SGC Rapport 2013:280

In-situ methane enrichment of raw biogas in the anaerobic digestion process

(Metananrikning av rågasen under rötningsprocessen)

Mikael Hansson, Johan Laurell, Åke Nordberg, Åke Rasmuson, Jing Liu, Mihaela Nistor, Sten Strömberg, João Costa

"Catalyzing energygas development for sustainable solutions"

SGC Svenskt Gastekniskt CenterAB

In-situ methane enrichment of raw biogas in the anaerobic digestion process (Metananrikning av rågasen under rötningsprocessen)

Mikael Hansson, Johan Laurell, Åke Nordberg, Åke Rasmuson, Jing Liu, Mihaela Nistor, Sten Strömberg, João Costa

Denna studie har finansierats av:
Energimyndigheten
Göteborg Energi AB
Avfall Sverige AB
EON Sverige AB
Kristianstad Biogas AB
LRF

Rapporten finns också publicerad av:
Avfall Sverige Utveckling – Rapport U2013:08

Postadress och Besöksadress
Scheelegatan 3
212 28 MALMÖ

Telefonväxel
040-680 07 60

Telefax
0735-279104

E-post
info@sgc.se

Hemsida
www.sgc.se

Svenskt Gastekniskt Center AB, SGC

SGC är ett spjutspetsföretag inom hållbar utveckling med ett nationellt uppdrag. Vi arbetar under devisen *”Catalyzing energygas development for sustainable solutions”*. Vi samordnar branschgemensam utveckling kring framställning, distribution och användning av energigaser och sprider kunskap om energigaser. Fokus ligger på förnybara gaser från rötning och förgasning. Tillsammans med företag och med Energimyndigheten och dess kollektivforskningsprogram *Energigastekniskt utvecklingsprogram* utvecklar vi nya möjligheter för energigaserna att bidra till ett hållbart samhälle. Tillsammans med våra fokusgrupper inom *Rötning*, *Förgasning och bränslesyntes*, *Distribution och lagring*, *Industri och hushåll* och *Gasformiga drivmedel* identifierar vi frågeställningar av branschgemensamt intresse att genomföra forsknings-, utvecklings och/eller demonstrationsprojekt kring. Som medlem i den europeiska gasforskningsorganisationen GERG fångar SGC också upp internationella perspektiv på utvecklingen inom energigasområdet.

Resultaten från projekt drivna av SGC publiceras i en särskild rapportserie – *SGC Rapport*. Rapporterna kan laddas ned från hemsidan – www.sgc.se. Det är också möjligt att prenumerera på de tryckta rapporterna. SGC svarar för utgivningen av rapporterna medan rapportförfattarna svarar för rapporternas innehåll.

SGC ger också ut faktabroschyrer kring olika aspekter av energigasers framställning, distribution och användning. Broschyrer kan köpas via SGC:s kansli.

SGC har sedan starten 1990 sitt säte i Malmö. Vi ägs av Eon Gas Sverige AB, Energigas Sverige, Swedegas AB, Göteborg Energi AB, Lunds Energikoncernen AB (publ) och Öresundskraft AB.

Malmö 2013

Martin Ragnar
Verkställande direktör

Swedish Gas Technology Centre, SGC

SGC is a leading-edge company within the field of sustainable development having a national Swedish assignment. We work under the vision of *"Catalyzing energygas development for sustainable solutions"*. We co-ordinate technical development including manufacture, distribution and utilization of energy gases and spread knowledge on energy gases. Focus is on renewable gases from anaerobic digestion and gasification. Together with private companies and the Swedish Energy Agency and its frame program *Development program for energy gas technology* we develop new solutions where the energygases could provide benefits for a sustainable society. Together with our focus groups on
Anaerobic digestion, *Gasification and fuel synthesis*, *Distribution and storage*, *Industry and household* and *Gaseous fuels* we identify issues of joint interest for the industry to build common research, development and/or demonstrations projects around. As a member of the European gas research organization GERG SGC provides an international perspective to the development within the energygas sector

Results from the SGC projects are published in a report series – *SGC Rapport*. The reports could be downloaded from our website – www.sgc.se. It is also possible to subscribe to the printed reports. SGC is responsible for the publishing of the reports, whereas the authors of the report are responsible for the content of the reports.

SGC also publishes fact brochures and the results from our research projects in the report series *SGC Rapport*. Brochures could be purchase from the website.

SGC is since the start in 1990 located to Malmö. We are owned by Eon Gas Sverige AB, Energigas Sverige, Swedegas AB, Göteborg Energi AB, Lunds Energikoncernen AB (publ) and Öresundskraft AB.

Malmö, Sweden 2013

Martin Ragnar
Chief Executive Officer

Förord

Till projektet med titel: ”*In-situ* methane enrichment of raw biogas in anaerobic digestion processes” har följande referensgrupp knutits:
Tobias Persson, SGC (programansvarig)
Håkan Eriksson, EON Sverige AB
Carl Lilliehöök, Kristianstad Biogas AB
Tore Sigurdsson, Kristianstad Biogas AB
Peter Malmros, Uppsala Vatten och Avfall AB
Tisse Jarlsvik, Göteborg Energi AB

Projektet har bedrivits i två delar där Mikael Hansson och Johan Laurell från JTI, Dr. Åke Nordberg från SLU och Prof. Åke Rasmuson från KTH främst varit verksamma i projektets ena del (del 1) medan Dr. Jing Liu och Dr. Mihaela Nistor från Bioprocess Control Sweden AB och Sten Strömberg tillsammans med João Costa från Lunds Universitet främst varit verksamma i projekts andra del (del 2).

Projektet har bedrivits under tiden 2012-03-01 till 2013-01-31.

Summary

Different aspects of *in-situ* methane enrichment as a method to increase the methane content in biogas have been studied. The study consisted of two separate parts:

1. Optimization of key process parameters using computer simulations
2. Lab based evaluation of different techniques for carbon dioxide removal.

Computer simulations have been carried out on in-situ methane enrichment of biogas from anaerobic digestion of sewage sludge. The sludge in the digester is continuously circulated through a bubble column for desorption of carbon dioxide by which the headspace gas in the digester becomes enriched by methane. The model is a combination of two separate models: a digester model, ADM1, implemented in the programming language C, and a desorption column model written in Matlab. ADM1 describes digestion of particulate composites as a 5-stage process involving disintegration, hydrolysis, acidogenesis, acetogenesis and methanogenesis, of which the last three process steps are represented by growth kinetics of the specific degrading biomass. The desorption model describes desorption of carbon dioxide and methane from anaerobic sludge in a bubble column operating at steady-state in the homogeneous flow regime. The liquid sludge phase and the gas phase are both described by the axial dispersion model and the contacting is counter current. The model accounts for desorption of methane and carbon dioxide, and the dissociation reactions of carbonate and ammonium. The two models are combined by the commercial tool for modeling, simulating and analyzing multi domain dynamic systems called Simulink, and the simulations account for the influence of the desorption on the digestion and *vice versa*. The combination of the column model and the ADM1 model is however not trivial since the desorption column model is a steady-state model in which the system of differential equations in space are solved by numerical methods without any time domain, while the ADM1 is a dynamic model that solves time dependent differential equations, using a time step length that changes in response to the results of the differential equations.

The results show that a methane slip below 2 % can be obtained simultaneously as a significant increase in the biogas methane concentration. As an example, simulation of a 2000 m^3 digester (active volume) and a desorption column of 30 m^3 with a sludge flow of 600 m^3/d and an air flow of 11 000 m^3/d gave an increase in the methane concentration from 58 % to 69 % with a methane loss of 1.3 %.To minimize the methane slip and to maximize the biogas methane concentration the sludge flow rate should be low and the gas flow rate should be high. A higher gas flow rate will significantly increase the biogas methane concentration, but have a minor negative effect on the methane slip when the sludge flow rate is low.

In the range studied, the influence of the volume of the desorption column is weak which needs to be further investigated to be fully understood. In addition, it has not been explored whether gas flow rates beyond the limitation of the homogenous flow regime can be favorable. Furthermore, it has not been sufficiently investigated, whether the reduced reaction rate of the bicarbonate to carbon dioxide conversion with increasing pH will set a limit to the achievable biogas methane concentration at increasing gas flow. Physical data of importance for the desorption process and parameters describing the mass transfer and

hydrodynamics of the bubble column contain uncertainties. However, these uncertainties appear to have less influence on the results than changes of processing conditions like the gas and sludge flow rates.

In the second part of the study, three different techniques to remove carbon dioxide from the produced biogas were investigated on a lab based platform, spread over six phases. The main objectives, besides developing the lab platform, were to find the most promising technique for carbon dioxide removal and prove the principle of *in-situ* methane enrichment.

During the first three phases, air and vacuum (0.4 bar) stripping were evaluated against a reference using a nitrogen rich substrate. The results showed poor performance for both methods, resulting in decrease in methane content and considerable pH increase in the digesters. Ammonia inhibition due to the nitrogen rich substrate, amplified by the pH increase, was believed to be the main reason for the poor performance. It was therefore concluded that increasing the methane content by removal of carbon dioxide was not possible with a substrate rich in nitrogen.

In the last three phases, air stripping as well as vacuum treatment with and without addition of organic acids were tested using a substrate mixture containing less nitrogen. All three techniques provided small increases in methane content. The combined treatment with vacuum and organic acids generated the largest increase of close to 12%-units. However, no method was able to produce biogas with an average methane content higher than 62%, which is far below a satisfactory level. Two of the main reasons were assumed to be a too high organic loading rate and too limited operation time (8 hours per day) of the stripping procedure. An interesting outcome of the study was that the carbon dioxide removal procedure seemed to reduce the effects from an overloaded system.

Sammanfattning på svenska

Olika aspekter för att öka metanhalten i biogas med en *in-situ* metod har undersökts. Studien genomfördes i två separata delar:

1. Vidareutveckling och optimering av processparametrar med datorsimuleringar
2. Praktisk utvärdering av olika tekniker för att avdriva koldioxid.

Datorsimuleringar har genomförts för processintern metananrikning av biogas från rötning av avloppsslam. Slammet i rötkammaren cirkuleras kontinuerligt genom en bubbelkolonn för desorption av koldioxid med ett luftflöde. Därmed kommer gasen från rötkammaren att anrikas med avseende på metan. Modellen är en kombination av två separata modeller: en rötkammarmodell, ADM1, implementerad i programspråket C och en modell för desorptionskolonnen implementerad i Matlab. ADM1 beskriver nedbrytning av partiklulärt material som en 5-steg process med sönderdelning, hydrolys, syrabildning, acetatbildning och metanbildning, varav de sista tre processtegen representeras av mikrobernas omsättningskinetik för de specifika ämnena. Desorptionsmodellen beskriver desorption av koldioxid och metan från slam i en bubbelkolonn vid ”steady-state” i det homogena flödesområdet. Slam- och gasfasen beskrivs båda av axiella dispersionsmodeller vid motströmsflöde. Modellen tar hänsyn till desorption av metan och koldioxid, samt dissociationsreaktioner för karbonat och ammonium.

De två modellerna kombineras med simuleringsverktyget Simulink för modellering, simulering och analys. Vid simuleringarna tas hänsyn till desorptionens påverkan på biogasproduktionen och vice versa. Kombinationen av ADM1 och kolonnmodellen är emellertid komplicerad eftersom kolonnmodellen är en steady-state modell där ingående differentialekvationer löses genom numeriska metoder utan tidsdomän, medan ADM1 är en dynamisk modell som löser tidsberoende differentialekvationer, med användning av en tidstegslängd som ändras beroende på resultatsvar från differentialekvationerna.

Resultaten visar att en metanförlust från kolonnen under 2 % kan erhållas samtidigt som en ökning i biogasens metankoncentration sker. Exempelvis gav simulering av en 2000 m^3 rötkammare (aktiv volym) kopplad till en 30 m^3 desorptionskolonn med slamflödet 600 m^3/d och luftflödet 11 000 m^3/d en ökning av metanhalten från 58 % till 69 % och en metanförlust på 1,3 %. För att minimera metanförlust och maximera metanhalt i rötkammaren ska slamflödet vara lågt och luftflödeshastigheten hög. En högre luftflödeshastighet kommer att avsevärt öka metankoncentrationen, men har en mindre negativ effekt på metanförlust när slammets flödeshastighet är lågt.

I de studerade intervallen verkar desorptionskolonnens volym inte påverka resultaten i någon större utsträckning. Detta är svårt att förklara och behöver studeras vidare för att öka förståelsen av systemet. Vidare har vi inte undersökt om luftflödeshastigheter bortom gränsen för det homogena flödesområdet kan vara gynnsam för hög metanhalt och låg metanförlust. Dessutom är det inte tillräckligt utrett om den reducerade reaktionshastigheten av bikarbonat till koldioxid med ökande pH-värde som resultat, kommer att sätta en gräns för vilken metanhalt som kan uppnås vid ökat luftflöde. Fysisk data som är av betydelse för desorptionsprocessen och parametrar som beskriver massöverföring och

hydrodynamik i bubbelkolonnen innehåller fortfarande en rad osäkerheter. Dessa osäkerheter verkar dock ha en mindre inverkan på resultaten än förändringar av gas- och slam flödeshastigheter, vilka är driftparametrar som kan styras.

I den andra delen av studien har tre stycken strategier för att öka metanhalten i biogas med en *in-situ* princip utvärderats genom praktiska försök. Under projektets inledande del designades och implementerades den experimentella plattformen som sedan användes för att utvärdera de olika teknikerna fördelat över sex stycken faser. Syftet var att dels utveckla och implementera en labbplattform som möjliggjorde utvärderingen samt att utvärdera vilken av de tre strategierna som var den mest lovande. Målet var följaktligen inte att optimera processen utan främst att åstadkomma en förändring så att så att en jämförelse var möjlig. De tre metoderna som undersöktes var luftstrippning och vakuum (0.4 bar) med eller utan tillsatser av organiska syror. Luftstrippning har vid flera tidigare tillfällen visat sig vara en effektiv metod medan vakuum med eller utan organiska syror är mer oprövade kort. Tanken med vakuumbehandlingen var att minimera rötslammets kontakt med syre men ändå bibehålla en drivkraft för att påskynda avdrivningen av koldioxid. Tillsatsen av organiska syror syftade till att minska alkaliniteten och således göra mer bikarbonat tillgängligt som koldioxid. För att möjliggöra en rättvis jämförelse genomfördes alla procedurer manuellt och satsvis och kunde således endast utföras under dagtid då labbet var bemannat. De parametrar som bevakades var totalt gasflöde, gassammansättning, pH och TS/VS vilket ansågs tillräckligt för att kunna genomföra jämförelsen mellan de tre metoderna.

Under de tre första faserna utvärderades luftstrippning och vakuumbehandling mot en referens med ett substrat rikt på kväve. Resultaten pekade på att metoderna fungerade dåligt eftersom både gasproduktionen och metanhalten var lägre jämfört med referensen. Anmärkningsvärt från perioden var också att behandlingen ledde till väldigt höga pH-värden (8.2-8.4). Med bakgrund av detta antogs processen vara kraftigt inhiberad av ammoniak och därför drogs slutsatsen att *in-situ* metananrikning inte kan appliceras på en process där ett kväverikt substrat används.

Under de tre avslutande faserna utvärderades luftstrippning, vakuum samt vakuum med tillsatser av organiska syror med en mer balanserad substratblandning för att möjliggöra en jämförelse under mer normala förhållanden. Tyvärr tvingades utvärderingarna av luftstrippningen och vakuumbehandlingen hållas väldigt korta på grund av projektets tidsbegränsning. Båda dessa metoder visade dock tendenser på ett ökat metaninnehåll i den producerade gasen jämfört med en referensreaktor. Under luftstrippningen kördes processen med en uppehållstid av endast 10 dagar vilket ledde till något instabila resultat med lågt metanutbyte. Vakuumbehandlingen, som hade en mer normal uppehållstid, påvisade mer stadiga värden men åstadkom en mindre ökning av metanhalten jämfört med luftstrippningen. Den mest framgångsrika tekniken visade sig vara vakuum tillsammans med organiska syror som gav en ökning på nära 12%-enheter. En intressant observation från denna fas var att pH värdet sjönk kontinuerligt efter att de organiska syrorna tillsats i kolonen trots att vakuum var applicerat. Detta tyder på att apelsinjuicen, som användes för att simulera de organiska syrorna, fortsatte att sönderdelas till starkare syror och att bortföringen av koldioxid inte skedde i tillräckligt stor utsträckning för att motverka den pH

sänkande effekten. Denna långvariga verkan innebär att ganska små mängder av de organiska syrorna krävs för att få önskad effekt. Eftersom apelsinjuice innehåller en stor mängd socker antas dock dessa effekter inte vara lika distinkta som om innehållet från en hydrolysreaktor används istället. Det ska också tas i beaktande att tillstatser av organiska syror minskar alkaliniteten vilket kan leda till en mer instabil process..

Trots att metanhalten var klart högre jämfört med referensreaktorn för tekniken med vakuum tillsammans och tillsatserna av organisk syra uppgick medelvärdet bara till strax över 61% och inte de 80-90% som man bör uppnå för att tekniken ska vara applicerbar. Detta är klart under vad tidigare studier uppvisat. Den främsta anledningen till att metanhalten inte blev högre, bortsett från att proceduren endast utfördes under en kort tid av dygnet, antas bero på en stressad process till följd av en för hög belastning. I tidigare studier har den organiska belastningen legat kring 1.5-2 gVS/L/dag vilket är avsevärt lägre än de 3 gVS/L/dag som användes i denna. Resultaten tyder således på att en relativt låg belastning krävs för att uppnå riktigt höga metanhalter, åtminstone i ett första steg tills processen har anpassat sig. Det ska dock tilläggas att en ökning av metanhalten från 49 till 61% innebär att nära 40% mindre koldioxid behöver avlägsnas i ett senare uppgraderingssteg. Samtidigt leder innebär tekniken också ökade investerings- och driftkostnader för anläggningen.

En annan intressant observation från studien var att avlägsnandet av koldioxid föreföll ha vissa stabiliserande effekter på en överbelastad process. Detta tros härstamma från faktumet att pH ökningen, som följer av bortförandet av koldioxid, gynnar de känsliga metanproducerande bakteriegrupperna.

För fortsatta studier rekommenderas att luftstrippning tillsammans med tillsatser av organiska syror används för att uppnå bästa resultat. Detta eftersom luftstripping bedömdes ha en kraftfullare avdrivningsförmåga av koldioxid jämfört med 0.4 bars vakuum, utan att vara mer hämmande för processen. pH sänkningen från de organiska syrorna bedömdes också ha en positiv effekt genom ökad löslighet av koldioxid och kombination av de två bör därför möjliggöra en maximal avdrivning. I ett nästa steg bör dessutom proceduren köras kontinuerligt med en lägre organisk belastning för att undvika inhibering och möjliggöra metanhalter över 85%.

Table of content

1 Background

With the increasing demand of biomethane production to be used as a vehicle fuel and injected into natural gas grid, the demand for cost efficient biogas upgrading technologies has increased, in particular at biogas production facilities with low gas flows, such as farm-scale plants. Biogas plants are required to operate not only at higher organic loading rates with a greater utilization of digester capacity, but also with a high methane content in digester off gas in order to ensure the plant profitability. Various technologies for biogas upgrading are commercially available including water scrubbing, organic physical scrubbing, chemical adsorption, pressure-swing-adsorption and membrane separation (Petersson and Wellinger, 2009). However, biogas upgrading plants based on these technologies are all expensive and can only be economic favorable for large-scale biogas plant. Thus, there is a demand on developing cost efficient upgrading technologies with focus on small or middle-size biogas production facilities. An alternative and potentially cost efficient technique to upgrade biogas is *in-situ* methane enrichment (Hayes et al 1990; Richards et al 1994).

1.1 Principle of *in-situ* methane enrichment

The *in-situ* methane enrichment technique is performed by pumping the digester sludge, rich in soluble CO_2, through a CO_2 desorption column and then back to the digester (Figure 1). The desorption of CO_2 is achieved by aeration of the sludge, based on the higher solubility of CO_2 compared to CH_4. At a pH of 7.0 and a temperature of 35 °C, e.g. CO_2 is 20 times more soluble than CH_4. The sludge being returned from the desorption column will not be saturated in CO_2, and will have a capacity to absorb a significant portion of the CO_2 produced in the anaerobic conversion of organic matter but will only absorb a small fraction of the less soluble CH_4. In principal, much higher methane content can be expected as the result of *in-situ* enrichment of digester off gas.

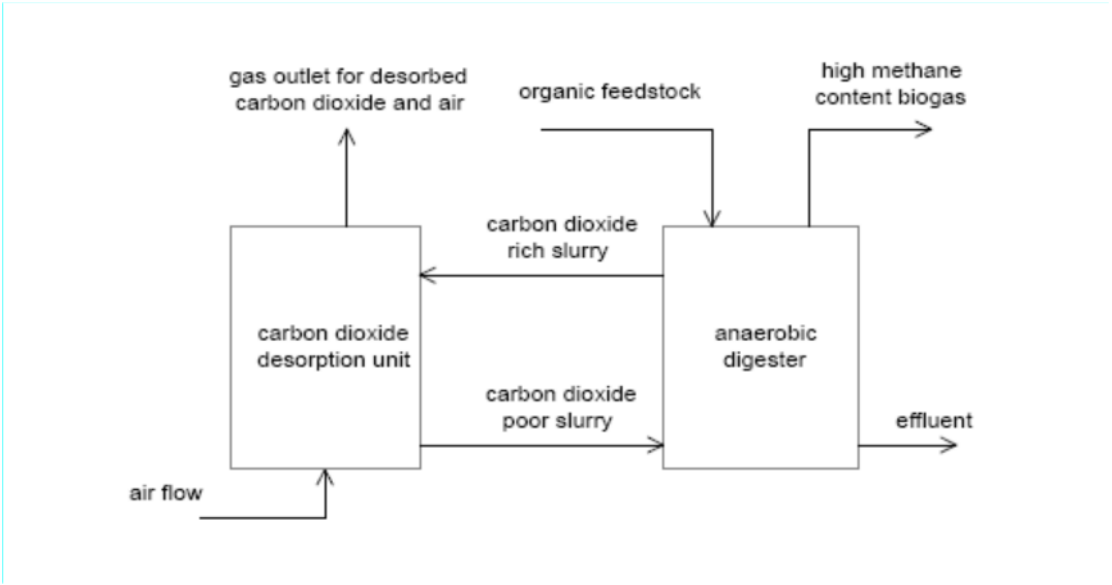

Figure 1: Schematic picture of in-situ methane enrichment based on air stripping.

1.1.1 Carbon dioxide solubility

Carbon dioxide's solubility in water is proportional to the partial pressure of carbon dioxide in the atmosphere in accordance with Henry's law (Equation 1 in section 2.1.4) (Stumm & Morgan, 1996). As a normal biogas process is an open system, the partial pressure of carbon dioxide can maximally reach slightly above the atmospheric one.

Carbon dioxide is a diprotic acid in aqueous solution where it mainly exists in four forms: carbonate ions (CO_3^{2-}), bicarbonate ions (HCO_3^-), carbonic acid (H_2CO_3) and carbon dioxide (CO_2). Normally the last two components can be grouped together (CO_2^*) since the conversion to carbonic acid is a fast and almost irreversible process. The reaction scheme of the carbonate system is presented below.

