., 2003).

In the case of using MEA for capturing CO_2 from flue gas of a coal fired boiler, MEA degradation occurs within CO_2 absorption and desorption processes (Gouedard et al., 2012). Side reactions of oxygen, NOx, SOx, ashes etc. with MEA first proceed in the absorber column (Fig. 1.2). Oxidative products are generated in this column where the column temperature is normally maintained in a range of 40 to 60 °C (Gouedard et al., 2012). Generated oxidative products together with other flue gas components are directed to the stripper column where thermal degradation proceeds at a column temperature of 100 to 120 °C (Gouedard et al., 2012). MEA carbamate and other side reactions' products formed in this column (Gouedard et al., 2012). Most MEA is regenerated by distillation or

vacuum distillation in this stripper column (Fig. 1.2). The recovered MEA solvent is used repeatedly in the reaction loop. The undesirable compounds generated by the irreversible transformation of MEA accumulate at the bottom of the stripper and is regularly collected for disposal (Islam et al., 2011). The complex chemical products generated from MEA degradation can arouse different operational problems, such as formation of volatile compounds, foaming, fouling and corrosion in the capture facilities (Thitakamol et al., 2009; Abdi and Meisen, 2010; Dawodu and Meisen, 1996). It is reported that solvent degradation causes solvent loss that accounts for around 10% of the total cost of CO_2 capture (Rao and Rubin, 2002). Approximately 2.2 kg of MEA needs to be reloaded to replace solvent MEA loss for capturing 1 tonne of CO_2 for effective CO_2 capture performances (Strazisar et al., 2003). The degradation products also represent health and environment threats and should be handled in responsible ways (Shao and Stangeland, 2009).

1.4 Proposed MEA Waste Treatment Methods

The MEA waste is classified as hazardous waste (Council Directive 91/689/EEC, 1991). Development of safe and efficient handling and treatment methods for such waste are therefore important to prevent or limit emissions of constituents that can be damaging to humans and the environment. The proposed treatment methods include: 1) Incineration, where waste is burned for energy recovery. 2) Landfilling, which demands specific locations and facilities for waste storage to prevent human and environment contaminations. 3) Biological treatment, applying organisms for assimilating and degrading organics, including the toxic chemicals in the waste. 4) Alternative techniques, such as advanced oxidation (Petala et al., 2008), electrolysis (Cho et al., 2009) and enzymatic treatment (Tavares et al., 2009).

Due to stricter emission controls and regulations inclining to safer and greener waste management methods, landfilling organics is becoming less attractive and hazardous waste landfilling is prohibited in European countries (Council Directive 1999/31/EC). Incineration can be an attractive option at some specialized waste treatment plants, such as cement factory in Porgrunn, Norway (Botheju et al., 2013). Biological treatment is applied for a wide range of industrial and domestic solid and liquid wastes. Extensive studies have been carried out and successful scaling ups of biological treatment plants have been carried out worldwide (Lettinga and Hulshoff Pol, 1991). This is proposed as an option for treating MEA waste by considering its ability of effectively assimilating organic substances and converting these to less harmful or even useful products, such as CH_4 as renewable energy from anaerobic digestion. The mentioned alternative techniques might serve as supplements to biological treatment and their capability and economic effectiveness still need comprehensive investigations.

1.5 Research Scope

Researches on effective and economical waste treatment methods are important for CCS technology that has a potential to be implemented worldwide for CO_2 mitigation. Understanding the treatment process and accumulate knowledge in terms of waste handling methods, treatment efficiency, treatment limitations, etc. can facilitate the public acceptance of the CO_2 capture technology and promote the development of CCS.

This study was focusing on anaerobic treatment of an industrial reclaimer MEA waste that was collected from an industrial scale coal fired boiler using MEA as the flue gas CO_2 capture solvent. Both theoretical and experimental studies were carried out in the research. Theoretically, the degradation status of MEA and other chemicals present in the MEA waste were investigated based on literature reviews. Modeling and simulations were used to evaluate assumptions and results from the experiments. The standard ADM1 model (Batstone et al., 2002) was expanded and applied to investigate the MEA waste degradation based on theoretical assumptions generated from experimental analysis. The experimental tests of anaerobic MEA waste degradation were performed in lab-scale reactor systems at defined temperatures and feed conditions. The degradation performances were assessed by mass balances monitoring performance parameters such as biogas yield and chemical oxygen demand (COD) removal according to standard methods. Other anaerobic digester products were also analyzed for more in depth understanding of the biological degradation processes, process inhibition factors and cultivation effects. Testing AD detoxifying effects on MEA waste were also performed for assessing the potential environmental effects of AD treatment.

1.6 Research Objectives

The anaerobic degradation tests of industrial reclaimer MEA waste were conducted to reveal the MEA waste degradation potential and limitations at defined conditions. This objective was approached by studying the effectiveness of AD waste degradation, in experimental tests with varying bioreactors and feed scenarios to reach the following goals: 1) Construct an AD digester that promotes effective growth and accumulation of an efficient culture. 2) Sustain the stable AD digester for continuous MEA waste degradation. 3) Perform experimental tests with appropriate chemical analysis to understand and quantify MEA waste degradation. 4) Reveal and understand limiting factors for AD of MEA waste. 5) Test the effectiveness of AD in detoxifying MEA waste. 6) Generate a mathematical model based on Anaerobic Digestion Model No.1 (ADM1) (Batstone et al., 2002) to facilitate MEA waste degradation simulations.

Chapter 2 Literature Review

This chapter presents a literature review of MEA degradation, both the unwanted degradation appeared in CO_2 capture and the desirable degradation occurring in biological waste treatment. Biodegradation of MEA waste is also presented.

2.1 MEA Degradation in CCS

MEA degradation in CCS facilities is complicated and dependents on the flue gas composition, the involved operational conditions and applied fuel pretreatment methods (Gouedard et al., 2012). The undesired side reactions in the CCS process lead to complex products generation (e.g. heat stable salts) (Gouedard et al., 2012). Identification and quantification of MEA degradation components are challenging due to methods and instrument limitations (Strazisar et al., 2003; Thitakamol et al., 2007). Two main types of MEA solvent degradation pathways have been proposed: thermal and oxidative degradation (Strazisar et al., 2010; Lepaumier et al., 2009a, b, c; Goff and Rochelle, 2004; Strazisar et al., 2003). Thermal degradation mainly proceeds in the stripper column where CO_2 reacts with solvent by the impact of temperature (at around 120 °C for MEA) (Davis and Rochelle, 2009). Oxidative degradation is mostly expected to occur in the absorber where there is oxygen from flue gas (da Silva et al., 2012). Protonation, polymerization and isomerization reactions can be involved in the MEA degradation pathways (Strazisar et al., 2001, 2003; da Silva et al., 2012).

Thermal degradation of MEA in absence of CO_2 has been extensively studied to understand the role of heating. The degradation causes dealkylation, dimerization and cyclisation (Gouedard et al., 2012). Ammonia and N-(2-hydroxyethyl)-ethylenediamine (HEEDA) are generated as the most important thermal degradation products (Gouedard et al., 2012). Thermal MEA degradation at high CO_2 partial pressure showed successive degradation compounds of Oxazolidin-2-one (OZD), HEEDA, N-(2-hydroxyethyl) imidazolidin-2-one (HEIA) and N, N'-bis-(2-hydroxyethyl) urea (Gouedard et al., 2012). Mechanisms for the generation of each of these main products have been proposed by Gouedard et al. (2012). Oxidative degradation of MEA generates some similar products such as ammonia and HEEDA (da Silva et al., 2012; Davis, 2009). Gouedard et al. (2012) presented the main oxidative reactions involved in CCS and the generated products. Except for the chemicals identified as thermal and oxidative degradation products, more than 60 other degradation products are mentioned in the literature but without specifying mechanisms (Gouedard et al., 2012). MEA degradation in industrial CCS contains more compounds than that which had been identified as degradation products in laboratory tests (da Silva et al., 2012). Those products constitute the most challenging part in analyzing MEA degradation (da Silva et al., 2012).

In industrial CCS process, generated MEA degradation products accumulated with other flue gas impurities (e.g. dust, SOx and NOx) and process additives (e.g. corrosion chemicals) at the bottom of the stripper column. The mixture contaminants with high boiling points make the MEA recovery in the stripper complicated. A slipstream of the contaminated solvent is normally sent to a solvent reclaiming system where a much higher temperature is applied for MEA recovery (Strazisar et al., 2003). After the reclaiming, the recovered lean MEA solvent is returned to the CO_2 capture unit for repeat use (Fig. 1.2). The concentrated reclaimer bottom solution, consisting of MEA, contaminants such as heat stable salts and other MEA degradation products, is collected for disposal (Strazisar et al., 2003). This reclaimer bottom solution is termed "amine waste" or, in the case of this study, "MEA waste", MEAw. The major degradation products identified in the reclaimer amine waste are shown in Table 2.1 and Table 2.2 (Strazisar et al., 2003). This particular reclaimer MEA waste was collected from an industrial scale coal fired power plant with CO_2 capture using MEA solution as the capture solvent (Strazisar et al., 2003). The MEA waste used in this thesis has the similar origin.

MEA was the dominant chemical component in this MEA waste which was the similar waste applied for the experimental test in this dissertation. Ammonia, carboxylic acids and other oxidative products that may act as precursors in complex chemicals' generation, such as HeGly (N-(2-hydroxyethyl) glycine) were also identified (da Silva et al., 2012). Oxidation rather than dimerization (thermal degradation) was considered to be the dominant pathway involved in this industrial MEA waste generation (Strazisar et al., 2003). Observed dissolved metallic ions (Table 2.2) may have catalytic effect to the oxidative degradation of MEA, leading to more oxidative products generation (Sexton and Rochelle, 2011).

Table 2.1 Degradation products of MEA induced by CO_2 capture from Strazisar et al., (2003)

No.	Name	Formula
1	N-formylethanolamine	$(C_3H_7NO_2)$
2	N-acetylethanolamine	$(C_4H_9NO_2)$
3	2-oxazolidone	$(C_3H_5NO_2)$
4	N-(hydroxyethyl)-succinimide	$(C_6H_9NO_3)$
5	N-(2-hydroxyethyl)-lanthamide	$(C_5H_{11}NO_3)$
6	1-hydroxyethyl-3-homopiperazine	$(C_7H_{14}N_2O_2)$
7	1-(2-hydroxyethyl)-2-imidazolidinone	$(C_5H_{10}N_2O_2)$
8	1-hydroxyethyl-2-piperazinone	$(C_6H_{12}N_2O_2)$
9	4-hydroxyethyl-2-piperizinone	$(C_6H_{12}N_2O_2)$
10	3-hydroxyethylamino-N-hydroxy-ethylpropanamide	$(C_7H_{16}N_2O_3)$
11	2-hydroxyethylamino-N-hydroxyethylacetamide	$(C_6H_{14}N_2O_3)$
12	Ammonia	(NH_3)
13	Acetic acid	$(C_2H_4O_2)$
14	Propionic acid	$(C_3H_6O_2)$
15	n-butyric acid	$(C_4H_8O_2)$
16	Monoethanolamine	(C_2H_7NO)
17	2,6-dimethyl-4-pyridinamine	$(C_7H_{10}N_2)$
18	2-imidazolecarboxaldehyde	$(C_4H_4N_2O)$
19	1-methyl-2-imidazolecarboxaldehyde	$(C_5H_6N_2O)$

Table 2.2 Ion concentrations in MEA waste adapted from Strazisar et al., (2003)

	Ion concentration (ppm)	
	Lean MEA	Reclaimer bottoms
Cations		
Sodium	80	821
Potassium	2.2	18
Calcium	1.1	1.3
Iron	1.4	1.1
Copper	0.2	0.1
Zinc	0.3	0.2
Aluminum	-	0.4
Selenium	-	17.4
Arsenic	-	1.7
Ammonia	a	a
Anions		
Fluoride	300	1500
Chloride	1600	49000
Bromide	0.9	80
Sulfate	2200	250
Nitrate	290	3100
Nitrite	130	a
phosphate	7.8	230
a, Not quantified		

2.2 MEA Waste Impacts

Loss of MEA due to degradation products generation in CCS demands MEA replacements for effective CO_2 captures. This adds operational cost. Replacement of new solvent accounts for about 10 % of the total cost of CO_2 sequestration (Rao and Rubin, 2002). High distillation temperature requirement for MEA recovering in the reclaimer unit also negatively impacts the CCS operating economics. Pipe corrosion, fouling, etc. due to increased solvent viscosity leads to elevated cost associated with pumping and other operations (Islam et al., 2011).

MEA and its degradation products can potentially cause various impacts to humans and the environment. MEA is a harmful and corrosive chemical according to EU regulations and directives (EU, 2000). The MEA degradation waste is classified as hazardous waste in accordance with hazardous waste Council Directive 91/689/EEC, (1991). Emissions of MEA vapor and the degradation products have been observed in CCS operations, causing increased human, terrestrial, freshwater and marine ecotoxicity potentials (Singh et al., 2011). MEA is water miscible and considered to be easily biodegradable in nature. A strong MEA and soil binding, however, can inhibit biodegradation (Hawthorne et al., 2005). High concentration of MEA persistence has been detected on a contamination site even after a 10 years decaying period (Hawthorne et al., 2005). Limited toxic effects information from MEA degradation products and the additives, such as corrosion inhibitors, degradation inhibitors and oxygen scavengers were summarized by Thitakamol et al. (2007). However, effects of many of the identified MEA degradation chemicals are still lacking. Regulations and laws for disposing such chemical waste (e.g. HEI (N-(2-hydroxyethyl) imidazole (da Silva et al., 2012)) are

also not sufficient (Thitakamol et al., 2007). Thus, researching MEA waste treatment methods and investigating detoxifying effects of such treatment are important for knowledge generation and for CCS deployment in general.

2.3 Biological MEA Degradation

The MEA waste investigated here consists of high concentration of MEA (over 10 wt%) and MEA degradation products generated in the carbon capture process (Wang et al., 2014 a). Published papers on biological MEA degradation and the consequat products are Ohtaguchi et al. (1995); Lai et al. (1996); Ohtaguchi et al. (1997); Eide-Haugmo et al. (2009). Researches show that MEA is a readily biodegradable organic in nature, however, it takes a relatively long adaptation period before the degradation process proceeds (Sorensen et al., 1997; Eide-Haugmo et al., 2009). Due to MEA's antimicrobial nature and its cell membrane destructive effects, only certain organisms are able to take MEA as en energy and carbon source (Wang et al., 2006; Speranza et al., 2006).

Ndegwa et al. (2004) suggested that the MEA degradation in soil involves two hydrolysis steps: The hydrolysis of MEA (C_2H_7ON) to ammonium and acetaldehyde (C_2H_4O), and the hydrolysis of acetaldehyde to ethanol and acetate (Fig. 2.1). Two mechanisms are used to explain the synthesis of acetaldehyde from the degradation of MEA. One is the deamination by coenzyme B12-dependent ethanolamine ammonia-lyase (Eq. 1) and the other mechanism is the rearrangement of the NH_2 group by the process of Acetobacterium sp., strain LuTria3 (Abend et al., 1999). Acetaldehyde is readily degraded to acetate by organisms through consuming CO_2 (Speranza et al., 2006) and can also serve as an electron donor for nitrification of ammonia to NO_2 or NO_3 in the aerobic condition. In anaerobic condition, the hydrolysis product of acetaldehyde (acetate and ethanol) reacts as electron donors that can be converted to CH_4, providing energy for synthesis of methanogenic organisms.

Experimental investigations showed that anaerobic MEA degradation rates were relatively low and about one tenth of those in aerobic conditions (Sorensen et al., 1997). Biodegradations of the MEA collected at a contaminated soil site was rapid in both aerobic and anaerobic conditions at a MEA concentration of 1.5 g MEA/kg (Ndegwa et al., 2004). High MEA removal efficiency (over 99 %) was obtained in experimental test by applying MEA (over 0.5 g/L) as feed substrate for biological nitrogen removal, achieving a nitrogen removal of 77 % (Hauser et al., 2013).

$$NH_3^+ \quad OH \qquad\qquad R^1 \quad O$$
$$R^1-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}-H \xrightarrow[\text{coenzyme } B_{12}]{EAL} H-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}-\overset{\displaystyle \|}{C} \;+\; NH_4^+$$
$$R^2 \quad R^3 \qquad\qquad R^2 \quad R^3$$

$R^1 = R^2 = R^3 = H$
$R^1 = R^3 = H, R^2 = CH_3$
$R^1 = R^2 = H, R^3 = H$
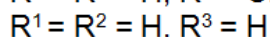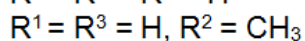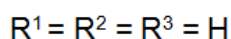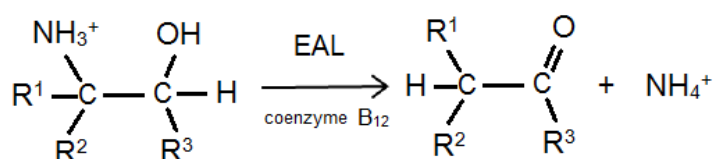
(Eq. 1)
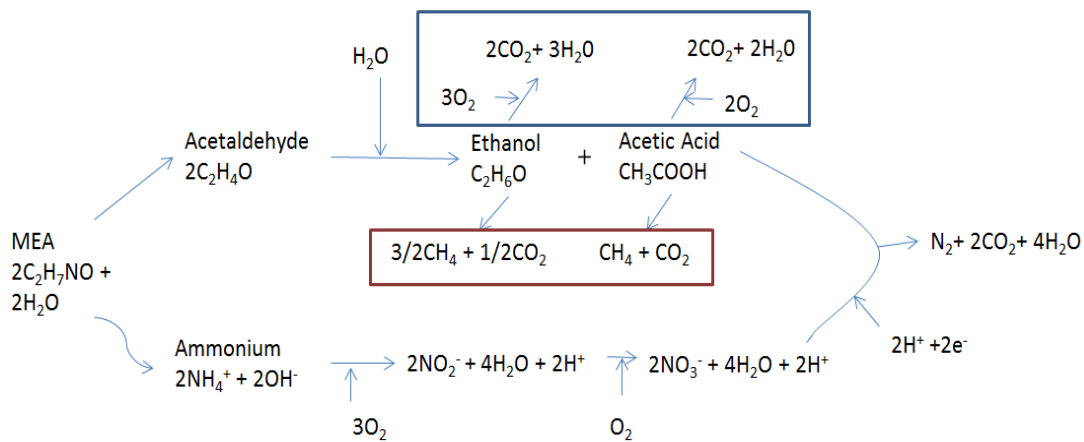
Fig. 2.1 Biodegradation paths of MEA (Ndegwa et al., 2004) for aerobic digestion (blue box) and anaerobic digestion (red box).

2.4 Biological MEA Waste Degradation

The biodegradation of industrial MEA waste involves not only MEA degradation but the degradation of chemicals (such as volatile fatty acids, HEIA and other MEA degradation organics) in the real waste. Industrial amine solvent solutions for CCS are designed for both stability and durability by adding specific chemicals (e.g. corrosion inhibitors). The accumulation of such anti-organisms constituents in reclaimer MEA waste makes the waste more resilient to biodegradation than natural amines (Eide-Haugmo et al., 2009). Biodegradation of such waste in terms of the interactions between organisms and the chemicals (e.g. kinetic rates and inhibitions) are unknown and the degradation processes are thought to be complicated. Schematic of proposed MEA waste degradation processes are shown in Fig. 2.2. Anoxic, aerobic, anaerobic and their combinations may lead MEA waste degradation to fertilizer and renewable energy generation (e.g. CH_4) which can maximize the utilization of such complex chemical waste (Botheju, 2010).
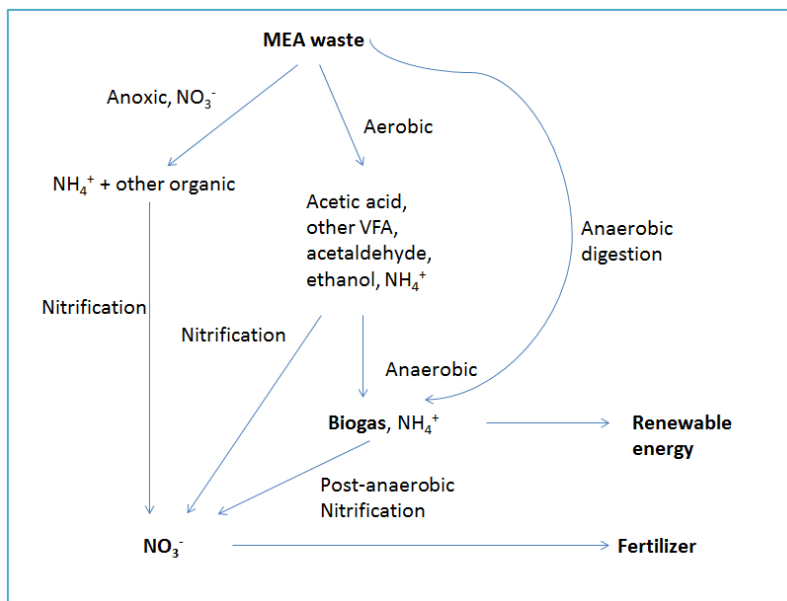
Fig. 2.2 proposed biological MEAw degradation pathways adopted from Botheju, (2010)

Only limited tests of industrial MEA waste biodegradation have previously been conducted (Hauser et al., 2013; Botheju et al., 2010, 2011). Hauser et al. (2013) mainly focused on MEA waste nitrogen removal in aerobic condition. Over 98 % MEA waste organics carbon removal and over 70 % of total nitrogen removal was achieved in her test. Anaerobic degradation (AD) of such complex waste has been suggested and trial tests were conducted by Botheju et al. (2011). However, detailed information on MEA waste degradability, waste removal efficiency and the possible inhibition effects in AD are lacking. Previous researches conducted in Telemark University College by Botheju revealed that anaerobic degradation of MEA waste alone was not successful, observing diminishing efficiency after months of operation. Botheju et al. (2011) proposed to add external easily degradable organics to enhance AD of MEA waste since the low concentration of accessible carbon in the amine waste limited anaerobic organisms' growth. Industrial carbonic wastes such as apple residues from apple juice processing factory and other easily accessible domestic waste (e.g. waste water) are potential co-digestion substances for MEA degradation. Digestion of a combined feed of MEA waste with easily degradable organics, nutrients, vitamins showed stable anaerobic operation and the waste was at least partly biodegradable at the co-digestion feed condition by applying mixed and adapted culture (Botheju et al., 2011).

Both aerobic and anaerobic biodegradation of MEA waste are possible alternatives. However, aerobic treatment of MEA waste involves aeration (air or oxygen pumping in to the digester), making such open systems with gasses and aerosol to the atmosphere. It can potentially cause emission that can pose human and environment threats. Demanding for external electrons and carbon sources (e.g. ethanol) for stabilizing aerobic digestion (Tchobanoglous et al., 2003) also negatively impacts the aerobic treatment efficiency. Such factors imply advantages of AD over aerobic digestion, such as:

Saving aeration energy; providing closed treatment system, preventing discharge of potentially harmful chemicals to the air; generating renewable energy (CH_4); reducing biomass generation and bioreactor volume. AD of MEA waste is therefore the focus of this project.

Challenges of anaerobic digestion of MEA waste also emerge. The organisms involved in AD are sensitive to toxic effects of ammonia, pH variations etc (Tchobanoglous et al., 2003). Methanogenesis is especially vulnerable to such factors (Chen et al., 2008). The AD biomass cultivation process is generally slow and easily inhibited (Chen et al., 2008). Additionally, slow adaptation of the anaerobic culture to toxic factors, due to slow growth of such, demands highly efficient biomass accumulation. These challenges are met in this project by design and construction of efficient and robust lab scale AD systems for long term MEAw bio-degradation tests by allowing culture adaptation and testing its limitations.

2.5 Preliminary Tests of Co-feed MEAw Digestion

Process design and construction in this project was partly based on experimental results from preliminary tests using apple juice as a co-feed substrate and a process of two sludge blanket reactors in series. These tests were carried out in the first phase of this PhD study to establish the methods required to reach the goals of the study. The protocols tested in this initial phase were based on studies previously carried out by Botheju et al., (2010). The preliminary tests did not generate any publishable results and are therefore not described in any detail in this dissertation. Some observations are, however, included in the following paragraph to give a theoretical introduction of how the methods were established.

The preliminary tests were performed at room temperature. Apple juice (pH = 5) was initially used as the sole co-feed substrate. pH of the co-feed MEAw solution was adjusted to neutral before it was fed in to the digester. Experimental results showed that the digester was unstable. Volatile fatty acids (VFA) concentrations were not stable, even when maintaining relatively neutral pH reactor condition. The lack of nutrients, vitamins etc. were considered to be possible causes of the failure. Undesirable biomass loss in the effluents was also observed that suggested inadequate biomass retention. Improvements of both feed substances and reactor structure by providing a mixture of co-feed nutrients, adapting the culture by slow step increase of feed loading and improved gas, liquid, solids separation for sustaining biomass, were therefore implemented. Additionally, operational procedures were simplified by these process improvements since high feed alkalinity made pH adjustment unnecessary. Minimal biomass flowed out of the digester and long term process stability was obtained (Wang et al., 2013b). The results presented in this thesis are all obtained from the improved digester design that was operated in two versions.

Chapter 3 Materials and Methods

This chapter presents the materials applied for the two main experimental tests conducted in this project: 1) Anaerobic digestion tests which include semi-continuously fed and batch syringe tests; 2) Detoxifying tests. The methods and experimental strategies used are given in the experimental management part. Applied experimental instruments and analytical software are added at the end of this chapter.

3.1 Anaerobic Digestion Treatment

3.1.1 MEA Waste

The reclaimer MEA waste (MEAw) used for anaerobic digestion (AD) test was collected from a full scale MEA based CO_2 capture facility at an industrial coal fired power plant. The waste settled in to two, liquid and solid phases in the storage tank. The solid phase was viscous paste of a mixture of liquid and solid particles. The liquid phase, which was the largest fraction of the waste, was the main focus in the project here. Composition measurements of this waste used as AD feed are given in Results and Discussion (Chapter 4.2).

The MEAw applied as feed in AD test contained various chemicals which are not well known. Complex combinations of organic and inorganic substrates in such waste have been reported: Table 2.1 and Table 2.2 (Strazisar et al., 2001 and 2003; Thitakamol et al., 2007). MEA, acetate, propionate and butyrate, were about 50 % of the MEAw COD and the other half was unaccounted chemicals. Inorganic cations (ammonia and metal ions such as copper, sodium and potassium) and anions (fluoride, chloride, nitrate sulfate etc.) have also been identified in such waste (Strazisar et al., 2003). The unaccounted chemicals can include toxic compounds such as corrosion inhibitors, catalytic agents and other chemicals that are inhibitory to microbial growth (Thitakamol et al., 2007).

3.1.2 Co-digestion Substrates

Organic substrates of starch, glucose, yeast extract and peptone which are considered as easily degradable organics for anaerobic degradation organisms were applied as co-substrates in the AD of MEA waste. Starch was replaced by glucose after a few months experimental test due to its accumulation in the digester feeding pipes. Physical and chemical characteristics of the co-digestion feeds are given in Table 3.1. The organic co-substrate contains easily degradable carbon sources, nutrients and minerals. The growth factors provided from co-substrates for organisms' growth and

synthesis can help to maintain strong biomass for reluctant substrates degradation and enhance the culture's tolerance to toxic effects.

Table 3.1 Physico-chemical characteristics of co-digestion feed

Characteristics	Starch[a]	Glucose[b]	Yeast extract[c]	Peptone[c]
Solubility in water at 1 %	insoluble	complete	complete	complete
pH (1 - 2 % solution)	5.0 – 8.0	6.0 - 7.0	5.5 – 7.2	6.2 - 7.2
Loss on drying (%)	≤ 20	≤ 8.9	≤ 5.0	≤ 6.0
Total nitrogen, TN (%)	-	0	≥ 10.5	12.2 – 13.4
α-amino nitrogen, AN (%)	-	0	-	3.5 – 5.0
AN/TN (%)	-	0	-	26 -41
Residue on ignition (%)	≤ 0.3	-	-	≤ 15.0
Chloride (as NaCl) (%)	-	-	≤ 5.0	≤ 8.0
Average Molecular weight (g/mol)	162*n	198.2	-	840 Daltons

- *Data not available; a, starch from potato (Roth); b, glucose (VWR); c, from Merck*

3.1.3 Minerals and Buffer Solutions

Organisms involved in anaerobic digestion, especially for methanogenesis are sensitive to changes of the environment conditions, such as pH. A buffer solution of 131 g/L (1.5 mol/L) of K_2HPO_4 and 102 g/L (1.5 mol/L) of KH_2PO_4 and a mineral solution (Table 3.2) were also prepared and added to the reactor system for stabilizing the minerals concentrations at the start of the test.