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^- + H^+ \rightleftharpoons H_2CO_3 \rightarrow CO_2(aq) + H_2O$$

In Figure 2, the carbonate system's distribution at different pH levels at 25 °C is shown. As seen in the figure, most of the carbonate exists in the form of bicarbonate at the normal pH interval for an AD (Anaerobic Digestion) process (i.e. 7-8). When carbon dioxide is removed in the stripping process, the equilibrium will slowly shift to the right with an increase in pH as a consequence. This shift is regulated by the disassociation constant (K_{a1}) of the bicarbonate and carbon dioxide relationship (Equation 3 in section 2.1.4).

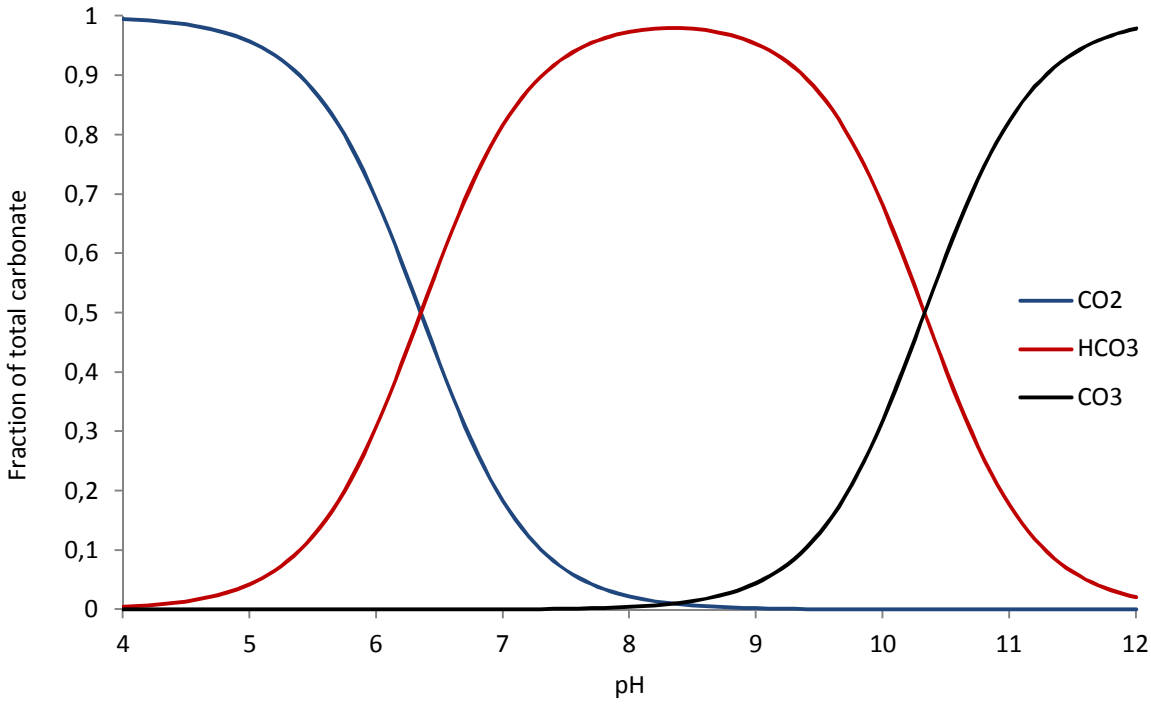

Figure 2: The distribution of carbonate species as a fraction of total dissolved carbonate in relation to solution pH

The concentration of bicarbonate, which contributes to the main part of the alkalinity of an AD system (Jarvis & Schnürer 2009), has an important role in deciding at what pH a certain methane content is achieved. In Figure 3, the

methane content as function of pH at different alkalinity (given in g $CaCO_3$ per liter) levels is plotted. It is assumed that the gas phase is open at atmospheric pressure and only consisting of methane and carbon dioxide that are both acting as ideal gases. Furthermore, bicarbonate is presumed to be the only buffering component in the alkalinity system. As seen in the figure, pH rice approximately 0.3-0.4 units when the methane content increase from 50 to 80%.

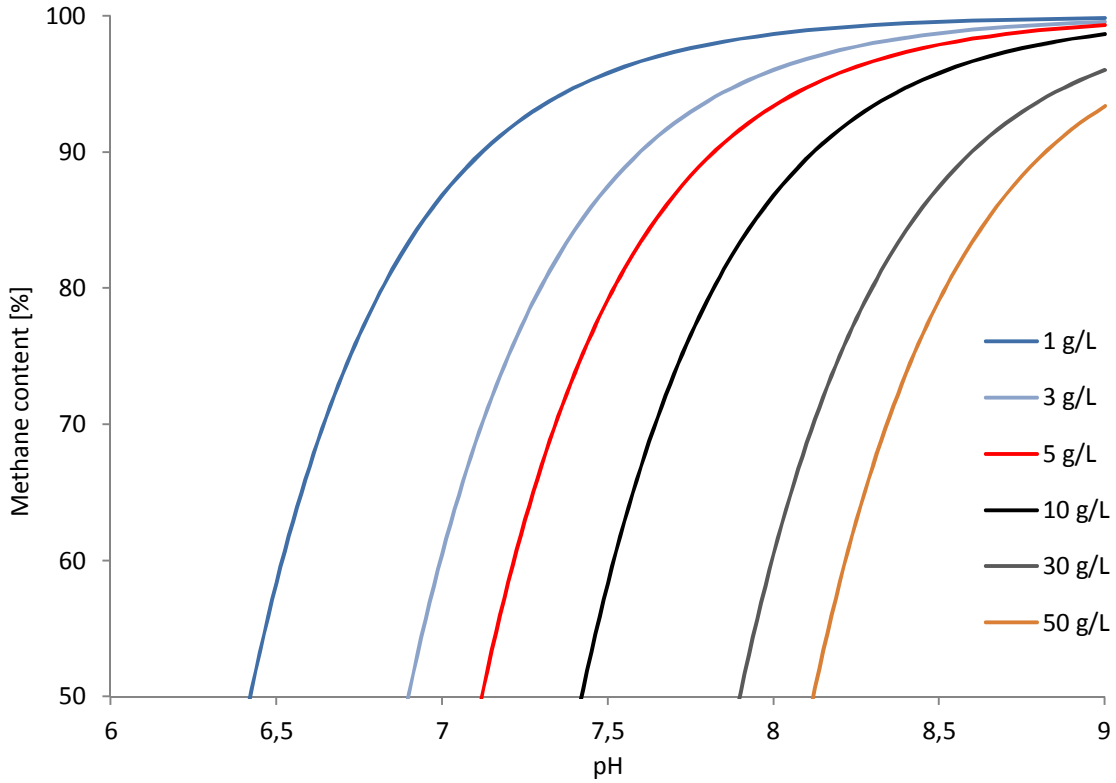

Figure 3: Methane content as a function of pH at different alkalinity levels (g $CaCO_3$/L)

One of the approaches that were evaluated in this study was the addition of organic acids to increase the driving force for the removal of carbon dioxide inside the stripping column. This is possible since the organic acids will lead to a decreased alkalinity, making more inorganic carbon available as carbon dioxide. When the sludge returns to the digester, the organic acids will be consumed, increasing the alkalinity again. As more carbon dioxide is available for removal in the stripping column, less volume of methane will be removed compared to volume of carbon dioxide. Therefore, the addition of organic acids will make it possible to achieve higher methane contents with smaller losses of methane.

1.1.2 Ammonia solubility

Another important relationship that might impact the carbon dioxide removal capability by manipulating the pH is the ammonium system (Figure 4). The solubility of ammonia is also regulated by Henry's law and mainly exists in two forms in a liquid solution: (Zhang et al. 2012): ammonium ions (NH_4^+) and ammonia ($\mathrm{NH_3}$).

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$

As seen in figure 4, most of the ammonium nitrogen is present at the normal pH interval as ammonium, ions which is regarded as relatively harmless for an AD process. Free ammonia, on the other hand, is commonly known to act as an inhibitor, especially for the acetoclastic methanogens (Hansen et al. 1998; Chen et al. 2008). As the fraction of free ammonia increases with increasing pH, large amounts of ammonium nitrogen together with a high pH often leads to inhibition of AD processes. Therefore, the pH level has to be kept low when a substrate rich in nitrogen is used.

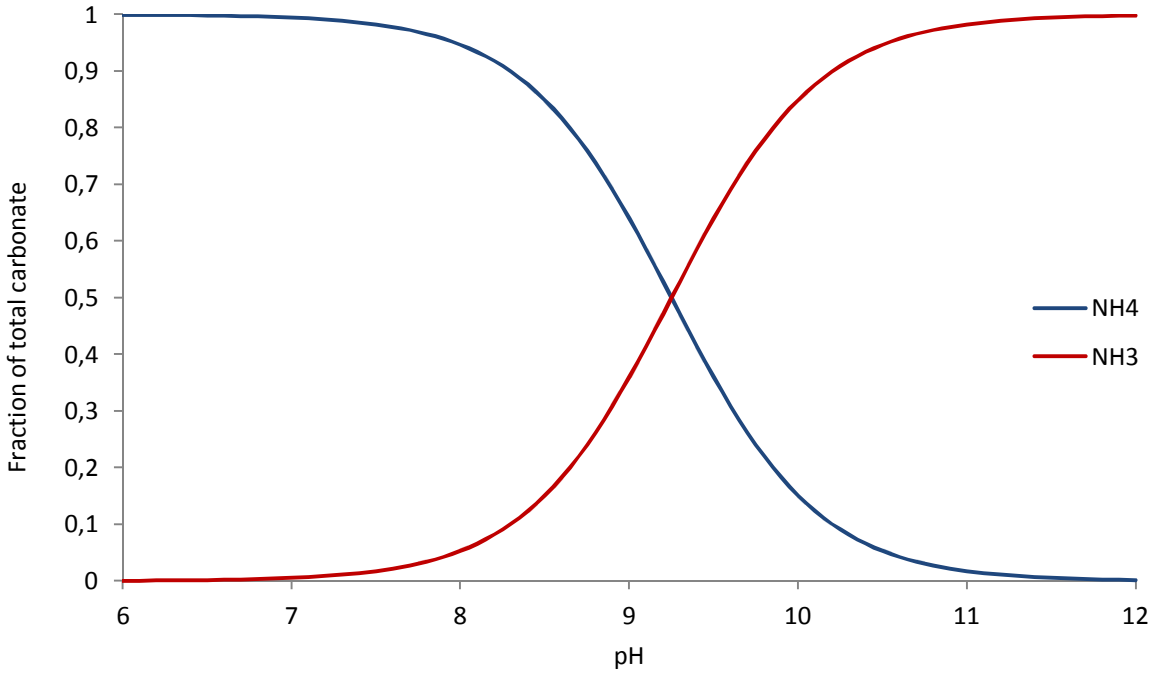

Figure 4: The distribution of NH_3 and NH_4^+ species as a function of pH.

As free ammonia is a gas at ambient temperature it can be desorbed in the same way as carbon dioxide during a stripping procedure. In fact, stripping of ammonia from anaerobic sludge has been shown to be effective on several occasions (Guštin and Marinšek-Logar, 2011; Liao et al. 1998; Bonmatí and Flotats 2003; Quan et al. 2010). Most of the previous studies also show that the removal effect is highly dependent on the pH with the most effective removal at pH 10-12. Stripping has also been shown to, in combination with additions of lime, be an efficient pretreatment step with pig slurry waste (Zhang and Jahng 2010; Zhang et al. 2012), whereas another study observed no such effect (Bonmatí and Flotats 2003). Removal of ammonia should lead to a decrease in pH since the equilibrium demands that ammonium ions replace the free ammonia leading to a release of hydrogen ions. This theory is supported by the results observed by Bonmati et al. which experienced a significant drop in pH during the air stripping of fresh pig slurry waste. As stripping of ammonia and carbon dioxide counteract each other with regards to their effect on the pH, the procedure might actually have double positive effect when a substrate rich in nitrogen is used. This is due to the fact that the pH decrease from the stripping of ammonia leads to less available free ammonia and more available carbon dioxide. However, considering the anaerobic bacteria's high sensitivity for free ammonia such a condition is difficult to achieve.

1.2 Previous studies on *in-situ* methane enrichment of biogas

The concept of *in-situ* methane enrichment was initially investigated by two research groups in Unite States from University of Illinois and Cornell University during the beginning of 1990s (Hayes et al 1990; Srivastava and Hill, 1993; Richards et al 1994). These research works were focused on using air stripping for carbon dioxide desorption (i.e. bubble column). No further research and development had been carried out until late 90s when a research group from the Swedish Institute of Agricultural Engineering (JTI) and the Royal Institute of Technology (KTH) started further investigation and evaluation of the concept based on the standard bubble column concept, i.e. air stripping for CO2 desorption.

The cooperation between JTI and KTH on *in-situ* methane enrichment started with a licentiate work where a mathematical model for the desorption process was developed (Lindberg, 2003; Lindberg and Rasmuson, 2006; Lindberg and Rasmuson, 2007). This was followed by empirical continuous experiments in pilot scale and further simulations with the desorption model (Nordberg et al 2005; Nordberg et al., 2012). Based on the findings in this study, the cost of *in-situ* methane enrichment based on standard bubble column was estimated to be one third of the cost of conventional techniques for a raw gas flow < 100 Nm^3/h. The computer modeling tool was further developed by KTH and JTI with funding support from FUTURA and Göteborgs Energi by coupling a model describing the anaerobic digestion process with the desorption model. The simulation results show that very careful optimization of the conditions and variables are required in further work in order to reveal if a concentration of 95% methane in the digester gas and a loss no more than 2% is feasible.

1.3 Objectives and aims

The study consisted of two parts: one focused on optimizing the process operation and configuration using a computer based model and second focused on experimentally proving the principle and evaluating different approaches to accomplish *in-situ* methane enrichment.

The objectives of the first part of the study were to further develop the coupled anaerobic digestion and desorption model for simulation of important process parameters such as column dimensions and sludge- and air flow including an estimation on the energy requirement for aeration and sludge pumping

The objectives of the second part of the study were to design and produce a lab platform that could successfully be used to prove the principle of *in-situ* methane enrichment. Further on, with the lab platform evaluate three different techniques (i.e. air stripping, vacuum stripping with and without addition of organic acids) in order to find the most promising approach to achieve a high methane content in the biogas without too large losses of methane and inhibition of the process.

2 Experimental

2.1 Part 1. Optimization of key process parameters using computer simulations

2.1.1 Description of Models

The model is a combination of two separate models – a digester model and a desorption column model together describing an *in-situ* methane enrichment plant

(Figure 5). The digester model, ADM1 (Anaerobic Digestion Model no 1) (Batstone et al, 2002), is implemented in the programming language C. The desorption model was originally developed by Lindberg and Rasmuson (2007) and is written in Matlab. The desorption model has been further extended by Yu and Rasmuson (2008).

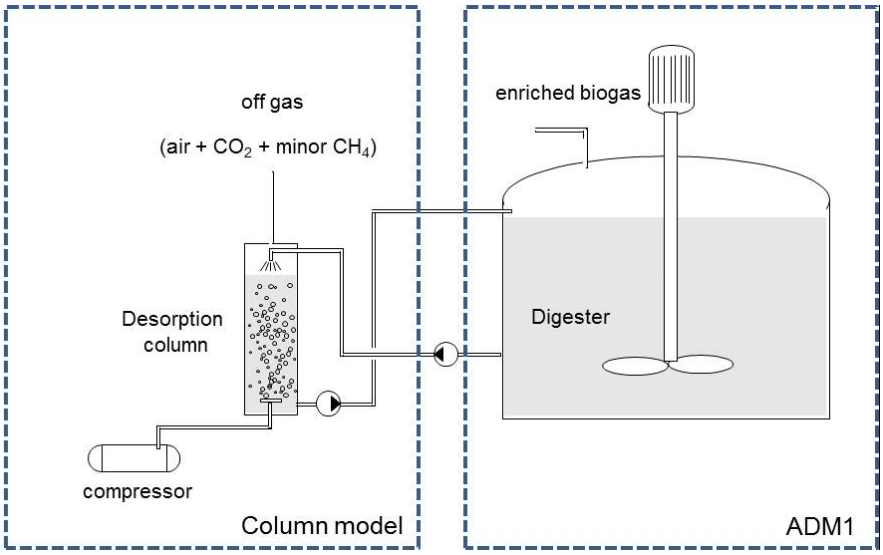

Figure 5: Schematic structure for combination of digester model and a desorption column model

2.1.2 Anaerobic digestion model no 1 (ADM 1)

The International Water Association (IWA) Task Group for Mathematical Modeling of Anaerobic Digestion Processes developed the Structured Anaerobic Digestion Model no.1 (ADM1) to describe the different process pathways in detail (Batstone et al., 2002). ADM1 describes digestion of particulate composites as a 5-stage process involving disintegration, hydrolysis, acidogenesis, acetogenesis and methanogenesis, of which the last three process steps are represented by growth kinetics of the specific degrading biomass (Figure 6). In the first step composite solids and cells of microorganisms are decomposed to their principal constituents including carbohydrates, proteins and fats. Additionally, inert particulate and soluble matter emerge which are not affected by the subsequent reactions. This process step is named disintegration and represents a characterization of the input substrate. Subsequently, the macromolecular products are subject to enzymatic degradation (hydrolysis) and transformed to monosaccharides, amino acids and long chain fatty acids (LCFA). Further anaerobic digestion leads from an acetogenic and a methanogenic phase to biogas production.
As mentioned, the model does not only produce a prediction of the methane but also several intermediates and end products. In this case the state variables carbon dioxide and ammonium in conjunction with a calculation of pH is of particular interest as input to the desorption model. To these, methane is added as input in order to calculate the loss of methane from the system.

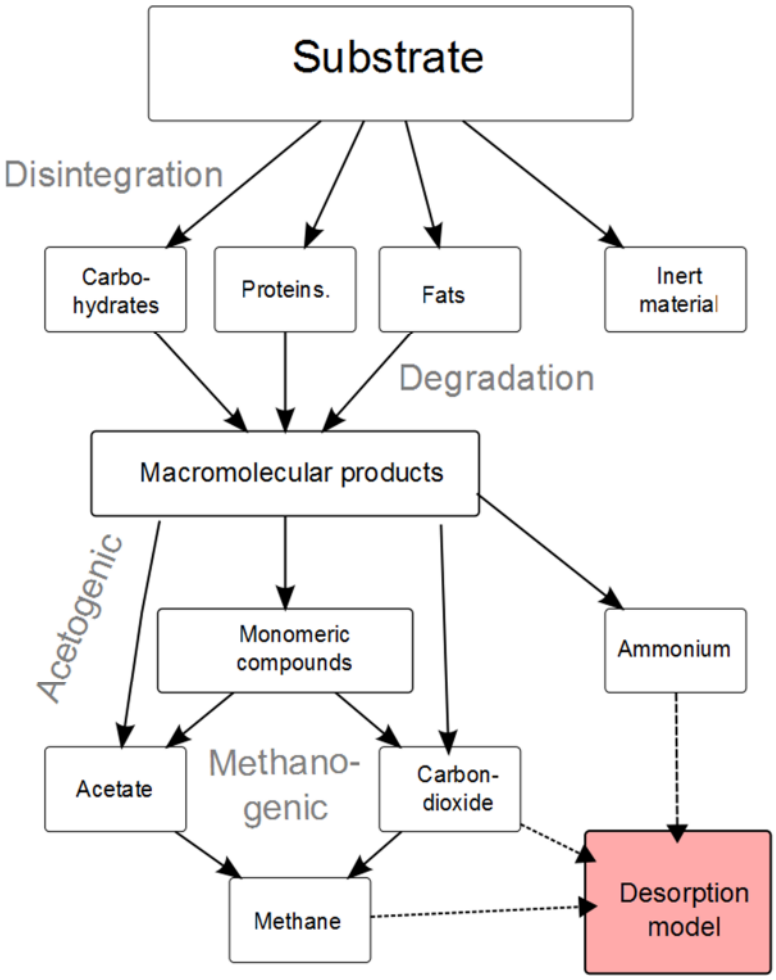

Figure 6: Schematic picture showing metabolic pathway of ADM1 and the three state variables exported to Desorption model (together with calculated pH). For the schematics of the dynamic model se Appendix 1.

2.1.3 The desorption model

The desorption model describes desorption of carbon dioxide and methane from anaerobic sludge in a bubble column operating at steady-state in the homogeneous flow regime. The version used in this work account for desorption of methane and carbon dioxide, but neglects the desorption of ammonia since the ammonia solubility is high and previous work has shown that this is a justified simplification. The liquid sludge phase and the gas phase are both described by the axial dispersion model and the contacting is counter current. The model accounts for that the concentrations vary along the column length both in the gas phase and in the liquid phase. The dispersion coefficients and concentration graphs over the column show that the back mixing is substantial especially in the liquid phase, i.e. a perfect plug flow model would not describe the process well. In the model, the dissociation reactions of carbonate and ammonium are included, while the reactions of phosphate, sulphide and volatile fatty acids are neglected since the concentrations of these compounds are very low. pK_a constants for carbonate and ammonium reactions are taken for mesophilic conditions (37 ^{o}C).

The model includes differential mass balances for carbon dioxide and methane in the sludge and in the gas phase, and for bicarbonate, pH and ammonium/ammonia in the liquid phase. In the code the column diameter *d* and height *L*, pressure p and temperature T, linear gas flow rate $\bar{u}_G$ and linear liquid flow rates u_L, and concentrations of species of interest in inlet liquid and gas streams can be selected. The two dispersion coefficients: E_G and E_L, the gas and liquid hold-up: ε_G and ε_L, and the mass transfer coefficients for methane and carbon dioxide on the liquid side, k_La, needs to be specified. No k_La-values or -correlations for this particular case are found in the literature and k_La may depend significantly on the liquid properties (Deckwer and Schumpe, 1993). For this reason the liquid side mass transfer coefficient for carbon dioxide has been determined by fitting the model to experimental results of Lindberg and Rasmuson, (2006). The mass transfer coefficient for methane is related to that of carbon dioxide via the diffusivities. The sum of the gas and the liquid hold-up of course equals unity.

2.1.4 Parameters

The desorption of methane is simple physical desorption and the equilibrium is described by Henry's law:

$$P_{CH_4} = He_{CH_4} c_{CH_4} \quad (1)$$

with He_{CH4} = 94,8 MPa/(kmoles/m^3). P here stands for partial pressure and c for concentration in the sludge. For carbon dioxide the Henry's constant is: He_{CO2} = 4.24 MPa/(kmoles/m^3). However, desorption of carbon dioxide from sewage sludge does not only incorporate physical desorption,

$$CO_2(dissolved) \rightarrow CO_2(gaseous) \quad (2)$$

but also chemical reaction producing carbon dioxide in the liquid phase:

$$HCO_3^- + H^+ \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} CO_2(dissolved) + H_2O$$

Defining the equilibrium constant as: $K_{a1} = \dfrac{[HCO_3^-][H^+]}{[CO_2(aq)]}$ (3)

Temperature dependence becomes:

$$\log K_{a1} = -3404.7/T + 14.843 - 0.03279 \cdot T \quad (4)$$

Where T stands for absolute temperature (K). The backward rate constant k_{-1} as defined in (3) (Danckwerts and Sharma, 1966):

$$\log k_{-1} = 329.850 - 110.541 \cdot \log T - 17265.4/T \quad (5)$$

Thus the expression for forward rate constant k_1 becomes:

$$\log k_1 = \log k_{-1} - \log K_{a1} = 315.007 - 110.541 \cdot \log T - 13860.7/T + 0.03279 \cdot T \quad (6)$$

For the ammonia/ammonium reaction:

$$NH_4^+ \underset{k_{-2}}{\overset{k_2}{\longleftrightarrow}} NH_3 + H^+ \quad (7)$$

The equilibrium constant equals $10^{-8.9}$, the backwards rate constant equals: $5*10^{10}$ s^{-1}. The forward rate constant is calculated as the product of the equilibrium constant and the backwards rate constant. The Henry's law constant is: 1673 Pa/(kmol/m^3) at 37 °C. Ammonia is very soluble and the desorption of ammonia is negligible at these conditions (Yu and Rasmuson, 2008).

The mass transfer coefficient, k_La, relation for desorption of carbon dioxide has been determined in previous work by fitting the model to experimental data (Lindberg and Rasmuson, 2006; Yu and Rasmuson, 2008). In the present work we use:

$$k_L a = 0.032 \cdot u_G^{1.27} \quad (8)$$

where the unit of the mass transfer coefficient k_La is 1/s, and u_G is linear gas flow rate in cm/s. The corresponding coefficient for methane is obtained from the carbon dioxide coefficient by diffusivity scaling. Dispersion coefficients and gas hold-up is calculated by relations presented in the literature (Lindberg, 2003).
In previous experimental work (Lindberg and Rasmuson, 2007), favorable desorption was obtained when the linear gas and linear sludge flow rates were: $u_G \in [0{,}25 - 2{,}2]$ cm/s and $u_L \in [0{,}3 - 0{,}8]$ cm/s. These conditions correspond to homogenous or bubbly flow, and hence we use (Hebrard et al, 1996):

$$\varepsilon_G = 4{,}0 \cdot u_G^{1{,}0} \quad (9)$$

which leads to a gas holdup ranging from 0,01 and 0,06.
In the present work, for the membrane sparger operating in the homogenous gas flow regime, we use for the liquid dispersion coefficient:

$$E_L = 0{,}43 g^{1/3} d^{4/3} u_G^{1/3} \left(\frac{e-1}{e} \right)^{1/3} \quad (10)$$

where E_L is in cm^2/s (Deckwer et al.1974) as was suggested by Hebrard et al. (1996) and is in good agreement with results of Joshi (1980). u_G is in cm/s and the column diameter*d* is in cm. For *e* the value of 1.07 is chosen as being a mean value of those of Hebrard et al (1996). G is the acceleration due to gravity
The gas phase axial dispersion coefficient is estimated by (Towell and Ackerman, 1972):

$$E_G = 0.2 d^2 u_G \quad (11)$$

The physical characteristics of sewage sludge are not very well documented and in addition they are expected to vary significantly over time and between different wastewater treatment plants. The following estimates have been used: diffusivity of CO_2 in sludge = 1.5×10^{-10} m^2/s; viscosity of sewage sludge = 10 cP and density of sewage sludge = 1050 kg/m^3 (partly using information from Holmström, 1981). The temperature of the sludge in the column is assumed to be 37°C.

2.1.5 Simulink modeling

The two models are combined by Simulink©, developed by The MathWorks. Simulink© is a commercial tool for modeling, simulating and analyzing multi domain dynamic systems. Its primary interface is a graphical block diagramming tool and a customizable set of block libraries. It offers tight integration with the rest of the MATLAB© environment and can either drive MATLAB© or be scripted from it. The construction of a model is simplified with click-and-drag mouse operations. Simulink includes a comprehensive block library of toolboxes for both linear and nonlinear analyses. Models are hierarchical, which allow using both top-down and bottom-up approaches. As Simulink is an integral part of MATLAB©, it is easy to

switch back and forth during the analysis process and thus, the user may take full advantage of features offered in both environments.

The combination of the column model and the ADM1 model is difficult due to the reason of time domains. The Column model is a steady-state model that iterates an output result from inputs without any time domain. ADM1 is a dynamic model that solves time dependent differential equations. The length of these time steps changes in response to the results of the differential equations. If the difference between the results of the time step is greater than a certain threshold the time step is shortened (otherwise it is increased).

When you combine these two models in Simulink it is easy to get into the situation where the results from the desorption model varies enough to trigger the step reduction at each step and thus steps through the model in the shortest step possible. As the desorption model takes about a minute (on a standard deskrtop computer) or two to iterate the results this will be a problem if the number of steps is in the range of five millions or so. In order to facilitate this problem the desorption model was given a fixed time step, meaning that the results from the desorption column is recalculated every 20 minute of model time. That has the effect that the desorption model delivers an input to the ADM1 model at a fixed interval without taking into account the magnitude of differences from an earlier step. Care has been taken to choose an interval long enough for the model to be reasonably fast, but short enough to avoid calculation oscillations and instabilities. The sludge from the digester reaching the desorption column is characterized by pH, and concentrations of carbon dioxide, methane, bicarbonate, and ammonium as calculated by the ADM1.The results from the Desorption model are then applied to the sludge recirculation back to the ADM1.

The results presented concerns steady state operation. However, to reach the steady-state the simulations are carried out in dynamic mode, i.e. starting from a digester running for itself, the sludge flow through the column is gradually increased to the desired level. Accordingly each simulation requires quite substantial computer time to reach the steady-state conditions. In total the models called *detailed* takes about a month to perform and most of the others between three days and a week.

2.1.6 Sensitivity analysis and Multivariate analysis

Multivariate data analysis (i.e. principal component analysis) was done using the Unscrambler® software package (CAMOA/S, Trondheim, Norway). Regressions of randomized parameters versus resulting model calculated CH_4 concentrations and CH_4 slip (Monte Carlo simulation) were done using partial least square regression (PLSR; Martens and Naes,1989).

When we perform a principal components analysis (PCA) on a multivariate data set we are interested in finding orthogonal components that explain maximal variance in the data set. In PLS, we in a similar way extract orthogonal components from a parameter set (X-matrix) that have maximal covariance with the response (Y-vector).

Partial least squares regression (PLSR) and principal component regression (PCR) are methods for prediction of scalar response variable Y from multivariate variables (X) where the basic idea in PLSR is to maximize the covariance between X and Y. The reason for use of PLSR is that an ordinary least squares (LS) problem becomes ill-posed due to many variables relative to few samples in the

modeling set and strongly collinear variables in Y. An important result of PLSR/PCR is also a compression of X into a few components. We also get scores (X) and loadings (Y) as part of the analysis and can draw a bi-plot of these scores. As all variables in the X matrix is normalized (using standard deviation and average) variables of vastly different scales and ranges can be compared in the same model.
We can then form the bi-plot and the locations of the sample points in the bi-plot are an approximation of the dependencies between the samples (X) and the results (Y). In this way complex interaction between parameters in the X matrix affecting Y can easily be displayed in a 2 dimensional graph. In this case it is used for two thing, identifying which X variables that affects Y variables and also which parameters affecting the sensitivity most i.e. is critical to have a correct value.

2.1.7 Previous modelling work

In previous work the combined model showed that a fairly good performance is obtained by a column having a volume of 5 % of the digester volume. However, the results suggest that reaching 90 % of methane in the digester headspace simultaneously as no more than 2 % total loss of methane will at least require very careful optimization of the conditions. Model simulations indicated that the mass transfer rate has a significant influence on the process, and may actually determine the success of *in-situ* methane enrichment. Unfortunately, the value of the mass transfer coefficient is quite uncertain and probably differs between substrates of different types. In short these point need to be taken in consideration.

- The mass transfer rate has a significant influence on the result. Faster mass transfer leads to overall more favorable results. Unfortunately the mass transfer coefficient is quite uncertain.
- For the base case mass transfer kinetics, it is not possible to reach the target of minimum 95 % methane in the headspace and less than 2 % methane loss. For the alternative mass transfer kinetics the outcome is clearly more favourable.
- In the range investigated, there is not a very strong influence of the column volume. However, this needs to be further investigated.
- It seems that a very tall column is not required, i.e. from an energy point of view it is favourable to widen the diameter rather than to increase the height as the energy of pumping against a higher water pillar do not result in an equivalent gain in methane value.

2.2 Part 2. Evaluation of different techniques for carbon dioxide removal

In second part of the study, the idea was to design and implement an experimental platform that allowed the evaluation of different techniques for carbon dioxide removal with an *in-situ* based procedure. This development and implementation was carried out during the period March to August 2012 followed by the experimental trials between September 2012 and January 2013. The objective was not to increase the methane content to a maximum level but rather to test the procedures on an equal basis and prove that the principle works. Therefore, to avoid a complicated lab setup and minimize technical and practical problems, as well as secure a standard for all treatment techniques, the procedures were always run manually in batch mode. Hence, the stripping process was only performed during the working hours and not throughout the nights or weekends. This will of course limit the potential of the technique significantly, however, it was deemed enough to prove the principle and make a comparison possible.

Table 1: Evaluated scenarios in the experimental part

Phase	Substrate	Treatment method	Digester
A1	Milk	None (Reference)	11.5 L
A2	Milk	Air	11.5 L
A3	Milk	Vacuum	11.5 L
B1	Milk + potato flour	Air	6.5 L
B2	Milk + orange juice	Vacuum	6.5 L
B3	Milk + orange juice	Vacuum + organic acids	6.5 L

The experiments were carried out by the classical approach with air stripping through a column, vacuum with and without the addition of organic acids to lower the pH and thus increase the driving force for desorption of carbon dioxide. The techniques were evaluated over a five month period divided into six phases presented in Table 1. In the first three (A1-A3), air stripping and vacuum treatment were compared against a reference using a nitrogen rich substrate. In the last three (B1-B3), air striping and vacuum treatment with and without additions of organic acids were evaluated using a substrate mixture with less nitrogen. For more details about the experimental design, please see section 2.2.4.

2.2.1 Experimental platform

One of the main objectives with the second part of the study was to develop and implement an experimental platform that would successfully allow the evaluation of the different carbon dioxide removal techniques. In this section the key components of this platform (i.e. digester, stripping column and hydrolysis reactor) are presented and in Figure 7 a photo showing the main part of the setup can be seen.

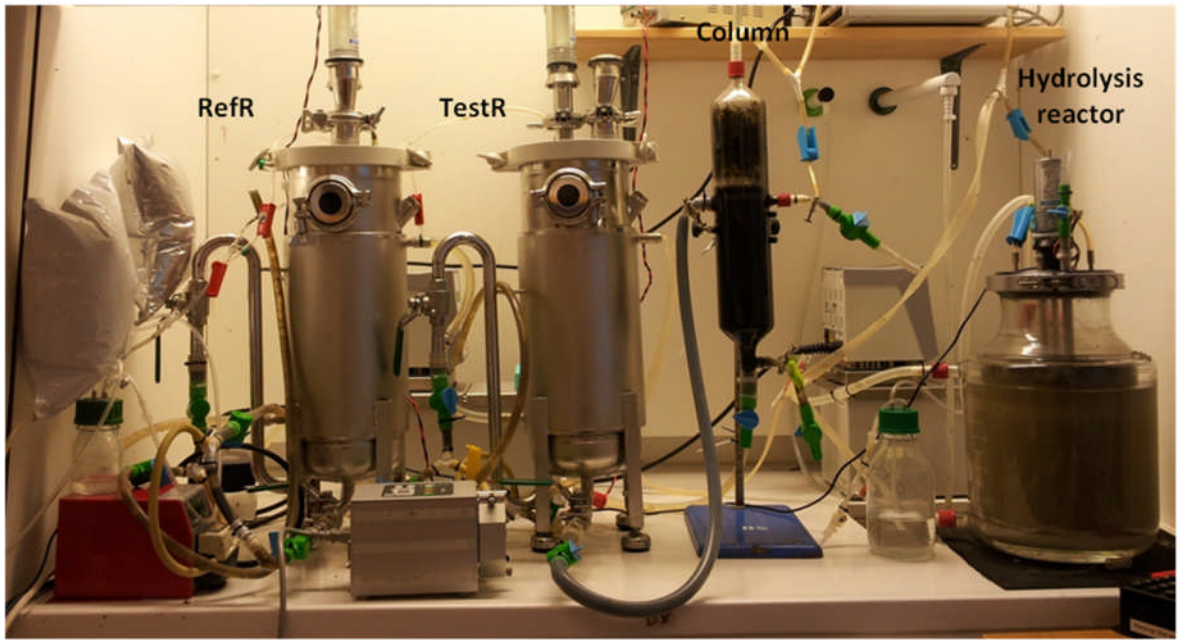

Figure 7: Photo of main part of the experimental setup during phase B3

Digester

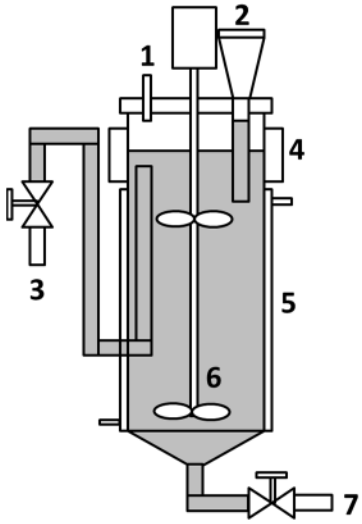

Figure 8: Drawing of digester used in the experimental platform with (1) gas outlet, (2) feeding funnel, (3) discharge outlet, (4) sight glass, (5) heating jacket, (6) mixer and (7) emptying outlet.

The digesters (Figure 8) were made of stainless steel with continuous mixing using a vertical mixer (6) with two impellers at different levels. For phases A1-A3 one reactor of 11.5 L was used whereas two reactors of 6.5 L were run in parallel during phases B1-B3. The heating was provided by a thermo water recirculation bath that pumped heated water through a jacket (5) surrounding the digester. Feeding was made through a submerged funnel (2) that also served as a liquid barrier for the sludge whereas the discharging took place from a tap (3) on the side that had its intake just below the liquid surface to minimize the risk of emptying the digester. The emptying was instead done using an outlet at the

bottom (7) with a larger diameter. The produced gas left the digester through an outlet at the top and two sight glasses (4) placed on opposite sides made it possible to see inside the digester.

Hydrolysis reactor

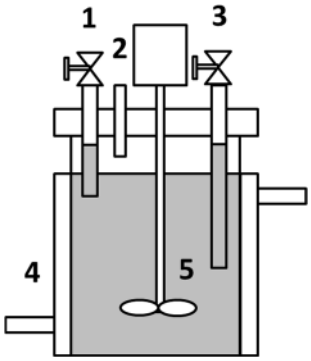

Figure 9: Drawing of hydrolysis reactor used in the experimental platform with (1) discharge outlet, (2) gas outlet, (3) feeding inlet, (4) heating jacket and (5) mixer.

The hydrolysis reactor (Figure 9) was made of glass and its content was continuously mixed using a vertical mixer with one impeller (5). As with the digester, heating was made with a temperature controlled pump that pumped heated water though a jacket (4) surrounding the reactor. The feeding (3) and discharging (1) were made from two in-/outlets at the top of the digester while the gas was collected from a third smaller outlet (2) next to them.

Stripping column

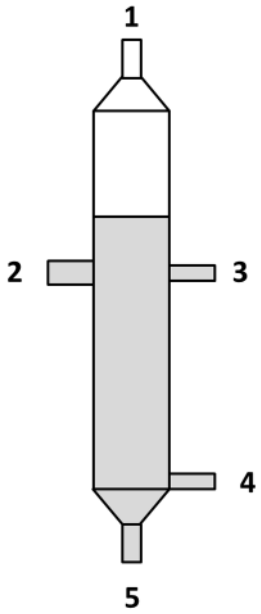

Figure 10: Drawing of column used in the experimental platform with (1) air outlet/ vacuum inlet, (2) sludge inlet, (3) organic acid inlet, (4) air inlet and (5) sludge outlet.

The column was made of glass with a total volume of 1.5 L and normal working volume of 1 L. The sludge was led into the column through an inlet in the middle (2) and led out through an outlet at the bottom (5). Additions of organic acids were

made through an inlet in the middle (3) of the column, on the opposite side of the one for sludge feeding. An inlet on the side at the bottom (4) was used to pump air through the column and an outlet at the top (1) served as exit for the air and inlet for the vacuum when that was applied.

2.2.2 Substrate

During phases A1-A3 cow milk (3% fat) was used as the only substrate. The reason for choosing a food product and not a waste material was to minimize the risk of having variations in the incoming feed. Cow milk was chosen as it is assumed to contain all the necessary nutrients for an anaerobic digestion to function properly. As an example, previous experience with running a continuous operation with only soy milk for half a year was problem free with a constant and even gas production. In Table 2, some key properties of the used substrates are given.

Table 2: Evaluated scenarios in practical test

Substrate	Carbohydrates [%]	Protein [%]	Fat [%]	VS[a] [%]	Theoretical methane yield[b] [NL/gVS]
Cow milk (3% fat)	4.8	3.4	3	11.2	0.60
Cow milk (1.5% fat)	4.9	3.5	1.5	9.9	0.53
Potato flour	79.0	0.1	0.1	79.2	0.42
Orange juice	9.0	0.7	0.3	10.0	0.43

a – VS is calculated as the sum of carbohydrates, protein and fat.
b – The theoretical methane yield is calculated with the energy values given in (*Angelidaki and Sanders, 2004)*

In Table 3, the substrate mixtures used in each phase are presented. Due to suspected problems with high contents of inorganic nitrogen and ammonia inhibition, the milk was diluted with water and supplemented with potato flour to increase the VS in phase B1. However, after experiencing problems with inconsistent properties of the hydrolysis reactor, this step was removed in phases B2 and B3 and an even mixture of milk and orange juice was directly fed to the system instead. The low pH (~4) of the orange juice was assumed to simulate acidic content of a hydrolysis reactor. However, as the orange juice contains large amounts sugars and other types of acids, some difference in effects were expected.

Table 3: Substrate mixtures used in each phase

Phase	Substrate 1	VS Fraction [%]	Substrate 2	VS Fraction [%]	VS [%]	Theoretical methane yield[b] [NL/gVS]
A1	Milk 3.0%	100	-	-	11.2	0.60
A2	Milk 3.0%	100	-	-	11.2	0.60
A3	Milk 3.0%	100	-	-	11.2	0.60
B1	Milk 1.5%	50	Potato flour	50	3.0	0.48
B2	Milk 1.5%	50	Orange juice	50	9.93	0.49
B3	Milk 1.5%	50	Orange juice	50	9.93	0.49

2.2.3 Anaerobic sludge

Two types of anaerobic sludge were used as the starting material. For phases A1-3 the digester was filled with sludge from a co-digestion plant outside of Kristianstad, Sweden. The plant treats a mixture of cow manure, household waste, industrial waste and slaughterhouse waste and has a sludge that is characterized by rather high VS contents (2-2.5%) and pH (7.8-7.9). During phases B1-B3, anaerobic sludge from a wastewater plant outside of Eslöv, Sweden was used instead. This plant mainly treats primary and secondary sludge from the wastewater treatment process together with some vegetable waste from the food industry. As with most sludge coming from wastewater treatment plants it is characterized by a lower VS (1-1.5%) and pH (7.3-7.4).

2.2.4 Experimental design

In order to evaluate the different procedures systematically, the project was divided into six different phases as described in Table 1. It should be noted that the original plan had to be changed on several occasions due to a number of technical challenges. Therefore, a summary of the implemented experiments and not necessarily the original plan is presented here. The first three phases (A1-A3) were performed with a nitrogen rich substrate in order to study the prospect of *in-situ* methane enrichment at high ammonia levels. The evaluated techniques were air stripping (A2) and vacuum (A3) that were compared against a reference (A1). In order to make a comparison under more normal conditions possible, a better carbon to nitrogen balanced substrate mixture was used during the last three phases (B1-B3). The evaluated techniques were air stripping (B1), vacuum with (B2) and without (B3) additions of organic acids. In this section a detailed description of each phase is given.

Between the A and B phases an experiment setup with liquid/solid separation was tested. However, due to a number of technical problems, the results from this period were not reportable and therefore not included in the report. The experimental setup and details about some of the problems is presented in Appendix II.

A1. Reference approach using a nitrogen rich substrate

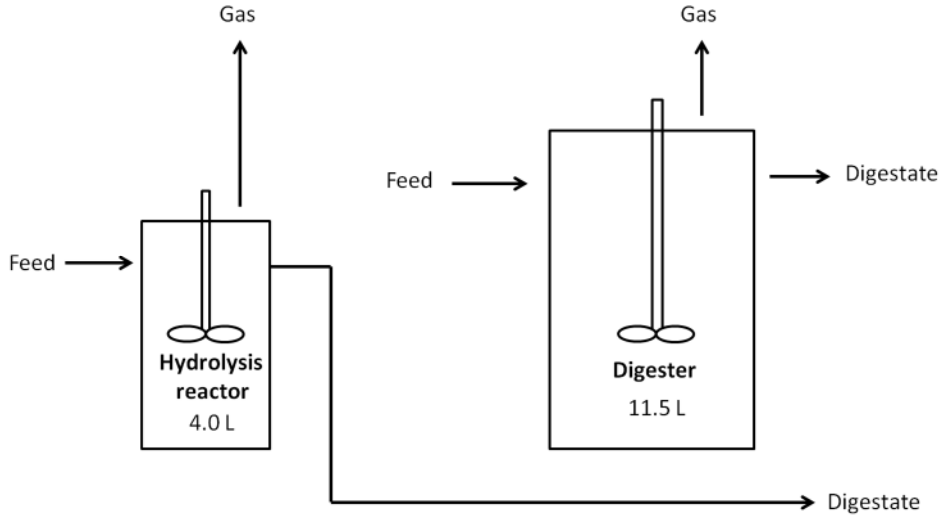

Figure 11: Process configuration in phase A1.

During A1, A2 and A3 one digester with an active volume of 11.5 L and a well-mixed hydrolysis reactor with an active volume of 4 L were used for the experimental part. The digester was operated as a normal continuously stirred tank reactor (CSTR) at 37 °C and fed with milk at an organic loading rate of approximately 2.5 g/L/day. The hydrolysis reactor was operated as a CSTR at 55 °C and fed with an organic loading rate of 10 g/L/day. At the end of the phase, the digester was fed from the hydrolysis reactor with a maintained organic loading rate. The objective of A1 was to establish a reference point/ baseline to compare with for the treatment methods in the other phases. A drawing of the setup is given in Figure 11 and in Table 4 the process operation details can be seen.

Table 4: Process operation parameters in phase A1

General	Substrate	Milk
	Anaerobic sludge	Co-digestion plant
	Reference in parallel	No
Digester	Organic loading rate	2.87gVS/L/day
	Hydraulic retention time	39.08 days
	Volume	11.5 L
	Fed from Hydrolysis	Yes
Hydrolysis reactor	Organic loading rate	10 gVS/L/day
	Hydraulic retention time	4 days
	Volume	4 L
Column	Treatment	None
	Retention time	2 days
	Air flow rate	-

A2. Air stripping using a nitrogen rich substrate

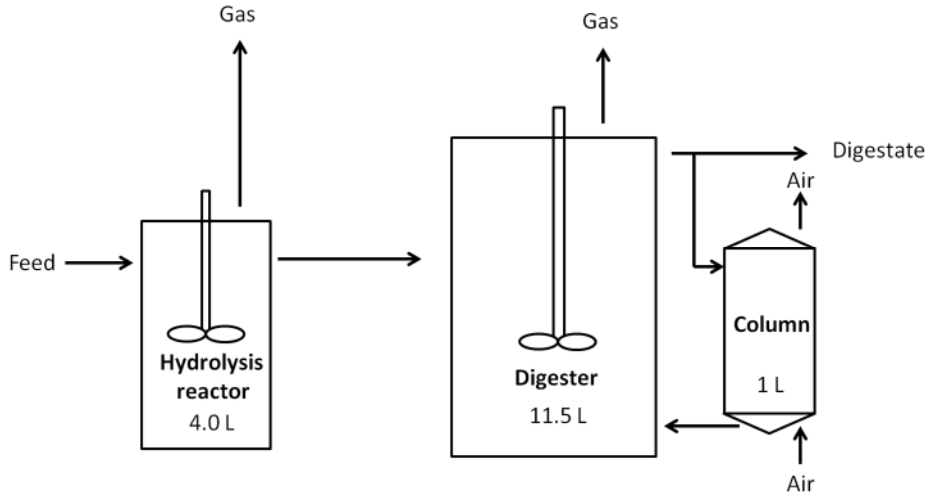

Figure 12: Process configuration in phase A2.