Table 3.2 Mineral solution composition

Chemical	Value (mg/L)
$MnSO_4 \cdot H_2O$	40
$FeSO_4 \cdot 7H_2O$	2800
$CuSO_4 \cdot 5H_2O$	60
$NiCl_2 \cdot 6H_2O$	92
$ZnSO_4 \cdot 7H_2O$	90
$CoCl_2 \cdot 6H_2O$	50
H_3BO_3	50
$(NH_4)_6Mo_7O_{24}$	50
$AlCl_3$	50
$Na_2SeO_3 \cdot 5H_2O$	50
EDTA	100

3.1.4 Inoculums

The MEA waste contains multiple chemicals with unknown anaerobic degradation possibilities. So a wide variety of organisms may be needed for successful degradation of recalcitrant compounds. A variety of biomass sources were introduced in the anaerobic reactor at the commencement of the test. Fresh anaerobic granular sludge from a pulp and paper industry wastewater treatment UASB (Upflow anaerobic sludge blanket reactor) in Norway constituted the main fraction of the biomass. The granular sludge was spherical at a dimension of around 2 mm. A polluted river bed sludge (Lilleelva river in Porsgrunn, Norway, that has been exposed to leachate from a mixed domestic and industrial landfill for decades) and biomass from other lab experimental tests (aerobic and anaerobic reactors treating domestic wastewater) were also added in the reactor to give higher biomass diversity. No taxonomical classification was carried out for the applied mixture of sludge.

3.1.5 Reactor Setups

Semi-continuous Feed Reactor

A hybrid lab-scale anaerobic digester which combined the concepts of suspended fluidized bed (Hickey and Owens, 1981) and attached biofilm reactors (Henze and Harremoes, 1983) was constructed for AD of MEA waste (Fig. 3.1). The reactor parameters are given in Table 3.3. The digester was designed to obtain high biomass retention time by allowing both suspended and attached (biofilm) biomass to accumulate. This should facilitate the development of a mixed culture containing organisms that can degrade the complex, recalcitrant and toxic substances that can be present in MEA waste (Table 2.1 and 2.2). It is not known whether such cultures are more easily evolved in biofilms or suspended cultures so a hybrid reactor was chosen to improve the odds of a successful experiment. This also allows for more local niches within the reactor that can favor certain degradation pathways and/or protect sensitive organisms from toxins.

The reactor was divided in three phases. Recycle line was applied by pumping liquid from the top suspended phase to the bottom suspended phase to simulate the upflow concept in an UASB system. A recycle rate of 25 mL/min was maintained during the test to generate an upflow velocity of ~ 0.5 m/h. The bottom suspended phase was incorporated as a conventional suspended sludge bed where feed substrates and biomass were added. A magnetic stirrer was employed for mixing to avoid sludge sedimentation and "dead zones" at the reactor bottom. In the center biofilm phase, a plastic net was used to frame the porous rock material (Light Expanded Clay Aggregates, "Leca" from Weber, Saint-Gobain) as the biofilm substratum. The upper suspended phase worked as a sedimentation zone to retain granular sludge and sludge particles from biofilm detachment in the reactor.
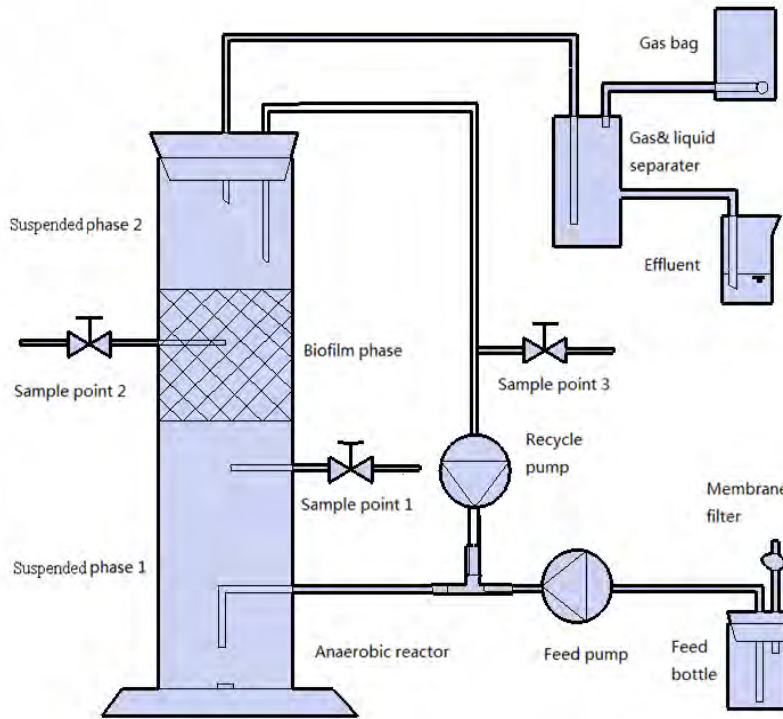
Fig. 3.1 Schematic configuration of the anaerobic hybrid reactor

Table 3.3 Parameters of the anaerobic reactor system

Component	Units	Value
Reactor height	cm	38
Reactor diameter	cm	7
Total work volume	L	1.25
Suspended phase 1	L	0.8
Biofilm phase	L	0.15
Suspended phase 2	L	0.3

Biogas generated in the reactor was collected in a biogas bag (Fig. 3.1). Its volumes were measured and the compositions were analyzed by gas chromatograph. Liquid effluents collected from the effluent bottle were used for COD, volatile fatty acid (VFA), alkalinity, ammonia and other analysis according to standard methods.

Syringe Batch Reactor

Several 100 mL syringes were used as batch reactors to test the degradation of co-feed MEA waste. Biomass cultivated in the semi-continuous feed reactor (used in the preliminary test) was applied as inoculum. Feed substrate was mixed with inoculum in the syringes and rubber stoppers were used to contain the biogas and liquid (Fig. 3.2).

The accumulated biogas volume was measured by reading the position of the syringe piston as it was pushed out by produced biogas (volume scale on the surface of the syringe). The gas was released after each reading for continuous accumulation of biogas in the syringe. When the biogas generation was almost ceased (approximately 25 days), liquid solutions from the reactors were collected for the measurements of pH, COD, VFA and ammonia concentrations.
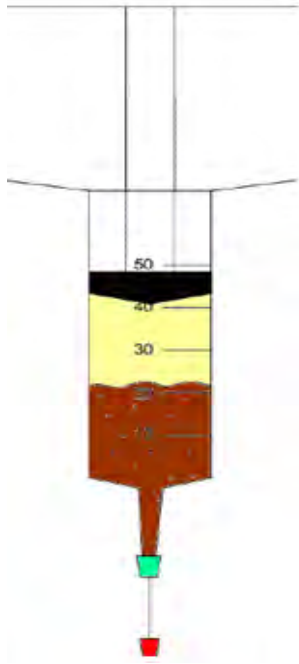
Fig. 3.2 An example of the syringe batch reactor

3.2 Detoxifying Tests

The detoxifying effects of AD on MEA waste was investigated by comparing the toxicity of MEA waste before and after AD in the hybrid reactor (Fig. 3.1) in a standardized toxicity test conducted in the Norwegian Institute for Water research (NIVA). Pure MEA (PM), reclaimer MEA waste (MEAw) and treated waste (TW: AD effluent from a steady state period) were used as test substrates. Algae *Pseudokirchneriella subcapitata*, crustaceaen *daphnia magna* and zebra fish, *Danio rerio* were used as the testing taxonomic groups.

3.3 Experimental Management

Three main tests performed in the course of the project, after an initial period of preliminary experiments, constitute the experimental basis for this dissertation. They are AD in semi-continuously fed hybrid reactor test, syringe batch test and AD detoxifying test.

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3.3.1 Semi-continuous Feed Test

The semi-continuous feed test was performed in the hybrid digester (Fig. 3.1) at room temperature (22 ± 2° C) continuously for 486 days. A series of feed scenarios were applied (Fig. 3.3 and Table 3.5). The co-digestion substrates were maintained constant in the feed solutions in the whole test period (Table 3.4). The feed MEAw COD ratio (MEAwr) was varied from 0.18 to 0.62 (Fig. 3.3). The feed substrate solutions were prepared by mixing MEAw and co-digestion substrates in deionized water and stored at 4 °C before feeding in to the digester. Buffers of KH_2PO_4 (0.15 g/L) and K_2HPO_4 (0.15 g/L) were added in the feed solution. The feed solution pH varied depending on the MEAw concentration and was 10.5 when 25 g MEAw/L was applied. The feed alkalinity was ~ 6 g/L $CaCO_3$ equivalent.

The feed was well mixed and fed to the reactor semi-continuously according to the determined organic loading rates, OLR (0.15 to 5.03 kg COD/m³·d, Fig. 3.3). The feed rate was set to 4 to 13 mL/min by adjusting the pump speed. A timer was employed for automatically controlling the feed pump at the selected times for substrate feeding.

Table 3.4 Compositions of the feed substrate

Component	Concentration (g/L)	COD (g COD/L)	Nitrogen concentration (g/L)
Starch (glucose)[1]	1.5 (1.7)	1.8	0.0
Yeast extract	3.6	3.3	0.4[2]
Peptone	3.0	4.5	0.4[3]
MEA waste	4.0-25.0	1.7-15.6	0.6-3.5[4]
Total	12.1 (12.3)-34.9 (35.1)	11.3-25.2	1.4-4.3

1 Starch was replaced by glucose in semi-continuously feed test at 250 days.

2 Product reference shows a nitrogen concentration of 10.5 % in this yeast extract.

3 Product reference shows a nitrogen concentration of 12-13 % in this peptone. 12.5 % was used in this calculation.

4 An approximate fraction value of 14 wt% of MEAw was measured and used here.
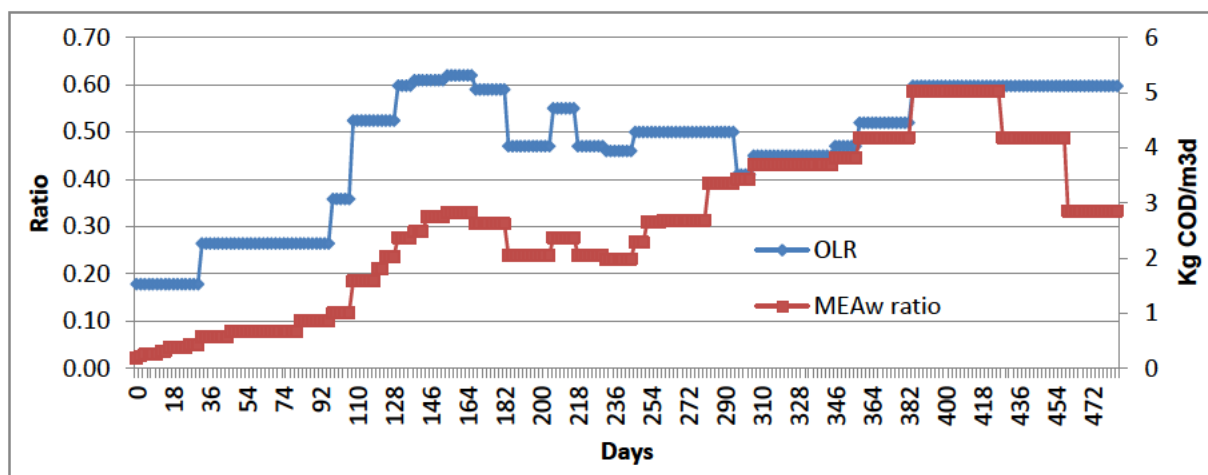
Fig. 3.3 Applied MEAwr (COD basis) in feed and the organic loading rates (OLR)

A period of three months' feed adaptation was applied at the commencement of the test. The mixed organisms' culture was cultivated by feeding co-substrates and MEAw to stabilize at the operational conditions. 10 mL of buffer and mineral solution (Table 3.2) were added initially to provide the necessary minerals in the adaptation period. After the initial addition, no external buffer (except that in feed) and minerals were applied in the reactor. Feed solution with MEAwr of 0.18 at OLR lower than 0.2 kg COD/m^3·d was fed to the digester to gradually acclimate the biomass in the adaptation period. The adaptation was considered complete when relatively constant biogas generation and pH were observed, after which the reported series of experimental tests were performed (Table 3.5).

3.3.2 Feed Strategy

The experimental tests were conducted continuously for 486 days, consisting of three distinct phases of experimental periods for different objectives (Table 3.5). The feed plan in the experiment was to increase the MEA concentration but maintain the co-substrates concentrations in feed (Table 3.4). The MEAw load increases applied depended on the process' ability to cope with the previous increase.

Phase one (0-184 days) was conducted by gradually increasing both the feed MEAwr and OLR to test the capacity of the digester and have an overview of the digester performance in terms of COD removal efficiency, methane yield, ammonia levels etc. The OLR was gradually increased from 0.15 to 2.82 kg COD/m^3·d. The MEAwr was from 0.18 to 0.62.

Phase two (185-296 days) was introduced when the COD removal efficiency was significantly reduced due to process overloading effects at the end of phase one. In this 2nd phase, a relatively constant and lower MEAwr was applied to investigate the process recovery ability and try to regain process stability. The OLR applied were from 2.01 to 3.35 kg COD/m^3·d and the MEAwr was around 0.5.

Phase three (297-486 days) was used to test process capacity and limitations after the relatively stable reactor performance achieved in phase two. The treatment capacity after long terms of reactor operation was tested by high feed loads. Scenarios of higher OLR (maximum 5.03 kg COD/m^3·d) at the MEAwr from 0.41 to a maximum 0.6 were investigated. The organisms' ability to cope with the inhibitory effects was examined by comparing the reactor performances in different phases.

Feed C/N ratio changed in the range 3 to 5 during the whole test period. Liquid effluents and biogas were continuously collected in the operation of the semi-continuously fed reactor. Liquid samples were collected for the measurements of pH, VFA, soluble COD, ammonia, alkalinity. Effluent pH was measured for every sample that was collected every two days. Alkalinity was measured occasionally. VFA and soluble COD concentrations were measured for every other sample. The volume of generated biogas and its composition (CH_4 and CO_2 partial pressures) were measured every two days.

Table 3.5 Summary of the applied feeds for the system in chronological order (Day zero was the last day of preliminary tests).

Phase	OL R (kg COD/m^3·d)	Feed COD (g COD/L)	MEAwr	HRT (d)	Duration (d)
Phase 1	0.25-0.42	9.7	0.18	39-23	1-31
	0.56-1.00	13.0-14.9	0.26-0.36	23-15	32-105
	1.58-2.03	20.2	0.52	13-10	106-127
	2.37-2.82	23.6-25.2	0.59-0.62	10-9	128-168
	2.62	23.4	0.59	9	169-184
Phase 2	2.04	18.2	0.47	9	185-206
	2.37	21.2	0.55	9	207-218
	2.01	18.0	0.47	9	219-232
	2.28-3.35	19.0	0.50	8-6	233-296
Phase 3	3.43	16. 3	0.41	5	297-306
	3.69	17.5	0.45	5	307-346
	3.82	18.1	0.47	5	347-358
	4.19	19.8	0.52	5	359-384
	5.03	23.8	0.6	5	385-428
	4.19	23.8	0.6	6	429-460
	2.86	23.8	0.6	8	461-486

3.3.3 Syringe Batch Test

The first scenario of anaerobic batch tests were performed at both room (22 ± 2 °C) and mesophilic temperatures (35 °C) with feed shown in Table 3.6. The batch reactors operated at 35 °C were placed

in an incubator. This test investigated the temperature effects on the degradation of co-feed MEAw and studied the MEAw's degradation ratio in selected conditions.

Three groups of feed substrates were used in the syringe batch tests (Table 3.6): Group A, feed with only easily degradable co-digestion organics; Group B, feed organics with MEAwr of 0.5; Group C, feed with only tap-water. Two parallels were prepared for each feed group at the two tested temperatures. Totally 12 batch reactors were operated.

Table 3.6 Summary of the applied feed for syringe batch test scenario one

Parameters	Group A	Group B	Group C
Glucose (g/L)	1.7	1.7	0
Peptone (g/L)	3.0	3.0	0
Yeast extract (g/L)	3.6	3.6	0
MEA waste (g/L)	0	20	0
Total COD (mg/L)	8645	17290	0
MEA waste ratio (COD basis)	0	0.54	0
Feed amount (mL)	5	5	5
Initial feed pH	7.2	10.6	7
Temperature (°C)	25/35	25/35	25/35

The inoculum had been cultivated in the preliminary test for approximately one year and stored in fridge before the batch test. 10 mL/d Group B substrate (Table 3.6) was fed to initialize the sludge and prepared for the test. The sludge was allowed to settle down for approximately 24 hours at the start of the batch test, so that all the sludge, including very small particles eroded from the granules was retained. 30 mL of well mixed sludge and 5 mL of each feed (Table 3.6) were added in each batch syringe reactor. The accumulated biogas volume was measured and recorded twice a day during the first two experimental days and once a day afterwards. The test lasted for approximately 25 days. Parameters of pH, COD, VFA and ammonia concentrations were measured for the suspension before and after the experiment.

The second scenario of anaerobic syringe batch test was conducted by applying feed of two pure chemicals N-acetylethanolamine and N-(2-hydroxyethyl)-ethylenediamine (HEEDA) (Table 3.7) that were identified by others (Strazisar et al., 2003 and Gouedard et al., 2012) in MEAw from the same source as that used in the main experimental study of this dissertation. N-acetylethanolamine is one of the major MEA degradation chemicals (Strazisar et al., 2003). It is believed to form as a result of MEA reaction with acetic acid which is produced in the oxidation degradation of MEA (Strazisar et al., 2003). HEEDA was mentioned in chapter 2.1. It is one of the most important thermal degradation products of MEA (Gouedard et al., 2012). However, the exact concentrations of N-acetylethanolamine

and N-(2-hydroxyethyl)-ethylenediamine in the MEAw which was applied for AD test were unknown. This batch test was conducted to verify the biodegradation ability of some major MEA degradation chemicals.

Batch reactors feeding with distilled water and standard feed substrate (MEAw + co-substrate) were used as reference (Group B, Table 3.6). The feed substrates (Table 3.7) were added to the batch reactors at 1 mL at day 0, 14, 16 and 18, and 2 mL at day 6. Inoculums were the same as that applied for scenario one.

Table 3.7 Summary of the applied feed for syringe test scenario two

Parameters	Formula	Concentration (g/L)
Tap-water		
Standard feed	MEAw + co-substrate[a]	
N-(2-hydroxyethyl)-ethylenediamine	$C_4H_{12}N_2O$	10
N-acetylethanolamine	$C_4H_9NO_2$	10

a, co-substrate components are given in Table 3.6 (feed Group B)

3.3.4 Detoxifying Test

The toxicity tests were performed by an external partner, Norwegian Institute for Water research (NIVA) in accordance with the standard procedures described in the OECD Guidelines OECD201, OECD 202 and OECD draft Guideline 'Zebra fish embryo toxicity test' (OECD, 2011). Pure MEA (PM), reclaimer MEA waste (MEAw) and treated waste (TW: AD effluent) were used as test substrates. The description of each test can be referred to Paper 3.

3.4 Analytical Methods

3.4.1 Gas Chromatograph (Hp 6890 serial C)

Gas chromatograph (Fig. 3.4) with a flame ionization detector and a capillary column (DB-FFAP 30 m long and 0.25 mm ID, 0.25 μm film) was used to analysis volatile fatty acids (VFA). Helium (at a flow velocity of 24 mL/min) was used as the carrier gas. Hydrogen and air were the detector gases. The temperatures of the injector and the detector were set to 200 °C and 250 °C, respectively. The oven temperature was programmed to go from 80 ℃, and hold for one minute, to 180 °C at a rate of 30 °C /min, then to 230 °C at a rate of 100 °C /min.

Fig. 3.4 Photo of the GC Hp 6890 serial C

3.4.2 Gas Chromatograph (Hp 5980 serial A)

Biogas composition was measured using a gas chromatograph (Hp 5980 serial A) (Fig. 3.5). It was a two column system. The Molsieve 5A column was used to separate H_2, O_2, N_2, CH_4, CO and The Porabond Q Tandem column was to separate air, CH_4, and CO_2. Argon was used as the carrier gas. Nitrogen was applied as the valve gas. The injection temperature and the detector were 120 °C and 150 °C, respectively. The oven temperature was kept constant at 40 °C.

Fig. 3.5 Photo of GC Hp 5980 serial A

3.4.3 Ion Chromatography

A non-suppressed cation chromatography (Fig. 3.6) was used to measure MEA and ammonium concentrations. A guard column SCG1 and a cation exchange analytical column SCS1 were used for

compounds separation. The column temperature was 35°C. Methanesulfonic acid (3 Mm) was applied as the eluent at a flow rate of 1 mL/min.

Fig. 3.6 Photo of the Ion chromatography

3.4.4 pH Meter and Other Measurements

pH measurements were obtained with a pH meter (Beckman). COD was analyzed according to the US standard 5,220D (APHA 1995). Alkalinity was measured by titrating the sample solution to pH 4.5. The three main forms of alkalinity (bicarbonate, carbonate, and hydroxide) are neutralized at pH 4.5. The titrant used was N/50 sulfuric acid. Alkalinity (mg/L $CaCO_3$ equivalent) was calculated based on Eq.3:

$$\text{Alkanility, } CaCO_3 = \frac{A \times N \times 50,000}{mL \text{ of sample}} \qquad \text{Eq.3}$$

Where A = mL standard acid used, N = normality of standard acid.

Free ammonia concentration was calculated based on total ammonia and pH measurements, according to Eq.4 (Angelidaki and Ahring, 1993).

$$[FAN] = \frac{[TAN]}{(1 + \frac{H^+}{k_a})} \qquad \text{Eq. 4}$$

FAN = $[NH_3]$ and TAN = $[TNH_3]$ are the free and total ammonia ($NH_3 + NH_4^+$) nitrogen concentrations, respectively. k_a is the ammonium dissociation constant (5.75 e^{-10} at 25 °C). The H^+ values are based on pH measurements.

3.4.5 Principe Component Analysis

Principal component analysis, PCA, is a statistical technique to identify patterns in data, and express the data in a way to highlight similarities and differences (Abdi and Williams, 2010). Commercial Excel add-in software XLSTAT was used for the PCA analysis.

3.4.6 Modeling and Simulation Tool

Anaerobic Digestion Model No. 1 (ADM1) (Batstone et al., 2002) was applied as a model base for analyzing anaerobic degradation of co-feed MEAw. Model extension by including state variables and kinetics of MEAw constituents and the co-feed organics was investigated. Experimental data was employed to facilitate AD of MEAw simulations.

Software AQUASIM 2.1f is a computer program for data analysis and simulation (Reichert, 1994). It was applied as a simulation tool for implementing the expanded ADM1 model.

Chapter 4 Results and Discussions

Results from the 486 days continuous operation of the hybrid digester were condensed and presented in this chapter. Papers 1 (Wang et al., 2013 a) and 2 (Wang et al., 2013 b) attached at the end of the thesis summarize the main results. Results of the syringe batch test are not published and are summarized here. The detoxifying effects of AD on MEA waste (MEAw), presented in Paper 3 (Wang et al., 2014 a) are also included. Modeling and simulation of co-feed MEAw AD as studied based on ADM1, are presented and summarized based on Paper 4 (Wang et al., 2014 b).

4.1 General Results

MEAw is a toxic and complex chemical mixture with a low carbon to nitrogen content ratio. Organisms' growth on such waste alone was observed to be difficult to sustain over extended periods of time in the preliminary experiments. Anaerobic co-digestion of this resilient waste with easily degradable organics was thus investigated by assessing biogas yields, total COD removal efficiency, ammonia, VFA accumulation etc. (Paper 1 and 2). Principle component analysis (PCA) was applied for analyzing the correlations between different parameters (e.g. pH, ammonia concentration, MEAwr) to the assessed variables and identifying inhibitory factors (Paper 2). Detoxifying effects of anaerobic digestion on MEAw were tested on three fresh water trophic groups (Paper 3). Accumulated AD experimental data were implemented in the expanded ADM1 model for assessing assumptions made regarding the AD process (Paper 4).

Generally, stable anaerobic degradation of co-feed MEAw was achieved and maintained for two years while exposed to challenging load conditions (Paper 2). AD of MEAw was limited by inhibitory effects from MEAw toxic factors and ammonia (Ppaer 2). These limitations were identified so that inhibition problems can be avoided in MEAw AD treatment processes. Gradual biomass adaptations to the inhibitory environment were also observed (Paper 2). It showed that the degradable organic COD constituted more than half of the total MEAw COD (Paper 2). The AD effluent toxicity was significantly reduced compared to that of untreated MEAw (Paper 3). The extended ADM1 model was able to predict reasonably accurate observed biogas generation, the inhibitory effects etc. without fundamental changes of process parameters from the standard ADM1 (Paper 4).

4.2 Stable AD of Co-feed MEAw

The MEAw used as feed consisted of water, MEA, VFA and unaccounted chemicals from MEA degradation and additions in the CCS process (Strazisar et al., 2003). Measurement shows that the water content in the liquid phase was 19.7 wt%. MEA was 25 wt%. Total nitrogen and organic carbon were 14 and 31 wt%, respectively. The chemical oxygen demand (COD) was about 1 g/g waste. The MEA waste has high alkalinity, 3 g CaCO$_3$/g MEAw equivalent. The heating value of the waste was

16 MJ/kg. During the storage of the waste, the MEA waste properties changed some with time, due to waste evaporation, continuous sedimentation and perhaps other unknown processes. Acquired samples' COD were measured in the range of 450 to 900 mg/g waste. The MEA contents were estimated to be 18 to 30 wt%. The concentrations of total nitrogen (7 - 14 wt% of the waste) and organic carbon concentrations, which were not regularly measured, were assumed to change proportional to the COD concentrations.

Anaerobic degradation of MEAw with co-substrate was sustained for 486 days in the semi-continuously fed test (Papers 1 and 2). Biogas yield, COD removal efficiency, VFA and ammonia concentrations are presented with respect to feed MEAwr (MEAw COD to total feed COD ratio) and OLR to assess the digester performances (Fig. 4.1-4.4). The maximum biogas yield was 0.43 L/g COD and the average was 0.35 L/g COD (Fig. 4.1), with ~ 80 % methane partial pressure obtained (Fig. 4.2). 70 % of feed COD removal was on average achieved (Fig. 4.3). Acetate constituted the major part (over 90 %) of VFA accumulation at inhibitory conditions (Fig. 4.2). pH was relatively stable in 7.0 - 8.0 (Fig. 4.4). Released ammonia due to digestion of co-feed MEAw led to reactor liquid concentrations within 2 g N/L and 90 mg N/L for ammonium and free ammonia, respectively (Fig. 4.4). Increased feed degradation was observed showing that the degradation was not just sustained but actually improved with time as the AD culture adapted to the waste (Fig. 4.3, Table 4.1).