During A2 the aim was to increase the methane content by stripping carbon dioxide with air. For this purpose, a 1 L column was connected to the digester in which the sludge was recirculated batch wise. In the column the sludge came in contact with air which was pumped from the bottom with an approximate flow rate of 200 L/day. The duration of every batch was around 1 hour and the retention time with regard to the digester volume was roughly 2 days. The column was not heated, thus the stripping procedure was started at 37 °C but ended at ambient temperature (22-23 °C) as the sludge cooled down. Feeding was performed directly from the hydrolysis reactor which at this time was assumed to have reached a stable concentration. Except for the additional column, the digester and hydrolysis reactor were operated in the same way as during phase A1. In Figure 12, a simple drawing of the setup for A2 is shown and in Table 5 the process operation details is given.

Table 5: Process operation parameters in phase A2

General	Substrate	Milk
	Anaerobic sludge	Co-digestion plant
	Reference in parallel	No
Digester	Organic loading rate	2.47 gVS/L/day
	Hydraulic retention time	36.23 days
	Volume	11.5 L
	Fed from Hydrolysis	Yes
Hydrolysis reactor	Organic loading rate	10 gVS/L/day
	Hydraulic retention time	4 days
	Volume	4 L
Column	Treatment	Air
	Retention time	2 days
	Air flow rate	200 L/day

A3. Vacuum stripping using a nitrogen rich substrate

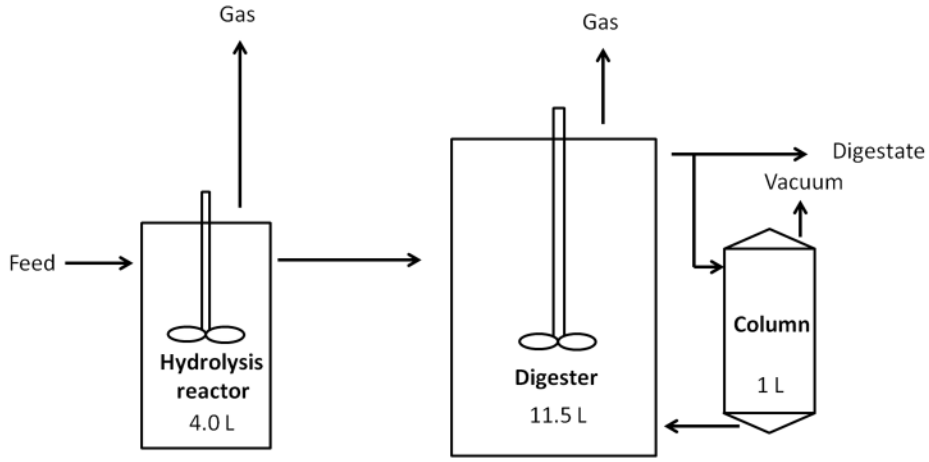

Figure 13: Process configuration in phase A3.

During A3 the aim was to increase the methane content by removing the dissolved carbon dioxide by applying vacuum to the external column (connected to the digester as described in section A2). The vacuum force was generated by a central vacuum pump and always applied at roughly 0.4 bar (~ 0.6 bar under pressure). Smaller pressures were not achievable as this led to leakage of air bubbles into the column. As in phase A2, the sludge was recirculated batch wise through the same column. A drawing of the setup can be seen in Figure 13 and in Table 6 the process operation details are given.

Table 6: Process operation parameters in phase A3

General	Substrate	Milk
	Anaerobic sludge	Co-digestion plant
	Reference in parallel	No
Digester	Organic loading rate	2.51 gVS/L/day
	Hydraulic retention time	36.40 days
	Volume	11.5 L
	Fed from Hydrolysis	Yes
Hydrolysis reactor	Organic loading rate	10 gVS/L/day
	Hydraulic retention time	4 days
	Volume	4 L
Column	Treatment	Vacuum
	Retention time	2 days
	Column pressure	0.4 bar

B1. Air stripping using a mixed substrate

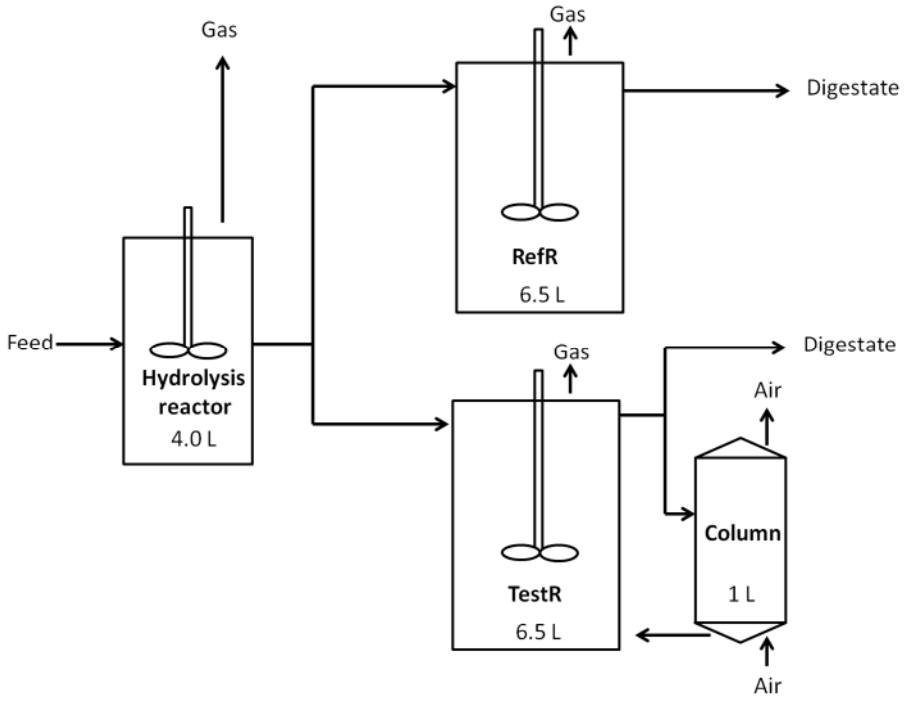

Figure 14: Process configuration in phase B1.

In phase B1 the feedstock was changed to a mixture of milk, water and potato flour in order to decrease the viscosity and reduce the nitrogen content of the substrate. This applied organic loading rate were 3 g/L/day with a hydraulic retention time of 10 days. Further on, two parallel digesters of 6.5 L were used instead of one to allow a real time reference. This setup was kept throughout B2 and B3 as well and in all these phases the reference is referred to as *RefR* and the one where the treatment method was applied *TestR*. Due to the smaller digester volumes, the retention time in the column was reduced to 1 day. Besides this, the process was run in the same way as in A2. In Figure 14 a drawing of the experimental setup used in phase B1 is shown and in Table 7 the process operation details are given.

Table 7: Process operation parameters in phase B1

General	Substrate	Milk + potato flour
	Anaerobic sludge	WWTP
	Reference in parallel	Yes
Digester	Organic loading rate	3
	Retention time	10 days
	Volume	6.5 L
	Fed from Hydrolysis	Yes
Hydrolysis reactor	Organic loading rate	10 gVS/L/day
	Retention time	1.2 days
	Volume	4 L
Column	Treatment	Air
	Retention time	1 day
	Air flow rate	200 L/day

B2. Vacuum stripping using a mixed substrate

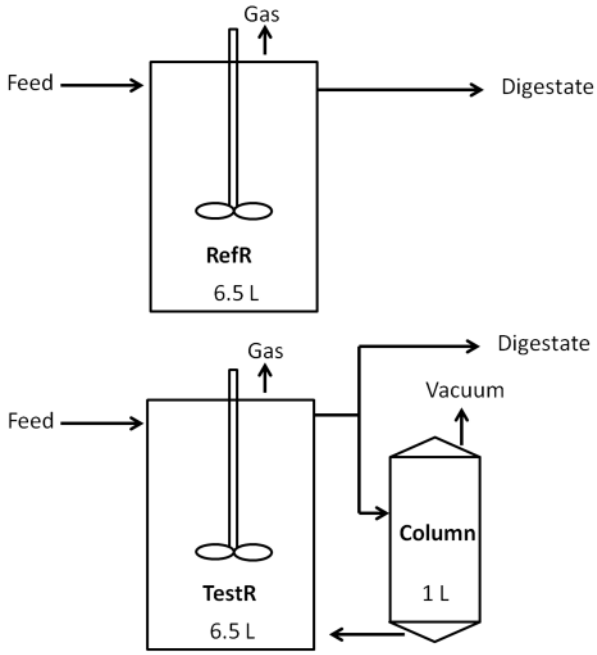

Figure 15: Process configuration in phase B2

In B2, vacuum was applied on the new setup with smaller digesters. Due to problems with irregular composition of the hydrolysis feed, the digesters were fed directly with a mixture of milk and orange juice instead. The duration, column pressure and retention time in the column was kept the same as in B1. In Figure 15 a schematic drawing of the experimental setup used in phase B2 is shown and in Table 8 the process operation details are given.

Table 8: Process operation parameters in phase B2

General	Substrate	Milk + Orange juice
	Anaerobic sludge	WWTP
	Reference in parallel	Yes
Digester	Organic loading rate	3.05
	Retention time	30.8
	Volume	6.5 L
	Fed from Hydrolysis	Yes
Hydrolysis reactor	Organic loading rate	-
	Retention time	-
	Volume	-
Column	Treatment	Vacuum
	Retention time	1 day
	Column pressure	0.4 bar

B3. Vacuum stripping with organic acid addition using a mixed substrate

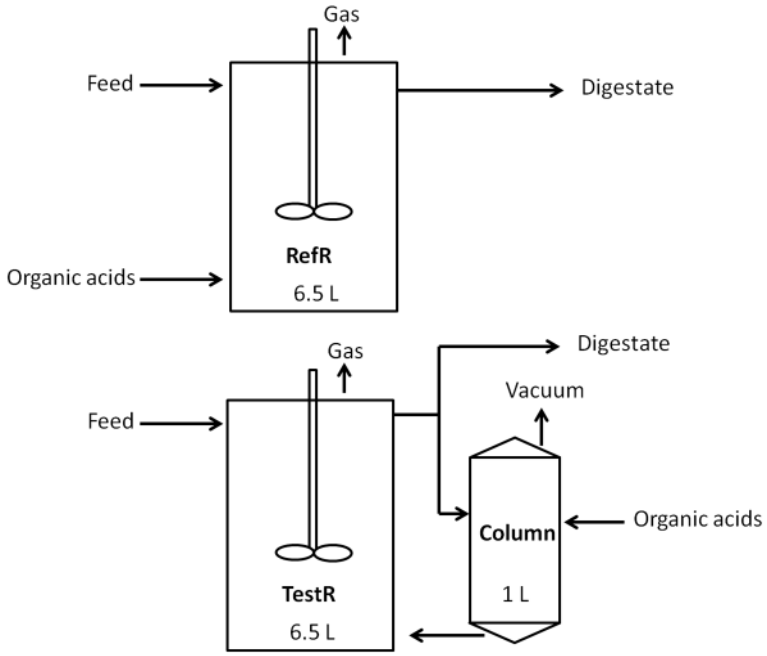

Figure 16. Process configuration in phase B3.

In B3, vacuum and additions of organic acids to lower the pH was applied. The orange juice was used as a source of organic acids and was added directly to the column with an evenly distributed dosage. In the operation of the column, vacuum was first applied for 30 minutes so that the sludge could cool down. The orange juice was then added and vacuum applied for an additional hour. The column pressure was kept at 0.4 bar during the vacuum procedure and retention time of the sludge was kept at 1 day as in phases B1 and B2. In Figure 16 a drawing of the experimental setup used in phase B3 is shown and in Table 9 the process operation details are given.

Table 9: Process operation parameters in phase B3

General	Substrate	Milk + Orange juice
	Anaerobic sludge	WWTP
	Reference in parallel	Yes
Digester	Organic loading rate	3.05
	Retention time	30.8
	Volume	6.5 L
	Fed from Hydrolysis	No
Hydrolysis reactor	Organic loading rate	-
	Retention time	-
	Volume	-
Column	Treatment	Vacuum + organic acid
	Retention time	1 day
	Column pressure	0.4 bar

2.2.5 Analysis equipment

Gas flow meter

The gas flow rate was monitored using the measurement device (Figure 17) from the BRS (BioReactor Simulator) from Bioprocess Control Sweden AB. The system consists of 6 parallel opening flow cells and monitors gas flow continuously using a technique based on liquid displacement and buoyancy with a measurement resolution of 10 ml. The measured flow is automatically normalized and presented at standard conditions with regard to temperature, pressure and water content. A cloud based software solution makes possible to store and handle the large amounts of data that is generated during a continuous test.

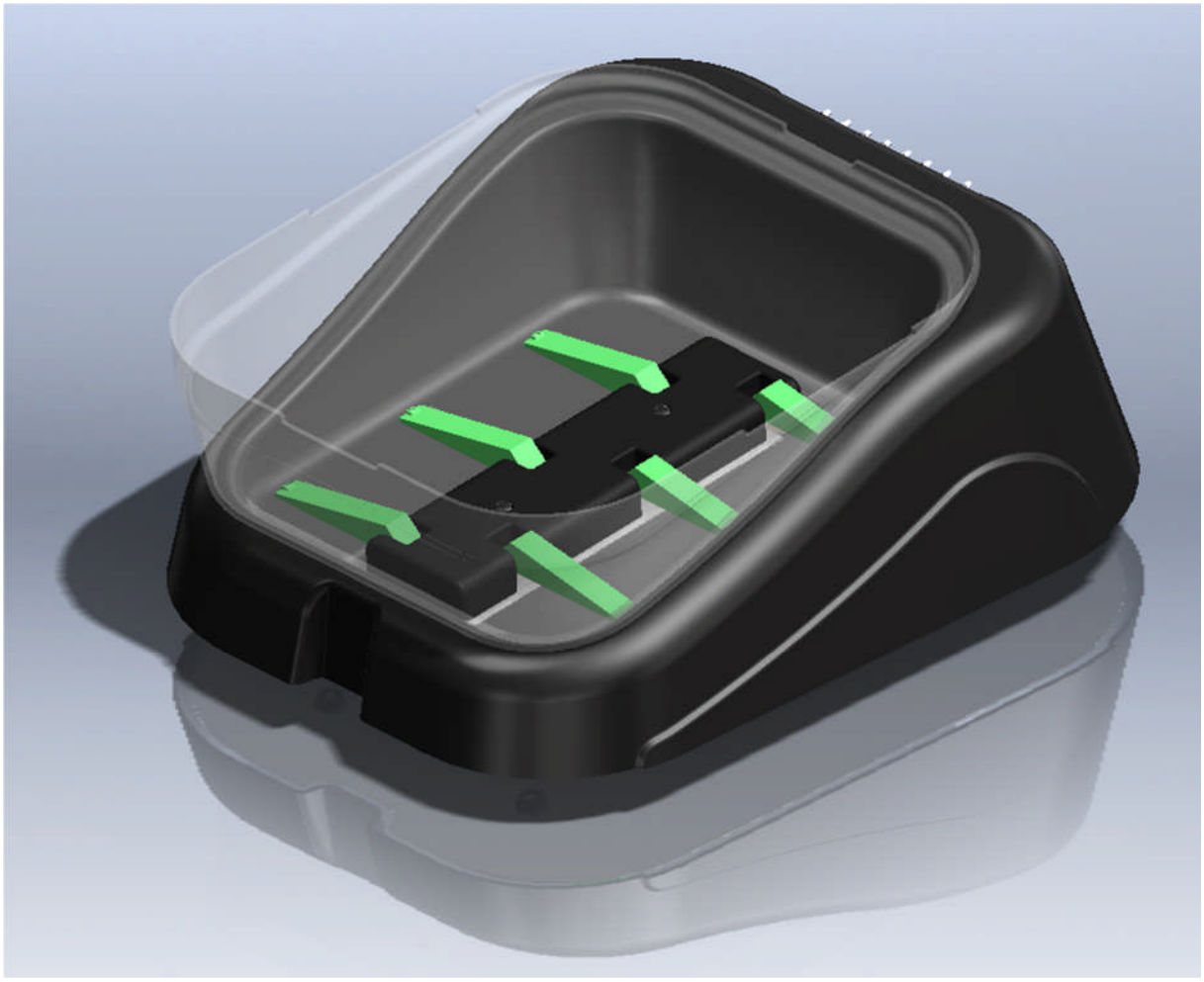

Figure 17: Measurement device for BioReactor Simulator (BRS)

Gas chromatograph (GC)

The gas composition was measured in two ways: a traditional approach with manual sampling using a conventional gas chromatograph (Clarus 400) and second approach that allows continuous monitoring with a small mobile gas GC (GCM-MB) which contains an automatic sampling system.

Clarus 400
All manual GC measurements were made on a Clarus 400 from Perkin Elmer. The GC was calibrated to analyze methane, carbon dioxide and air using helium as the carrier gas.

GCM-MB1
For continuous monitoring of the gas composition, a Gas Microbox GCM-MB1 from SLS Microtechnology GmBH (Figure 18) was used. This is a small scale mobile gas chromatograph that includes an automatic sampling device allowing continuous measurements which are then stored and analyzed on an external computer. In the current project the GCM-MB1 was calibrated to analyze the composition of methane, carbon dioxide and nitrogen with argon as carrier gas. During phases B1-B3 it was mainly connected to *TestR* where the carbon dioxide removal technique was performed.

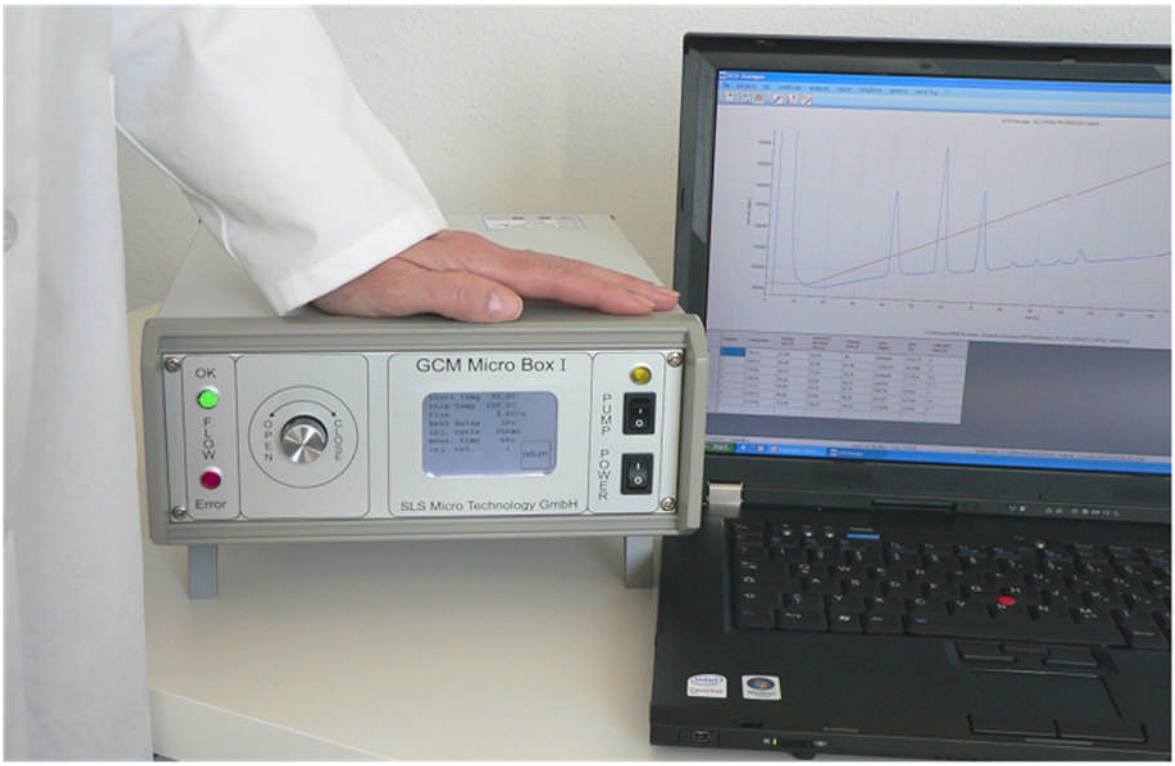

Figure 18: Product photo of the Gas Microbox GCM MB1

pH meter
pH was monitored manually using an Orion 4 star pH/Conductivity meter from Thermo Scientific.

Oven and moisture analyzer for TS and VS analysis
TS (Total Solids) and VS (Volatile Solids) were determined by the traditional gravimetric method of heating the sample at 105 °C for 20 hours and after that for 2 hours at 550 °C. A moisture analyzer (AnD ML-50) was also used in parallel in phase B3 for quicker results.

2.2.6 Process operation

Running the experimental setup presented in section 2.2.1 and 2.2.4 required substantial manual work. In this section a brief description of the different steps is given.

Feeding and discharging

The digesters were mainly fed one time per day in the morning. The applied amount of substrate was always weighed before added into the process. Before the feeding, the same amount of sludge was withdrawn in order to avoid that any substrate were removed. Gas bags were connected after the gas outlet in order to make the discharging possible and serve as gas storage for the continuous GC measurements.

Liquid sampling

Liquid samples of the sludge for measurements of pH and TS/VS were taken on regular intervals using the discharge outlet (point 3 in Figure 8). In order to make sure that representative samples were taken, 200 ml of sludge was always withdrawn and return to the digester before the actual sampling process.

Gas sampling

Gas sampling was carried out through air tight sampling ports placed after the gas bag with 1 ml syringes. Samples were taken with different frequencies throughout the project with one sample per day, just before feeding the digester, during A1-A3, three samples or more during B1-B2 and finally five samples or more during B3.

Column operation

The column was mainly operated manually in batch mode. Below follows a short description of this operation:

1. The content was emptied and pH was measured.
2. The column was filled up with 1 L of fresh sludge from the digester and pH was measured.
3. Air stripping or vacuum was applied.
4. The air stripping or vacuum was stopped after 1 hour and the procedure started over from point 1.

During phase B3 with the addition of organic acids the following extra steps were done:

5. Vacuum was stopped abort after half an hour and the organic acids were added. A pH measurement was taken before and after adding the organic acids. The vacuum was then resumed.
6. The treatment was stopped after 1 hour and the procedure started over from point 1.

2.2.7 Process parameters

A number of different process parameters were calculated in order to evaluate the performance of the digesters. In this section, the equations behind them are presented.

Organic loading rate
The organic loading rate was calculated according to Equation 11 where OLR is the organic loading rate, F is the in and out flow to the digester, C_S is the substrate concentration and V_R is the active reactor volume.

$$OLR = \frac{F \times C_S}{V_R} \quad (11)$$

Hydraulic retention time
The hydraulic retention time was calculated according to Equation 12 where HRT is the hydraulic retention time, V_R is the active reactor volume and F is the in and out flow to the digester.

$$HRT = \frac{V_R}{F} \quad (12)$$

Specific gas production
The specific gas production was calculated according to Equation 13 where SGP is the specific gas production, G is the total gas flow and V_R is the active reactor volume.

$$SGP = \frac{G}{V_R} \quad (13)$$

Specific methane production
The specific methane production was calculated according to Equation14 where SMP is the specific methane production, G is the total gas flow, X_{CH_4} is the average methane content of the gas and V_R is the active reactor volume.

$$SMP = \frac{G \times X_{CH_4}}{V_R} \quad (14)$$

Specific gas yield
The specific gas yield was calculated according to Equation 15 where SGY is the specific gas yield, G is the total gas flow, F is the in and out flow to the digester and C_S is the substrate concentration.

$$SGY = \frac{G}{F \times C_S} \quad (15)$$

Specific methane yield
The specific methane yield where calculated according to Equation 16 where SMY is the specific gas yield, G is the total gas flow, X_{CH_4} is the average methane content of the gas, F is the in and out flow to the digester and C_S is the substrate concentration.

$$SMY = \frac{G \times X_{CH_4}}{F \times C_S} \quad (16)$$

2.2.8 Data handling

Due to the cyclic behavior of many of the monitored parameters, special consideration had to be given to present representative values. As an example, values over the weekend when no feedings were made had to be disregarded since they did not represent the organic loading that was used for the rest of the week. The same consideration had to be given to parameters that were measured manually on a daily basis. Many of the monitored parameters were highly dependent of the feeding and since no manual measurements were taken during the night, the data only represents the values around the feeding point. Therefore, it can only be compared with other data points from the same time of the day. Thus, the reported values from pH, GC (Clarus 400) measurements and TS/VS may not represent the correct average over the whole period. However, as the measurements were the same time of the day they could be used for comparison purposes.

The reported data from the GCM-MB1 were correlated with the data from the conventional Clarus 400 to make sure that similar and presumably accurate results were given. Since GCM-MB1 consumed a substantial amount for each sample as well as during operation this was compensated in the reported gas flow.

In order to make calculations with each compound possible, the raw data from GCM-MB1 was piecewise interpolated using the function *pchip* in Matlab to produce a value for each hour. This was deemed reasonable since the GCM-MB1 sampled almost every hour which makes the effect from the interpolation minimal. The interpolations yielded data series based on the same time vector, making mathematical operations possible. Below follows a short description of the three different gas compositions values that are presented in the second part of this report.

Gas composition (Gas flows)

These values were based on the measurements of the GCM-MB1 and the measured flow rate and were calculated as the fraction of all produced methane, carbon dioxide or nitrogen divided by the sum of all produced gas. Since this method is based on the total volumetric relationship and not an average of concentrations, these values were assumed to be more accurate and were therefore used for the calculations of the process parameters. However, since these values were calculated as the fraction of two sums, a standard deviation could not be calculated and thus does not provide any information of the how the gas composition differed from day to day.

Gas composition (GCM-MB1)

These values were calculated as the average of the daily average of the measured gas composition by GCM-MB1. Thus, these values did not consider changes in the flow rate which could have led to an error in the reported values if the flow fluctuated substantially. However, it offered a good opportunity to study the daily stability of the methane content since a standard deviation easily could be calculated.

Gas composition (Clarus 400)
These values were calculated as the average of the daily average of the measured gas compositions by Clarus 400 and were considered to be more accurate than the measurements from GCM-MB1. However, since these measurements were only sampled during the working hours, they may not represent the gas composition with regard to all 24 hours of the day. Therefore these values were mainly used to compare the different

3 Results and discussion

3.1 Part 1. Optimization of key process parameters using computer simulations

3.1.1 Start-up of work

The ADM1 model – Column model connection was not fully implemented in the previous project and the model needed streamlining and optimising as the simulations demanded a large number of iterations. The model was continuously improved during the project in the end of the project the simulations runs about three times faster than at the start. This is both due to improved computer code and better knowledge of the interactions between the column and ADM1 and thus finding steady state faster (see Figure 19)

In April the work started with finalising the model constructed in the earlier project. This work can be divided in two parts; the first was to actually connect the Desorption model to the dynamic recirculation flow in the ADM1 model, and not just using ADM1 for creating input into the Desorption model. The second part was to optimise the working of the model in general in order to speed up the simulation process. The first part was of this proved to be of a greater obstacle than expected and some unsatisfactory compromises had to be accepted.

In parallel with these two major tasks also the simulated substrate was further adjusted to be as close to as possible the WWTP sludge analysed in the earlier project.

In May the simulation started with several screening simulations. They were based on 3 to 5 different levels of air and sludge flows respectively, in order to find suitable limits for the air and sludge flows to be used, as well as to decide what volumes to use for the Desorption column.

The detailed simulations were done at several different volumes and as much as ten airflows and ten sludge flows. Each detailed simulation took between two and three weeks and thus a set of computers running in parallel was necessary. The code and processing time was continuously improved during this work.

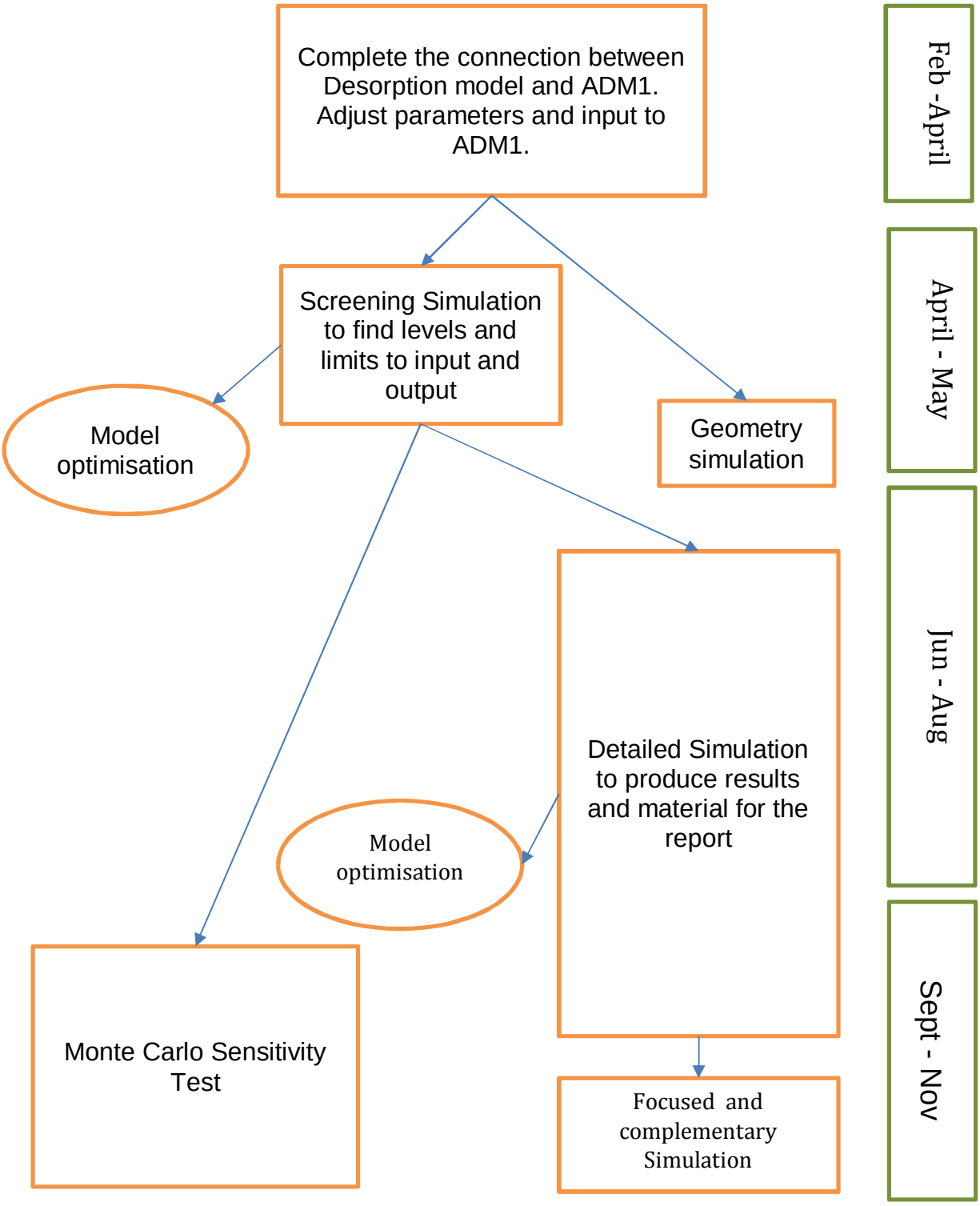

Figure 19: Schematics of the work path of the project.

3.1.2 General simulation structure

The simulations have been done for an active digester volume of 2000 m^3 and a headspace volume of 500 m^3 operated on municipal sewage sludge with a hydraulic retention time (HRT) of 30 days and an organic loading rate (OLR) of 1.5 kg COD/m^3/d (Table 10).

Table 10: Baseline operation parameters (no desorption column connected).

Operation parameter	Baseline value
Active Volume	2000 m^3
Headspace Volume	500 m^3
HRT	30 days
OLR	1,5 kg COD/m^3/d
Specific Biogas production	0.9 $m^3/m^3_{reactor}$/d.
Methane concentration	58 %

After start up of ADM1, the simulated pH oscillated during the first five days. This was due to common simulation model (mathematical) start up behaviour and modelled effects from differences between inoculum and substrate (Figure 20). Thereafter, the pH was stabilised at 7.2. The connection of ADM1 to the desorption column model at day seven resulted in an increase in the pH, which stabilised at pH 7.45. Thus, the introduction of the desorption column had a positive effect on the process by stabilising the pH at a higher level. The extent of this positive effect has not been investigated further in this work.

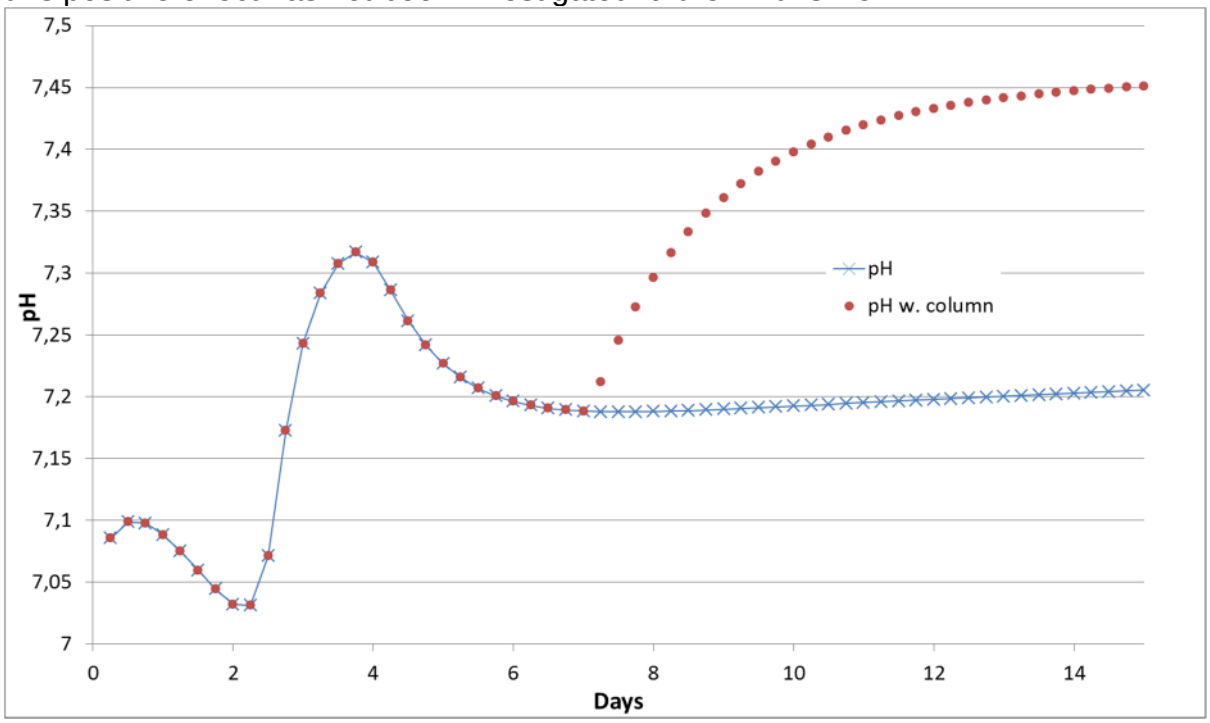

Figure 20: Example of simulated pH in sludge from ADM1, connected to desorption column at day 7 (red dots). The blue line shows the pH without connection to the desorption column. The oscillation of the curve of day 0 to 5 stems from two sources; common simulation model (mathematical) start up behaviour, and modeled effects from differences between inoculum and substrate.

3.1.3 Detailed mapping of the effects of air flow and sludge flow

Several screening simulations were done using three different column volumes, 1, 5, and 10% of reactor volume. From this material we have chosen to present the results of the 5% volume column simulations for two different dimensions of the column.

The parameters used for the first simulation of a ten by ten matrix at different levels of sludge and air flows and a column height of 4.0 m and column diameter

of 5.6 m are presented in Table 11 The results on methane concentration in the digester and the methane slip from the column are presented in Figure 21.

Table 11: The main parameters for the first simulation matrix (Figure 6).

Parameter	Values	Notes
Column Volume	5% (100 m^3)	Of reactor volume
Sludge flow	100-2400 m^3/day	Through column
Air flow	100-11000 m^3/day	Through column
Initial methane conc.	58%	Without column
Column Height	4 m	
Column diameter	5.6 m	

In general, the simulation shows that the combination of a high sludge and air flow will increase the methane concentration in the digester headspace (Figure 21 a). A sludge flow of >2 200 m^3/d and an air flow of >10 000 m^3/d is needed to achieve >80 % methane concentration in the headspace. However, an increased sludge and air flow will also increase the methane loss in the column (Figure 21 b). At 80 % methane concentration in the headspace, the methane loss will be 5-6 %. If the methane loss should be limited to 2-3 %, the methane concentration in the digester headspace can reach 70-75 % at a sludge flow of 1 000 m^3/d and an air flow of 10 000 m^3/d. Thus, the simulations indicate that a combination of low sludge flow and high air flow will increase the selective desorption of carbon dioxide, i.e. the ratio between carbon dioxide and methane desorption.
In the second simulation, the geometrical configuration of the column was changed to 6 m height and 4.6 m diameter, thus an increase in the height to diameter ratio, but still maintaining the same volume as in the first simulation (Table 3). The methane concentration in the head space of the digester did not change compared to the results presented in Figure 21 a. However, the results showed that the methane loss slightly decreased due to the change in column shape (Figure 22). This indicates that the selective desorption of carbon dioxide is facilitated by a higher height to diameter ratio of the column.

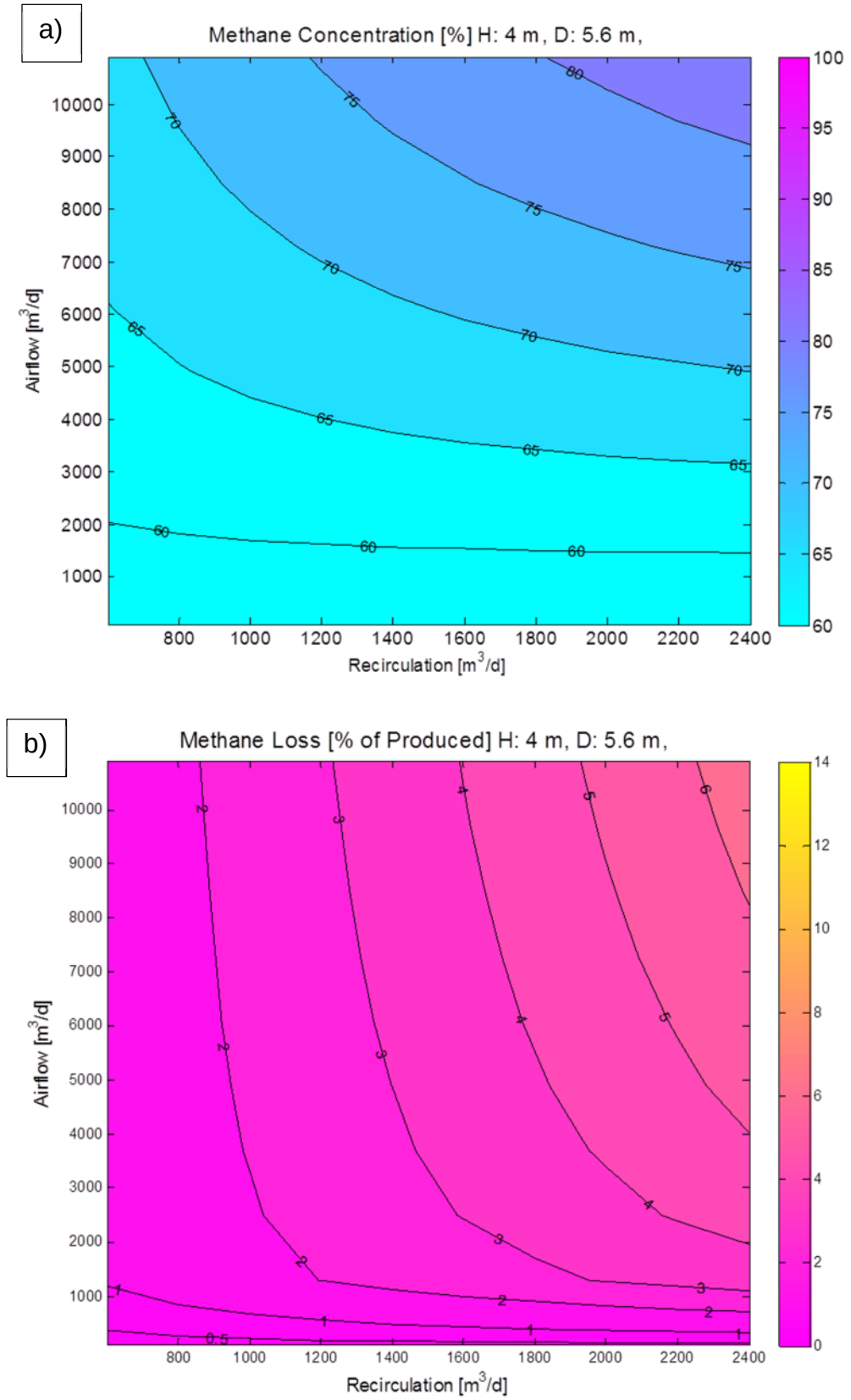

Figure 21: The effects of different sludge- and airflows for a column geometry of 4.0 m height and 5.6 m diameter a) the methane concentration in the headspace of the biogas reactor and b) the methane slip from the desorption column.

Table 12: The parameters used for the second simulation matrix.

Parameter	Values	Notes
Column Volume	5% (100 m^3)	Of reactor volume
Sludge flow	100-2400 m^3/day	Through column
Air flow	100-11000 m^3/day	Through column
Methane conc.	58%	Without column
Column Height	6 m	
Column Diameter	4.6 m	

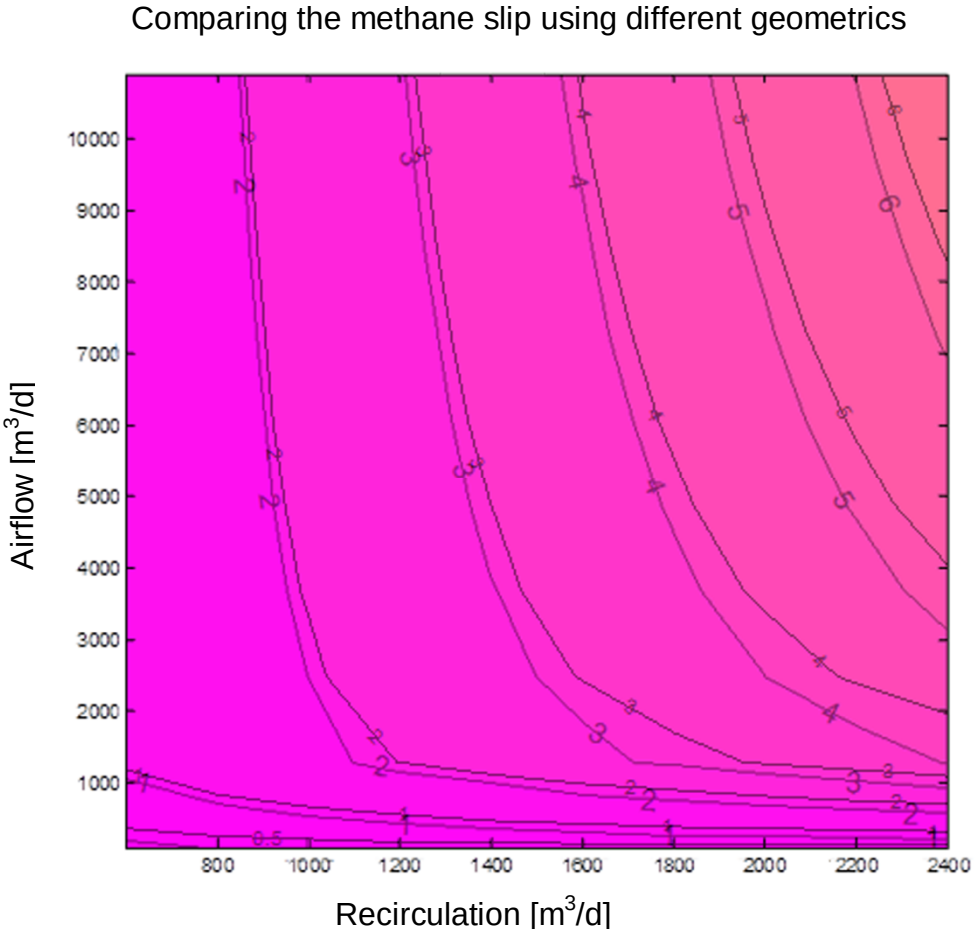

Figure 22: Comparison of the methane slip for two different column geometrics. The isolines shift from right to left when the column has a higher height to diameter ratio (from small numbered lines to large numbered lines). The methane concentration was the same as in Figure 21 a.

3.1.4 Geometric dependencies simulation

In the next part of the simulation work we took a different approach of what parameters to use as base vectors (Table 13). A fixed value of air- and sludge flow was used which in the previous simulation generated around 2% methane slip for a 5% column volume with a height of 6m. The column geometry was instead freely varied between 1 to 7 meters in both height and diameter (and thus in volume).

This was made in order to study how the methane slip and the methane concentration was affected by the geometry and to find the limits for the geometry of the desorption column (Figure 23).

Table 13: The parameters used for the geometric effect analysis of the column model.

Parameter	Values	Notes
Column Volume	0.03 – 13 %	Of reactor volume
Column Diameter	1 to 7 m	
Column Height	1 to 7 m	
Sludge flow	1000 m^3/day	Through column
Air flow	8000 m^3/day	Through column

The ranges of methane concentration (66-73 %) and of methane loss (2.05-2.40 %) are rather small at the set sludge- and air flow. At column heights below 2 m, the methane concentration in the head space of the digester is not much affected by the diameter (or total volume). However, at column heights over 5 m, there is an indication that a decrease in the diameter will increase the methane concentration and shrinking the methane loss. This is probably a result of a higher linear air flow in columns with a smaller diameter.