4.2.1 Biogas Yield

Biogas yield steadily increased from 0.35 to a maximum of 0.43 L/g COD at MEAwr lower than 0.2 during the adaptation phase prior to the test phases presented in Fig. 4.1. Biogas yield gradually decreased as OLR increased in phase 1. Simultaneously increasing MEAwr and OLR to a maximum of 0.6 and 3 kg COD/m^3·d, respectively in the last part of phase 1 greatly reduced the biogas yield to less than half of the highest value. Clear negative effects were observed here. However, higher and relatively constant biogas yields were obtained at each feed scenario (Phases 1 -3) when MEAwr were below 0.6.
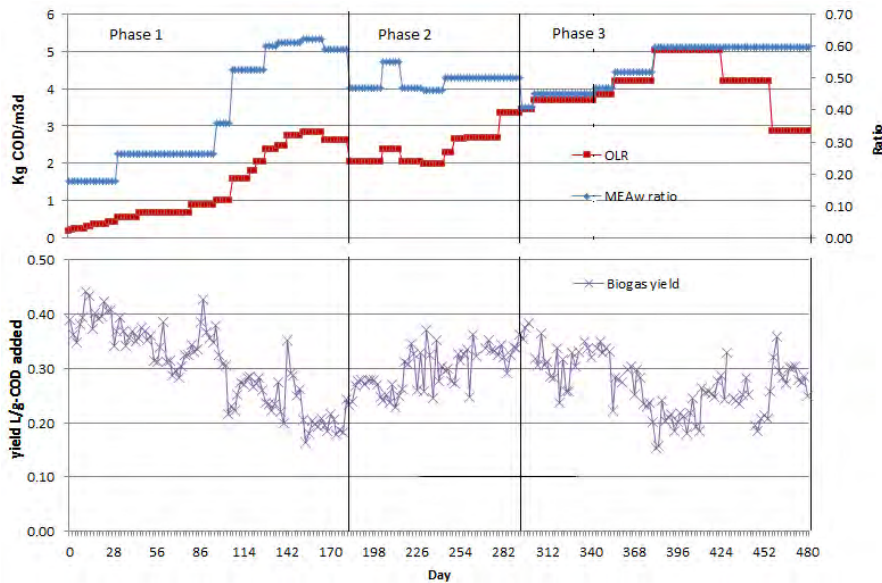
Fig. 4.1 Biogas yield at different feed OLR and MEAwr

Biogas yield recovery from 0.2 to 0.35 L/g COD was achieved by reducing load and feed waste ratio, MEAwr, in phase 2 (185-296 days). Biogas yield remained high when again increasing OLR to over 3 kg COD/m^3·d while maintaining relatively stable MEAwr (~ 0.5) at the end of phase 2. Biogas yield decreased again to 0.2 L/g COD when the feed MEAwr increased from 0.4 to 0.6 in phase 3. OLR increased to 5 kg COD/m^3·d in this phase only due to the MEAwr increments (Chapter 3). The inhibitory effect from high MEAw content in the feed was clear and similar biogas yield was obtained at MEAwr of 0.6 and OLR of 3 and 5 kg COD/m^3·d in phases 1 and 3, respectively. However, gradual biogas yield increase was observed after a few weeks operation at the inhibitory load level in phase 3 (385-428 days). The biogas yield at the end of phase 3 was 0.3 L/g COD, increased 50 % comparing to that at a similar feed (OLR= 2.8 kg COD/m^3·d and MEAwr= 0.6) in phase 1. It indicates that an increased portion of MEAw was degraded after a long period of operation. This was attributed to biomass acclimation effects.

These test results confirm the negative impacts from MEAwr on the biogas yield also show that the negative impact lessens with time. Feed OLR was increased in two ways in the experimental test, either by increasing MEAw concentration in feed or increasing the feed loading rate at selected MEAw concentrations. In phase 1, both steps were applied. So the effects of OLR and MEAw on overloading were not clear. In phase 2, MEAw was kept around 0.5, while feed loading rate was increased to check the OLR effects. The biogas yield recovered gradually at constant MEAwr = 0.5 while OLR increased which show that the AD organisms tolerate MEAwr = 0.5. Meanwhile, a 25 % higher OLR was applied than the maximum OLR in phase 1 (Fig. 4.1). In phase 3, the OLR increase was only due to the feed MEAwr to 67 % more than that of phase 1. The max MEAwr applied in phase 3 was at a similar level as that in phase 1. The biogas yield first went down during the load increase in phase 3 as it did during the overloading in phase 1, but then gradually increased about 50 %

at the highest MEAwr (Fig. 4.1). This improved performance in phase 3 is attributed to culture's adaptation to this challenging feed. OLR effects during the load increase period (from day 190 to day 424) were directly related to the feed concentration of MEAw. Feed MEAwr over 0.5 led to inhibition effects.

4.2.2 Methane Partial Pressure and VFA Accumulation

Methane yield had a similar trend as total biogas yield during the whole test period (Paper 2), since methane partial pressures was quite stable at around 0.8 of the generated biogas (Fig. 4.2). The remaining 20 % was CO_2 (Fig. 4.2). The CH_4/CO_2 ratio at an average of 4 through the reported operation of the AD digester is quite high compared to most reported AD plants.
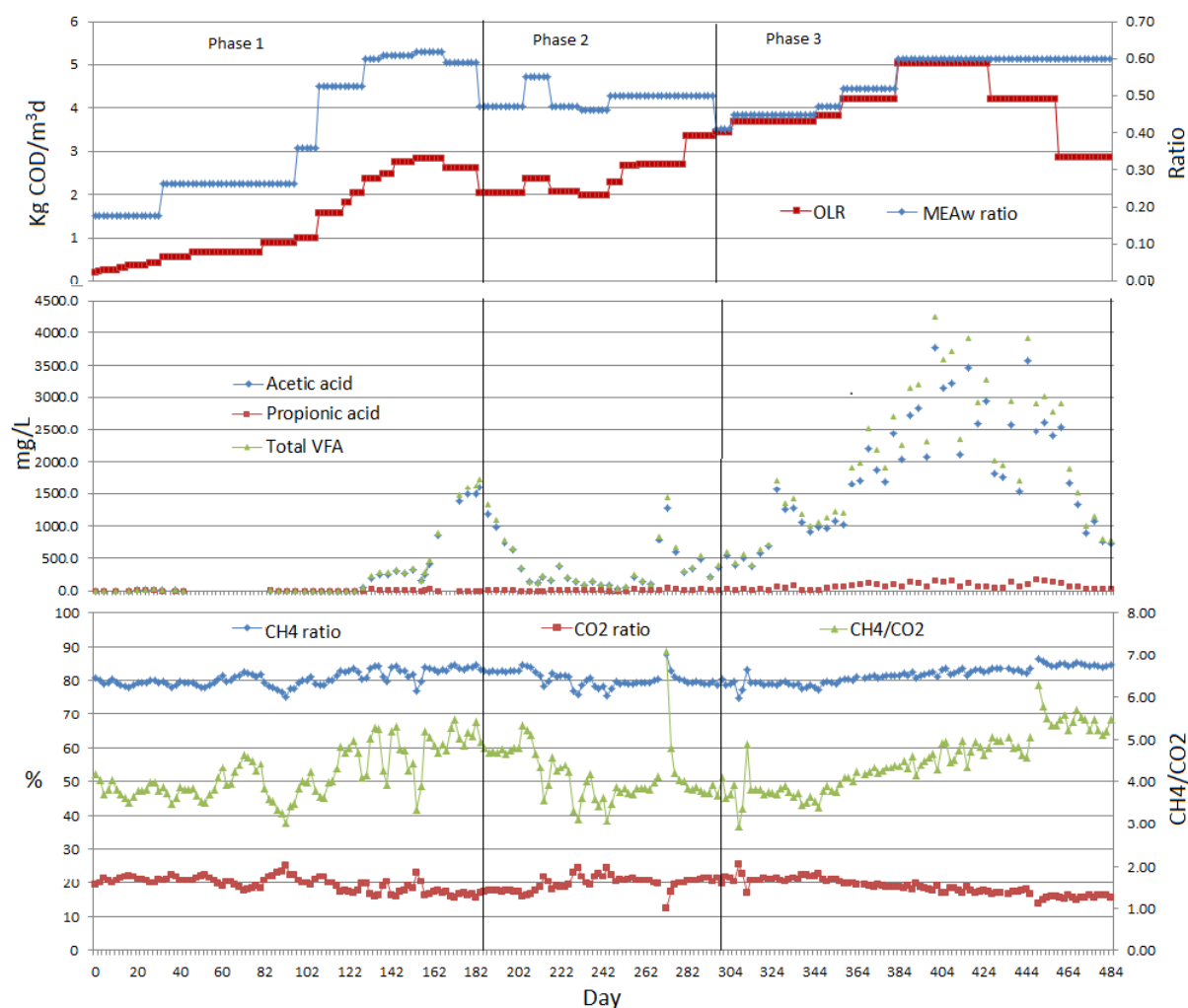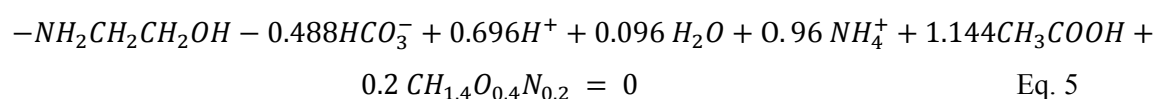

Fig. 4.2 Partial pressure of CH_4 and CO_2 in the generated biogas and VFA accumulation

The relatively high methane partial pressure and CH_4/CO_2 ratios in the obtained biogas (Fig. 4.2) were mainly attributed to the bicarbonate consumption due to degradation of ethanol amines in MEAw (Eq.

5) and the effects of VFA accumulation (Fig. 4.2). MEA degradation at anaerobic condition is considered to follow Eq. 5. About 0.5 mol of bicarbonate is consumed by degrading 1 mol of MEA, generating acetic acid as the main product. Bicarbonate consumption results in H_2CO_3 dissolution and form new inorganic carbon balance between the gas and liquid phases (Tchobanoglous et al., 2003). Additionally, because of higher solubility of CO_2 than CH_4 in the digester liquid, more CO_2 dissolution in the liquid was expected than at equilibrium (Krich et al., 2005). On the other hand, VFA accumulation limits CO_2 generation, causing reduced CO_2 accumulation in the gas phase. It is thus believed that increased degradation of MEA from MEAw and the accumulation of acetic acid led to CO_2 partial pressure reduction in the gas phase. Empirical formula $CH_{1.4}O_{0.4}N_{0.2}$ ($C_5H_7O_2N$) (Eq. 5) was used to represent biomass (Eastman and Ferguson, 1981)

$$-NH_2CH_2CH_2OH - 0.488HCO_3^- + 0.696H^+ + 0.096\,H_2O + 0.96\,NH_4^+ + 1.144CH_3COOH +$$
$$0.2\,CH_{1.4}O_{0.4}N_{0.2} = 0 \qquad\qquad \text{Eq. 5}$$

VFA started to accumulate when the feed MEAwr was over 0.6 in phase 1 (Fig. 4.2). The VFA concentration stayed lower than 0.5 g/L in most of the time in phase 2 and increased to 4 g/L with MEAwr step increase in phase 3 (Fig. 4.2). Acetate constituted more than 90 % of the accumulated VFA and some minor other fatty acids were also observed in the digester (Fig. 4.2 and Paper 2). Acetoclastic methanogenesis was, therefore, evidently especially sensitive to the factors causing the inhibition. Direct MEAw inhibitory effects and some other common AD inhibitors (e.g. ammonia, from the degradation of MEAw and co-substrates (Fig. 4.4)) may have caused the observed inhibition of the degradation of co-feed MEAw (Paper 2).

4.2.3 COD Removal

The maximum COD removal efficiency was above 90 % and the minimum was 45 %, with an average of 70 % in the whole test period (Fig. 4.3). Over 90 % of feed COD was removed when MEAwr was below 0.5 at the OLR lower than 1 kg COD/m^3·d (Fig. 4.3). Continuous efficiency reduction was observed when MEAwr was increased to 0.6 together with OLR increased to 2.8 kg COD/m^3·d in phase 1. Afterwards, the efficiency rapidly recovered from 45 % to above 80 % when reducing MEAwr to ~ 0.5 in phase 2. In phase 3, the removal efficiency reduced to 60 % with the MEAwr increase (Fig. 4.3). High MEAwr is evidently challenging for the involved organisms while they can handle high OLR quite well (Fig. 4.1-4.2, Paper 2). This implies that efficient treatment can be achieved as long as at least an equal amount of easily degradable co-substrate, such as domestic wastewater, is available and the culture is adapted to such feed.

Adaptation of biomass to the inhibitory feed conditions was confirmed by observing that the COD removal efficiency was significantly increased in phases 3 compared to phase 1 at a similar feed condition (MEAwr of 0.6 and OLR of 2.8 kg COD/m^3·d) at days 470 and 170, respectively. A higher portion of complex co-feed MEAw was degraded in the later phase.
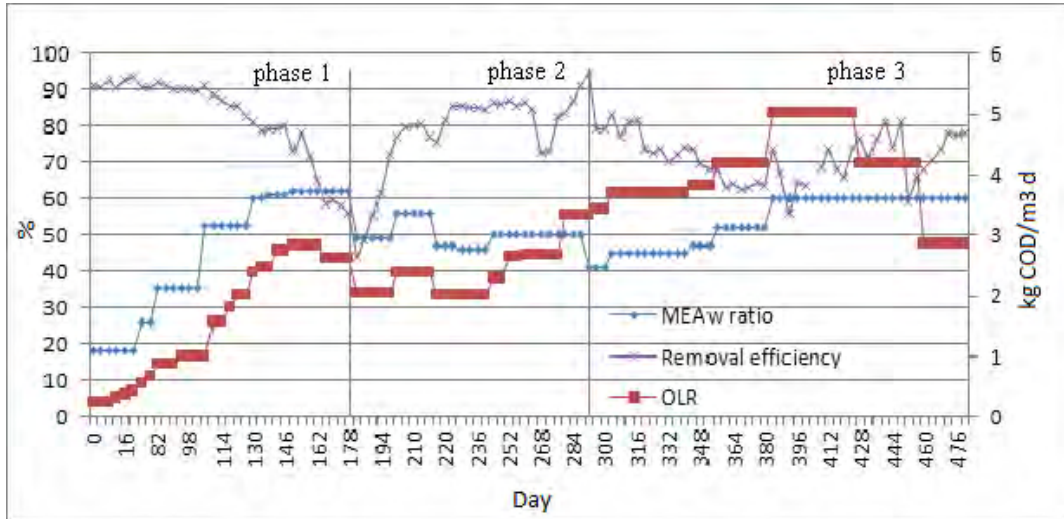
Fig. 4.3 COD removal efficiency (%) under different feed OLR and MEAwr in feed

4.2.4 Ammonia Generation

Inorganic ammonia with the two main forms of free ammonia (NH_3) and ammonium (NH_4^+) was released in the digester due to breakdown of nitrogenous organics in both MEAw and the co-digestion substrates. Ammonium is mainly dissolved in the liquid phase. Free ammonia balance in liquid-gas phase is dependent on the environmental conditions of pH, temperature and ammonium concentrations (Eq. 4). The digester was maintained at room temperature of 22 ± 2 °C with pH stayed in the range of 7.0 to 8.0. Gradually pH increased was observed during the test period without applying pH adjustment (Fig. 4.4). High feed MEAw alkalinity (5.9 g/L $CaCO_3$ equivalent for 18 g MEAw/L solution) as well as the buffer capacity from accumulated ammonia can stabilize AD from acute pH variations (Zhao and Viraraghavan, 2004) and was considered to cause the pH increase.

Total inorganic ammonia nitrogen (TAN) concentration reached a maximum of 2.2 g N/L at the end of both phase 1 and 3 (Fig. 4.4). The TAN concentrations varied in between 1.5 and 2 g/L in phase 2 (Fig. 4.4). Average free ammonia nitrogen (FAN) concentration, according to Eq. 4 was 50 mg N/L, with a maximum of 90 mg N/L, obtained at the end of phase 3 (Fig. 4.4). TAN was not significantly increased in phase 3 while due to the pH increase at the end of phase 3, FAN was much higher (90 mg N/L) than that in the early phases.
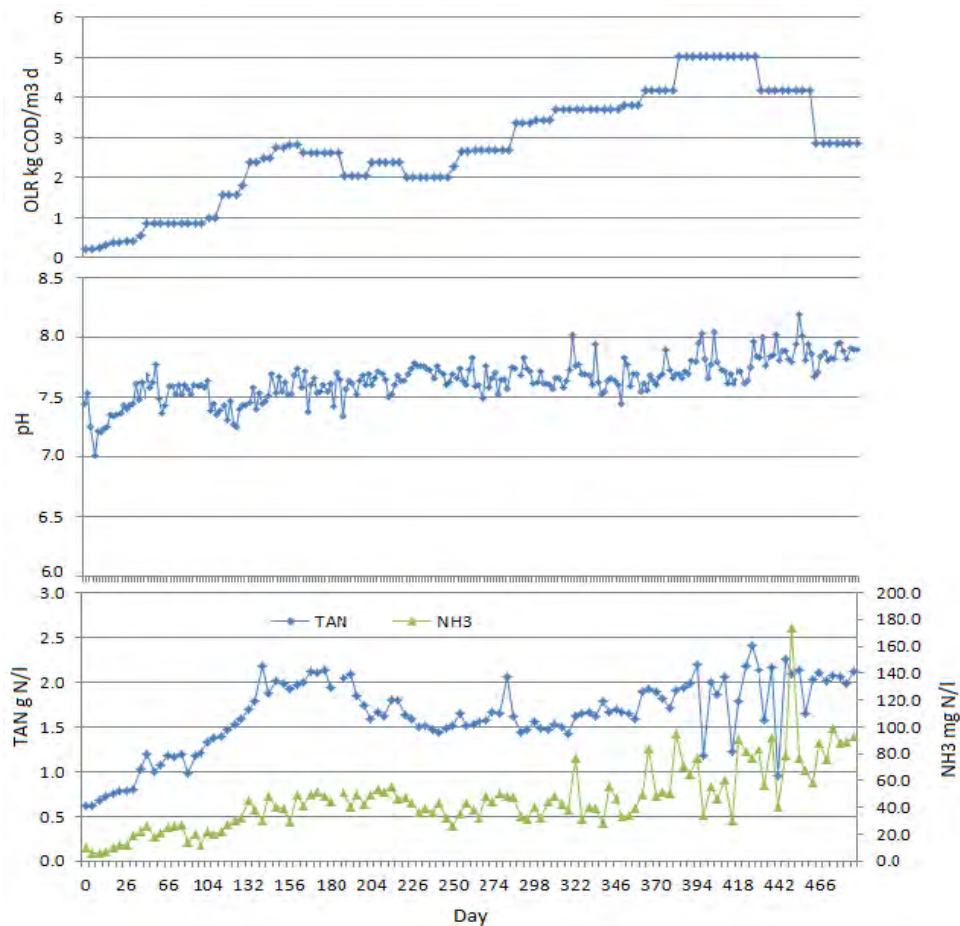
Fig. 4.4 Reactor effluent pH and total and free ammonia nitrogen (TAN and FAN) concentrations under varying feed organic loading rate (OLR) during the test period

Calculated nitrogen conversion rates (calculated as feed organic N minus total ammonia N divided by time) at three feed scenarios are given in Table 4.1 where relatively stable ammonia concentrations were obtained at the selected feed scenarios (Fig. 4.4). Average N conversion rates gradually increased (0.08, 0.11 and 0.17 g N/L·d) with the time (Table 4.1). It reveals a developing biomass capacity in degrading nitrogen containing organics. Increasing inorganic N generation rates suggested improved nitrogenous MEAw organics degradation with the maturity of AD biomass.

Table 4.1 Nitrogen conversion rates in selected feed scenarios

Parameters	Units	Scenario 1	Scenario 2	Scenario 3
Experimental days	days	222-246	310-346	462-486
OLR	kg COD/m^3·d	2.01	3.69	2.86
MEAw ratio (COD basis)	-	0.47	0.45	0.60
Average feed N	g N/L	2.26	2.14	3.45
Average effluent TAN	g N/L	1.52	1.61	2.06
N degradation rate	g N/L·d	0.08	0.11	0.17
Average COD removal efficiency	%	85	75	74
Average pH	-	7.7	7.7	7.9

4.3 Inhibitory Factors and Acclimation

Observed reduced biogas yield (Fig. 4.1), decreased COD removal efficiency (Fig. 4.3) and elevated VFA concentrations (Fig. 4.2) show inhibitory effects of feed MEAw on AD (Paper 2). The large amount of acetate accumulation (Fig. 4.2) indicates that acetoclastic methanogenesis was the limiting step for the complete AD. Inhibition of the methanogens that converts acetate to methane, the main methane generating pathway (Fig. 4.2, Tchobanoglous et al., 2003) was evidently especially inhibited. MEAwr is, therefore, considered to be one of the main inhibitive factors in AD of co-feed MEAw (Fig. 4.5, Paper 2). The question is "how"? Answers to this can make it easier to avoid such process disturbances and understand why the AD culture is able to adapt to such feed.

4.3.1 Inhibition factors

Anaerobic digestion is sensitive to toxic and inhibitory factors such as ammonia, overload, pH variations (Chen et al., 2008). Methanogenesis is especially sensitive to optimal operational conditions compared to the other processes (e.g. acidogenesis) in AD (Kayhanian, 1994). Principle component analysis (PCA) for interpreting the correlations of variables showed that MEAwr, OLR and total ammonia nitrogen (TAN) were the three main inhibitory factors to methane yield here. The effects were MEAwr > OLR > TAN > VFA > NH$_3$ and pH (Fig. 4.5). Accumulation of VFA was strongly correlated to TAN and feed OLR and less to pH, free ammonia nitrogen (FAN) and MEAwr (Fig. 4.5).

MEAwr as the most inhibitive factor to methane yield indicates that the constituents of MEAw and/or degradation products from it had significant negative effects on methanogenesis. It has been demonstrated that the degradation of MEAw alone was not successful in the preliminary test due to

lack of nutrients, high nitrogen content, low accessible carbon etc. and evidently due to strong inhibition. Stable digestion of MEAw was obtained after adding the required growth factors (Papers 1 and 2). While the inhibitory effects were especially clear at MEAwr above 0.5 (Fig. 4.1-4.3). Batch tests also demonstrated that by applying easily degradable feed with MEAw added, the biogas accumulation rates were depressed (Fig. 4.7, Table 3.5). Methane was generated much slower with than without MEAw at both temperatures tested, while the total biogas potential was much higher with (Fig. 4.7).

The relatively high negative effects from OLR observed can be attributed to inhibition caused by MEAwr since the OLR increase associated with VFA accumulation were imposed by increasing MEAwr in feed (Fig 3.2, Table 3.5 and Chapter 4.2.1). Total and free ammonia accumulation to levels of 2 g N/L and 90 mg N/L, respectively, can inhibit AD, causing VFA accumulation. Ammonia, especially free ammonia (FA) is considered to be the main inhibitory factor in AD of high nitrogen content feed organics (Chen et al., 2008). The PCA analysis (Fig. 4.5) suggests that this was not so much the case in AD of MEAw. TAN effects were stronger than FAN on VFA accumulation (Fig. 4.5).

The PCA correlation cycle shows that FAN is almost orthogonal to methane yield, implying that they are not significantly correlated (Fig.4.5). FAN is, however, closely related to VFA accumulation which may be a more direct indicator of inhibition of acetoclastic methanogenesis when almost all the VFA is acetic acid. It is reported that AD cultures can slowly adapt to TAN concentrations of over 7 g/L and FAN close to 1 g/L (Yenigun and Demirel, 2013). The 486 days of experimental operation with long sludge retention times, at relatively low TAN and FAN concentration may have enabled biomass to gradually adapt and overcome inhibitory effects from ammonia. Alternative pathways can be established to overcome inhibition. It seems like that some syntrophic acetate oxidation (Schnürer et al., 1994) may have developed to avoid ammonia inhibition in the reported AD of MEAw. This may explain how the culture became less inhibited with time.
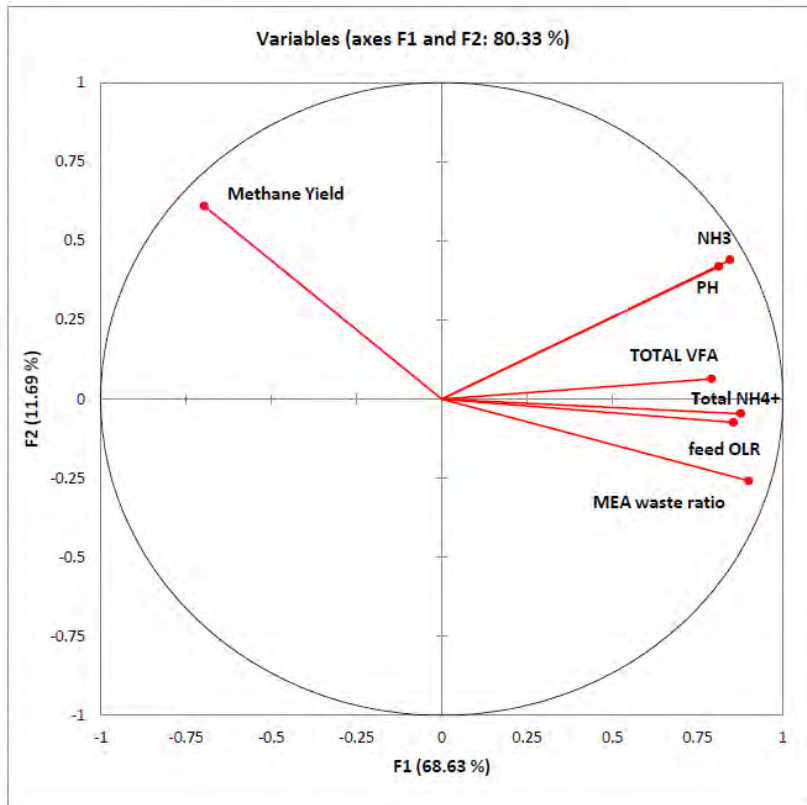
Fig. 4.5 Correlation circle shows a projection of the initial variables in the factors space, indicating the correlations between different variables. (When two variables are far from the origin, if they are close to each other, they are significantly positively correlated; when they are opposite from each other, they are negatively correlated; when they are orthogonal to each other, they are not significantly correlated.)

A degradation ratio calculated as CH_4 plus VFA COD divided by the total feed COD was applied to reveal the feed COD degradation degree independent of the degree of inhibition of methanogenesis (Fig. 4.6). The degradation ratio was as expected lower at high MEAwr (Fig. 4.6). Only 45 % of the feed COD was broken down at the feed with maximum MEAwr (~ 0.6) in phase 1. The degradation ratios were in the range of 0.5 to 0.8 when maintaining MEAwr around 0.5 in phase 2. In phase 3, however, the degradation ratio was close to the average obtained at lower MEAwr. It demonstrates that anaerobic digestion has developed and gradually adapted to the inhibitory conditions and degraded almost all feed substances to methane and acetic acid (Fig. 4.6).

Fig. 4.6 Combined VFA and CH$_4$ COD to the feed COD ratio under different applied MEAwr in feed in the tested three phases; Error bars represent one standard deviation

4.4 MEAw Degradation Ratio

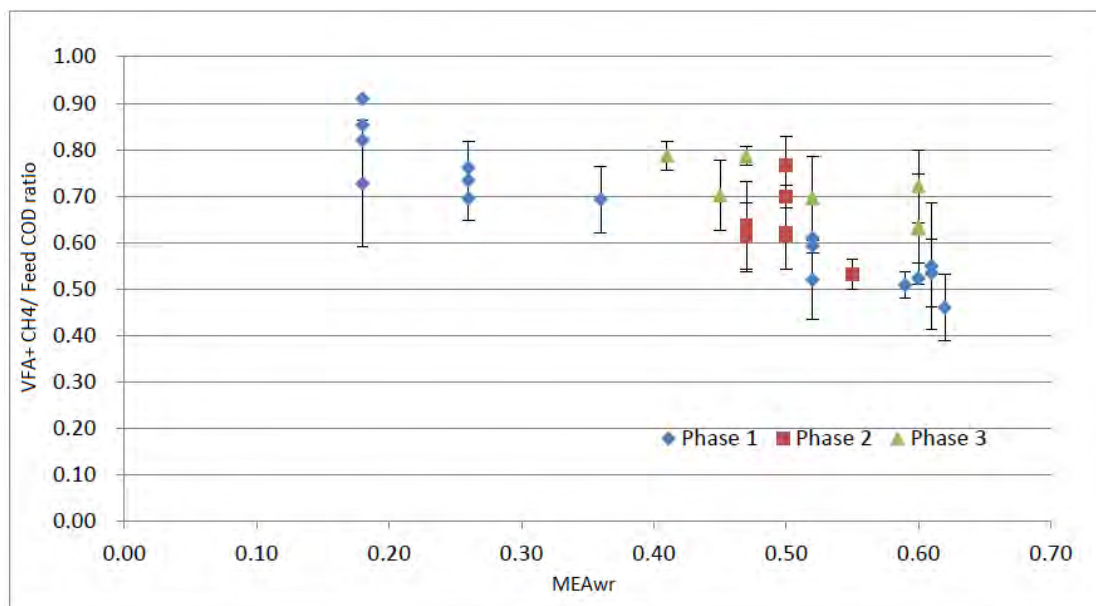MEAw degradation ratio of over 50 % was obtained in the batch anaerobic degradation of MEAw (Table 4.2). More unidentified and resilient organics in MEAw were evidently broken down after biomass adaptation during a year of operation of the semi-continuously fed digester (Fig. 4.9 and 4.10) with the degradable organic ratio over 70 % (Fig. 4.8). The identified chemicals, N-acetylethanolamine (C$_4$H$_9$NO$_2$) in the similar MEAw was biodegradable in AD (Fig. 4.8) while N-(2-hydroxyethyl)-ethylenediamine (C$_4$H$_{12}$N$_2$O) was not (Fig. 4.8).