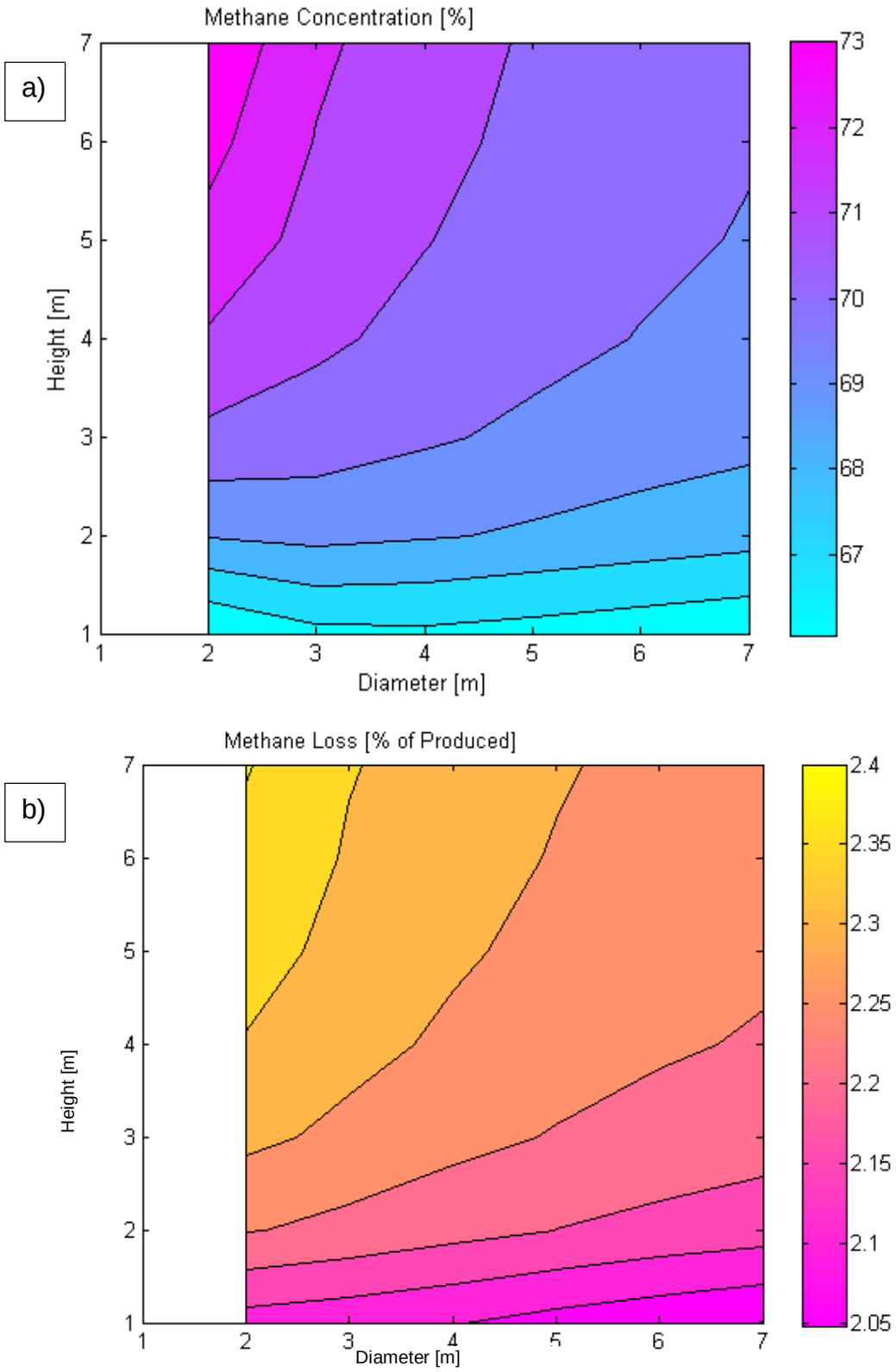

Figure 23: The methane concentration in the headspace a) and the methane slip b) dependence of the geometry of the desorption column. The white are to the left in the figure is where which the airflow is higher than threshold for the desorption model.

3.1.5 Sensitivity test using multivariate methods

The different parameters (X-variables) and variances for the desorption column used in the Monte Carlo simulations are presented in Table 14. The variance of the chemical parameters (i.e. coefficients and constants) was ± 50 %, while the variance of the operational parameters (sludge and air flow) was ± 80 %. There was a considerable problem to vary the dimensional parameters (i.e. column volume and height) in the same range as the other parameters. The reason for this was not further investigated but probably stems from the fact that some configurations that was generated created to high linear airflows in the column, so the random range factor was set much lower (± 5 %) for column volume and height. The actual range for the operational- and dimensional parameters differs to some extent from the chosen variance range as the Monte Carlo method randomly selects values within the specified range. Thus some parts of the range may become unused (Table 15).
The results from the Monte Carlo simulation are presented as a two biplots from the PLSR created, including both the X- and Y-variables (Figure 24 and 25).
The PLSR of the chemical parameters is shown in Figure 24.The explained X-variance were both 11 %, while the explained Y-variance was 33 % for PC1 and not significant (2 %) for PC 2. Thus, the effect of the chemical parameters on the methane concentration and the methane slip is very limited.
The explained X-variance for PC 1 and PC 2 in Figure 25 (including also the dimensional and operational parameters) were both 11 %, while the explained Y-variance was 80 % and 4 % for PC 1 and PC 2, respectively. Thus, the majority of the variance is not affecting the model. However, the PLSR of the Monte Carlo sensitivity test still shows several interesting results. The variables marked with red are the target (Y) variables and the other variables (X) seen in the graph is varied randomly. The four variables underlined are those who affect the target variables the most, and are thus critical for the result of the model. The equilibrium constant of bicarbonate to carbon dioxide reaction and Henrys law constant of carbon dioxide are the two parameters that are most important to have a correct value of in this type of non-ideal environment. However, in comparison with the effect of airflow and sludge flow their effects are secondary. Another observation is that the desorption column design (Volume, Height, and Diameter) have a much lower effect on the result than expected.

The resulting relative standard deviation of the target parameters was 36% for methane Slip and 11% for methane concentration (Table 16). The much lower value for the methane concentration could stem from the fact that the area chosen for the simulation was in a high methane concentration area. But it also indicates that Methane slip is more sensitive for changes in parameters.
In Figure 25, both the relative information content of the different axis and the effects of co-variation of variables (i.e. methane concentration and methane slip) have to be taken into account. Thus, the distance along the x-axis is more important than the distance along the y-axis due to the high explained variance in PC 1 compared to PC 2. Therefore, the location of EqC Bicarb indicates that it is similar in importance to Henry CO2 but with opposite sign.
However, the variables marked with green indicate that there are some parameters that can be studied or manipulated in order to separate the methane

slip and methane concentration. The most interesting feature is perhaps the height –diameter relation. However, as the information weight of the PC2 is low, this has to be studied further. The relative high value of Height in the PC2 axis supports the observation demonstrated in Figure 22.

Table 14: A collation of the chosen variances for the Monte Carlo simulation and the estimated importance (see Figure 24).

Parameter [units]	Name in Graph	Value	Set Monte Car-lo Variance	Importance
Coefficient for k_La	Coeff kLa	0.32	±50%	Low
Exponent for k_La	Exp kLa	1.27		Low
Coefficient for gas hold-up ε_G	Coeff Gas Hold	4.0		Low
coefficient for gas phase dispersion E_G	Coeff Gas Disp	0.2		Low
Coefficient for liquid phase dispersion E_L	Coeff Liq Disp	0.43		None
Henry's law constant of CO_2 [Pa/(kmol/m^3)]	Henry CO2	4.24×10^6		Moderate
Henry's law constant of CH_4 [Pa/(kmol/m^3)]	Henry CH4	9.48×10^7		Low
Equilibrium constant for $HCO_3^- \leftrightarrow CO_2$,	EqC Bicarb	$10^{-6.305}$		Moderate
Rate constant $HCO_3^- \rightarrow CO_2$ [kmol/m^3/s]	Rate Bicarb	1.15×10^5		Low
Equilibrium constant for $NH_3 \leftrightarrow NH_4^+$	Eq Ammonia	$10^{-8.9}$		Low
Column Volume [m^3]	Volume	100	±5%	Low
Column Height [m]	Height	4		Low
Sludge flow [m^3/day]	Sludge flow	2000	±80%	High
Air flow [m^3/day]	Air flow	10000		High

Table 15: Actual Range of model parameters for the sensitivity test.

Parameter	Actual Values	Notes
Column Volume	95 – 105 m^3	
Column Height	3.9 – 4.1 m	
Column Diameter	3.8 – 4.2 m	
Sludge flow	430-4300 m^3/day	Through column
Air flow	2000 - 20000 m^3/day	Through column

Table 16: Results from the Monte Carlo Sensitivity test. The relative standard deviation of the methane slip is three times larger than the standard deviation of the methane concentration.

	Average	Range	Realtive stddev
Methane Concentration	88 %	57-98%	11 %
MethaneSlip	13 %	1-20 %	36 %

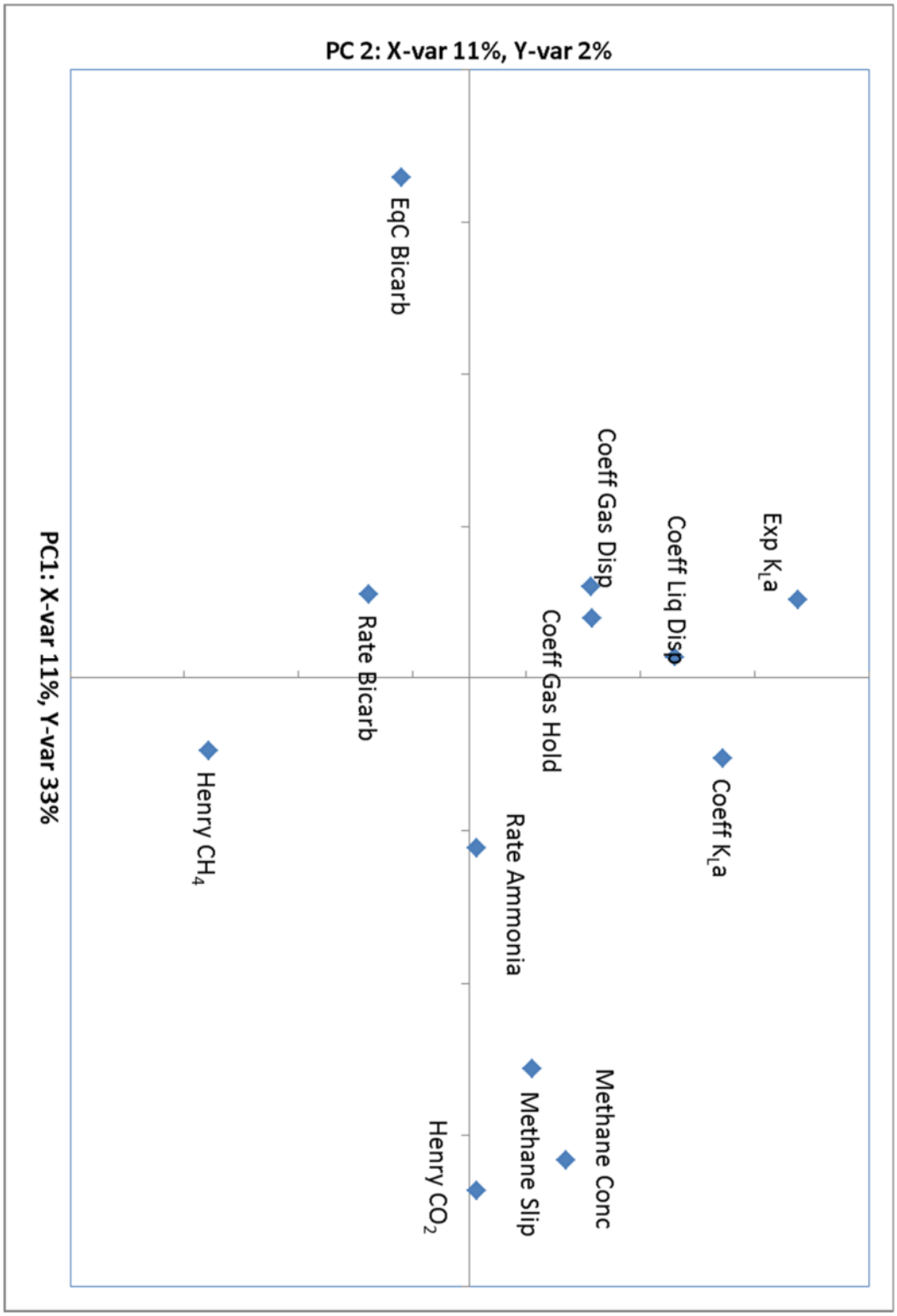

Figure 24: PLRS of chemical parameters. Observe that the Y varaiable explained in PC2 is non-significant and thus the placement in that direction is more or less irrelevant. Also the low total X-var explanied in relation to the Y-var suggests that the Monte Carlo variation only effects the output in a limited amount ie the model is stable and an small error in the parameters value will not have great effect on the result.

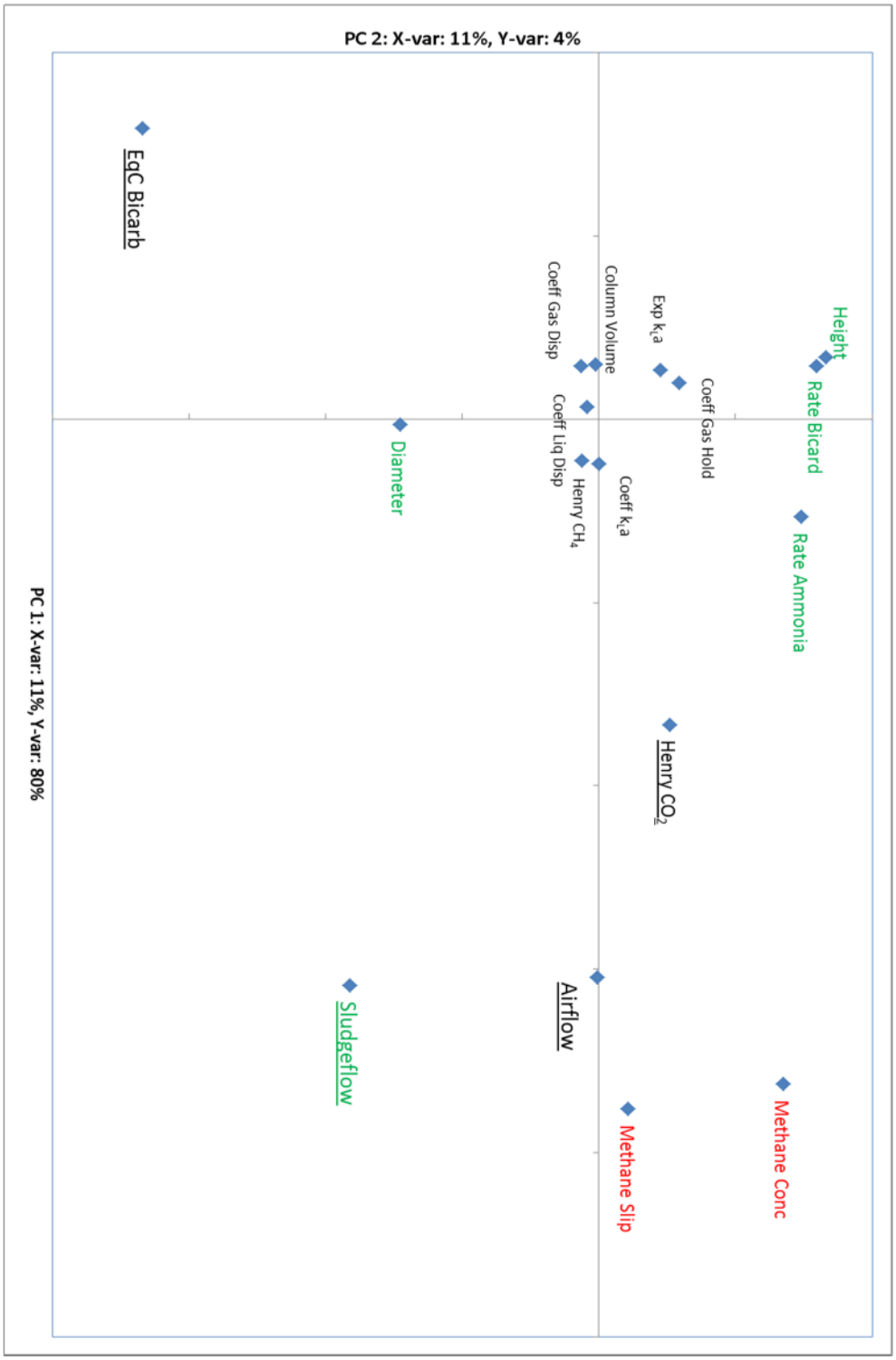

Figure 25: Biplot plot from the PLSR created from the Monte Carlo data. The colour markings indicates as : Red: target variables (Y-variables), Green. Parameters that separates Methane Slip and Methane Concentration. Underlined parameters indicates the most influential parameters.

3.1.6 Collation of results

When results from different simulations are plotted in a graph as methane concentration versus methane slip several trends reveal themselves (see Figure 26 and Figure 27). In Figure 27 the effect on the methane concentration and slip of one constant sludge flow with increasing air flow is displayed.

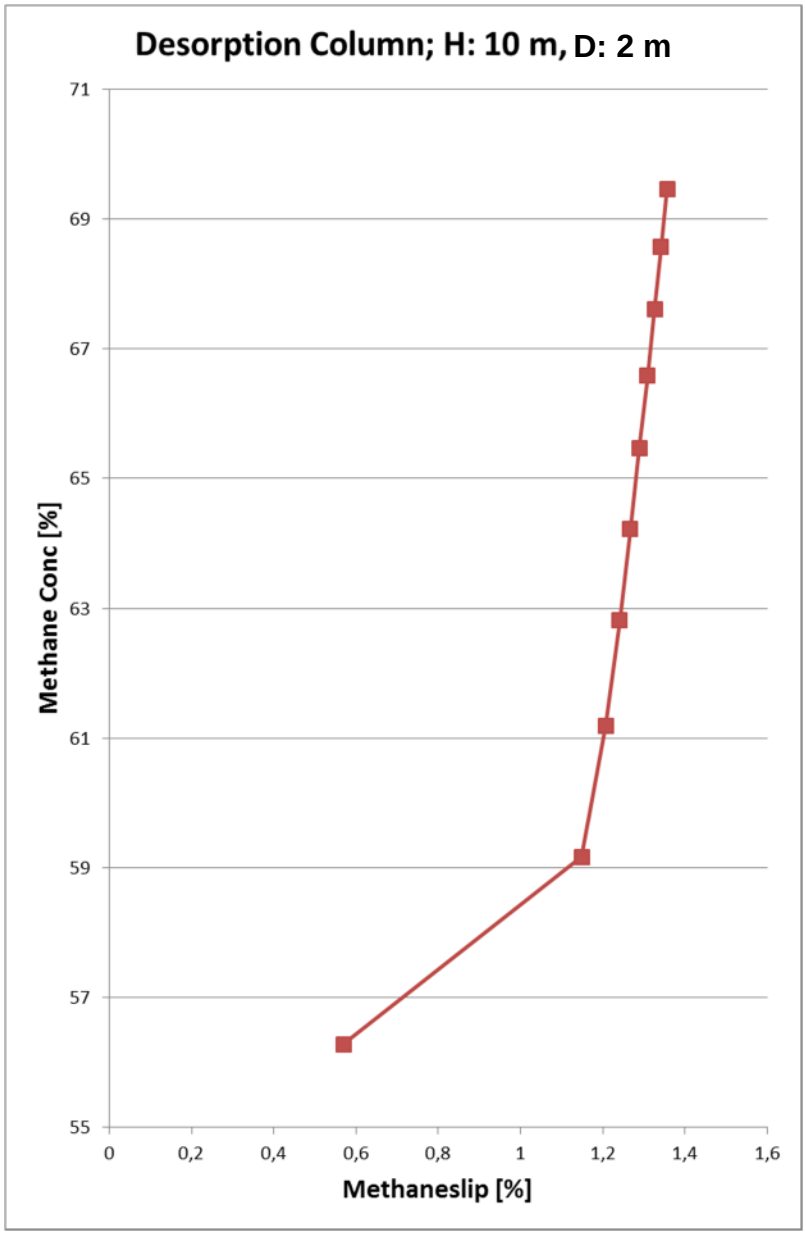

Figure 26: Displaying Methane Concentration in reactor vs. methane slip at sludge flow 600 m^3/d, airflow varies between 100 and 11000 m^3/d. The observation can be made that an increase in the airflow gives a dimishing return in methane concentration in the biogas reactor. At an airflow of 100 m^3/d there was no significant effect on the metane concentration in the biogas reactor, although a small methane slip was observed.

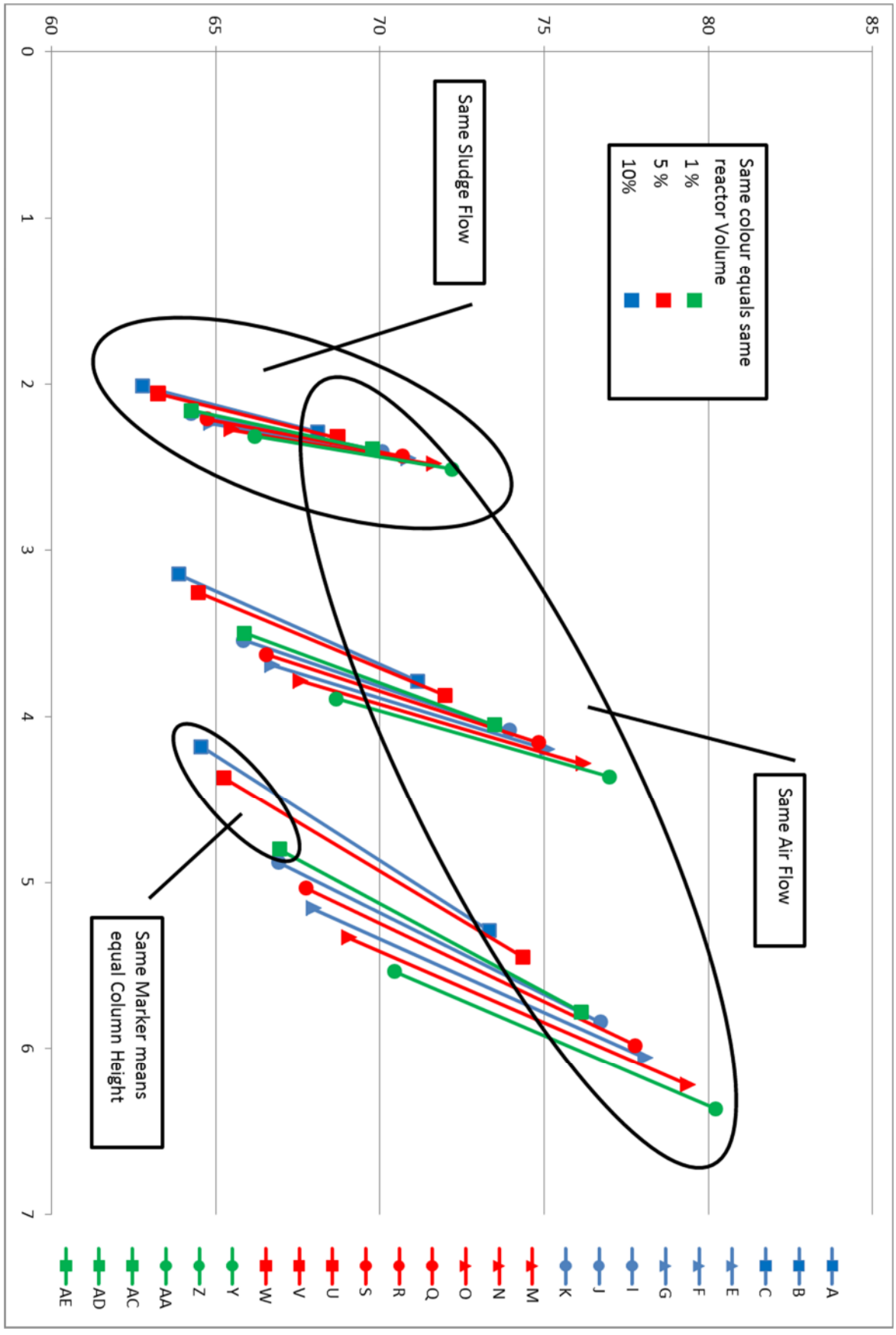

Figure 27: Methane concentration versus Methane slip for various sludge- and air flows including different geometrics of the desorption column.

Table 17: Geometrical properties of the simulations in Figure 27.

	Height [m]	Diam [m]	Vol [%]
A,B,C	2	11,3	10
E,F,G	6	6,5	10
I,J,K	4	8	10
M,N,O	6	4,6	5
Q,R,S	4	5,6	5
U,V,W	2	8	5
Y,Z,AA	4	2,5	1
AC,AD,AE	2	3,6	1

Table 18: The air flows and sludge flows used in 27.

Parameter	Value [m^3/d]
Sludge flow	200,1300,2400
Air flow	4100,8100

In Figure 27 is shown the result of simulations of three different sludge flow rates and two different gas flow rates, using three different column volumes of the desorption column. The Figure shows that:

- The methane slip increases with sludge flow rate and hence needs to be kept low to meet the requirement of less than 2 % slip.
- An increasing gas flow rate will significantly increase the biogas methane concentration while the increase in the methane slip is less, especially at low sludge flow rates.
- An increasing desorption column volume at constant height reduces the biogas methane concentration and the methane slip but the influence is not very strong, and becomes weaker as the sludge flow rate decreases.
- The sludge flow is affecting the methane slip in a major way; this is in line with theoretical calculations and indicated from the position of the sludge flow parameters placement in the biplot of PLSR (Figure 25).

3.1.7 The energy consumption

A preliminary estimation on the energy requirement for *in-situ* methane enrichment was done based on an air flow of 8 000 m^3/d and a sludge flow of 600 m^3/d. The column height was set to 5 m and a column volume of 1 % of the digester volume (ca 20 m^3). The power requirement, W_E, of a compressor at adiabatic compression is given by:

$$W_E = \frac{k}{k-1}\frac{Q_1 P_1}{\xi}\left[\left(\frac{P_2}{P_1}\right)^{(k-1)/k} - 1\right] \qquad (18)$$

where ξ is an efficiency factor usually in the range of 0,7 – 0,9.

$$k = \frac{C_P}{C_V} \tag{19}$$

and equals about 1,40 for air at room temperature. Q_1 is the volumetric gas flow rate (m^3/s) and P_1 is outlet pressure ($Pa=N/m^2$). Tables for air are available on the term:

$$X = \left[\left(\frac{P_2}{P_1} \right)^{(k-1)/k} - 1 \right] = (r^{0,283} - 1) \tag{20}$$

r	1,1	1,2	1,3	1,4	1,5	1,6	1,7	1,8	1,9
X	0,0273	0,0530	0,0771	0,0999	0,123	0,142	0,162	0,181	0,199

Inserting numerical values for air in equation 20 becomes:

$$W_E = \frac{1}{\xi} 3.5 Q_1 P_1 \left(r^{0,283} - 1 \right) \tag{21}$$

The equation above shows that the energy consumption is directly proportional to the required gas flow. It can be shown that the pressure drop dependency is quite linear, e.g. if the pressure drop (Δp) decreases by 20 % the energy consumption will decrease almost by 20 %. Hence, the energy consumption is directly proportional also to the pressure drop. For $\xi = 0{,}8$, equation 12 becomes

$$W_E \approx 53{,}8 * Q_1 \left(r^{0,283} - 1 \right) \quad \text{[kW]} \tag{22}$$

which in example for a pressure drop of about 50 kPa (5 m vp) and a gas flow of 8000 m^3/day becomes: 5 kW.

Unless the column is very short, the most important contribution is the liquid head, i.e. liquid depth in the column. The liquid head pressure drop will depend on the dispersion density and hence the gas holdup. However, unless the linear gas flow rate is very high the gas holdup will be less than 10 %, and correction will not be needed in approximate calculations. From aeration of waste water, a rough estimate of the pressure drop in the bubble generator is 1 m vp loss in the orifice to each diffuser and perhaps 0.5 m vp in the actual membrane. The latter value will gradually increase over time – perhaps 0.3 m vp over 5 years.

With a compressor power of 5 kW, the electricity requirement will be 120 kWh/d. The electricity requirement for pumping sludge was 0.33 kWh/m^3 sludge according to our previous pilot study (Nordberg et al 2005), thus 198 kWh/d with a sludge flow of 600 m^3/d. The total electricity requirement will then be 318 kWh/d. The daily methane production from a 2000 m^3 digester with 0.9 nm^3 biogas/m^3 digester volume/d and 58 % methane concentration will be 1044 nm^3 methane /d, i.e. ca 10 230 kWh/d. Hence, the electricity needed for pumping sludge and aeration is ca 3 % of the energy in the methane produced.

3.2 Part 2. Evaluation of different techniques for carbon dioxide removal

3.2.1 A1. Reference approach using a nitrogen rich substrate

During A1 the digester was run at normal conditions with an organic loading rate of 2.87±0.06 gVS/L/day. The goal was to achieve a reference point for evaluation of the effects from the different carbon dioxide removal techniques. As seen in Figure 28, both gas flow rate and methane content varied substantially with each feeding. Also during weekends when, no feedings were made (October 13 to 14 in Figure 28), the gas production and methane content differed greatly. In order to reduce these fluctuations, an automatic feeding system with four feeding cycles per day was tested (represented by the smaller peaks in the gas production between October 5 and 10). However, due to problems with coagulation of the milk in the tubes, this idea was discarded and instead the rest of the experimental test was carried out with just one manual feeding per day and none during the weekends. Starting from October 12, the reactor was fed with the content from the hydrolysis reactor. Unfortunately, the concentration in the hydrolysis reactor varied during this period leading to that different organic loading rates were applied to the reactor. As seen in Figure 28, this generated rather unstable conditions that were considered unfit to serve as a reference point. Therefore, it was decided that only the period October 8 to12 would be used as reference as this were considered to constitute the most representative part of the phase.

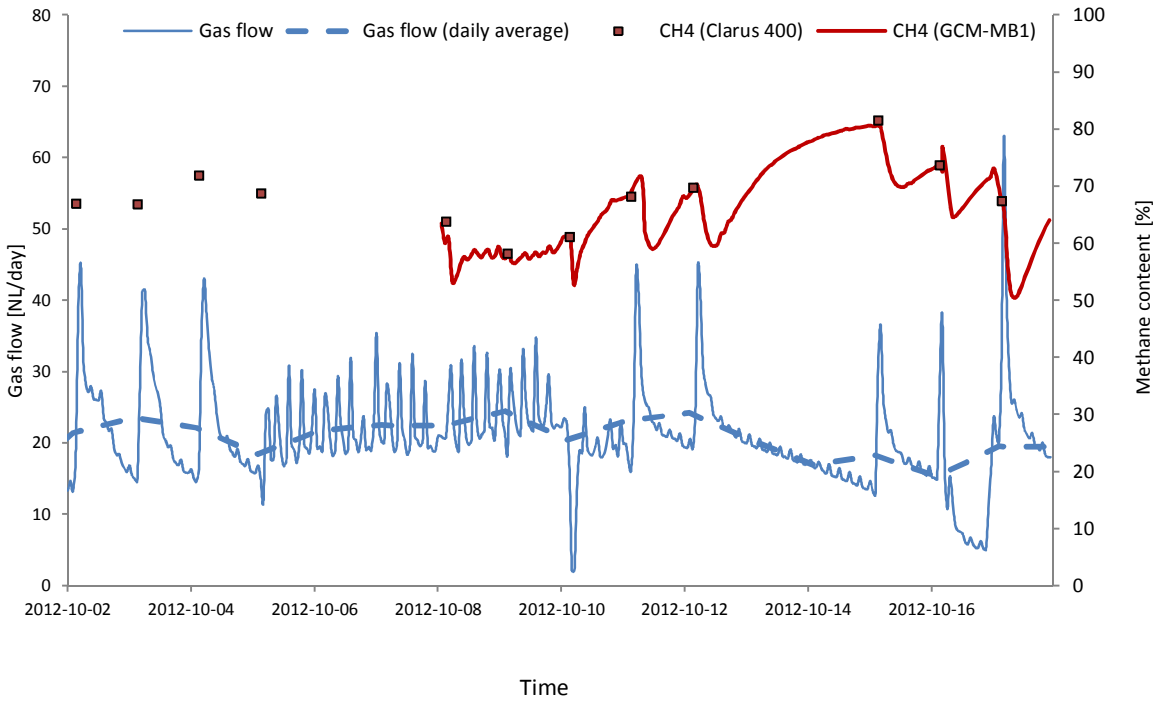

Figure 28: Gas flow rate and methane content of produced gas during A1

As seen in Figure 29, the digester pH decreased or remained rather stable during the week and then returned to a higher value after the weekend. The pH measurements were always taken prior to the feeding and therefore represent the highest pH of the day and not necessarily the average. This is the reason a lower value was observed on October 8 when the process had been fed continuously and thus experienced more stable conditions.

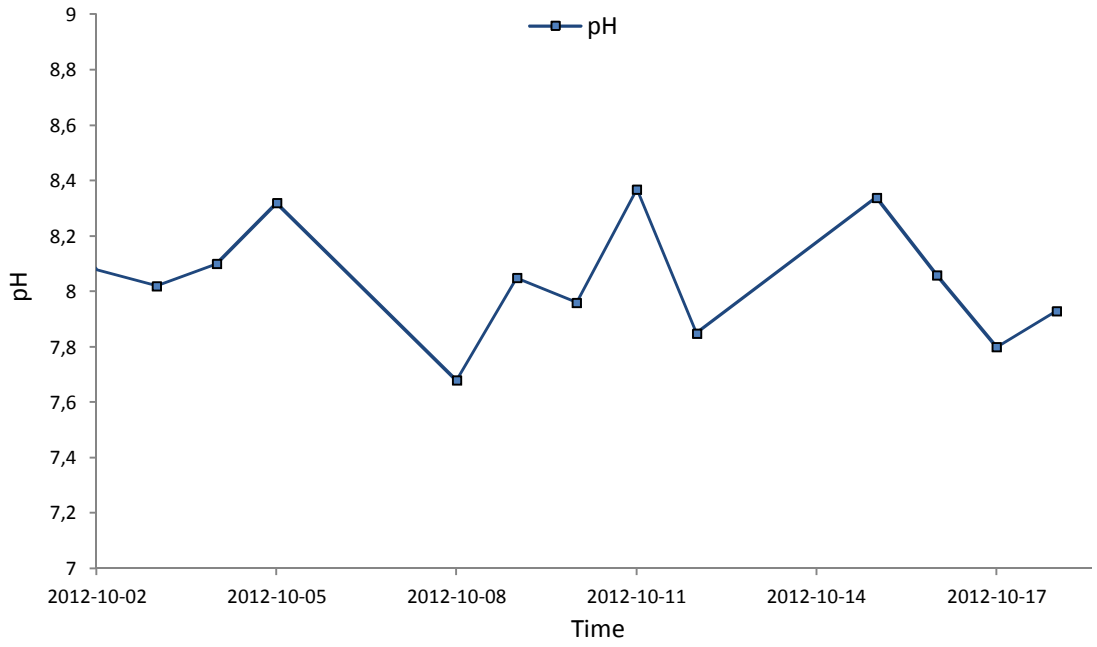

Figure 29: Digester pH during phase A1

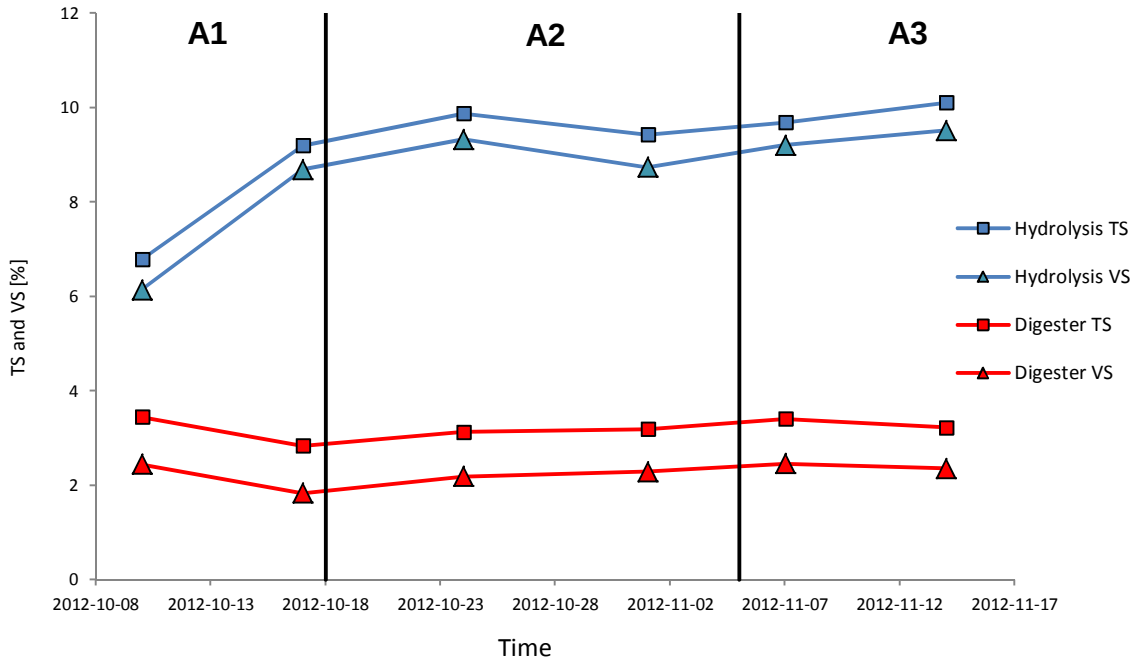

Figure 30: TS and VS content of the digester and hydrolysis reactor during phases A1-3.

All key process parameters from phase A1 are presented in Table 19. As seen, the average gas production during the reference period was 23.3±1.9 NL/day which corresponded to a specific gas production of 2.02±0.16 NL/m^3/day. The specific methane yield (0.44±0.06 NL/gVS) was as expected lower compared to the theoretical yield (0.60 NL/gVS) which partly can be explained by the high VS content in the digestate (See Figure 30). A notable point was the high pH (8.13±0.26) which is believed to be a cause of the large nitrogen content in the

milk as well as a high pH (7.8) from the original sludge. However, as discussed above, this value represents the highest pH value of the day and not the average.

Table 19: Summary of results from A1-A3

Parameter	A1	A2	A3	Unit
Process parameters				
OLR	2.9 ± 0.1	2.5 ± 0.1	2.5 ± 0.1	gVS/m^3/day
HRT	39 ± 1	36 ± 1	36 ± 1	days
SGP	2.02 ± 0.16	1.46 ± 0.13	1.39 ± 0.11	NL/m^3/day
SMP	1.26 ± 0.18	0.85 ± 0.10	0.80 ± 0.07	NL/m^3/day
SGY	0.71 ± 0.12	0.59 ± 0.06	0.55 ± 0.05	NL/gVS
SMY	0.44 ± 0.06	0.34 ± 0.04	0.32 ± 0.03	NL/gVS
Gas flows				
Total	23.3 ± 1.9	16.8 ± 3.0	12.8 ± 0.8	NL/day
CH_4	14.4 ± 1.3	9.8 ± 0.6	7.6 ± 0.5	NL/day
CO_2	8.8 ± 1.3	6.9 ± 2.6	5.2 ± 0.3	NL/day
N_2	0.08 ± 0.04	0.04 ± 0.01	0.04 ± 0.1	NL/day
Gas composition (Gas flows)				
CH_4	62.1	58.4	57.8	%
CO_2	37.6	41.4	42.0	%
N_2	0.3	0.24	0.23	%
Gas composition (GCM-MB1)				
CH_4	62.1 ± 3.8	59.5 ± 7.0	57.9 ± 1.7	%
CO_2	37.5 ± 3.7	40.3 ± 7.1	41.9 ± 1.7	%
N_2	0.3 ± 0.2	0.2 ± 0.1	0.2 ± 0.2	%
Gas composition (Clarus 400)				
CH_4	69.2 ± 1.9	65.9 ± 4.1	63.2 ± 6.0	%
CO_2	30.9 ± 1.9	34.1 ± 4.1	36.8 ± 6.0	%
Air	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	%
pH				
Digester	8.1 ± 0.3	8.3 ± 0.3	8.3 ± 0.3	-
Before column	-	8.2 ± 0.1	8.1 ± 0.1	-
After column	-	8.6 ± 0.1	8.4 ± 0.1	-
Shift column	-	0.4 ± 0.0	0.3 ± 0.1	-

As seen in Figure 28, there were big fluctuations in the methane content with values just above 50% after a feeding, up to 80% after a weekend. This clearly shows the importance of continuous monitoring of the gas composition when only one feeding per day is made. As with the pH, the gas composition from Clarus 400 represented the state prior to feeding and therefore had a higher methane content compared to the gas compositions based on GCM-MB1 measurements, which were taken continuously. An average methane content of 62.0 % is considered to be fairly normal when using milk as substrate. However, considering the high pH of the sludge, a higher value could have been expected

3.2.2 A2. Air stripping using a nitrogen rich substrate

The variations in gas flow and methane content during phase A2 can be seen in Figure 31. As seen in the graph, the methane content surprisingly decreased during the week when the treatment was applied. On the other hand, a slowly increasing trend in the total gas production was also observed during this period. Nevertheless, the distinct decrease in methane content clearly demonstrates that the air stripping was unsuccessful. As with A1, large daily and weekly fluctuations were observed.

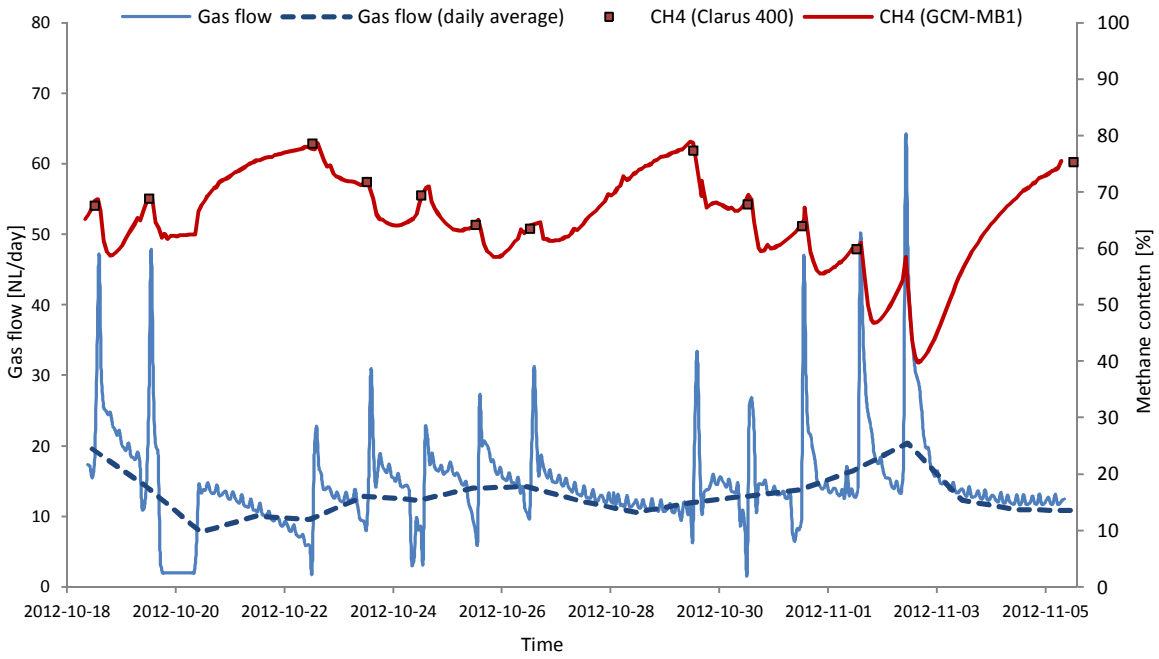

Figure 31: Gas flow rate and methane content of produced gas during A2

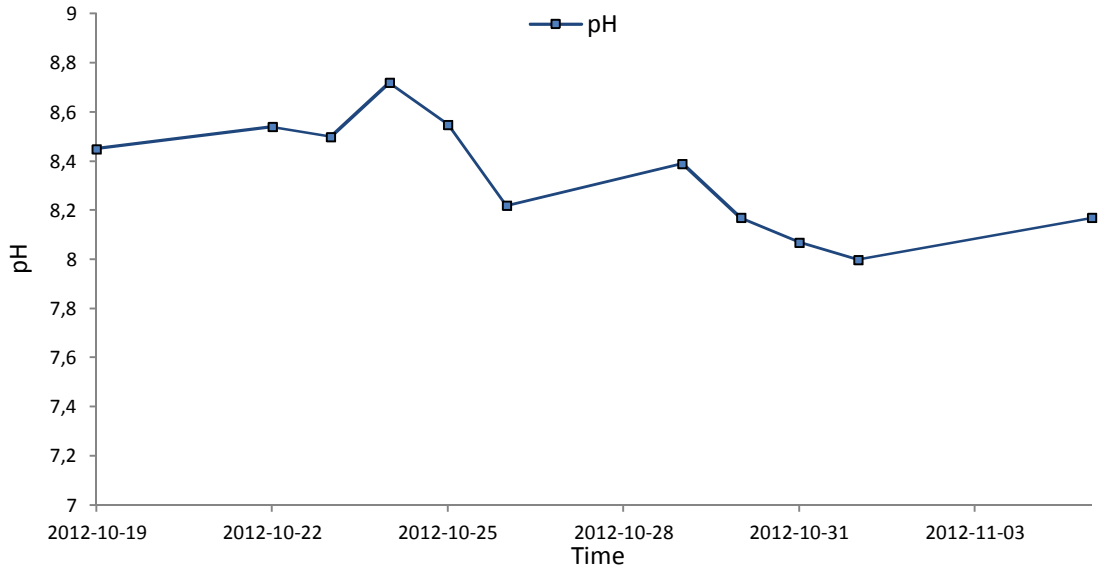

Figure 32: Digester pH during phase A2

As seen in Figure 32, there was a slight drop in pH during the procedure. As the air treatment was expected to increase the pH, this has to be seen as quite surprising. The decreasing trend could partly be explained by stripping of ammonia but a more likely explanation is the acidic content of the hydrolysis reactor that was used as feedstock. The average pH was 8.32±0.27, which was still higher compared to the reference. With regard to the column there was an average increase in pH in from 8.2±0.1 to 8.6±0.1 which suggests that at least some of the inorganic carbon was removed.