4.4.1 Batch Test

Anaerobic degradation of MEAw in batch reactors was conducted at two temperatures (25 and 35 °C) since temperature is considered to be an important factor for digestion rate, in particular the rate of hydrolysis and methane formation in AD (Tchobanoglous et al., 2003). Results show that temperature increase of 10 °C positively affected the degradation rates of both feed substrates with and without MEAw (Fig. 4.7). At 35 °C, the maximum biogas generation rates for both feeds were close to 2.5 mL/d (A, Fig. 4.7), while at 25 °C, the rates were about 1.1 mL/d (B, Fig. 4.7). Biogas generation rates of feed with MEAw are slowed down by the inhibitory effects from MEAw, apparently in the same way at both temperatures tested (Fig. 4.7). It suggests that temperature does not influence the mechanisms involved in MEAw degradation much, but temperature is generally an important factor in design of treatment plants.

Calculation shows that the generated methane COD to the total feed COD ratios were 0.89 and 0.70 (by assuming 80 % of the biogas was methane, Fig. 4.2) for the two different feeds at 35 °C (Table

4.2). The ratios were 0.69 and 0.58, respectively at 25 °C (Table 4.2). MEAw COD degradation ratio was ~ 50 % at both temperatures (Table 4.2).

(A) 35 °C   (B) 25 °C
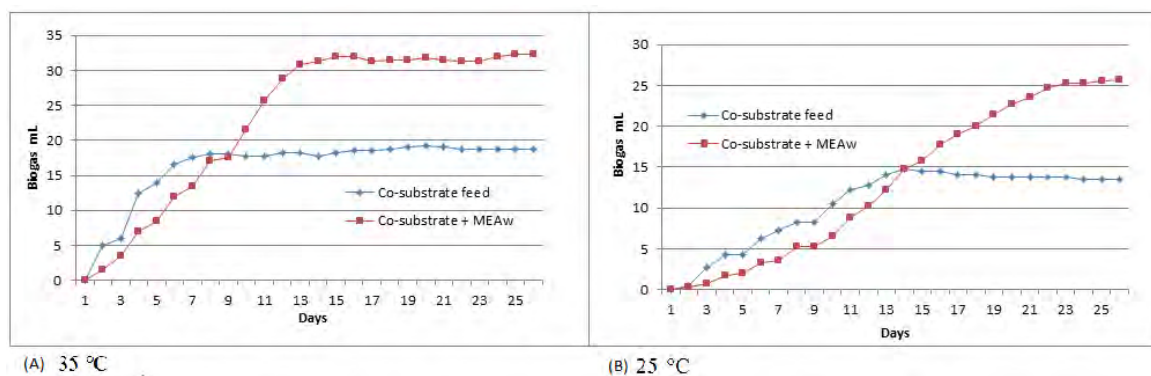
Fig. 4.7 Biogas generation from feed added at time zero at two temperatures (A), 35 °C and (B), 25 °C

Table 4.2 Feed and effluent characteristics of the batch experiments at both 25 and 35 °C

Parameters	Co-substrate feed	Co-substrate + MEAw	Co-substrate feed	Co-substrate + MEAw
Temperature (°C)	35	35	25	25
Feed COD (kg/L)	8.6	18.6	8.6	18.6
Feed pH	7.2	10. 6	7.2	10. 6
Effluent pH	8.2	8.3	7.9	8.1
Feed NH_4^+ (g/L)	0.05	0.14	0.05	0.14
Effluent NH_4^+ (g/L)	1.2	1.3	1.1	1.3
Biogas volume (mL)[a]	19	32	14	26
CH_4 volume (mL)[b]	15	26	11	21
CH_4/feed COD ratio	0.89	0.70	0.69	0.58
MEAw degradation ratio[c]	-	0.53	-	0.48

a, Value obtained by subtracting blank biogas generation; b, CH_4 partial pressure was assumed to be 80 v/v %; c, Calculated based on methane yield and feed MEAwr

Biogas accumulation for the syringe tests feeding with standard feed and two pure chemicals identified in the similar MEAw showed that degradation of $C_4H_9NO_2$ was close to that of feed with co-substrate and MEAw (Table 4.2). Feed with $C_4H_{12}N_2O$ in the batch reactor had almost no biogas accumulation (Fig. 4.8). It implies that this chemical was not readily degradable by the applied AD culture. It was also demonstrated that $C_4H_{12}N_2O$ has poor biodegradation ability in seawater (Eide-Haugmo et al., 2009).

Fig. 4.8 Biogas accumulation during the batch experiment feeding with pure chemicals

4.4.2 Semi-continuous Feed Test
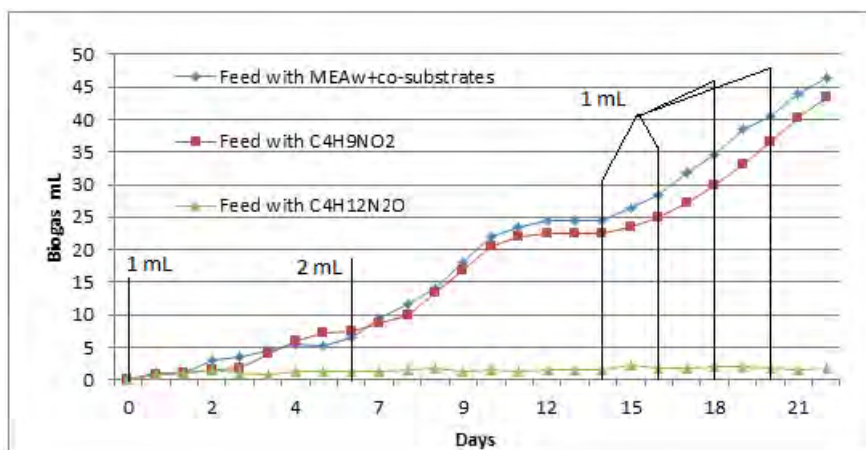
Mass balance shows that over 80 % of the feed COD is accounted for by summing up the COD from effluent sCOD and CH_4 (Fig. 4.9). The rest COD may have been used for biomass synthesis and some may have been retained in the digester by attaching to and accumulating in the biofilms (Paper 1). No attempt was made to confirm and quantify this. Degradation ratio ((VFA + CH_4)/Feed COD (Fig. 4.6 and 4.9) illustrates the degradation efficiency of feed organics. Average degradation ratios at each feed OLR periods tested are shown in Fig 4.9. The degradation ratios were 0.5 at high inhibitory condition and were maximum 0.9 when there was little MEAw in the feed. An average of 0.7 of the feed COD was converted to degradation products of VFA and methane in the semi-continuously fed digester (Fig. 4.9).

MEA was 14 - 30 wt% of the MEAw used in this test, accounting for almost half of the MEAw COD. MEA was found to be fully degraded in the semi-continuously fed AD of MEAw (Fig. 4.10). Another major MEAw constituent N-acetylethanolamine ($C_4H_9NO_2$) can also be degraded by this culture (Fig. 4.8). Other unidentified chemicals in the MEAw were also broken down to levels that were not detectable after AD treatment (peaks in Fig. 4.10). At least 50 % of MEAw COD was converted in the semi-continuously fed AD test and over 70 % of MEAw COD was convertible (Table 4.2 and Fig. 4.9).
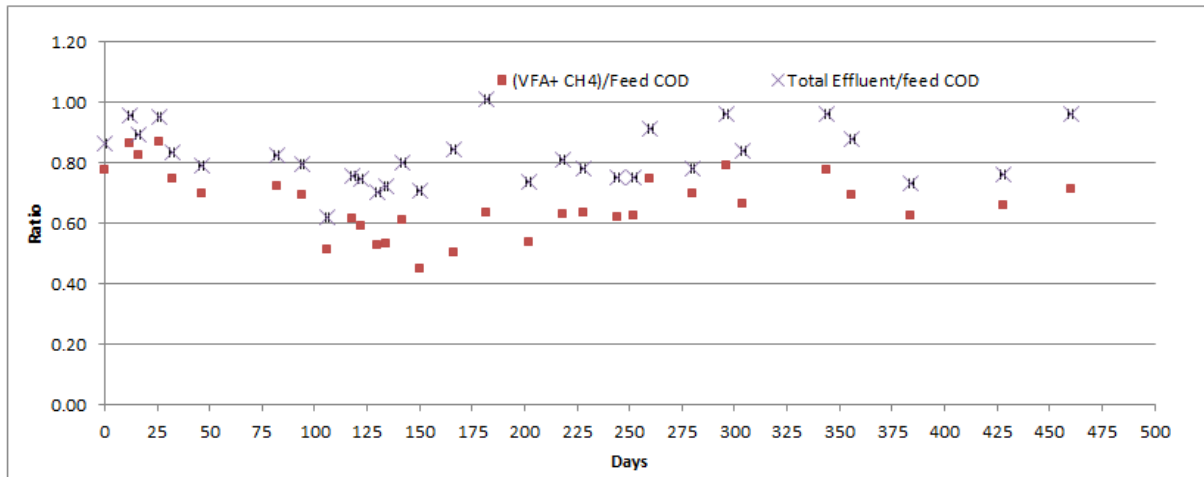
Fig. 4.9 Ratios of degradation products to total feed COD (($VFA+CH_4$)/Feed COD), soluble COD to total feed COD ratio (sCOD/Feed COD) and total effluent (sCOD+CH_4) to feed COD ratio.
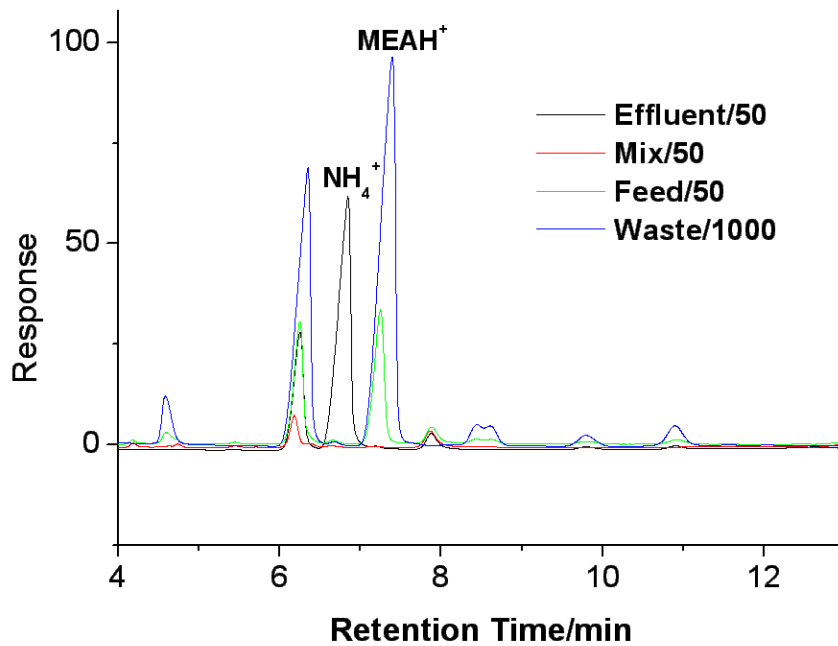
Fig. 4.10 IC analysis of samples (at 150th day): Black line – reactor effluent (50 times diluted); Red line - co-digestion substrates (50 times diluted); Green line - feed substrate (MEAw + co-digestion substrates, Table 3.5) (50 times diluted); Blue line - 1 g MEA waste (1000 times diluted).

4.5 Detoxifying Effects

Toxicity tests provide useful results for protecting human, aquatic organisms and the environment in general from contamination due to discharge of waste substances. Eco-toxicity tests of pure MEA, effluents from the semi-continuously fed AD digester treating MEAw and untreated MEAw were conducted (Paper 3). EC_{50} determined as 50 % growth rate inhibition for the unicellular algae

Pseudokirchneriella subcapitata, 50 % acute immobilization for crustacean *Daphnia magna* and 50 % lethal effects concentrations for embryos of the zebra fish *Danio rerio* were analyzed (Table 4.3). Toxicity of the untreated MEAw which consisted of 18 wt%MEA and other complex identified/unidentified chemicals with a measured COD of 630 mg COD/g MEAw was applied as a reference. Experimental test showed that this MEAw contained more toxic substances than pure MEA (Paper 3). Toxicity of the AD digester effluents was 126, 42 and 10 times lower than that of the untreated MEAw to the respective trophic groups (Table 4.3, Paper 3). Unidentified MEAw chemicals and ammonia generated from feed nitrogenous organic degradation may have contributed to the remaining AD effluent toxicity (Paper 3).

The AD effluent samples collected from the semi-continuously fed anaerobic digester treating co-feed MEAw was sustained at constant feed MEAwr (~0.59 (challenging level)) and OLR (1.6 kg COD/m^3·d) with stable digester performances (Paper 3). The methane yield was 0.2 L/g COD. Effluent samples contained about 114 mg COD/L of VFA where acetate constituted over 90 % of the concentration. The digester pH was stable at around 7.9. Total ammonia nitrogen (TAN) and free ammonia nitrogen (FAN) were 2.0 g/L and 68 mg/L, respectively and COD removal efficiency was 86 % (Paper 3).

EC_{50} concentrations of the pure MEA to the three trophic groups were 151, 209 and 618 mg/L, respectively (Table 4.3). MEAw had much stronger toxicity and the equivalent toxicity EC_{50} were calculated to be at MEA concentrations of 0.04, 0.18 and 0.44 mg/L (Paper 3). Thus, other toxic chemicals in MEAw (e.g MEA degradation products, corrosion inhibitors and inorganic salts) were important in contributing to the MEAw toxicity, as also observed by da Silva et al. (2012). Toxicity of the AD effluent showed that EC_{50} concentrations were increased 126, 42 and 10 times comparing to that of the untreated MEAw (Table 4.3).

Due to biodegradation, MEA was not detected in the AD effluents applied for the toxicity test (Fig. 4.10). Ammonia was the major degradation product and some unidentified chemicals were also detected to be degraded to levels that were not detectable by ion chromatography (Fig. 4.10). Ammonia, especially free ammonia (NH_3) is considered to be toxic to aquatic animals. The TAN and FAN concentrations measured at EC_{50} for each trophic groups were 49 and 1.6 mg N/L, 69 and 2.3 mg N/L and 102 and 3.4 mg N/L, for algae, Daphnids, zebra fish, respectively. Those concentrations are beyond the suggested threshold values for environmental protection and close to the acute toxicity that can be caused by ammonia (Gersich and Hopkins, 1986 and Camargo and Alonso, 2006). This implies that the toxicity of the AD effluents can be caused by its ammonia. Remaining unidentified organics in the effluent that are suspected to contribute to the inhibition of methanogenesis at high feed loads may also be toxic to the tested trophic groups. The relative inhibition importance of ammonia vs. unknown

chemical has not been determined yet, in either case. If ammonia is the main problem it can easily be solved, such as by standard processes for nitrification (Hauser et al., 2013).

Table 4.3 Summary of ecotoxicity endpoints for the three test chemicals corresponding to the three trophic groups

Test chemical	Trophic group	EC_{10}[a]	EC_{50}[a]
MEA (mg/L)	Algae	30	151
	Daphnids	128	209
	Zebra fish	165	618
MEAw (v/v %)	Algae	0.0089	0.019
	Daphnids	0.060	0.081
	Zebra fish	0.034	0.194
TW (v/v %)	Algae	0.74	2.4
	Daphnids	2.2	3.4
	Zebra fish	-	1.91

a, ECx: The concentration which results in x % reduction in growth rate, immobilization or lethal effects compared to the control.

4.6 Modeling and Simulation

Anaerobic digestion model No.1, ADM1 (Batstone et al., 2002) was expanded and applied for modeling and simulating AD of MEAw at room temperature (Paper 4). The new model ADM1_MEAw (Fig. 4.11) was based on assumptions: 1) MEAw COD consisted of 44 % MEA and 56 % complex organics (CO), in which degradable organics and inerts accounted 26 % and 30 %, respectively; 2) MEA and acetate were hydrolysis products of the degradable organics. 3) MEA was degraded to ammonium and acetate (Eq. 5); 4) Monod kinetics and standard organisms for amino acids degradation were applied for MEA uptake (Botheju et al., 2010); 5) Observed MEAw and ammonia inhibition on acetoclastic methanogenesis were included in the inhibition factor; 6) The long AD sludge retention time was accounted for in the model by a parameter t_{res},x that allows particles (X) to be retained in the reactor longer than the liquid.

The model ADM1_MEAw kinetics was calibrated by batch AD tests (Chapter 4.4.1), as illustrated by simulated biogas generation in Fig. 4.12. Reasonably accurate sCOD, pH, ammonia concentrations and VFA accumulation were simulated by ADM1_MEAw for the semi-continuous feed AD of MEAw at room temperature when applying the calibrated kinetics (Fig. 4.13-4.15 and Paper 4). Combined Inhibitory effects from free ammonia and MEAw on acetoclastic methanogenesis simulated the

inhibitory levels reasonable well, where free ammonia inhibition was overall stronger than that of MEAw (Fig. 4.15). Due to the difficulties of implementing accurate feed inorganic concentrations in to the model, the simulated pH showed deviations to the experimental results. This also caused the inhibitory effects from ammonia deviating from actual levels. The apparent low direct inhibition from the assumed potentially toxic constituents of MEAw suggests that such constituents were broken down by AD (Paper 4).

4.6.1 Model Parameters

The kinetics of the added biochemical processes of hydrolysis of CO to MEA, inerts, acetate and inorganic nitrogen (IN) and anaerobic degradation of MEA to acetate and ammonium in ADM1_MEAw (Fig. 4.11 and Paper 4) determined in batch AD tests at 35 °C, are given in Table 4.4. Adjustments for kinetics due to temperature effects to simulate the semi-continuously fed AD operated at 22 ± 2 °C are also given. Inhibitory effects on acetoclastic methanogenesis observed in the experiment were assigned in modeling acetate uptake by the K_I parameters given in Table 4.4 (Paper 4). Feed MEAw and co-digestion substrates concentrations in the 486 days of semi-continuously fed experiment expressed in units consistent with ADM1 simulations are given in Table 4.5.

Table 4.4 Specifications of parameters values

Parameter	Description	Units	Batch model	Semi-continuous feed model
K_{hyd_ch}	*First order carbon hydrate hydrolysis rate*	d^{-1}	10^a	6^c
$K_{hyd\ CO}$	*First order CO hydrolysis rate*	d^{-1}	10^b	10
K_{m_MEA}	*Monod maximum specific uptake rate of MEA*	d^{-1}	5^b	3^c
$K_{s\ MEA}$	*Half saturation constant of MEA*	kg COD/m^3	0.48^b	0.48
K_{I_MEAw}	*50 % inhibitory MEAw concentration*	kg COD/m^3	1^b	1
Y_{MEA}	*Yield of biomass on MEA*	kg COD B/kg COD S	0.08^a	0.08
$K_{I\_nh3\_ac}$	*50% inhibitory concentration of NH_3*	kmol/m^3	0.0018^a	0.0018

a, Standard ADM1 values; b, Estimated for batch test; c, Adjusted based on temperature effect (Eq. 6 and 7)

Table 4.5 Implemented feed concentrations in ADM1_MEAw

Composition	Units	Feed concentration
Total carbohydrates	g-COD/L	2.6
Particulate carbohydrates	g-COD/L	1.8 (0)^a
Soluble carbohydrates	g-COD/L	0.8 (2.6)^a
Amino acid	g-COD/L	7.0
MEA	g-COD/L	0.8-6.9
Complex organics (CO)	g-COD/L	1.0-8.8
Inorganic carbon (IC)	kmol/m^3	$8*10^{-3}$-$4*10^{-2}$

a, when glucose was used instead of starch after 250 days in the semi-continuously fed test (Wang et al., 2013 b)

Fig. 4.11 COD flux for the original ADM1 (black) and the expanded ADM1_MEAw (red + blue). HBu - Butyric acid, HPr – Propionic acid, HVa – Valeric acid, LCPA - long chain fatty acid, MEA – monoethanolamine, MEAw – monoethanolamine waste, CO – complex organics, IN – inorganic nitrogen.

4.6.2 Simulation Results
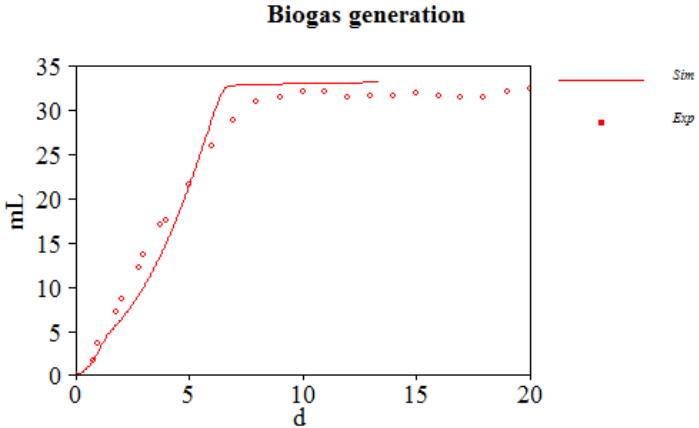
Fig. 4.12 Simulated and experiemntal biogas accumulation in the batch test.

ADM1_MEAw simulations of the semi-continuously fed test show that effluent sCOD (soluble COD), biogas flow rates, inorganic nitrogen concentrations etc. comply with the experimental data (Paper 4).

Some deviations in the simulated effluent sCOD appear when relativaly large feed load changes were applied (e.g. 100 – 200 days, Fig. 4.13). At relative stable AD operation (period 200 - 300 days, Fig. 4.13), the effluent sCOD was overestimated and the simulated inerts COD was almost equal to the sCOD observed in the experiment. It indicates that parts of the inerts content (30 %) in MEAw estimated from the batch calibration test are not really inerts and have been degraded by the acclimated culture in the long term experiment. This adaptation is not accounted for and predicted by the model (Paper 4).
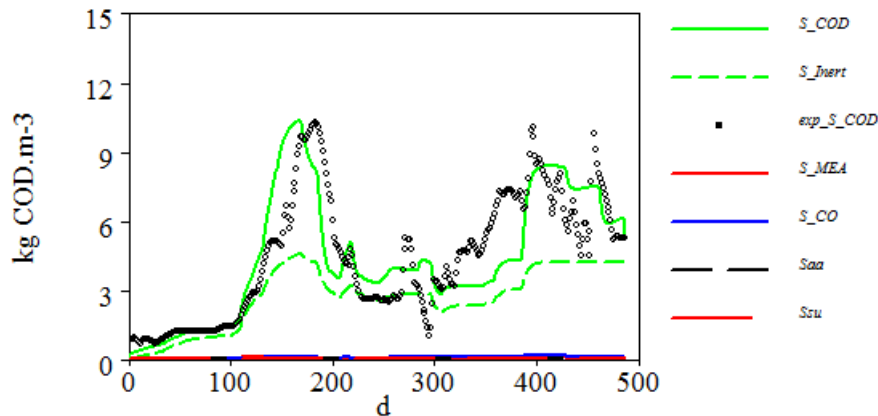
Fig. 4.13 Simulated and experimental effluent COD concentrations (s_COD and exp_s_COD). Saa and Ssu are simulated amino acid and sugar concentrations, respectively.

Inorganic carbon (IC) is an important factor in determining the pH and CO_2 balance between gas and liquid phases in the digester (Paper 4). The input IC concentrations were specified in the ADM1_MEAw (Paper 4) to account for its effects on pH. Predicted pH generally complied with experimental measurements (Fig. 4.14). An underestimation of pH and overestimation of biogas CO_2 partial pressure before 110 days in the simulation (Fig. 4.14) suggesting that IC model inputs were higher than the actual values. No obvious reason for the apparent input IC overestimation causing an increased buffer capacity before 110 days (Fig. 4.14) has been found.
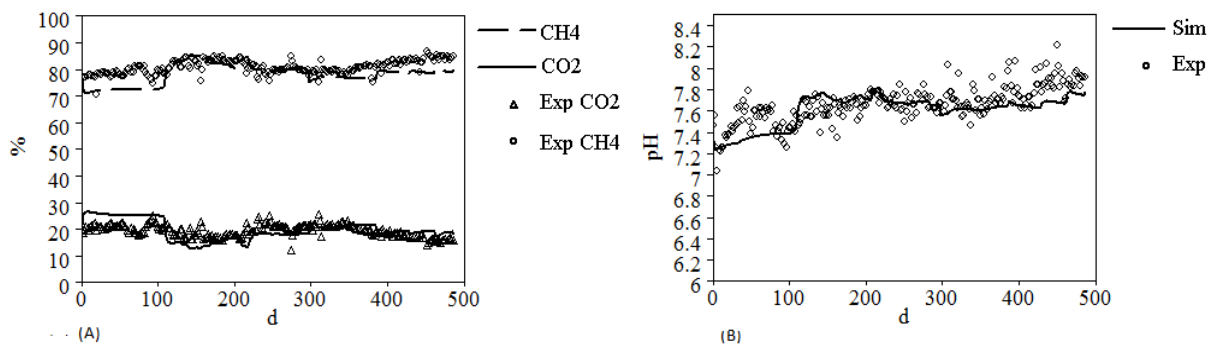
Fig. 4.14 Simulated and experimental CH_4 and CO_2 partial pressures (A) and pH (B).

Observed VFA accumulation episodes were predicted by the model with acetate constituting most of the VFA accumulation (Fig. 4.15). The VFA accumulated period and amounts were not so well simulated at the beginning of VFA accumulation (Fig. 4.15).

Acetate uptake in ADM1_MEAw was modeled by applying inhibitory effects of free ammonia and MEAw. The inhibition factor I_{MEAw} is assigned to the MEAw concentration in the AD digester, which decreases along with the MEAw degradation (Eq. 6, Paper 4).

$$I_{ac} = I_{pH,ac} I_{IN,lim} I_{NH_3} I_{MEAw} \qquad \text{Eq. 6}$$

The inhibition levels appeared to be correctly simulated before 100 days. After 180 days, the simulated inhibition effects also caused VFA accumulation quite in accordance with experimental observations (Fig. 4.15). Free ammonia was observed to be more effective than MEAw in inhibition of acetate uptake (Fig. 4.15). The overestimation of VFA accumulation (between 100 and 180 days) was attributed to free ammonia over prediction associated with the simulated relatively high pH (Fig. 4.14). Sensitive analysis showed that acetate accumulation was not sensitive to the free ammonia inhibitory coefficient ($K_{I\_nh3\_ac}$) (Table 4.4), which complies with the statement that this value is a low variability parameter between systems in continuous reactors (Siegrist and Batstone, 2001). VFA accumulation was more sensitive to MEAw inhibitory coefficient, K_{I_MEAw} and extended retention of solid, t_{res_x2}, than $K_{I\_nh3\_ac}$ (Fig. 4.15). K_{I_MEAw} was assigned a value of 1 and t_{res_x2} was 20 in the simulation, they both contribute low errors to the VFA accumulation in the model (Fig. 4.16), while the standard inhibition concentration $K_{I\_nh3\_ac}$ contributed relatively lager errors during the fluctuations of VFA concentrations (Fig. 4.16). All these show that the $K_{I\_nh3\_ac}$ value demands precise specification to reduce simulated VFA errors. Such was not conducted in the model calibration since the simulated results illustrated the experimental observations quite well by maintaining the standard ADM1 parameters.
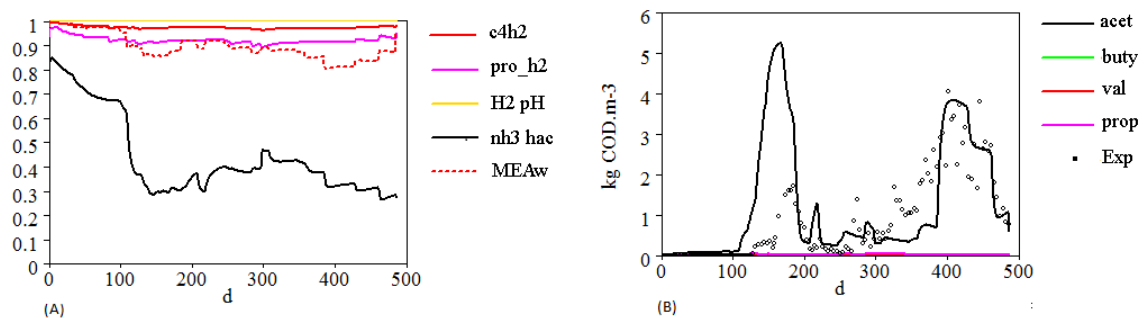
Fig. 4.15 Simulated inhibition effects (A) in AD of MEAw. c4h2 and pro_h2, hydrogen inhibition on butyrate and propionate degradation; H2_pH, pH inhibition on hydrogen degradation; nh2 hac and MEAw, free ammonia and MEAw inhibition on acetate degradation. Simulated VFA accumulation (B), acet, acetate; buty, butyrate; val, valerate; prop, propionate and Exp, experimental results.
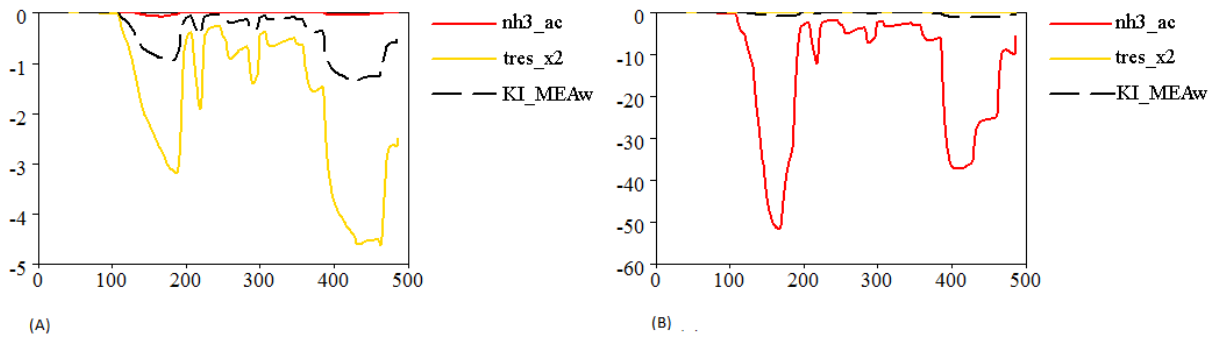
Fig. 4.16 Acetate concentration sensitivity to the selected parameters nh3_ac, free ammonia inhibition on acetate degradation; tres_x2, extended retention of solid; KI_MEAw, MEAw inhibition on acetate degradation (A) and their error contributions to the acetate concentrations (B).

Chapter 5 Conclusions

5.1 Conclusions and Implication

This thesis presents detailed experimental and theoretical studies of the anaerobic digestion of an industrial post CO_2 capture reclaimer MEAw. The lab-scale experimental tests involved subtasks of constructing and maintaining efficient anaerobic digester systems and performing experimental tests on MEAw degradation in both semi-continuously and batch fed manners at selected feed and temperature scenarios. Anaerobic MEAw degradation was evaluated by chemical analysis of the AD COD removal, biogas yield, ammonia accumulation etc. Inhibitory factors of AD of MEAw were detected and their effects are discussed. The detoxify effects of AD on MEAw was also accessed by conducting toxicity tests of MEA, MEAw and effluent from AD of MEAw on three typical fresh water taxonomy groups. Theoretical evaluations of AD of MEAw were conducted by literature review, establishing and operating a mathematical model, ADM1_MEAw based on the sophisticated model ADM1 and assumptions accumulated in the experimental study. The ADM1_MEAw model was applied to facilitate the understanding of AD of MEAw and its performance was evaluated by assessing the simulation results to the experimental data.

Some important observations in the study of AD of MEAw and their implications are summarized here.

1). Applying both the concepts of fluidized bed and biofilm reactor in the lab-scale anaerobic digester greatly improved the sludge retention and culture cultivation in this study. Enhancing the biomass diversity by employing cultures of various backgrounds is important to sustain and cultivate effective cultures to degrade challenging MEAw.

2). Adequate nutrients and minerals supplements are essential to the cultures' development for sustaining healthy organisms and stable reactor performances.

Lack of nutrients and minerals was considered to be one of the reasons that caused the anaerobic digester failure in the preliminary tests. Applying easily degradable and nutrients rich organics as co-substrates and improved digester structure enabled a stable anaerobic digestion of reclaimer MEAw. It implies that a successful anaerobic digestion of MEAw can possibly be achieved in a larger scale process where a similar digester structure, cheaper and easily accessible co-substrates, such as domestic waste water are used.

3).The anaerobic digester was stabilized at low feeding loads and MEAwr at the commencement of the test, while adaptation enabled the lab-scale digester to handle MEAwr up to 0.6 and an OLR of 5 kg COD/m^3·d.

4). Feed MEAwr over 0.5 is considered to be inhibiting to AD of MEAw. Increased feed MEAw in the semi-continuous feed test caused ammonia concentration in AD to reach inhibitive concentrations to acetoclastic methanogenesis. Acetate accumulation indicates that acetoclastic methanogenesis was mainly the inhibited organisms in AD of MEAw.

5). Increased MEAw degradation ratio was observed in the experimental phase after long period sludge adaptation was applied. Culture's acclimation to recalcitrant MEAw was considered to be the reason.

Inhibition of MEAw degradation in this experimental study was observed at MEAwr over 0.5. Complex and recalcitrant chemicals in MEAw and/or their degradation products, including ammonia can be the causes of the inhibited AD performance. When it comes to sustain stable AD from inhibition effects, it is important to prevent overloading. Synthesis of anaerobic organisms is a slow process, especially if potential inhibitory substrates are imposed during the culture cultivation. Maintaining suitable feed MEAw loads and applying adapted cultures in anaerobic digesters are important to avoid systems' failure due to inhibitory effects.

6). pH adjustment was not applied in the anaerobic degradation of MEAw. Stable digester pH ($\sim$ 8) within the optimal range for methanogens was obtained. Relatively high feed MEAw alkalinity was considered to contribute to the stable pH in the AD digester in handling feeds pH of $\sim$ 10 and VFA accumulations.

7). Over 70 to a maximum 93 % of the total MEAw COD degradation at tested conditions were achieved in the semi-continuously feed experimental test.

8). Methane yield reached a maximum of 0.34 L/g COD, at an average of 0.25 L/g COD. 80 % of the generated biogas was methane.

9). Temperature does not influence the mechanisms involved in AD of MEAw much, but temperature is generally an important factor in design of treatment plants.

The anaerobic digestion of MEAw together with easily degradable co-substrates achieved stable and high waste removal efficiency. Most of the waste was degraded to easily convertible forms of COD such as VFA and methane. The relatively high conversion ratio of MEAw and the generated methane rich biogas imply that AD of MEAw is a promising choice for both waste treatment and energy recovery. Adding AD of MEAw at CCS plant can be of economic interest for handling generated waste components and incorporating recovered energy to existing power intense systems.

10). MEAw toxicity was reduced by 10 to 126 times after anaerobic digestion treatment at a challenging feed condition with MEAwr of 0.6 by using an adapted culture.

11). Ammonia and/or other un-degraded toxic constituents from MEAw that survived AD of MEAw can be the remaining toxicity factors.

Anaerobic digestion of MEAw generally degraded most of the waste constituents. Applying nitrification for ammonia removal can potentially reduce the environment toxicity from ammonia and making the AD effluent safe for discharge. Reduced toxicity after AD digestion, renewable energy recovery and avoiding release of volatile toxicants are some advantages of anaerobic digestion over other treatments, such as aerobic MEAw degradation.

12). Model ADM1_MEAw applied standard ADM1 parameters and calibrated kinetics based on batch test for AD of MEAw was able to closely predict the reactor performance under varying feed scenarios.
13). All feed MEA was simulated to be degraded which complied with the experiment observations. Simulated COD removal, pH and inorganic nitrogen concentrations are in accordance with the experimental data.
14). Model ADM1_MEAw predicted overall stronger free ammonia inhibition than MEAw imposed on acetoclastic mathanogenesis in AD of MEAw. Simulated pH deviations are partly the cause of simulated free ammonia concentration errors which overestimated the free ammonia inhibitory effects.

The ADM1_MEAw based on ADM1 and assumptions made based on experimental results showed promising simulation results for AD of MEAw. The assumptions made to expand ADM1 to ADM1_MEAw were thereby determined to be reasonable. Simulation showed less inhibition from the assumed potentially toxic constituents of MEAw than inhibition effects from ammonia. It suggests that MEAw inhibitory constituents were broken down by AD which is also supported by the toxicity test. This model can also be used as a prediction tool to plan more experimental tests, conduct theoretical analysis and eventually to design treatment plants. Lab or larger scale tests by applying domestic wastewater for example can be an interesting topic that can be assisted by such a tool.

The conclusions can be summarized as follows: Anaerobic degradation of reclaimer MEAw was tested to be efficient and successful under the lab condition and applied scenarios in this study. An efficient bio-digester was constructed and operated stably and continuously for two years. Over 70 % of MEAw was degradable and the biogas was rich (80 %) in methane. The toxicity of the reclaimer waste was also significantly reduced by the anaerobic digestion. Limitations of digestion of MEAw were observed due to recalcitrant and inhibitory effects from MEAw and ammonia, the dealing of which can be interesting research topics for further test. The digestion model based on ADM1 successfully predicted the digester behavior in many perspectives and it can be a useful tool for understanding the digestion process and arranging further tests.

All the mentioned work and results presented and conclusions summarized in this thesis achieved the established research objectives of the project and are within the research scope. This research contributed to the knowledge of industrial waste treatment, as well as extended the possibility of biological waste treatment implementations. The knowledge accumulated of efficient and safe biological CCS waste treatment can facilitate the acceptance of CCS for the public and promote safe and environmental friendly CCS development.

5.2 Recommendation for Future Work

Research topics related to the experimental test of AD of MEAw degradation and some of the conclusions generated above can be further investigated. Followings are some examples together with the proposed examination methods:

The MEAw used in this AD test was from an industrial CO_2 capture facility. Some components in such waste, for example MEA and VFA concentrations were qualified and quantified. However, the majority of the MEAw components were not qualified or quantified in the test. Some of the waste components cannot even be identified. Due to storage and other environmental condition changes, the MEAw composition is also varying. How to conserve this MEAw and quantify its composition are challenging tasks, however, the clarification of which is important for understanding the AD of MEAw degradation as well as the inhibitory effects. For the known MEAw components, to understand the degradation ability of each component in anaerobic condition is important to understand the degradation of MEAw in general. Two pure chemicals in such MEAw were tested in this dissertation, one of which was clearly resistant to AD and the other was not. Proposal is made that by identifying the main MEAw components, quantifying their concentrations and testing their degradability, an in depth understanding of MEAw anaerobic degradation can be achieved.

The Anaerobic digestion of MEAw showed that over 70 % of MEAw was degraded in the digester. The "un-degraded" part of the MEAw composition was unknown. To identify and quantify those "residuals" are essential in understanding the effects of inhibition in AD of MEAw and its remaining toxicity effects. Both MEAw components and ammonia concentrations were considered to be inhibitive to AD of MEAw in the dissertation. Simulation results showed generally stronger inhibitory effects of free ammonia. As ammonia concentration is relatively easy to alter and monitor. A proposal is made to identify ammonia effects by manually altering ammonia concentrations independent of MEAw load in the anaerobic digester and investigate the digester behaviors.

Initially, granular sludge from a UASB reactor treating pulp and paper wastewater was mainly applied as inoculums in the AD of MEAw test. Some other inoculums sources were also added in the digester to diverse the biomass culture. The culture slowly adapted the feed substrates of MEAw and acclimated to the environmental conditions of high ammonia and other MEAw toxicants. It would be an interesting topic to monitor the conversion of biomass cultures in such adaption process and

identify the possible biological pathways that promote such adaptation. Taxonomical classification of organisms within clusters can be carried out and FISH (Fluorescence in situ hybridization) and DGGE (Denaturing gradient gel electrophoresis) are two applicable technics for such purpose.

The toxicity test of effluent from AD of MEAw showed increased fresh water taxonomy groups' tolerance comparing to the untreated MEAw. While relatively high free ammonia concentrations in the effluent can be the most important remaining toxic factor to the taxonomy groups. The role of free ammonia as well as MEAw "residulas" in posing toxicity to the water trophic groups can be clarified by conducting some post treatments test. For example, by nitrifying the ammonia in the AD effluent to get rid of ammonia effects and assessing the remaining toxicity.

Co-substrates applied in the dissertation are manufactured organics of high purity and economic values. Applying such co-substrates is not economically efficient in a larger scale test for MEAw degradation, for example treatment plant. Obtaining easily accessible and cheaper co-feed substrates are thus important to improve the economics of AD of MEAw. Domestic wastewater is one of the options, the use of which together with MEAw can be studied in future tests. An integration of wastewater treatment together with MEAw handling by obtaining and utilizing energy from MEAw anaerobic digestion is an interesting topic. The possibility of using residuals of AD of MEAw as fertilizer is also an attractive study topic. Modeling and testing how AD can be combined with aerobic processes to also remove TAN is also an interesting topic to establish the industrialized MEAw treatment.

The ADM1_MEAw model was construed based on the experimental studies conducted. As mentioned above, several future tests can be conducted for clarifying the remaining questions. The results generated in the future tests provided more detailed information about MEAw components, inhibitory effects etc. which would facilitate the construction of an even more structured AD model of MEAw degradation.

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Appendix A

Matrix of biochemical rate coefficients and kinetic rate equations for AD of MEAw is given in Table A-1.

Table A-1 Matrix of biochemical rate coefficients and kinetic rate equations for AD of MEAw (yellow mark)

Paper II:

Efficiency of the anaerobic digestion of amine wastes.

ORIGINAL RESEARCH PAPER

Efficiency of the anaerobic digestion of amine wastes

Shuai Wang · Jon Hovland · Rune Bakke

Abstract Laboratory-scale anaerobic degradation of monoethanolamine waste (MEAw) with co-substrate organics was conducted at room temperature and organic loading rates from 0.19 to 5.03 kg COD/m^3 day for 486 days in a hybrid digester. 90 % feed COD conversion to methane was obtained at the lower loads and only 45 % at the highest MEA waste/COD ratio (MEAwr) of 0.62 due to inhibition of methanogenesis. Inhibition at comparable loads decreased with time, implying that the culture adapted to the challenging feed. Methane yield was negatively correlated to MEAwr applied and inhibition avoided at MEAwr \0.5. Acetate accumulation implies inhibition of acetoclastic methanogenesis that can be caused by ammonia, a product of MEAw degradation. Moderate total ammonia nitrogen and free ammonia nitrogen accumulation, maximum 2.2 g N/l and 90 mg N/l, respectively suggests, however, that other components of MEAw, and/or degradation products of such, also inhibit methanogenesis, disturbing the digester performance.

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Introduction

There has been increasing focus on CO$_2$ capture (CC) as a measure to mitigate greenhouse gas emissions. In CC, alkaline amine solvents used for absorption of CO$_2$ [e.g. monoethanolamine (MEA)] is considered to be the most mature technology (IEA 2012). MEA and other alkanolamines are also commonly used for the absorption of acidic gases (CO$_2$, H$_2$S etc.) from natural gas and in refineries. The solvents are repeatedly used by regeneration through distillation in the capture process (Barchas and Davis 1992). Over time, the amine solvents degrade due to oxidation, thermal degradation, carbamation and reaction with SO$_x$, NO$_x$ and dust in the flue gas as well as by other means (Goff and Rochelle 2004; Davis and Rochelle 2009). A concentrated solution of reclaimer waste accumulates at the bottom of the reclaimer facility after distillation. This concentrated solution is classified as hazardous waste and must be stored and disposed of accordingly.

Biological MEA waste (MEAw) treatment has been suggested and investigated (Hauser et al. 2013; Botheju et al. 2011; Wang et al. 2013). Anaerobic

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digestion (AD) is a means to both break-down wastes and recover energy from it as methane. AD is a synergistic biological process that involves various types of organisms. AD of MEAw is challenging due to its relatively high N:C ratio and high content of complex chemicals. Inhibition and low chemical oxygen demand (COD) removal efficiency was observed at high loading during co-digestion of MEAw with easily degradable organics (Wang et al. 2013). AD is, though, vulnerable to toxic effects from ammonia and feed organics (Chen et al. 2008). Ammonia is a degradation product of MEA that can be inhibitory to the AD process (Hansen et al. 1998). Additionally, chemicals from MEAw may also stress the organisms.

The aim of this study was to examine the anaerobic degradation of MEAw to determine the limitations of waste loading. The study is a continuation of a previously published experiment (Wang et al. 2013) running the reactor for more than a year to investigate how waste degradation limitations change as the culture adapts to the feed. The AD capacity was tested by measuring the methane yield, COD removal efficiency and ammonia and volatile fatty acid (VFA) accumulations. Principle component analysis (PCA) was applied to investigate the relative significance of possible inhibitory compounds.

Materials and methods

Feed and nutrient

Reclaimer monoethanolamine MEA waste with combined easily-degradable organics was applied as feed substrate (Table 1). The MEAw investigated was collected from a full-scale MEA-based, CO_2 capture facility at a coal-fired power plant. The waste contained complex components that were not well identified. The measured COD of the waste varied between 450 and 900 mg COD/g waste, the N content was $\sim$7–14 % (w/w) and the MEA accounted from 18 to 30 % (w/w). Detailed information about similar wastes can be found in Strazisar et al. (2003) and Thitakamol et al. (2007).

Starch, replaced by glucose after 250 days (due to the detection of starch accumulation on the inner wall of the feeding pipe, to avoid flow disturbances and inconsistent mass balances that it could cause),

peptone and yeast extract mixture was applied as the co-substrate feed. The co-substrates were used to provide necessary nutrients, minerals and various easily degradable organics to maintain biomass that can tolerate exposure to toxic and inhibitory chemicals from the MEAw. Preliminary but unpublished tests show that methanogenesis cannot be maintained on MEAw alone as feed substrate. Constant concentrations of first starch, then glucose, peptone and yeast extract were used in the whole test period (Table 1). KH_2PO_4 (0.15 g/l) and K_2HPO_4 (0.15 g/l) were also added to the feed as buffers.

Feed solutions were prepared by mixing the MEAw and co-substrate in deionized water and stored at 4 °C. The pH of the feed mixture was around 10–11 (varying depending on the MEAw content).

10 ml buffer (102 g KH_2PO_4/l; 131 g K_2HPO_4/l) and mineral solutions (Table 2) were added to the system at the start-up of the digester to stabilize pH and provide the necessary minerals in the pre-adaptation period. No external buffer and minerals were supplied after the initial addition.

Biomass

A mixture of inocula from various sources were added in the reactor at the commencement of the test. 200 ml of settled fresh granular sludge, with relatively equal size ($\sim$2 mm) from a pulp and paper industrial wastewater treatment Upflow anaerobic sludge blanket reactor (UASB) in Norway, was applied as the main inoculum. Some polluted river bed sludge (Lilleelva river in Porsgrunn, Norway) and biomass from other laboratory experimental tests (aerobic and anaerobic reactors treating domestic wastewater) were also added in the reactor to give higher biomass diversity. No taxonomical classification was carried out. No extra biomass was added after the experiment startup.

Experimental set-up

The applied anaerobic reactor set-up is shown in Fig. 1. The reactor was made from a transparent acrylic tube, which was divided into two suspended fluidized bed phases by a fixed biofilm phase, making it a hybrid reactor combining attached and suspended biomass. The total working volume was 1.25 l. Magnetic stirring was employed in the bottom suspended phase

Table 1 Compositions of the feed substrate added during the experimental period

Component	Concentration (g/l)	COD (g COD/l)	Nitrogen concentration (g/l)
Starch (glucose)[a]	1.5 (1.7)	1.8	0
Yeast extract	3.6	3.3	0.4[b]
Peptone	3	4.5	0.4[c]
MEA waste	4–25	1.7–15.6	0.6–3.5[d]
Total	12.1–33.1	11.3–25.2	1.4–4.3

[a] Starch was replaced by glucose at 250th day

[b] Product reference shows a nitrogen concentration of 10.5 % (w/w) in this yeast extract

[c] Product reference shows a nitrogen concentration of 12–13 % (w/w) in this peptone. 12.5 % (w/w) was used in this calculation

[d] An approximate N fraction of 14 % (w/w) was measured and used here

Table 2 Mineral solution composition used at the startup of the digester

Chemical	Value (mg/l)
$MnSO_4 \cdot H_2O$	40
$FeSO_4 \cdot 7H_2O$	2,800
$CuSO_4 \cdot 5H_2O$	60
$NiCl_2 \cdot 6H_2O$	92
$ZnSO_4 \cdot 7H_2O$	90
$CoCl_2 \cdot 6H_2O$	50
H_3BO_3	50
$(NH_4)_6Mo_7O_{24}$	50
$AlCl_3$	50
$Na_2SeO_3 \cdot 5H_2O$	50
EDTA	100

(0.8 l) to avoid sludge sedimentation and "dead zones" at the reactor bottom. Feed was pumped intermittently into this phase using a peristaltic pump. The 0.15 l biofilm phase contained a porous rock material (Light Expanded Clay Aggregates, "Leca" from Weber, Saint-Gobain) as the biofilm substratum contained within a plastic net. The upper suspended phase (0.3 l) was intended as a second sludge bed reaction zone and sedimentation zone to retain sludge in the reactor. The reactor design was intended to achieve long solid retention times compared to hydraulic retention time to enable efficient cultivation of MEAw consuming

biomass and allow relatively high OLR. A recycle rate of 25 ml/min was maintained by a peristaltic pump to fluidize the sludge.

Experimental management

The experiment was performed at $22 \pm 2\ °C$. A pre-adaptation period of three months was applied first to adapt the inoculum to the feed substrate with MEAw. Then, 486 days of experimental data were collected and analyzed. The total feed COD concentrations applied varied in a range of 10–25 g/l, of which MEAw was 1.7–15 g COD/l. The co-substrate had a constant concentration of ~ 9.6 g COD/l (Table 1).

In the pre-adaptation, MEAw concentration in the feed and OLR were kept low and increased carefully (upto ~ 4 g MEAw/l) to avoid biomass loss due to toxic and inhibitory effects. This adaptation period ended when continuous and relatively stable biogas generation was observed. After pre-adaptation, the experimental test was continuously operated with three distinct phases of different feeding strategies (Fig. 2). In phase 1 (0–181 days), MEAwr in feed COD was increased from 0.18 to a maximum of 0.62, the corresponding OLR applied was from 0.25 to 2.82 kg COD/m^3 day. This period was designed to get an overview of the digestibility of MEAw substrate and system capacity and data analysis on this period is published by Wang et al. (2013). Process stability was investigated in phase 2, where MEAwr was kept at around 0.5 (182–281 days) and the OLR was in the range of 2–2.62 kg COD/m^3 day. High loads were tested in phase 3 (282–486 days), where MEAwr was elevated from 0.4 to 0.6 and OLR from 2.66 to a maximum of 5.03 kg COD/m^3 day. OLR was reduced to 2.86 kg COD/m^3 day while maintaining MEAwr at 0.6 at the end of phase 3. The feed COD variations were imposed by changing MEAw concentrations while the co-substrate COD concentrations remained constant (Table 1). The applied loads were varied by modifying either the MEAwr or increasing the feed loading (flow) rate.

The generated biogas was collected continuously in a gas bag (Cali-5-Bond) during the experiment (Fig. 1). The biogas volume and its composition were measured every 2 days. Liquid samples were collected from sample point 3 every 2 days (Fig. 1) for the measurements of pH, VFA, ammonia and soluble COD (sCOD) concentrations. The pH was analyzed
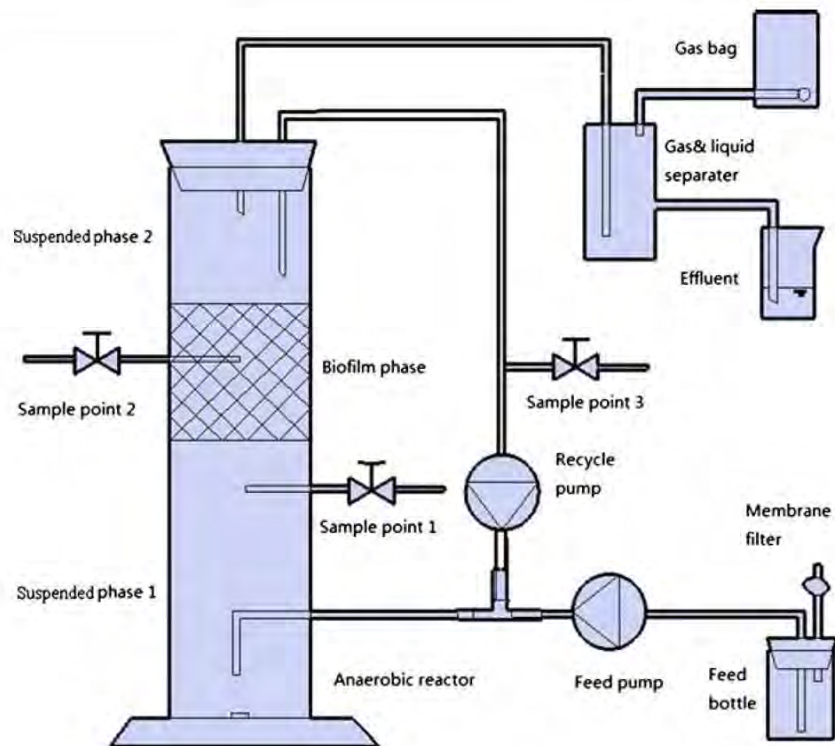
for each sample, while the analysis of VFA, ammonia and COD were conducted for every other sample due to the relatively small amount of samples collected.

Analytical methods

The analytical methods used for the measurements of VFAs, biogas composition, COD, MEA and ammonia concentrations and the calculation of total and free ammonia nitrogen concentration can be referred to Wang et al. (2013).

Principal component analysis, PCA, is a statistical technique to identify patterns in data, and express the data in a way to highlight similarities and differences (Abdi and Williams 2010). Correlation circle generated from PCA analysis was used to interpret the

Fig. 2 Feed and MEA waste COD concentration and organic loading rate (OLR) applied in the experiment test

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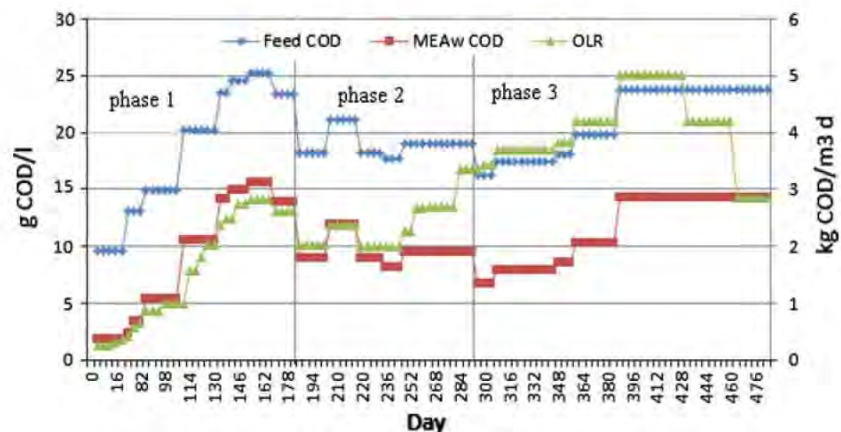
correlation between different variables used. Commercial Excel add-in software XLSTAT was used for the PCA analysis.

Results and discussion

The 486 days of anaerobic digester performance data were recorded and analyzed by assessing the COD and MEA waste removal efficiency and methane yield, showing that the extent of methane generation from waste degradation varied significantly. The influences of operational conditions and inhibition factors on anaerobic MEAw degradation are examined. Data from the first part of this experiment, published elsewhere (Wang et al. (2013)), are repeated here to more clearly show the digestion efficiency development during a long time span and compare results from a wide range of load conditions tested.

COD removal

The COD removal efficiency based on the influent and effluent soluble COD concentration measurements are given in Fig. 3. The COD removal efficiency was generally above 90 % before day 108. Afterwards, it gradually decreased to 45 % when the applied MEAwr increased above 0.5 to a maximum of 0.6 with OLR in the range from 1.5 to 2.8 kg COD/m^3 day (109–181 days). In light of the apparent impending system failure, MEAwr was reduced to around 0.5 while the OLR was maintained between 2 and 3 kg COD/m^3 day in phase 2 (182–282 days). During this period, COD removal efficiency recovered to about 80 % in one month and then remained relatively constant at MEAwr of 0.5 and an OLR of about 2.5 kg COD/m^3 day.

In phase 3, the COD removal efficiency reached up to 90 % again from 283 to 292 days, at a MEAwr of 0.5 and OLR of 3.43 kg COD/m^3 day. The relatively high efficiency at a much higher OLR than that applied in phase 1 indicated that high OLR in the later part of phase 1 (2.82 kg COD/m^3 day) was not the reason of the decreased removal efficiency. A stepwise increase of OLR to 5.03 kg COD/m^3 day by increasing feed MEAwr from 0.4 to 0.6 decreased the removal efficiency again to about 65 % (293–428 days). This decline reveals that the increase of MEAwr does negatively affect the removal efficiency. High MEAwr

is evidently more challenging for the involved organisms than high MEAw loading rate. The system has high capacity in terms of organic loading.

A comparison of removal efficiency at a similar feed MEAwr to that applied in phase 1 around 160 days and after 400 days shows that the removal efficiency was higher in the latter case even at higher loading rates. It indicates that the organisms continued to adapt to the complex feed substrate and inhibitory factors that this feed may have presented or inhibitory products of MEAw degradation (e.g. NH$_3$) through the whole test.

Mass balance

Mass balance for the main COD constituents, calculated at each sampling time based on the measured average methane generation, effluent VFA and effluent sCOD concentrations are shown in Fig. 4. Data, normalized to total feed COD, shows that 80–90 % of the feed COD was recovered as methane and sCOD. A varying fraction of the sCOD was VFA, reaching a maximum of ~50 % during the highest load in phase 3. The COD not accounted for in Fig. 4 (when total effluent/feed COD <1) can be produced biomass accumulating in the reactor and/or leaving as particulate COD. Observed sedimentation of some feed starch on the wall of the feeding pipe may have contributed to loss of feed COD and mass balance errors. Glucose was used instead of starch after 250 days in the feed solution to avoid this potential error. Afterwards, methane COD and effluent sCOD added up to approx. 0.9 times feed COD, showing that 10 % of the feed COD was converted to biomass and some was probably lost as recalcitrant chemicals absorbed to particles/biomass.

Figure 5 shows the combined methane and VFA COD to feed COD ratio with respect to applied MEAwr in feed to show how much of the feed was hydrolyzed and acidified (termed degradation ratio). Data from phase 1 shows that the degradation ratio decreased by a linear trend from about 0.8–0.5 at the maximum MEAwr applied. Only about 50 % of the feed COD was broken down at the highest MEAwr. The degradation ratio increased during the long adaptation period in phase 2 while maintaining relatively high MEAwr. After that the degradation efficiency during phase 3 was consistently higher than in phase 1 in the MEAwr range (0.4–0.6) tested. This clearly demonstrates the biomass adaptation to feed

Fig. 3 COD removal efficiency (%) under different feed OLR and MEA waste ratios in feed
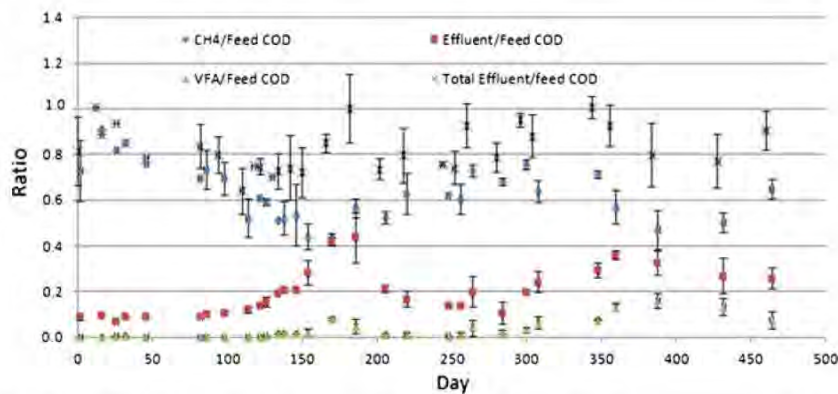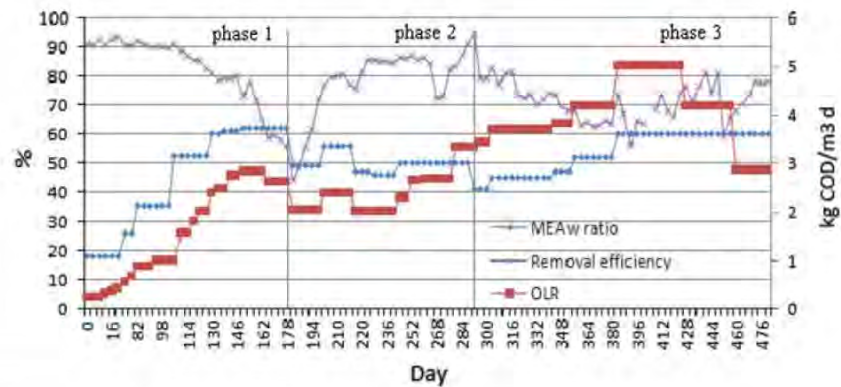

Fig. 4 Ratios of methane, VFA and effluent soluble COD to the total feed COD. *Error bars* represent one standard deviation

MEAw discussed above. The fraction of undetected substances in the feed that were reduced and degraded to methane and VFA still increased after hundreds of days of reactor operation.

pH and ammonia

The MEAw used had high alkalinity (16 g $CaCO_3$/l equivalent, for a 50 g MEAw/l solution in distilled water). The feed solution pH varied depending on the MEAw concentration and reached 10.5 when 25 g MEAw/l was applied. The digester effluent pH was measured in the range of 7.0–8.0 in the whole test period without applying pH adjustment in the AD. Even at the highest VFA accumulation (402–420 days, Fig. 7) the pH was well above 7, attributed to the high alkalinity buffer capacity of the feed solution as well as the accumulated ammonia concentration (Fig. 6). The effluent VFA concentrations varied from 0 to a

maximum of 4 g/l and total and free ammonia nitrogen (TAN and FAN) reached maximums of 2.2 g/l and 90 mg/l, respectively (Figs. 6, 7).

Figure 6 shows the ammonia concentration variations in the digester for the whole test period. The TAN concentration reached a maximum of about 2.2 g N/l at around 181 days and the highest FAN was 50 mg N/l in phase 1. TAN and FAN concentrations decreased simultaneously as OLR and MEAwr reduced and then stayed relatively constant in phase 2. Ammonia concentration increased again when feed MEAwr increased in phase 3. TAN and FAN varied more in phase 3 and were 2.2 g N/l and 90 mg N/l, respectively, at the end of the test.

Inhibition

Acetate was more than 90 % of the VFA accumulated in the digester with minor accumulations of several

Fig. 5 Combined VFA and methane COD to the feed COD ratio under different applied MEA waste COD ratios (MEAwr) in feed in the tested three phases; *Error bars* represent one standard deviation
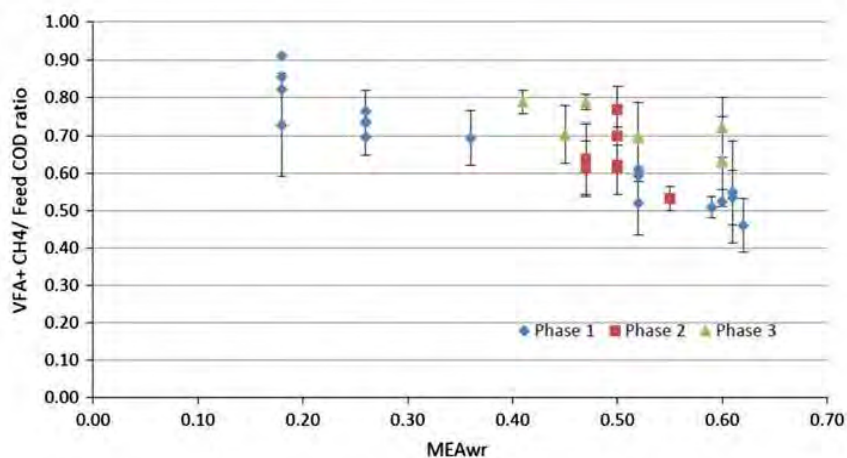

Fig. 6 Reactor effluent pH and total and free ammonia nitrogen (TAN and FAN) concentrations under varying feed organic loading rate (OLR) during the test period
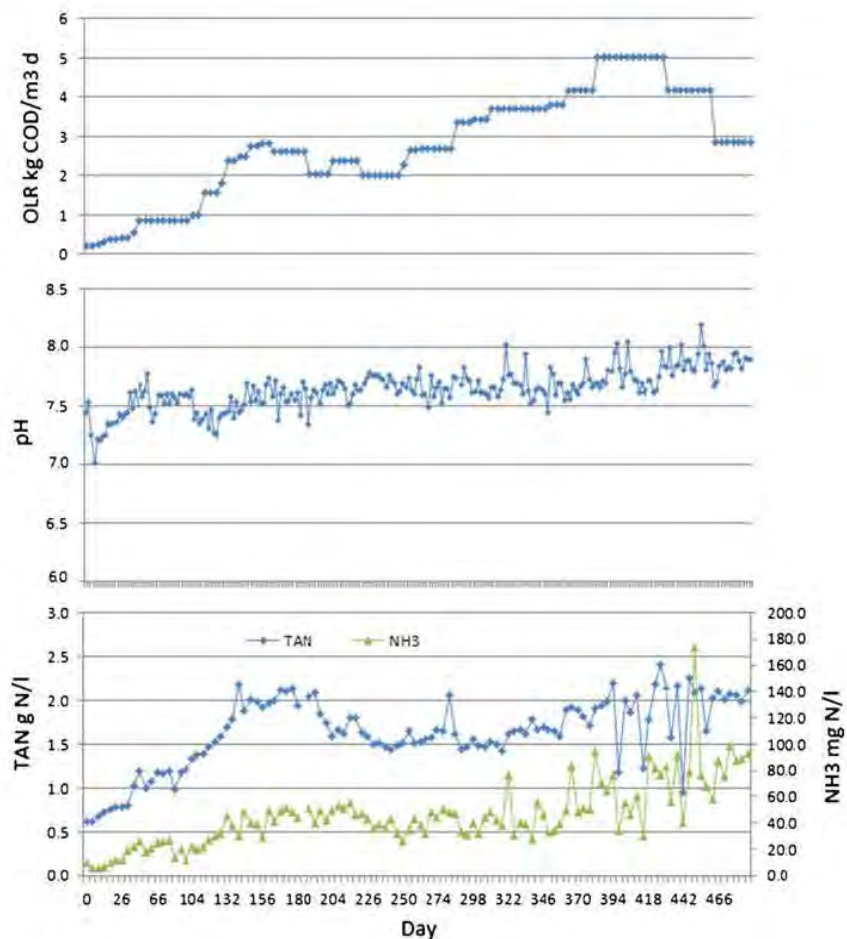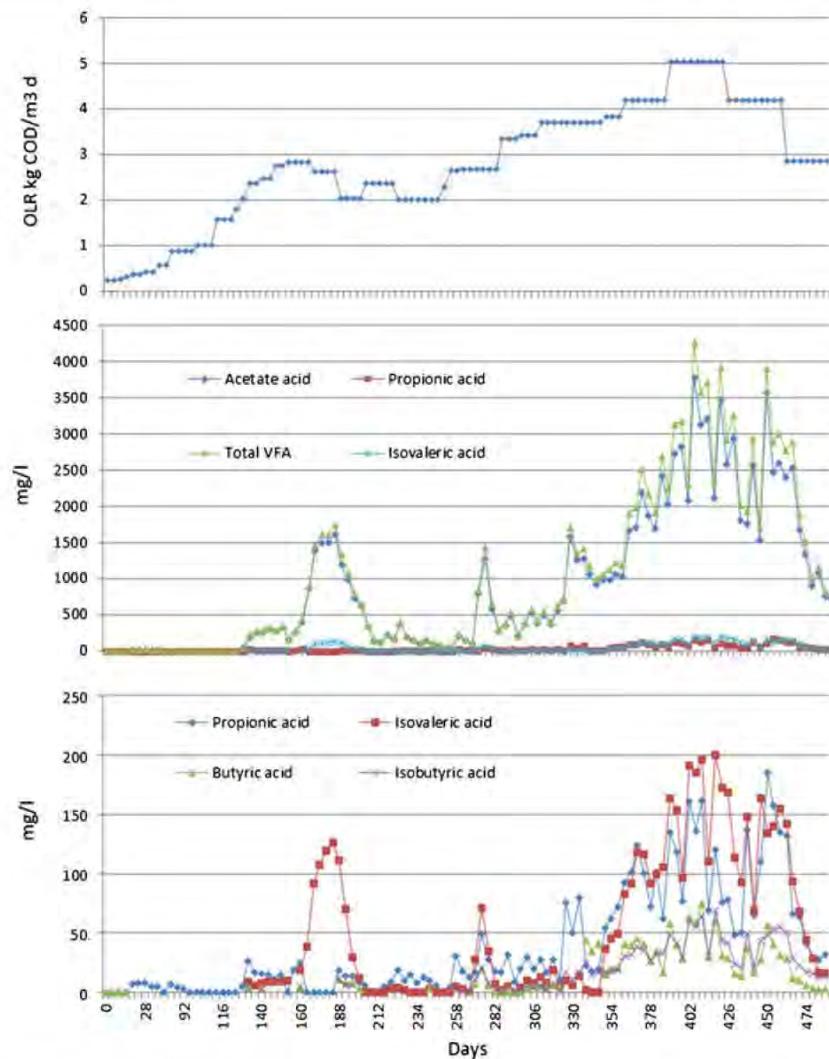
Fig. 7 Volatile fatty acid
(VFA) accumulations under
varying feed organic loading
rate (OLR)

other fatty acids. Isovaleric, propionic, butyric and isobutyric acid were detected when acetate concentrations were high (Fig. 7).

VFA accumulated when the methane yield decreased, implying that inhibition of VFA consuming organisms is a reasonable explanation of the diminished methane yield during periods of high MEAwr. Acetoclastic methanogenesis is evidently especially sensitive to the factors causing the inhibition since most of the accumulated VFA was acetate (Fig. 7). High concentrations of free ammonia can also cause such inhibitions, but the levels observed here were low compared to those reported to cause inhibition (e.g. observed inhibition coefficient K_i (50 %) is 30–90 mg

N/l) (Gallert et al. 1998; Batstone et al. 2002). High tolerance of 800 mg N/l was observed (Calli et al. 2005). It therefore, seems likely that some other constituents of MEAw and/or degradation products thereof contribute significantly to the observed inhibition. Complex and recalcitrant chemicals from MEAw may inhibit the anaerobic degradation and cause VFA accumulation. Anaerobic microbial consortia can adapt to high ammonia by establishing an alternative pathway (Schnürer et al. 1994). The observation of less VFA accumulation at similar feed MEAwr and OLR (0.6 and 2.82 kg COD/m^3 day) at the end of phase 3 compared to phase 1 (Fig. 7) suggests that such an adaptation may have occurred.
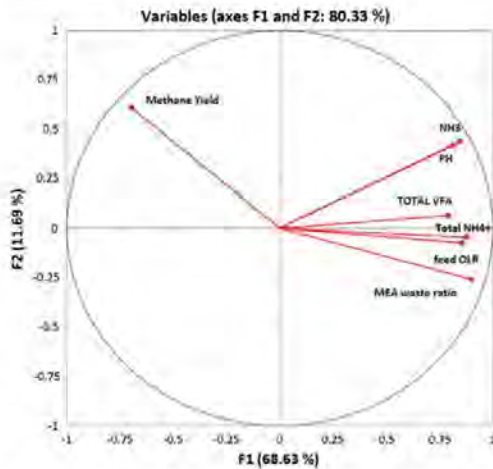
Fig. 8 Correlation circle (below on axes F1 and F2) shows a projection of the initial variables in the factors space, indicating the correlations between different variables. When two variables are far from the origin, if they are close to each other, they are significantly positively correlated; when they are opposite from each other, they are negatively correlated; when they are orthogonal to each other, they are not significantly correlated

This is supported by the observation that TAN was at a similar level in those two feed conditions while FAN concentrations were at a higher (90 mg/l comparing to 50 mg/l) level due to higher pH in phase 3 (Fig. 6). If FAN was the main inhibitory factor in phase 1, it indicates that the biomass consortium gradually acclimated to the inhibitory ammonia, possibly by establishing the alternative pathway described by Schnürer et al. (1994).

Figure 8 shows the correlation circle from PCA, where a projection of the initial variables (methane yield, pH, NH_3, total VFA, feed OLR, total NH_4^+ and MEAwr) are shown in the factors space. The correlation between variables can be interpreted through the angles of variable projections. When two variables are far from the origin and they are close to each other, such as pH and NH_3, they are significantly positively correlated (r close to 1). Methane yield is almost orthogonal to pH and NH_3, implying that they are not significantly correlated (r close to 0). MEAwr is on the opposite side of the center from methane yield, implying that they are significantly negatively correlated (r close to –1). OLR and total ammonia which varied with the MEAwr applied are also quite on the opposite side of Methane yield, implying that these

two variables may also strongly affect the methane yield. Total ammonia concentration and accumulated VFA may also cause stress in the methanogenic pathways and contribute to variations of the methane yield (Lü et al. 2013).

MEAwr played an important role in providing feed nitrogenous organics and thereby contributed to the ammonia accumulation when MEAw was degraded. PCA shows that MEAwr in feed is the most important impact negative factor to the methane yield, more so than FAN and TAN (Fig. 8). This supports the claim that some other constituents of MEAw and/or degradation products from such are the cause of, or contribute significantly, to the observed inhibition.

Conclusion

Anaerobic degradation of MEAw with easily degradable co-digestible substrates was conducted in a hybrid anaerobic digester for 486 days at room temperature. The mixed feed substrate degradation ratio reached a maximum of 93 % when no inhibition effects were observed at low MEAwr (<0.5) and OLR <3 kg COD/m^3 day. Principal component analysis showed a strong negative correlation between MEAwr and methane yield in the load range tested, MEAwr >0.5 reduced methane yield. VFA, mainly as acetate, accumulated with high MEAwr causing inhibitory conditions implying that acetoclastic methanogenesis was the step that was mainly inhibited. Complex and recalcitrant chemicals in MEAw and products of degradation, including ammonia, may be the cause of the inhibited AD performance. Significantly less inhibition was observed after a year of operation compared to the first phase of the experiment implying some microbial adaptation to the inhibiting factors. High MEA waste removal efficiency by AD can thus be achieved by cultures adapted to such feed in an appropriate co-substrate mixture. Relatively stable system performance can be obtained given moderate load changes.

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Paper III:

Detoxifying CO$_2$ capture reclaimer waste by anaerobic digestion

Detoxifying CO_2 Capture Reclaimer Waste by Anaerobic Digestion

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Abstract The decrease in toxicity of carbon capture reclaimer monoethanolamine (MEA) waste (MEAw) during anaerobic degradation of such waste together with easily degradable organics was investigated. Samples were collected from a bioreactor at steady state with 86 % organic chemical oxygen demand removal at room temperature, which had been running on MEAw for 2 years. The toxicity of the digester effluents were 126, 42 and 10 times lower than that of the MEAw to the tested freshwater trophic groups of *Pseudokirchneriella subcapitata*, *Daphnia magna* and embryos of *Danio rerio*, respectively. The toxicity of the tested taxonomic groups after anaerobic digestion was mainly attributed to the ammonia generated by the degradation of MEAw.

Introduction

Carbon capture and storage (CCS) is a technology proposed in energy intensive industries (e.g. power plant) to mitigate greenhouse gas effects [1]. Large scale CCS plants will generate potentially hazardous contaminates such as solvent and solvent degradation products. Life cycle assessment has shown that CCS systems can achieve a significant reduction in greenhouse gas emissions, although there are multiple environmental trade-offs to consider, such as increased human and environmental toxicity potential [2].

The CCS solvents that are normally used include monoethanolamine (MEA), methyldiethanolamine (MDEA), etc., which can cause environmental harm [3]. Complex solvent degradation products are generated in CCS process due to solvent reaction with flue gas impurities, thermal degradation, etc. and are difficult to qualify and quantify [4, 5]. Corrosion inhibitors added to increase the durability, and effectiveness of amine solvents can be resilient to biodegradation [6]. MEA waste from CCS is a complex mixture of solvent, MEA degradation products, substances other than CO_2 captured from the flue gas, corrosion inhibitors and corrosion products. The amine waste arises as the bottom product from the distillation unit when thermal reclaiming

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of the solvent is used. According to EU regulations and directives [7], the waste is classified as hazardous waste in accordance with hazardous waste Directive 91/689/EEC [8]. Anaerobic digestion (AD) that combines assimilating and degrading organics and recovering energy (in the form of methane) is a promising amine waste treatment method investigated [9–11].

The aim of the presented research was to investigate the detoxifying effect of AD treatment on MEA reclaimer waste (MEAw) collected from a coal fired power plant. A hybrid anaerobic reactor with an adapted culture that has been treating MEAw together with an easily degradable co-substrate since 2010 [9, 10] was employed and operated at steady state when effluent samples were collected for toxicity assessments. The freshwater toxicity of this treated waste (TW) was compared to toxicity of pure MEA and MEAw by using standard regulatory Organisation for Economic Co-operation and Development (OECD) bioassays [12] for the unicellular algae *Pseudokirchneriella subcapitata*, the freshwater crustacean *Daphnia magna*, and the embryos of the zebra fish *Danio rerio*. The effect concentration (EC) endpoints causing 50 % growth reduction, acute immobilisation and morality, respectively, were compared.

Material and Methods

Anaerobic Digestion

Feed

The MEAw used in this study was the waste product of the MEA solvent distillation from the 'reclaimer unit' in a full scale CO_2 capture plant treating flue gas from a coal fired power plant boiler. The MEA concentration in the MEAw applied here was 18 wt%. Nitrogen content was about 10 wt%. The measured MEAw chemical oxygen demand (COD) was 630 mg COD/g MEAw. Other components in the waste were not quantified but information for similar waste types can be found in [4, 5, 13].

Easily degradable organics were applied as co-substrate (41 % of feed COD) together with MEAw (59 % of feed COD) as the feed for the anaerobic digester. The co-substrate was used to provide necessary nutrients, minerals and easily degradable organics to maintain biomass that can tolerate exposure to toxic and inhibitory chemicals from the MEAw and to increase the relatively low carbon to nitrogen ratio in the MEAw that could otherwise inhibit microorganisms, especially methanogenesis [9, 10]. Properties and quantities of the co-substrate are shown in Table 1.

Anaerobic Reactor and Inoculums

Detailed information about the applied lab-scale hybrid anaerobic digester (Fig. 1) and the feed scenarios used for the long-term culture adaptation are given in [9].

Experimental Management

The anaerobic digester was operated at 22 ± 2 °C. Feed substrate used in the anaerobic digester is shown in Table 1. Feed solutions were prepared by mixing the MEAw and co-substrate in deionized water and stored at 4 °C before use. Buffer (0.15 g/L K_2HPO_4 and 0.15 g/L KH_2PO_4) was added in the prepared feed solution. The feed pH was 10. The feed substrate was pumped in to the reactor by a peristaltic pump semi-continuously at a feed speed of 11 mL/min for 8 min a

Table 1 Compositions of the feed substrate

Component	Concentration (g/L)	COD (g COD/L)	Nitrogen concentration (g/L)
Glucose	1.7	1.8	0.0
Yeast extract	3.6	3.3	0.4[a]
Peptone	3.0	4.5	0.4[b]
MEA waste	22.0	13.9	2.2[c]
Total	30.3	23.5	3.0

[a] Product reference shows a nitrogen concentration of 10.5 % in this yeast extract

[b] Product reference shows a nitrogen concentration of 12 13 % in this peptone, and 12.5 % was used in this calculation

[c] A fraction of 10 wt% of MEAw was used here

day at eight different times. A hydraulic retention time (HRT) of 14 days was maintained. The applied feed organic loading rate (OLR) was 1.6 kg COD m^{-3} day^{-1} in the test period. Effluents were collected for pH, ammonia and COD measurements. Effluents for the toxicity test were collected when steady state reactor performance was observed. The analytical methods, except the toxicity tests, are given in [9].
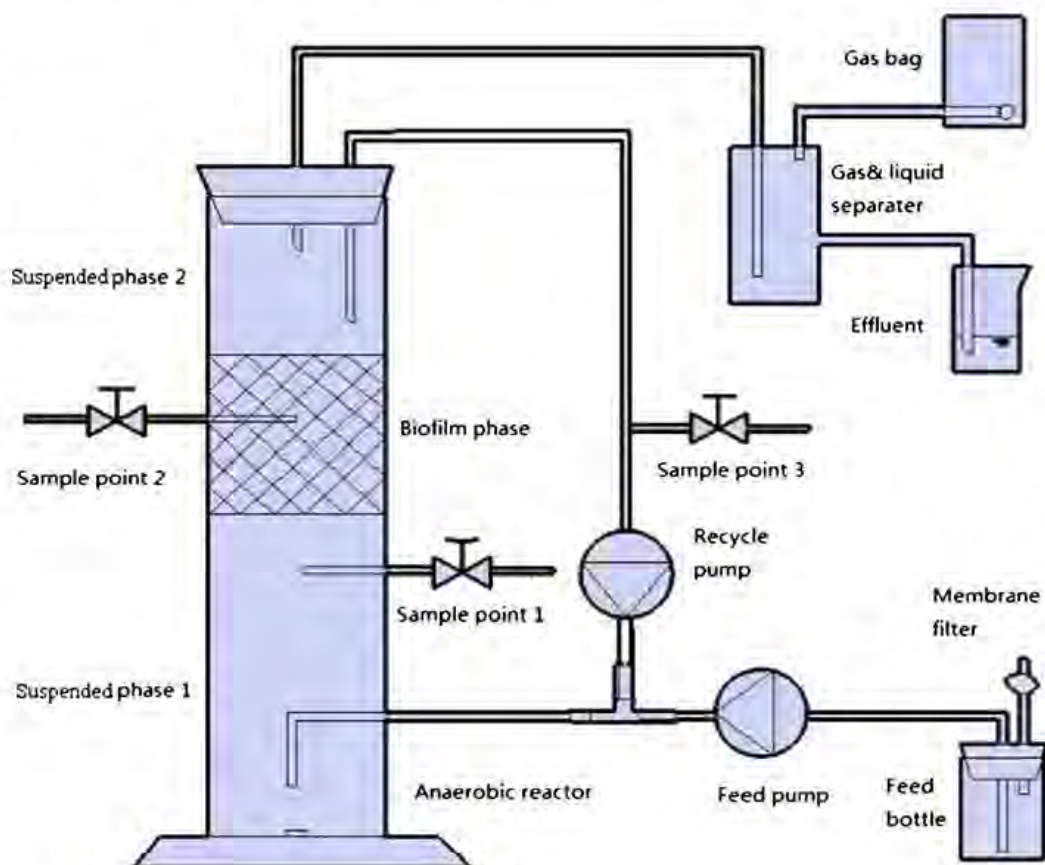

Fig. 1 Schematic configuration of the anaerobic hybrid reactor system [9]

Toxicity Tests

The toxicity tests were performed in accordance with the standard procedures described in the OECD guidelines OECD201, OECD 202 and OECD draft guideline 'zebra fish embryo toxicity test' [12]. Pure MEA (PM), reclaimer MEAw and TW (AD effluent) were used as test substrates. A brief description of each test is provided.

Growth inhibition of the algae *P. subcapitata* was performed in accordance with OECD guideline 201 [12]. A fully defined growth medium was used (OECD TG201). Cell counts were performed every 24±2 h for the duration of the test with a Beckman Coulter Multisizer 3 (Beckman Coulter, USA). There were six control replicates and three replicates per test concentration. Test concentrations were made from dilution of a stock solution and inoculated with an algal culture in exponential growth to a concentration of 5×10^3 cells mL^{-1}. The tests were incubated at 20±2 °C on an orbital shaker in continuous light from cool white fluorescent tubes (Philips TLD 36 W/950). The average growth rate for each test concentration was calculated from initial cell concentration and cell concentration at the time of the last cell count using the equation:

$$\mu = \frac{\ln(N_n) - \ln(N_0)}{t_n - t_0} \tag{1}$$

N_n=cell density at time t_n, N_0=cell density at time zero (t_0)

The percentage inhibition of growth rate as compared to the control was calculated for each treatment. Effect concentration values were determined with non-linear regression analysis using a Microsoft Excel macro, 'REGTOX' [14].

Acute immobilisation of *D. magna* was performed in accordance with OECD guideline 202 [15]. Five neonates (<24 h old) were added to the test vessels containing 40 ml of test media. Four replicates were used per test concentration. Test vessels were examined under the microscope every 24 h for the duration of the test (48 h) and immobilised or dead animals in each treatment were recorded. The EC_{50} values were calculated with non-linear regression analysis.

Embryos of the zebra fish, *D. rerio*, were obtained from the Norwegian Veterinary Institute, Oslo. The test method was based on the OECD draft guideline 'zebra fish embryo toxicity test'. The test was initiated immediately after fertilisation and continued for 96 h in duration. Lethal effects were recorded every 24 h and were based on four apical observations including: coagulation of the embryo, non-detachment of the tail, non-formation of somites and non-detection of the heartbeat. Observations of any one of these four malformations were indicative of lethality. This was compared to the occurrence in the dilution water control to provide sufficient information to calculate lethal concentration (LC) toxicity endpoints.

The physiochemical properties of MEAw and TW are given in Table 2, where properties of feed MEAw + co-substrate are also provided.

Results and Discussion

Anaerobic digestion results presented below were obtained and analysed at an OLR of 1.6 kg COD m^{-3} day^{-1} and a MEAw ratio of 0.59 (COD based).

Anaerobic Digestion of MEAw

Methane yield, ammonia level and other reactor performance parameters at steady state process operation when samples for the toxicity tests were taken is shown in Table 3.

Table 2 Measured parameter values of the three waste mixtures

Parameter (g/L)	MEAw (reclaimer MEAw)	Feed MEAw + co-substrate	TW (AD effluent)
COD	700	30.3	3.4
NH_4	0.8	0.01	2.4
K^a	–	0.23	0.19
Na	68.8	1.1	0.9
pH	11.1	9.8	7.9
Conductivity	11.3	6.2	15.2
Salinity	4.8	2.8	8.5

COD chemical oxygen demand

[a] Due to the high chemical oxygen demand, the waste water mixtures required dilution by 10,000 times its original concentration before analysis. This dilution resulted in [K] falling below the detection limit and is not reported

Table 3 shows a methane yield of 0.2 L/g COD and a volatile fatty acid (VFA) concentration of 114 mg COD/L, where acetic acid constitutes over 90 % of the VFA. The released methane and accumulated VFA are degradation products of the feed and are about 63 % of the total feed COD.

The digester was running at stable conditions with pH at around 7.9, which was considered suitable for methanogenesis. The total ammonia nitrogen (TAN=NH_4^+ + NH_3) concentration was 2.0 g N/L with a free ammonia, FAN, concentration of 68 mg N/L. Ammonia concentrations gradually increased during the 2 years of reactor operation prior to this test and degradation of MEAw was the main source of ammonia [9, 10].

Ecotoxicity

The results of the toxicity tests for pure MEA, MEAw and TW (Table 3) on the three trophic groups are given in Table 4. It shows that the algae were the most sensitive of the three tested species to the pure MEA and MEAw, followed by daphnids and zebra fish embryos. Zebra fish embryos were the most sensitive group to TW, followed by algae and daphnids, although the sensitive concentrations of TW were quite close for all three.

Table 3 Parameter values of the steady state operation AD during the study

Parameter	Units	Values[a]
OLR	kg COD m^3 day^1	1.6
MEAw ratio	MEAw COD/total COD	0.59
Feed COD	g COD/L	22.5
Feed amount	mL/day	88
CH_4 yield	L/g COD added	0.20 (0.02)
Total ammonia nitrogen (NH_4^+ + NH_3)	g N/L	2.0 (0.4)
Free NH_3	mg N/L	68 (19)
pH	–	7.9 (0.1)
VFA	mg COD/L	114 (37)
Effluent COD	g COD/L	3.4 (0.6)
Removal efficiency	Percentage	85.9 (0.9)

[a]Standard deviations in the bracket

Table 4 Summary of ecotoxicity endpoints for the three test chemicals corresponding to the three trophic groups

Test chemical	Trophic group	EC_{10}[a]	EC_{50}[a]	COD (mg COD/L)[b]
MEA (mg/L)	Algae	30	151	198
	Daphnids	128	209	274
	Zebra fish	165	618	809
MEAw (v/v %)	Algae	0.0089	0.019	0.15
	Daphnids	0.060	0.081	0.61
	Zebra fish	0.034	0.194	1.54
TW (v/v %)	Algae	0.74	2.4	81.5
	Daphnids	2.2	3.4	116
	Zebra fish	–	1.91	64.9

[a] ECx: the concentration which results in x percentage reduction in growth rate, immobilisation or lethal effects compared to the control

[b] At EC_{50}

The 50 % growth rate inhibition (EC_{50}) for unicellular algae, 50 % acute immobilisation for crustacean *D. magna* and 50 % lethal effects concentrations for embryos of the zebra fish were observed at MEA concentrations of 151, 209 and 618 mg/L, respectively. MEA constituted 18 wt% and was the main chemical identified in the MEAw used. Based on the calculation, the MEA concentration in the feed substrate was 4 g/L, which is much higher than the observed EC_{50} thresholds for the tested tropic groups.

MEAw had much stronger toxic effects than just MEA (Table 4). The EC_{50} for the three trophic groups were observed to be at MEAw dilution ratios of 5,000, 1,250 and 500, corresponding to MEAw concentrations of 0.24, 0.98 and 2.44 mg/L, respectively. The MEA concentrations were calculated to be 0.04, 0.18 and 0.44 mg/L, respectively at the three MEAw EC_{50} concentrations. These levels were much lower than the pure MEA EC_{50} concentrations (Table 4). MEAw evidently contains more additional toxic substances other than MEA. MEAw contains a mixture of chemicals, and some have been identified [4, 5], whilst the chemical composition is often dependent on which analytical method and/or instrumentation is applied [16]. The information on toxicity effects of the detected chemicals is limited. It is expected that MEA degradation of organic and inorganic salts (10 wt%) in the waste due to the addition of sodium carbonate, in addition to corrosion products generated and inorganic anions formed from compounds in the flue gas (nitrate from NOx and sulphate from SOx) contributed to the toxicity effects of MEAw.

The COD concentrations were calculated for MEA, MEAw and TW at their EC_{50} for each trophic group (Table 4). MEAw COD concentrations at their EC_{50} were the lowest in the test chemicals. It indicates that if the toxicity was caused by organic components, then their concentrations were at relatively low levels. Inorganic materials (e.g. NH_3) that cannot be oxidised by dichromate may have also contributed to the observed toxicity.

The toxicity test of TW for the three trophic groups shows that the EC_{50} concentrations increased 126, 42 and 10 times after anaerobic treatment comparing to that of MEAw (Table 4). The remaining toxicity in TW after AD is not due to MEA since MEA was not detected in effluent samples due to biodegradation (Fig. 2) [9]. Some unidentified chemicals in MEAw were also degraded to below detection levels in the effluent samples. Ammonia was the major degradation product in the effluent water detected by ion chromatography (Fig. 2). Unidentified toxic organics in the effluent after the AD that are suspected to inhibit

Fig. 2 IC analysis of samples: *black line* effluent (50 times diluted), *red line* co-digestion organics (50 times diluted), *green line* feed substrate (50 times diluted), and *blue line* 1 g MEA waste (1,000 times diluted) [9]
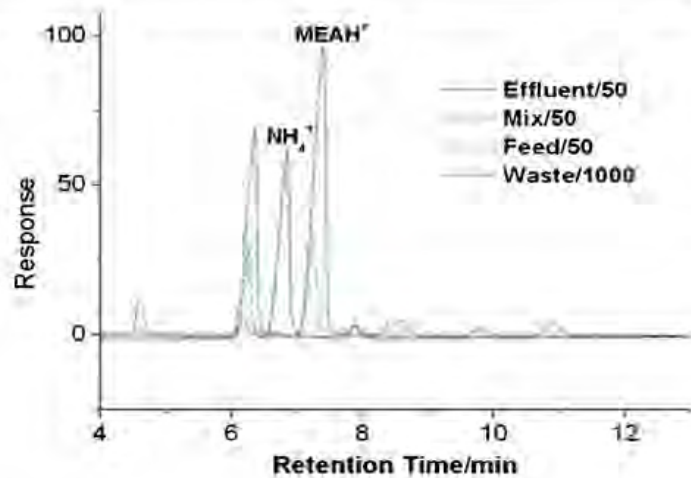
methanogenesis at high feed loads [10] may also contribute to the toxicity in TW after AD observed here.

The TW COD concentrations corresponding to the EC_{50} were much higher than that of MEAw (Table 4), suggesting that toxic organic substances were removed by AD. VFAs, mainly acetic acid, were the main organics detected in TW (Table 3). Although COD is not a standardised unit for assessing toxicity effects, it can be used as a proxy for organic substances, and variations in COD may indicate changes of toxic components. Toxic components from MEAw may have been degraded, while inert and residual (14 % of feed COD) components and ammonia from the feed substrates degradation may contribute to the remaining toxicity to the tested trophic groups.

TW toxicities to the three trophic groups show that EC_{50} were not significantly different (Table 4). TAN (NH_4^+ and NH_3) and FAN concentrations that were above 2.0 and 68 mg N/L, respectively (Table 3) in the TW can potentially be the main cause of the observed remaining toxicity of TW. Low ammonia can be beneficial to aquatic organisms (e.g. algae), but elevated ammonia concentrations in the aquatic environment are toxic. The negative impacts of ammonia can be due to inhibiting photosynthesis of algae [17, 18], damaging fish gill epithelium, repressing immune system, disrupting blood vessels, etc. [19].

The threshold concentrations of TAN in freshwater that result in unacceptable biological effects were suggested to be 3.48 mg N/L at pH 6.5 and 0.25 mg N/L at pH 9.0 [20]. Free ammonia (NH_3), however, is considered to be more toxic to aquatic animals than ionised ammonia. Concentrations of less than 0.05–0.35 mg NH_3-N/L for short-term exposures and less than 0.01–0.02 mg NH_3-N/L for long-term exposures have been recommended to protect aquatic animals [19]. TW that gave EC_{50} for algae was at TAN and FAN concentrations of 49 and 1.6 mg N/L, respectively. The value was 69 and 2.3 mg N/L, respectively, for Daphnids, which was quite close to the FAN EC_{50} concentration (2.94 mg N/L) observed by Gersich and Hopkins [21]. The TW EC_{50} for embryos of the zebra fish had TAN and FAN concentrations of 102 and 3.4 mg N/L, respectively. Both the TAN and FAN concentrations of TW (Table 3) were much higher than that proposed for environmental protection and close to the acute toxicity of the free ammonia concentration. This implies that the observed toxicity of TW can be largely due to high ammonia concentration in the TW. A proper post-treatment of the anaerobic digester effluents to reduce ammonia content, such as by nitrification, can therefore potentially eliminate or reduce the waste toxicity to lower levels.

Conclusion

The toxicity of MEAw was reduced by 10 to 126 times by anaerobic digestion at steady state by an adapted culture, shown as 126, 42 and 10 times higher EC_{50} tolerance concentrations of digester effluents than for the untreated MEAw to three freshwater trophic groups. The remaining toxicity of the treated MEAw can largely be attributed to ammonia generated from MEAw degradation. Other toxic constituents may, however, also survive AD of MEA reclaimer waste. Anaerobic digestion of MEAw combined with ammonia removal can potentially reduce the environment toxicity to enable safe effluent discharge.

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Paper IV:

Modeling and simulation of lab-scale anaerobic co-digestion of MEA waste

Modeling and simulation of lab-scale anaerobic co-digestion of MEA waste

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Abstract

Anaerobic digestion model No.1 (ADM1) was applied and expanded in this study to model and simulate anaerobic digestion (AD) of an industrial carbon capture reclaimer MEA (monoethanolamine) waste (MEAw) together with easily degradable organics. The general structure of ADM1 was not changed except for introducing state variables of MEA and complex organics (CO) in the waste and biochemical reactions of MEA uptake and CO hydrolysis in the model ADM1_MEAw. Experimental batch test results were used for calibrating kinetics variables. The obtained kinetics were employed in the ADM1_MEAw to simulate semi-continuously fed experimental test for 486 days at room temperature ($22 \pm 2°C$). The validation results show that the ADM1_MEAw was able to predict the process performance with reasonable accuracy, including process pH, biogas generation and inorganic nitrogen concentrations, for a wide range of feed scenarios. Free ammonia inhibition, was observed to be the main inhibitory effects on acetoclastic methanogenesis, leading to volatile fatty acids (VFA) accumulation at high loads. Inhibition assumed to be caused by potentially toxic constituents of MEAw appears to be much less important than ammonia, suggesting that such constituents were broken down by AD.

Introduction

The anaerobic digestion model No.1 (ADM1) is a sophisticated model generated by the IWA Task group for Mathematical Modeling of Anaerobic Digestion Processes (Batstone et al., 2002). The model includes

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26 dynamic state variables, 19 biochemical and 3 gas-liquid transfer kinetic processes. It describes the AD processes of complex particulates through disintegration, hydrolysis, acidogenesis, acetogenesis to methanogenesis (Batstone et al., 2002). Disintegration is a physical process and the rest four biochemical processes are catalyzed by intra- or extracellular enzymes. The ADM1 model has been implemented to simulate AD of different industrial wastes and proved to be successful (Derbal et al., 2009; Ozkan-Yucel and Gokcay, 2010). Some extensions of the ADM1 were also established to account for the effects of micro-oxygen (Botheju et al., 2010), the degradation of phenolic compounds (Fezzani and Cheikh, 2009), and the formation and emission of odorants (Parker and Wu, 2006). Modifications that focus on specific process functions such as hydrolysis regarding the characteristics difference of feed organics (Yasui et al., 2008; Ramirez et al., 2009) were also implemented in ADM1. The ADM1 model is widely acknowledged as a powerful tool for investigating AD processes at various operating conditions and helpful in predicting the behavior of anaerobic digesters (Batstone et al., 2006).

Challenges in application of the ADM1 model also emerge. The structured model demands detailed characterizations of the organic compounds feeding in to the anaerobic digesters, including organics compositions of carbohydrates, protein, lipids and the inerts fractions to get reasonable model predictions (Kleerebezem and van Loosdrecht, 2006). However, characterizations of the individual variables are generally not practical, at least not on a regular basis. Reasonably approximations are commonly made depending on the available characterization of the raw material and the waste measurements (such as Chemical Oxygen Demand (COD), Total Kjeldahl Nitrogen (TKN)) (Ramirez et al., 2009). The kinetic values of disintegration, hydrolysis and other biochemical processes can also vary in a large range, which require specifications for different investigated cases (Batstone et al., 2002).

In this study a new model ADM1_MEAw based on ADM1 was generated to investigate the AD of industrial reclaimer MEAw with easily bio-degradable organics. MEAw degradation processes and the observed inhibitory effects associated with MEAw degradation (Wang et al., 2013 b) were included in ADM1_MEAw. Newly applied kinetic parameters were calibrated based on batch experimental study. The recommended kinetic parameters in standard ADM1 were mostly maintained with adjustments of the maximum uptake rates based on temperature effect. The aim was to assess to what extend the expanded model can simulate and predict the degradation process without applying fundamental changes in the ADM1 parameters. 486 days of lab-scale semi-continuously fed digester experimental data was applied for verifying the model parameters by comparing with simulation results. Biogas generation, pH, VFA accumulation etc. were simulated to assess the performance of model ADM1_MEAw.

Materials and Methods

The model ADM1_MEAw was implemented in a software platform AQUASIM 2.1f, which is a computer program for data analysis and simulation (Reichert, 1994). Applied experiental feed MEAw and easily degradable organics (Wang et al., 2013 b) were assigned in the model based on their contents.

Co-feed organics specification

Easily degradable organics: starch, glucose, peptone and yeast extract (Wang et al., 2013 b) were used to co-digest with MEAw in AD. The co-feed substrates were used to provid necessary nutrients, minerals and easily degradable organics for cultivating healthy biomass that can tolerate exposure to toxic and inhibitory chemicals from the MEAw. Components of the easily degradable organics were specified according to the provided prouducts' analysis information which contained mainly carbonhydrate and amino acids (Table 1) and their feed concentrations expressed in units consistent with ADM1 simulations are given in Table 2.

MEA waste specification

The MEAw used in the experimental AD test was obtained from an industrial reclaimer unit for solvent recovery at a coal fired power plant where MEA was used as the CO_2 capture solvent. The MEA waste was generated due to MEA degradation, reactions with flue gas impurities etc. in the carbon capture process and accumulated together with added chemicals (e.g. corrosion inhibitors) at the bottom of the reclaimer unit after the solvent regeneration (da Silva et al., 2012; ElMoudir et al., 2012). The waste contained complex and not well identified chemicals, including MEA, organic chemicals from MEA degradation, corrosion inhibitors, heat stable salts and other inorganic components (Strazisar et al., 2003 and Thitakamol et al., 2007). The detected chemicals were not well quantified, while MEA, N-acetylethanolamine (Eq. 1) and carboxylic acids (acetic, propionic and n-butyric acid) were supposed to be the main components in the MEAw used for the AD test (Strazisar et al., 2003 and 2001).
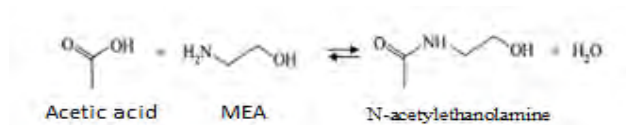
Eq. 1

Implementation of all detected MEAw compounds to ADM1_MEAw is practically impossible and can easily cause errors due to the limited quantification data. Thus, MEAw composition was simplified to MEA and complex organics (CO) which contained inerts, degradable organics (e.g. N-acetylethanolamine) etc. Measurements showed that MEAw COD varied in a range from 450 to 900 mg-COD/g-waste, where MEA COD was assumed to be constant at ~ 44% of the MEAw COD and the rest (~ 56%) was CO COD. According to measurements and calculations, the MEA and nitrogen fractions were around 18 to 30 wt% and 7 - 14 wt%, respectively (Wang et al., 2013 b). Alkalinity of the applied MEAw was measured to be ~

0.31 g/g MEAw ($CaCO_3$ equivalent) and was used to calculate the feed inorganic carbon concentrations in the model (Table 2).

CO (Strazisar et al., 2003) was assumed to consist of mainly N-acetylethanolamine (0.46), inerts (0.54) and inorganic nitrogen (Table 1). A portion of 30 % of the feed MEAw COD was termed as inerts (Table 1 and 2) based on the conclusion that over 70 % MEAw was degraded in AD (Wang et al., 2013 b). These inerts was determined to be not biodegraded and reluctant to biodegradation in the 486 days simulation of semi-continuously fed experimental test.

Table 1. Characterizations of the feed organics

Stoichiometric parameters (COD basis)	Names	Values
f_{ch_Sta}	*Particulate carbon hydrate fraction in starch*	1
f_{su_Glu}	*Monosaccharides fraction in glucose*	1
f_{aa_Ye}	*Amino acid fraction in yeast extract*	1
f_{aa_Pep}	*Amino acid fraction in peptone*	0.83
f_{su_Pep}	*Monosaccharides fraction in peptone*	0.17
f_{ac_CO}	*Acetate fraction in CO*	0.20[a]
f_{MEA_CO}	*MEA fraction in CO*	0.26[a]
f_{SI_CO}	*Soluble inerts fraction in CO*	0.54[b]
f_{IN_CO}	*Inorganic nitrogen released from CO*	0.0029-0.0039[c]

a, According to Eq. 1. b, Specified according to batch test with an assumption of 30 % inerts in the feed MEAw COD. c, calculated based on IN content in the MEAw.

Table 2. Implemented input feed concentrations in ADM1_MEAw.

Composition	Units	Feed concentration
Total carbohydrates	g-COD/L	2.6
Particulate carbohydrates	g-COD/L	1.8 (0)[a]
Soluble carbohydrates	g-COD/L	0.8 (2.6)[a]
Amino acid	g-COD/L	7.0
MEA	g-COD/L	0.8-6.9
Complex organics (CO)	g-COD/L	1.0-8.8
Inorganic carbon (IC)	kmol/m³	$8*10^{-3}$-$4*10^{-2}$

a, when glucose was used instead of starch after 250 days in the semi-continuously fed test (Wang et al., 2013 b)
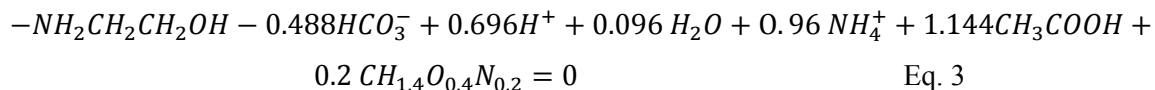
Suggested modification to ADM1

Modification of the basic ADM1 structure

Anaerobic degradation of MEAw involves mainly the degradation of MEA and MEA degradation products (e.g. N-acetylethanolamine) formed in the carbon capture process. Two hydrolysis processes were proposed for MEA degradation (Ndegwa et al., 2004). They are the hydrolysis of MEA to ammonium and acetaldehyde and the hydrolysis of acetaldehyde to ethanol and acetate. Two mechanisms are used to explain the synthesis of acetaldehyde from the degradation of MEA. One is the deamination by coenzyme B_{12}-dependent ethanolamine ammonia-lyase (Eq. 2) (Abend et al., 1999) and the other mechanism is the rearrangement of the NH_2 group by the process of bacterium LuTria3 (Speranza et al., 2006). Acetaldehyde can be directly degraded to acetate by consuming CO_2 in the anaerobic condition (Speranza et al., 2006).

$$R^1 = R^2 = R^3 = H$$
$$R^1 = R^3 = H, R^2 = CH_3$$
$$R^1 = R^2 = H, R^3 = H$$
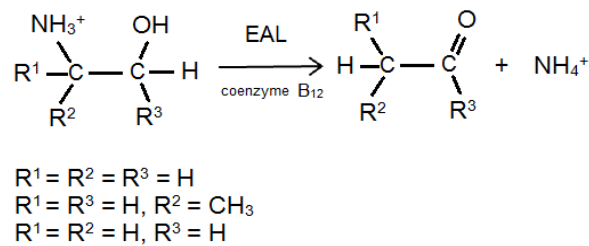
Eq. 2

To generally represent the degradation processes involved in AD of MEAw and comply with the composition simplifications, biodegradation of MEA to ammonium and acetate was included in ADM1_MEAw without considering the intermediate product acetaldehyde (Eq. 3). The biomass yield, Y_{MEA} was assumed to be 0.08 kg-COD biomass/kg-COD MEA (assumed to be the same as the standard organisms growing on amino acid) (Bothejua et al., 2010). Empirical formula $CH_{1.4}O_{0.4}N_{0.2}$ ($C_5H_7O_2N$) (Eq. 3) was used to represent biomass (Eastman and Ferguson, 1981). Ethanol, which was not included in the standard ADM1 for its low concentration in AD digesters (Batstone et al., 2002) was also not considered here.

$$-NH_2CH_2CH_2OH - 0.488HCO_3^- + 0.696H^+ + 0.096\,H_2O + 0.96\,NH_4^+ + 1.144CH_3COOH +$$
$$0.2\,CH_{1.4}O_{0.4}N_{0.2} = 0 \qquad\qquad \text{Eq. 3}$$

The degradation of other MEAw organics was simplified to hydrolysis of CO. CO was assumed to consist of mainly N-acetylethanolamine, inerts and inorganic nitrogen (Table 1). N-acetylethanolamine can be hydrolyzed to MEA and acetate (Eq. 1). In order to reduce the involved state variables, N-acetylethanolamine state variable was not created but its degradation products MEA and acetate were assumed to be released directly from CO hydrolysis. Inerts and inorganic nitrogen (IN) were also assumed

to be released due to hydrolysis of CO in the digester (Table 1) to allow for a COD balance and an exact stoichiometric analysis. Inerts were defined as the organics that are not degraded in AD, for simplicity and avoiding an extra state, even if they may be degradable by giving favorable conditions. The schematic of the ADM1_MEAw is shown in Fig. 1.
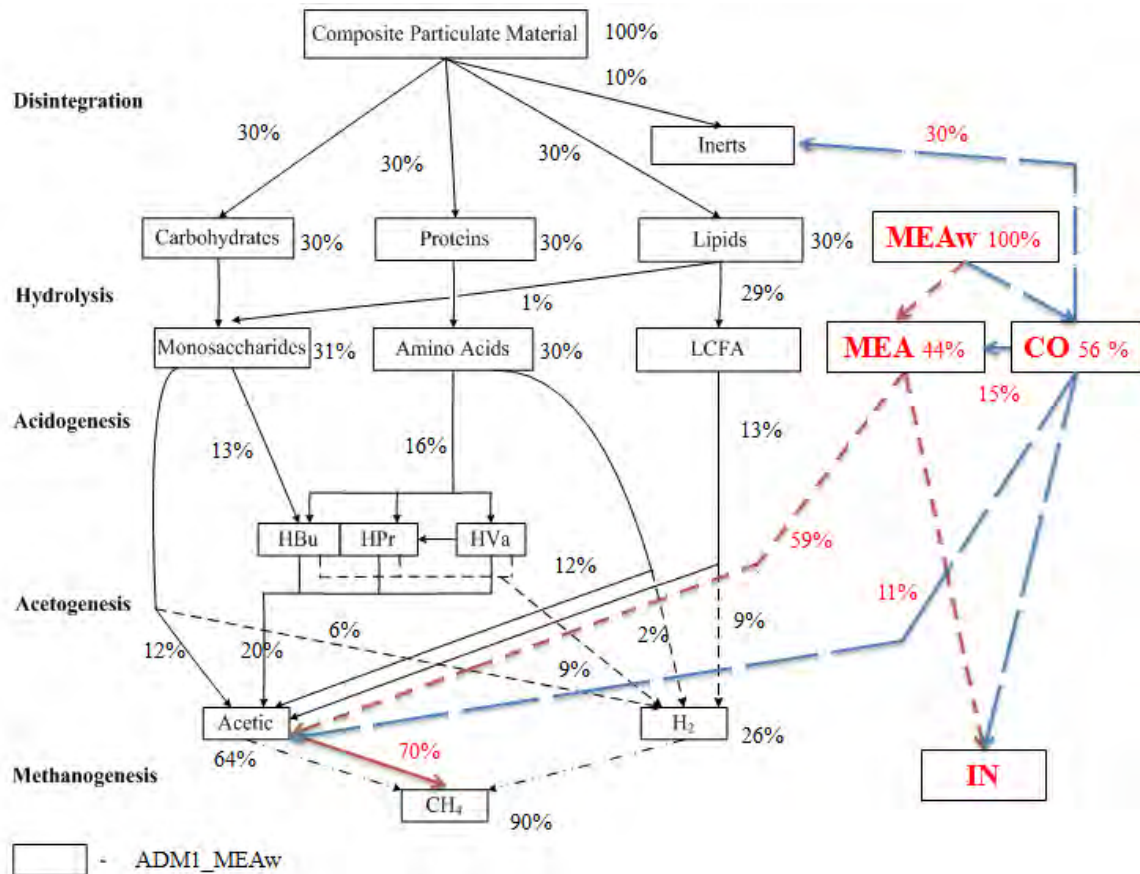

Fig. 1 COD flux for the original ADM1 (black line) and the expanded ADM1_MEAw (color dashed lines). HBu - Butyric acid, HPr – Propionic acid, HVa – Valeric acid, LCPA - long chain fatty acid, MEA – monoethanolamine, MEAw – monoethanolamine waste, CO – complex organics, IN – inorganic nitrogen.

First order kinetics was used for simulating CO hydrolysis. Monod kinetics was applied for the biodegradation of MEA (Botheju et al. 2010). Due to the organic structure similarity of MEA and amino acid, the MEA consuming biomass was assumed to be the standard amino acid degradation biomass, avoiding an extra state variable (Botheju et al. 2010). The added kinetics was shown in Table 3. Initial standard ADM1 biochemical processes were unchanged in the extended model.

Inhibition simulation

The feed MEAw contains recalcitrant chemicals, for example corrosion inhibitors that are slowly or non-biodegradable and that may also inhibit microbial growth (Eide-Haugmo et al. 2009). A commonly used

non-competitive inhibition function was applied in the extended ADM1 to account for the possible toxic effects on acetoclastic methanogenesis due to inhibition from the input MEAw and/or its degradation products (I_{MEAw}, Table 3) (Wang et al., 2013 b and 2014). Inhibition effect from free ammonia, included in the original ADM1 was the other inhibition factor anticipated in the AD of the MEAw due to the release of inorganic nitrogen. Together with the standard inhibition factors (pH, free ammonia and inorganic nitrogen limitation) (Batstone et al., 2002), the new acetate uptake inhibition is given in Eq. 4. Other inhibition factors in the original ADM1 processes were maintained.

$$I_{ac} = I_{pH,ac}I_{IN,lim}I_{NH_3}I_{MEAw} \qquad \text{Eq. 4}$$

The MEAw inhibition, I_{MEAw} was formed as in Eq. 5:

$$I_{MEAw} = \frac{1}{1+S_{MEAw}/K_{I_{MEAw}}} \qquad \text{Eq. 5}$$

Table 3 State variables and parameters added in the extended ADM1.

Parameter	Description	Units
S_{CO}	*Complex organics (CO)*	kg-COD/m^3
S_{MEA}	*MEA*	kg-COD/m^3
k_{hyd_CO}	*First order CO hydrolysis rate*	d^{-1}
K_{s_MEA}	*Half saturation constant of MEA*	kg-COD/m^3
K_{m_MEA}	*Monod maximum specific uptake rate of MEA*	d^{-1}
Y_{MEA}	*Yield of biomass on MEA*	kg-COD B/kg-COD S
I_{MEAw}	*Inhibition function of MEAw*	-
K_{I_MEAw}	*50 % inhibitory MEAw concentration*	kg-COD/m^3

Temperature effect

The lab-scale semi-continuously fed experiment was performed at room temperature (22 ± 2℃), while batch experimental test and the original ADM1 were implemented in AQUASIM at standard 35 ℃. Temperature is an important factor in determining the digestion rate, particular the rate of hydrolysis and methane formation (Tchobanoglous et al., 2003). Therefore, the temperature effects on the maximum uptake rates were accounted for in the extended model and modified by applying van't Hoff-Arrhenius relationship as shown in Eq. 6, with a simplification in Eq. 7 (Tchobanoglous et al., 2003):

$$\frac{d(lnk)}{dT} = \frac{E}{RT^2} \qquad \text{Eq. 6}$$

Where, k = reaction rate constant, T = temperature, K= 273.15 + ℃, E = a constant characteristic of the reaction, J/mol, R = ideal gas constant, 8.314 J/mol·K.

Temperature coefficient θ was generated according to Arrhenius' equation:

$$\frac{k_2}{k_1} = \theta^{(T_2 - T_1)}$$ Eq. 7

Where, T_1 and T_2 are the two temperatures and k_1 and k_2 are rate constants before and after adjustments, respectively. Typical values for θ vary from 1.02 to 1.10 for some biological treatment system (Tchobanoglous et al., 2003). A value of 1.05 was used to adjust all maximum uptake rates in the model from standard values given at 35 °C (Batstone et al., 2002).

Simple kinetic model development

A lab-scale hybrid digester was used in semi-continuously fed AD of MEAw (Wang et al., 2013 a, b). The digester has two suspended phases and a biofilm phase in between and stacked in a plastic cylinder to retain long sludge retention times (Wang et al., 2013 a, b). To comply with this concept, biomass retention factor $t_{res,X}$ (solids retention time in addition to hydraulic retention time) was employed in the expanded ADM1 and assigned a specific value. The mass balances for all the soluble and particulate state variables were modeled as given by Eq. 8, 9 and 10 (Batstone, et al., 2002):

$$V\frac{dS}{dt} = Q(S_{in} - S) - r_s V$$ Eq. 8

$$V\frac{dX}{dt} = QX_{in} - \frac{X}{t_{res,X}/V + 1/Q} + \mu X V$$ Eq. 9

$$r_s = \mu\frac{X}{Y} = \frac{\mu_m S}{K_s + S}\frac{X}{Y}$$ Eq. 10

Where S_{in} and S (kg-COD/m^3) represent the COD feed in and flow out of the digester, respectively; V is the reactor working volume (m^3); Q is the flow rate (m^3/d); r_s is the COD consumption rate (kg-COD/m^3·d). X_{in} and X are biomass flows of the system, μ is the specific biomass growth rate (d^{-1}). Y (kg-COD biomass/kg-COD) is the biomass yield. K_s is the half saturation constant (kg-COD/m^3) and μ_m is the maximum biomass growth rate (d^{-1}).

Ion balance

The charge balance equation in ADM1 was modified to account for the MEA acidification (Eq. 11). MEA has a pKa of 9.5 with buffer capacity and can influence the pH values in the AD reactor.

$$S_{H^+} - S_{OH^-} = S_{HCO_3^-} + \frac{S_{ac^-}}{64} + \frac{S_{pro^-}}{112} + \frac{S_{bu^-}}{160} + \frac{S_{va^-}}{208} + S_{An^-} - \frac{S_{MEA^+}}{80} - S_{Cat^+} + S_{NH_4^+}$$ Eq. 11

Where S_{MEA^+} is the MEA ion concentration implemented in the ADM1, the concentration was calculated as follows:

$$S_{MEA,total} = S_{MEA^+} + S_{MEA} \qquad\qquad \text{Eq. 12}$$

The algebraic equation was formulated as

$$S_{MEA^+} - \frac{S_{MEA,total} * S_{H^+}}{K_{a,MEA^+} + S_{H^+}} = 0 \qquad\qquad \text{Eq. 13}$$

Results and discussion

Model ADM1_MEAw based on ADM1 was calibrated first by implementing batch experimental data from the AD of MEAw with easily degradable organics at 35 °C. The calibrated kinetics and inhibitory factors (Table 4) were then employed in ADM1_MEAw for the simulation of the semi-continuously fed digester performance at room temperature. 486 days of experimental data (Wang et al., 2013 b) was used to compare with the model simulations.

Batch model simulation

The calibrated kinetic values for the batch model are given in Table 4. An inhibition factor including both free ammonia and MEAw was introduced in the model (Eq. 4 and 5), where the digester MEAw concentration was considered to be inhibitive to aceoclastic methanogenesis (Wang et al., 2013 b) and the inhibition effects reduced along with the waste degradation. It is shown that simulated biogas accumulation complied with the experimental data reasonably well (Fig. 2, A). The simulated methane partial pressure accounted for 80 % in the biogas (Fig. 2, B), which was in similar level as that obtained in the semi-continuously fed experimental test (Wang et al., 2013 b).
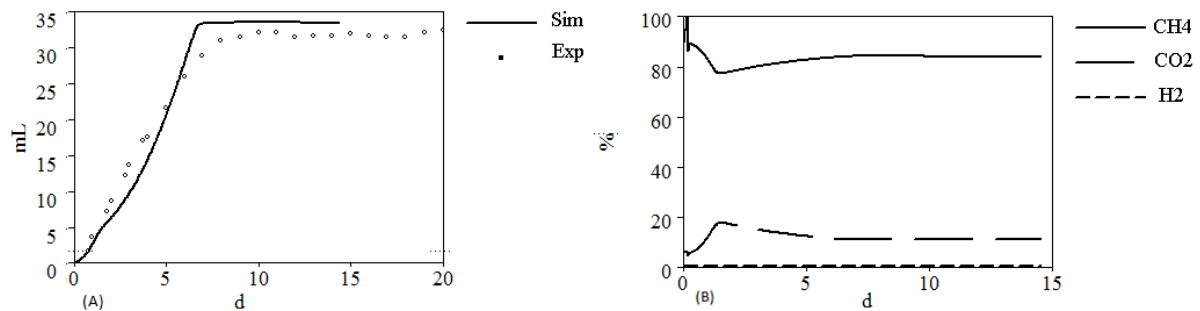

Fig. 2 Biogas accumulation (A) and partial gas pressure (B) simulated by the extended model

Simulated pH varied and stabilized around 8.0 (Fig. 3, A) when the biogas generation almost ceased after 7 days of retention (Fig. 2, A). The simulated finial pH was close to the measurement of pH 8.2. Simulation showed that acetate uptake was inhibited mainly by free ammonia (Fig. 3, B). The inhibition from MEAw and hydrogen (Batstone et al., 2002) were strong at the beginning of the test and gradually reduced with time, attributing to the degradation of the inhibitory chemicals (Fig. 3, B). VFA accumulation was not observed at the end of both the test and simulation.
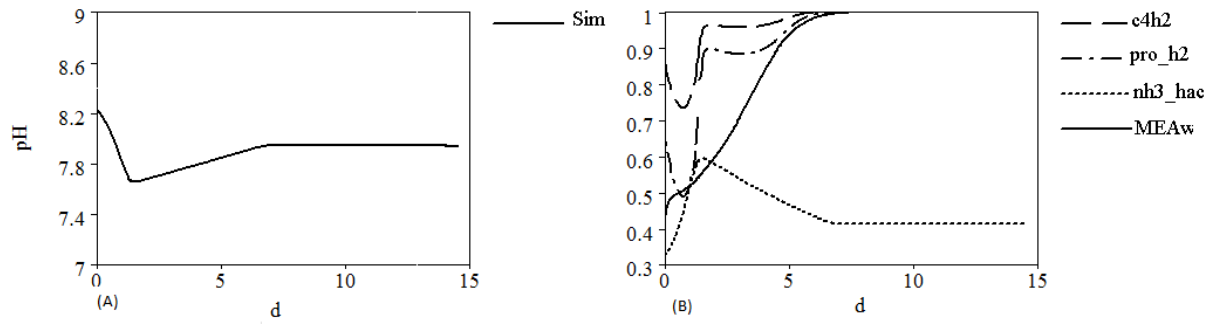
Fig. 3 Simulated pH (A) and inhibition effects (B), c4h2, pro_h2, nh3_hac and MEAw are inhibitions of hydrogen on butyrate, propionate degradation, free ammonia and MEAw on acetate degradation, respectively.

Table 4 Parameters' value specification

Parameter	Description	Units	Batch model	Semi-continuous feed model
K_{hyd_ch}	*First order hydrolysis rate of particulate carbohydrate*	d[-1]	10[a]	6[c]
K_{hyd_CO}	*First order hydrolysis rate of CO*	d[-1]	10[b]	10
K_{m_MEA}	*Monod maximum specific uptake rate of MEA*	d[-1]	5[b]	3[c]
K_{s_MEA}	*Half saturation constant of MEA*	kg-COD/m^{3}	0.48[b]	0.48
K_{I_MEAw}	*50% inhibitory MEAw concentration*	kg-COD/m^{3}	1[b]	1
Y_{MEA}	*Yield of biomass on MEA*	kg-COD B/kg-COD S	0.08[a]	0.08
$K_{I}\_nh3\_ac$	*50% inhibitory concentration of NH_3*	Kmol/m^{3}	0.0018[a]	0.0018

a, Standard ADM1 value; b, Estimated for batch test; c, Adjusted based on temperature effect (Eq. 6 and 7)

Semi-continuously fed digester simulations

The standard and calibrated kinetic parameters from the batch model (Table 4) were employed in ADM1_MEAw for simulating AD of MEAw in the semi-continuously fed digester at 22 ± 2 °C (Wang et al, 2013 a, b). The kinetic values were adjusted based on temperature effects according to Eq. 6 and 7. 486 days of experimental data was used to verify the parameters and test the model flexibility in predicting MEAw degradation at different feed scenarios (Wang et al., 2013 b).
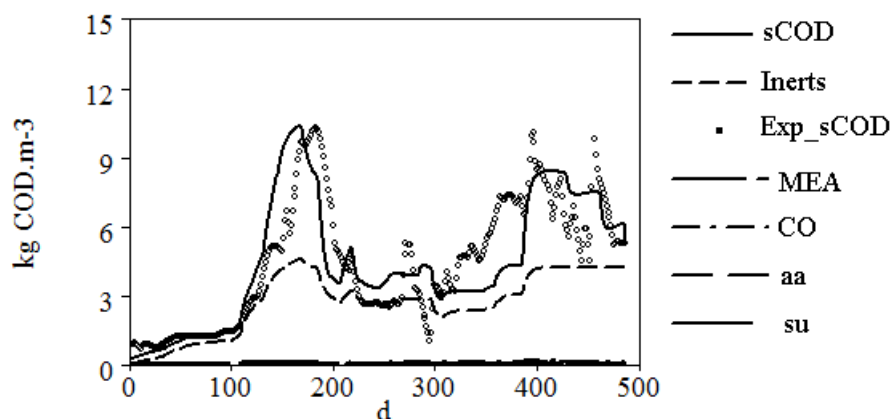
Fig. 4 Simulated and experimental effluent components concentrations (COD based). aa, amino acid; su, monosaccharides.

The simulated effluent soluble COD (sCOD) concentrations were generally close to the experimental measurements with some deviations observed at high load scenarios (Fig. 4). During 100 – 200 days, simulated effluent sCOD accumulated earlier than the experimental observations. The simulated effluent sCOD was overall higher than the measured data between 200 and 300 days (Fig 4), suggesting an underestimated feed degradation in the simulation. Simulation showed that inerts COD constituted the main part of the effluent sCOD and was almost equal to the measured effluent sCOD during this period (Fig. 4). It indicates that the assumed 30 % inerts COD in the feed MEAw was higher than the actual portion. When in the experiment about 80 % of feed COD was degraded during this period (Wang et al., 2013 b). Biomass acclimation was believed to lead to the increased feed MEAw degradation ratios (Wang et al., 2013 b), while the effects were not accounted for in the model. From 300 to 400 days, an underestimation of sCOD accumulation was shown in the simulation, which was attributed to the predicted low inhibition levels (Fig. 5). Other feed organics (e.g. MEA) were observed to be mostly degraded which was in accordance with the experimental observations (Wang et al., 2013 b).

Inhibition

The accumulation of sCOD in AD effluent was attributed to feed MEAw inerts and the organics' (e.g. acetate) accumulation due to the inhibition effects on organisms from MEAw and/or its degradation products and ammonia (Wang et al., 2013 b). Experimental observation showed that feed MEAw had strong negative effects on biogas yield (Wang et al., 2013 b). Complex MEAw chemicals may impose inhibition on ancetoclastic methanogenesis, while no specific inhibition factor has yet been identified. MEAw effects were accounted for in the model by adopting feed MEAw concentration (Eq. 4 and 5), causing acetate accumulation. The free ammonia inhibition coefficient (0.0018 M) was maintained as in the standard ADM1 since it is considered to be a low variability parameter between systems in continuous reactors (Siegrist and Batstone, 2001).

Simulation showed that acetate uptake was mainly affected by free ammonia in AD (Fig. 5 A). Inhibitory effects of MEAw were observed to be in comparably low levels (Fig. 5 A). PCA (principle component analysis) (Wang et al., 2013 b) showed that VFA concentration was closely related to free ammonia and feed MEAw concentration (Wang et al., 2013 b). The simulated stronger free ammonia inhibition effects indicate that the inhibitory chemicals in MEAw were broken down by AD and caused less acetoclastic methanogensis inhibition. Other inhibitions (e.g. hydrogen inhibition) (Fig. 5 A) were also observed in the simulation which affected the degradation of propionic acid for example.

Accumulated VFA was mainly acetic acid with other acids observed in much lower levels (Fig. 5 B) which complied with the experimental observations (Wang et al., 2013 a, b). However, the acetate accumulation was simulated to be much higher and started at an early phase (108 days) than experimental data (124 days) (Fig. 5 B). The simulation predicted a relatively high pH value at 108 days (Fig. 6 A), which led to a free ammonia overestimation (Fig. 6 B). VFA accumulation soared immediately after the overestimation of free ammonia (Fig. 5 B). The combined effects from inhibition of free ammonia and MEAw in the model (Fig. 5 A) amplified the inhibition effects and led to a higher VFA accumulation during 100 – 220 days. Simulated acetate accumulation at the end of the test was very close to that observed in the experiment (Fig. 5 B), which indicates that the combined inhibition effects were in reasonable levels at these stages of simulation.
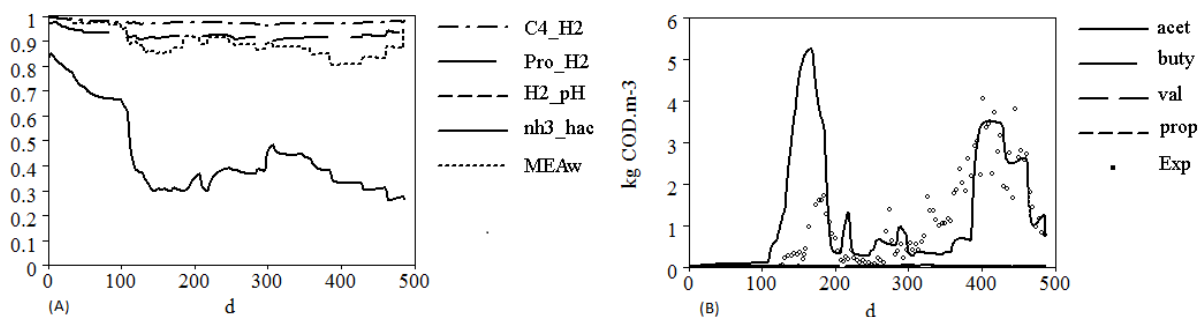

Fig. 5 Simulated inhibition effects (A) from H_2 on butyrate and propionate degradation (C4_H2 and Pro_H2), pH effects on hydrogen degradation (H2_pH) and NH_3 and MEAw effects on acetate degradation (nh3_hac and MEAw) in AD of MEAw. VFA accumulation (B), acet, acetate; buty, butyrate; val, valerate; prop, propionate.

pH and ammonia

Ammonia (ammonium + free ammonia) nitrogen in the AD digester was originated from nitrogenous content organics in both MEAw and co-feed substrates. The simulated ammonia concentration was generally close to the experimental observations with some under/overestimation in before 200 days (Fig. 6 B and Fig. 7). Free ammonia concentrations were calculated based on equilibrium of pH, ammonia and temperature (Angelidaki and Ahring, 1993), of which temperature was constant in the simulation. Simulated free ammonia variations were mainly determined by the pH (Fig. 6 A) and total ammonia concentrations (Fig. 7) from model prediction, the relatively low accuracy of those two state variables can lead to the variations of inhibitory effects in Fig. 5.

pH was simulated in ADM1 by accounting for different chemicals' ions concentrations in charge balance (Batstone et al., 2002). Inputs inorganic nitrogen (IN) and carbon (IC) are two important parameters in determining pH values in the model, whose concentrations were assigned in state variables of S_{An^-} and S_{Cat^+} (Eq. 11), respectively in ADM1 when implemented in AQUASIM. However, IN, IC and other ions concentrations were not well quantified in the applied feed MEAw. An overall feed inorganic carbon concentration was calculated based on the measured MEAw alkalinity, which was from the sodium carbonate addition for MEA regeneration in the reclaimer (Strazisar et al., 2003). IN concentration from input MEAw was ignored here since the measured values were quite low, but IN was accounted for in the hydrolysis of complex organics. The simulation results show that CO_2 partial pressure overestimation was observed at the beginning of the test (Fig. 8), which indicates that the inorganic carbon concentration was overestimated. This overestimation of IC can also contribute to the digester pH reduction during this period (Fig. 6 A) due to the buffer capacity from CO_2 dissolution in the liquid. More detailed specifications of input alkalinity and ions concentrations can achieve better prediction of pH values.
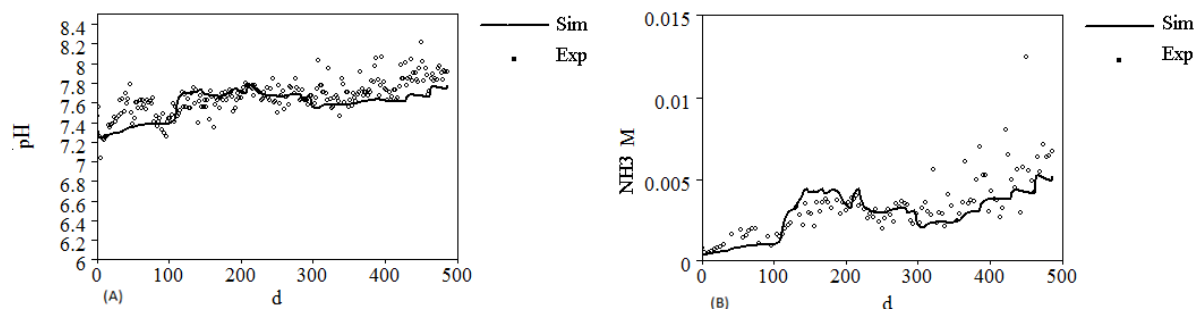

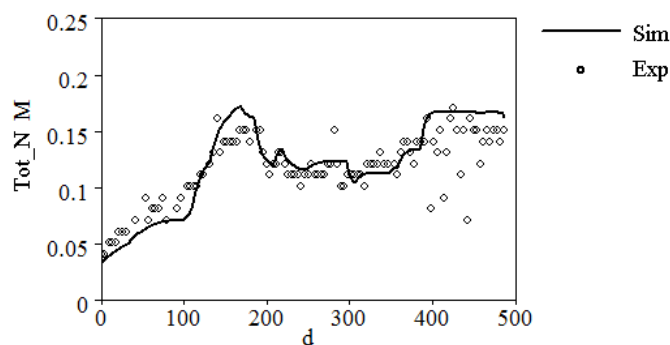Fig. 6 Simulated and experimental pH (A) and free ammonia concentration (B)

Fig. 7 Simulated and experimental total ammonia concentration

Biogas generation

Simulated biogas flow rates show a comparable good correlation with the experimental results (Fig. 8 A). Biogas overestimation was observed at around 200 days, when in the experiment, VFA peak showed (Fig. 5 B). The overestimation was attributed to the simulated relatively early VFA accumulation at around 160 days due to inhibition effects (Fig. 5). From 300 days to the end, simulated biogas flow rates are in the high

range of the measured biogas flows that fluctuate very much in the experiment (Fig. 8 A). The simulated CO_2 partial pressure was relatively high before 110 days (Fig. 8 B) attributing to the inaccurate IC input in the model. The partial pressure of both methane and CO_2 were in good correlation with the experimental data after 110 days (Fig. 8 B).
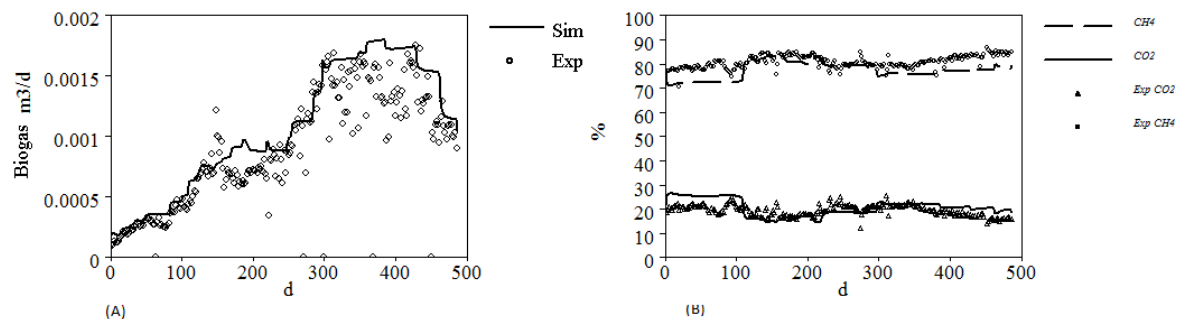

Fig. 8 Simulated and experimental biogas generation (A) and CH_4 and CO_2 partial pressures (B)

Anaerobic digestion of MEA is coupled with consuming CO_2 as a reactant (Eq. 3 and Speranza et al., 2006). Accurate prediction of MEA and other ethanol amine concentrations in the MEAw are thus important for biogas simulations, especially for the biogas partial pressure predictions. It showed in the experiment that the biogas generation was gradually increasing in inhibitory conditions due to acclimation effects (Wang et al., 2013 b), while these effects were not included in the model. The $t_{res,X}$ (extended retention of solid) applied in the model was observed to play an similar role as acclimation effects that with increased biomass retention, increased feed degradation rate and reduced inhibition effects were obtained. Other biochemical processes (e.g. syntrophic acetate oxidation (Schnürer et al., 1994)) may have also occurred in the digester which was not specified experimentally or implemented in the model.

Simulation validation

Root mean square deviations (RMSD) were calculated for the ADM1_MEAw simulations with respect to the data for eight key process variables for each of three experimental phases conducted in the experimental test. The distinctions of the three phases are described in greater detail in Wang et al., (2013 b). These three separate RMSD values are shown in Table 5 together with an overall RMSD value for the complete 486 days experiment. The RMSD values of the three phases are generally in the same order of magnitudes as the RMSD values for the entire experiment. Relatively lower RMSD values of simulated CH_4 partial pressure, IN, acetate concentrations and pH in experimental phase 2 may be a result of a less load variations than during the other two phases. The absence of other patterns in the calculated deviations (Table 5) shows that the model predicts the process behavior with similar precision for the entire 486 d experiment. Generally the simulations comply well with the experimental data.

Table 5. Calculationed RMSD for the simulation and experimental results for the entire 486 d experiment and for phase 1-3 with distinctly different operational conditions.

Variables	Units	0-486 days	Phase 1 (0-184 days)	Phase 2 (185-296 days)	Phase 3 (297-486 days)
Biogas flow	*m^3/d*	2.35E-04	1.25E-04	1.85E-04	3.28E-04
CH_4 partical pressure	*%*	4.63	5.28	2.12	5.02
CO_2 partial pressure	*%*	3.56	4.53	3.01	2.63
IN	*M*	0.02	0.02	0.01	0.03
Free ammonia	*M*	1.35E-03	8.50E-04	5.28E-04	1.91E-03
Acetate	*$Kg\text{-}COD/m^3$*	1.17	1.48	0.49	0.80
pH	*-*	0.16	0.17	0.08	0.19
sCOD	*$Kg\text{-}COD/m^3$*	1.61	1.43	1.74	1.68

Conclusion

The model ADM1_MEAw was generated based on ADM1 for the simulation of anaerobic degradation of MEA waste with easily degradable organics at room temperature. The model was based on the assumptions of 1) MEAw COD consisted of 44 % MEA and 56 % complex organics (CO), in which degradable organics and inerts accounted 26 % and 30 %, respectively; 2) MEA and acetate were hydrolysis products of the degradable organics. 3) MEA was degraded to ammonium and acetate (Eq. 3); 4) Monod kinetics and standard organisms for amino acids degradation were applied for MEA uptake (Botheju et al., 2010); 5) Observed MEAw and ammonia inhibition on acetoclastic methanogenesis were included in the inhibition factor; 6) The long AD sludge retention time was accounted for in the model by a parameter $t_{res,x}$ that allows particles (X) to be retained in the reactor longer than the liquid.

The expanded model ADM1_MEAw based on ADM1 and assumptions according to experimental investigation of AD of MEAw was constructed in this study. ADM1_MEAw applied standard ADM1 variables and kinetics of the newly added biochemical processes calibrated based on batch test were able to successfully predict the reactor performance under varying experimental scenarios. Simulated COD removal, pH, inorganic nitrogen concentrations etc. through large feed input variations complied well with the 486 days of semi-continuously fed experimental data. Predicted acetate accumulation generally complied with the experimental observations, with deviations attributed to less accurate predicted inhibitory effects. Most feed MEAw was degraded in the simulation and its inhibitory effects on acetate uptake were comparably lower than free ammonia which was the dominant inhibitor in acetate degradation.

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