As seen in Table 19, a lower gas production compared to the reference was experienced. The specific methane yield was only 0.34±0.05 NL/gVS vs. 0.44±0.06 NL/gVS during A1. Lower values for the methane content were also observed (58.4% vs. 62.1% for the gas flow calculation and 65.9% vs. 69.2% for Clarus 400). Furthermore, the high standard deviations for the gas composition from GCM-MB1 indicate a rather unstable process. The nitrogen content was only 0.2% which was even lower than the reference (0.3%), suggesting that negligible amounts of nitrogen were absorbed during the air treatment.

The lower methane content and higher pH, compared to the reference, suggests a very high alkalinity in the solution. This can most likely be explained by a high concentration of ammonium ions (Jarvis & Schnürer 2009). As the methane production also was lower, some kind of inhibition was probably active in the process as well. One reason for the poor performance could be the exposure of oxygen inside the column. This is supported by the fact that the methane content decreased during the week, when the procedure was applied. However, the total gas production also increased during this period and the average methane production was quite stable at 9.8±0.6 NL/day, whereas the carbon dioxide production fluctuated more with 6.9±2.6 NL/day. This suggests that, even though the methane producing bacteria may have been inhibited by the exposure to oxygen, they were not getting worse. A more likely explanation for the poor performance is instead inhibition from too high amounts of free ammonia, which was amplified by the pH increasing effects from the carbon dioxide removal. As described in the introduction, free ammonia mainly inhibits the acetoclastic methanogens whereas the hydrogenotrophic populations remain less affected (Hansen et al. 1998; Chen et al. 2008). It has also been suggested that too high contents of free ammonia shifts the metabolic degradation of acetate towards the syntrophic acetate-oxidizing pathway instead (Westerholm, 2012). This should lead to an accumulation of inorganic carbon followed by an increase in carbon dioxide content and possible drop in pH.

Clearly, air stripping at a high pH with suspected high amounts of ammonium nitrogen is not effective and the potential stripping of free ammonia cannot make up for the removal of carbon dioxide.

3.2.3 A3. Vacuum treatment using a nitrogen rich substrate

The variations in gas flow and methane content during phase A3 can be seen in Figure 33. Once again, the daily and weekly fluctuations of the two parameters were distinct. Compared to the air treatment, the values for the vacuum procedure were more stable during the weeks. However, no increase in methane content was observed from applying the method, instead the daily values were rather constant at a low level.

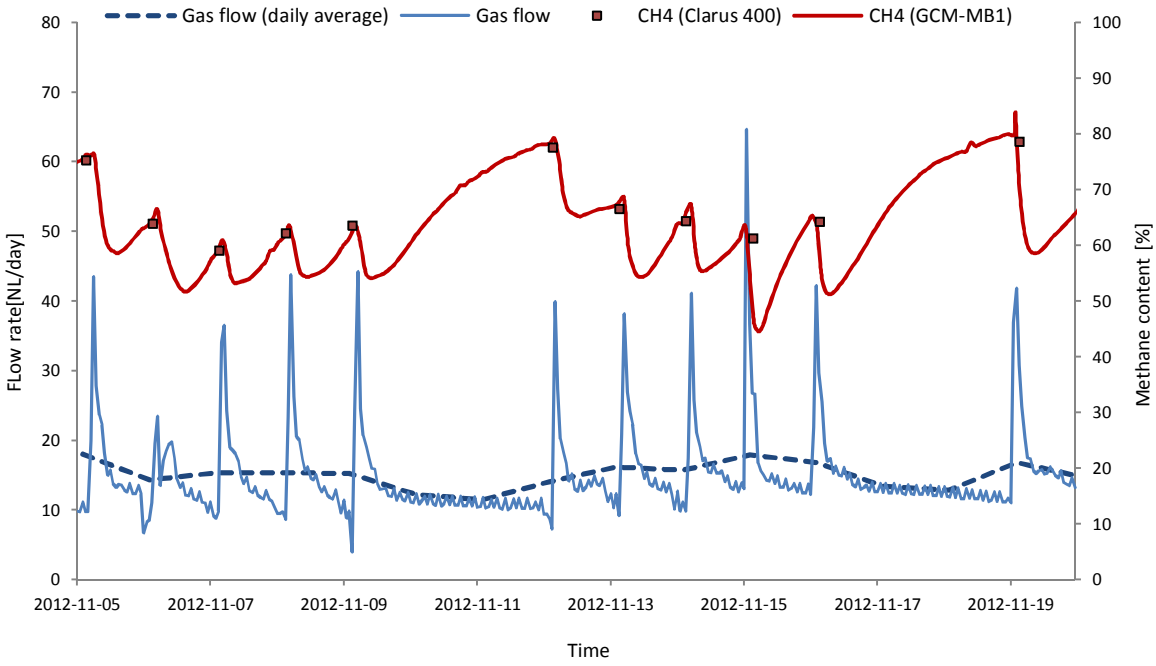

Figure 33: Gas flow rate and methane content of produced gas during A3

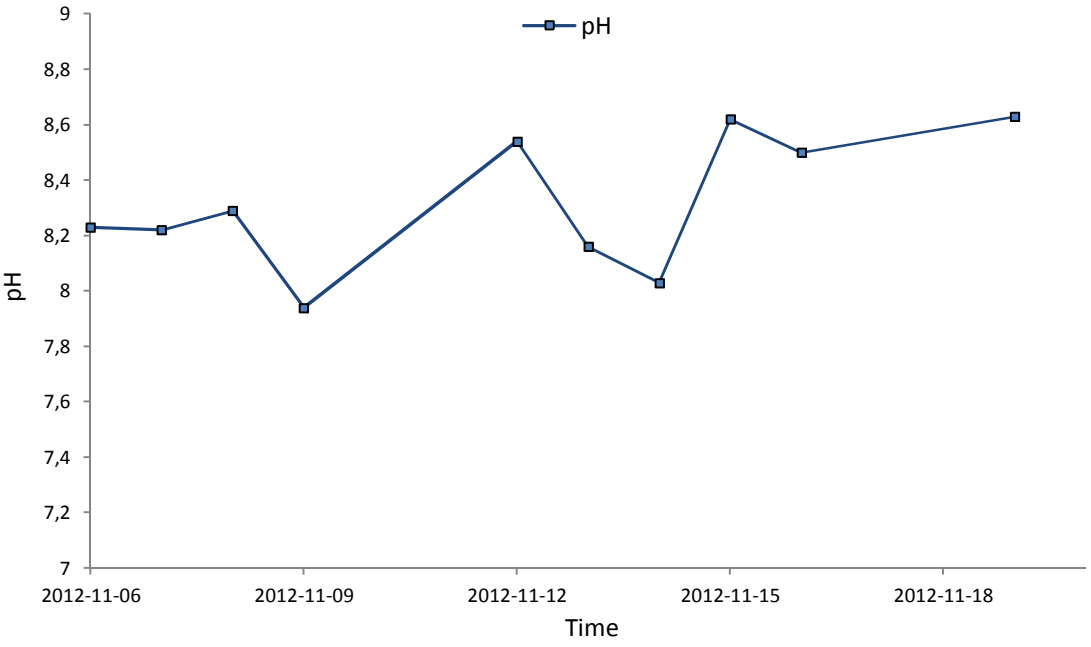

Figure 34: Digester pH during phase A3

As seen in Figure 34, the digester pH during phase A3, in contrast to A2, increased during the procedure. However, as seen in Table 21, the average pH (8.2±0.3 vs. 8.3±0.3) was similar whereas the increase inside the column was less (0.3±0.1 vs. 0.4±0.0).

By studying the parameters presented in Table 19 it is clear that the vacuum treatment was performing even worse compared to the air treatment. The specific methane yield was as low as 0.33±0.05 NL/gVS and the methane content only

57.8%. As with the air treatment, a low average concentration of nitrogen (0.2%) was registered in the biogas.

Surprisingly the vacuum treatment produced even less methane than the air treatment step. This can be seen as another proof that the oxygen itself was not the main contributor to the inhibition, since the exposure should have been quite limited during the vacuum procedure. Another theory could be that the vacuum itself inhibited the bacteria further by disrupting the internal transportation systems. However, the most likely explanation is that the ammonia inhibition has had grown more severe due to a slowly increasing concentration of ammonia nitrogen.

Based on the observations in this phase, it can be concluded that vacuum stripping of carbon dioxide does not work at high pH levels and suspected ammonia inhibition. Moreover, the smaller shift in column pH and lower methane content suggests that vacuum is a less powerful method compared to air stripping. A possible explanation for this is that the partial pressure of carbon dioxide is still high in the column at 0.4 bar pressure and therefore constitutes a small driving force for removal. However, it should be mentioned that, since the vacuum procedure was evaluated after the air stripping, the poor results could be due to an already growing reactor imbalance and thus should be viewed with caution.

3.2.4 B1. Air stripping using a mixed substrate

The variations in gas flow and methane content for the test (*TestR*) and reference (*RefR*) digester during phase B1 can be seen in Figure 35. Unfortunately this period was forced to be kept rather short due to the time limitations of the project. As seen in the figure, *TestR* experienced a little bit higher methane content during three of the sampled days. However, *TestR* also experienced a lower and more unstable gas production. It should be pointed out that a short retention time (10 days) was applied during this phase which surely contributed to the unstable data.

As seen in Figure 36, the digester pH varied quite a lot but followed the same trend until the last few days of the procedure where *TestR* remained stable and even increased slightly while *RefR* dropped substantially down to 6.74. The difference in pH is also confirmed by the average values which were 7.3±0.2 for *TestR* compared to 6.96±0.19 for *RefR*. Furthermore, as seen in Table 22, the procedure increased the pH significantly from 7.4±0.3 to 7.8±0.3 inside the column.

The process parameters presented in Table 20 show that the digesters were performing poorly with specific methane yields of 0.23±0.06 and 0.31±0.02 for *TestR* and *RefR* respectively. The most likely explanation for this was the short retention time which must have caused a wash out of bacteria. The average methane content based on measurements from Clarus 400 confirms that *TestR* (63.3±8.4) had a higher methane content compared to *RefR* (55.0±9.0). However, once again the high standard deviations show that the process was unstable. Compared to phases A1-3, the nitrogen content in the gas was higher which might be a response to the increased exposure to air in the stripping process (one day retention time compared to two). On the other hand, the air content measured by Clarus 400 did not differ much between *TestR* and *RefR*.

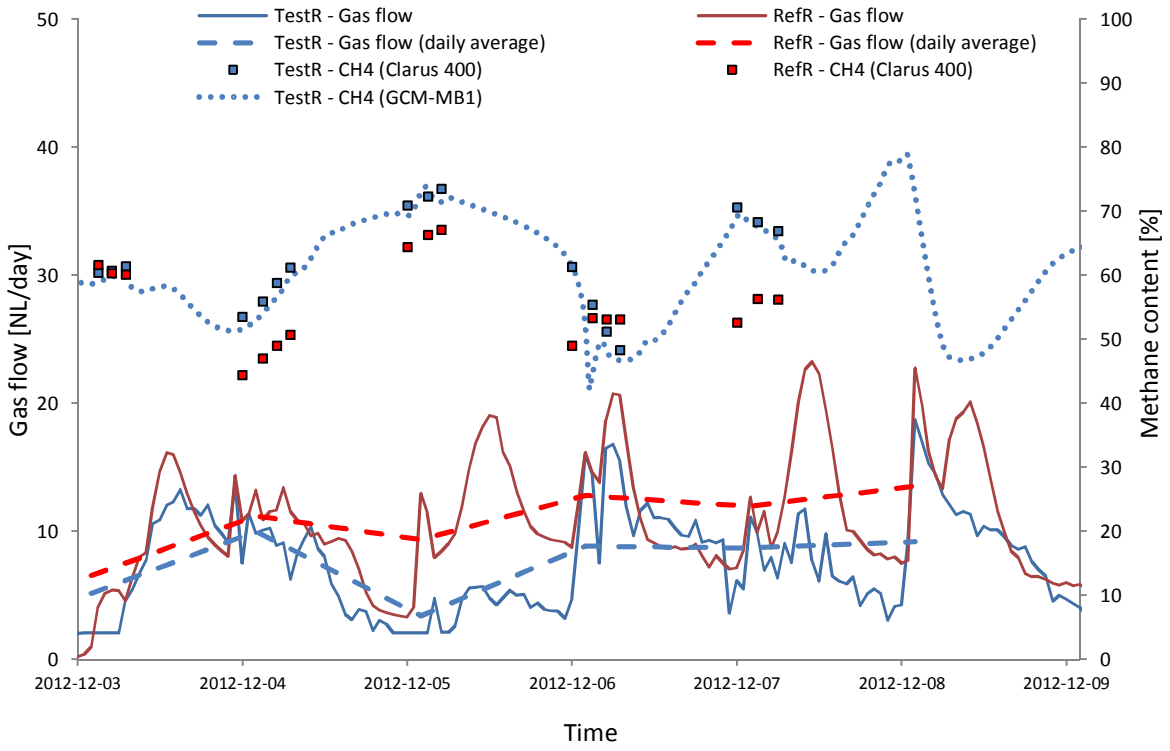

Figure 35: Gas flow rate and methane content of produced gas during B1

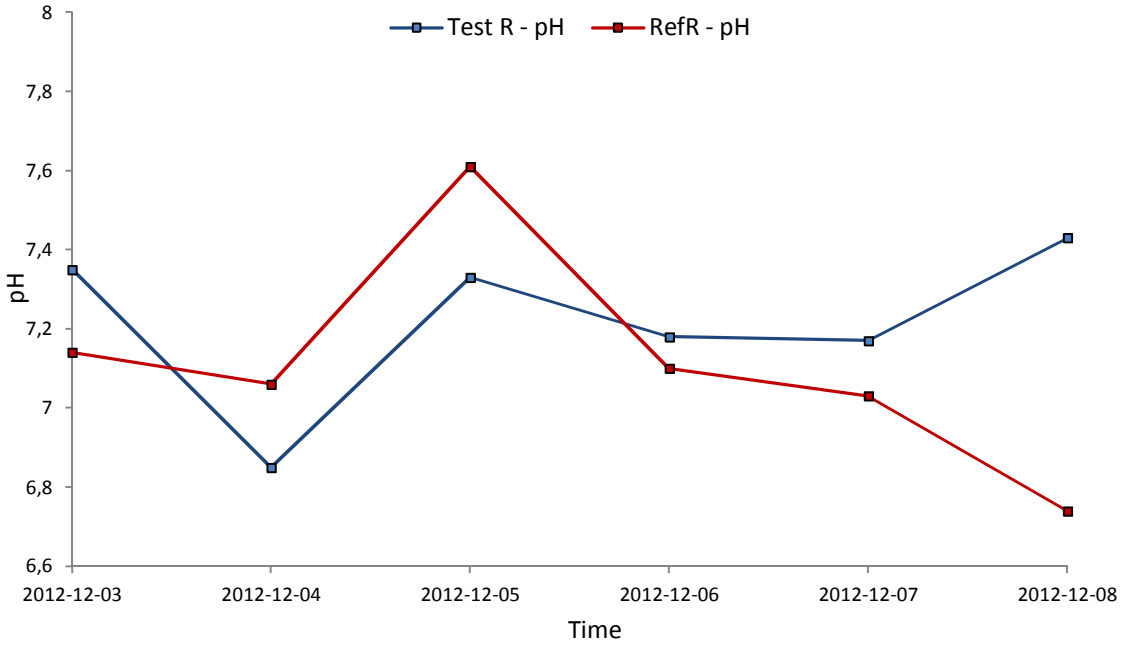

Figure 36: Digester pH of TestR (blue) and RefR (red) during B2

Table 20: Summary of results from B1

Parameter	RefR	TestR	Unit
Process parameters			
OLR	3	3	gVS/m^3/day
HRT	10	10	days
SGP	1.76 ± 0.11	1.18 ± 0.32	NL/m^3/day
SMP	0.92 ± 0.05	0.70 ± 0.19	NL/m^3/day
SGY	0.59 ± 0.04	0.39 ± 0.11	NL/gVS
SMY	0.31 ± 0.02	0.23 ± 0.06	NL/gVS
Gas flows			
Total	11.4 ± 0.6	7.7 ± 2.1	NL/day
CH_4	-	4.5 ± 0.7	NL/day
CO_2	-	3.1 ± 1.4	NL/day
N_2	-	0.10 ± 0.05	NL/day
Gas composition (Gas flows)			
CH_4	-	59.0	%
CO_2	-	39.7	%
N_2	-	1.3	%
Gas composition (GCM-MB1)			
CH_4	-	61.0 ± 7.1	%
CO_2	-	37.9 ± 6.9	%
N_2	-	1.1 ± 0.2	%
Gas composition (Clarus 400)			
CH_4	55.0 ± 8.1	63.3 ± 8.4	%
CO_2	45.0 ± 8.2	36.6 ± 8.2	%
Air	0.4 ± 0.0	0.5 ± 0.1	%
pH			
Digester	7.0 ± 0.2	7.3 ± 0.2	-
Before column	-	7.4 ± 0.3	-
After column	-	7.8 ± 0.3	-
Shift column	-	0.5 ± 0.1	-

Due to the unstable conditions it is difficult to draw more conclusions besides that air stripping increases the methane content in the gas at lower alkalinity levels and pH around 7.3- However, based on the results in this study, the increase is small and the total production of methane might decrease instead. On the other hand, it should be noted that while *RefR* were heading for digester failure with a quickly declining pH at the end, *TestR* experienced its highest methane production and an increasing pH at this time. This could be a sign that the air stripping stabilizes the process by maintaining a higher pH. Unfortunately, seven days of data is not enough to properly evaluate a method likes this.

3.2.5 B2. Vacuum treatment using a mixed substrate

The variations in gas flow and methane content of *TestR* and *RefR* during phase B2 can be seen in Figure 37. Unfortunately, this phase was also forced to be kept short due to the time limitation as well as a long start-up time due to the problems from the previous phase. As seen in the figure, the methane content did not differ much between *TestR* and *RefR*. However, looking at the first point taken each day, as well as all the points during the last day, when no feeding was made, *TestR* always had a higher content. This suggests that the vacuum treated process might have experienced higher methane contents during the night when no measurements were made. The trend of the measurements also gives an indication that *TestR* was more sensitive to the feedings since it experienced severe drops in methane content after each feeding. The gas production was rather stable during this period with *TestR* having slightly lower values.

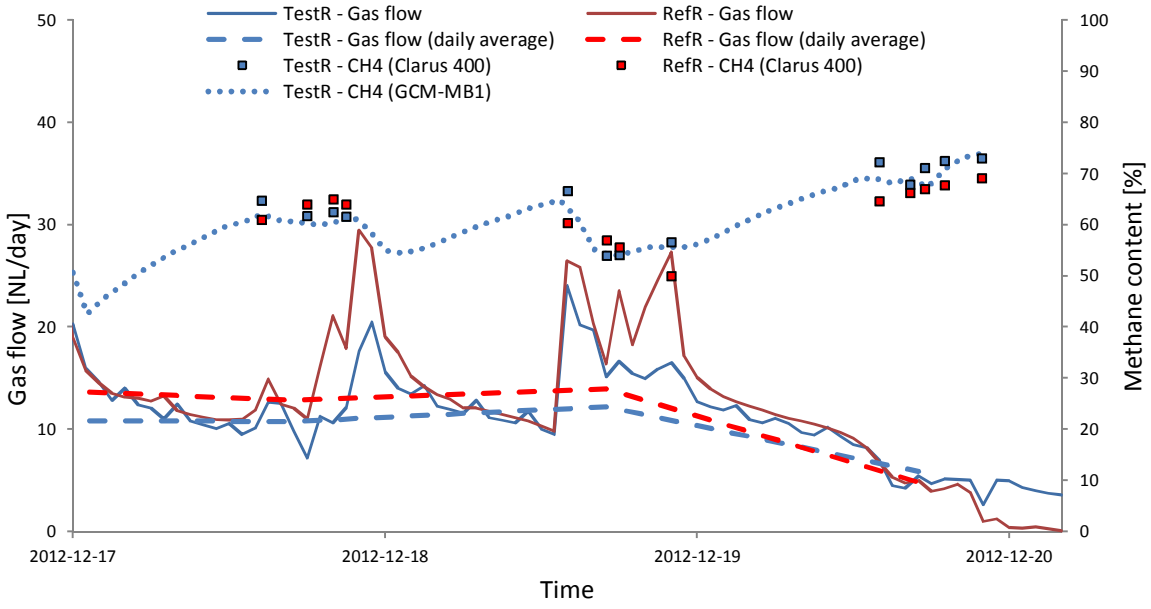

Figure 37: Gas flow rate and methane content of produced gas during B2

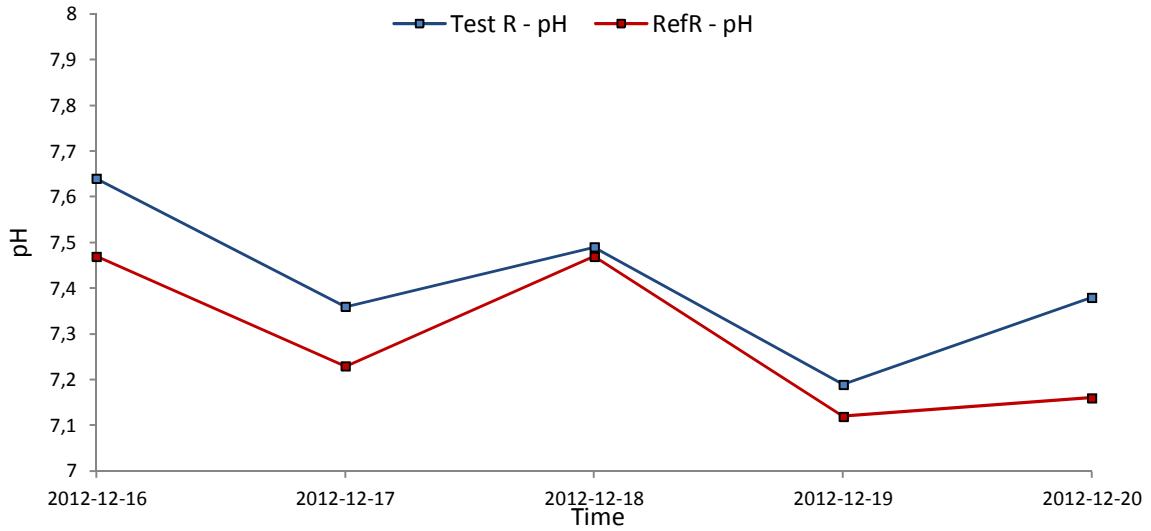

Figure 38: Digester pH of TestR (blue) and RefR (red) during B2

As seen in Figure 38, the digester pH of *TestR* and *RefR* follows the same decreasing trend with *TestR* having slightly higher values. The decrease in pH might be explained by the acidic feedstock with orange juice and a slow accumulation of VFA due to this.

Table 21: Summary of results from B2

Parameter	RefR	TestR	Unit
Process parameters			
OLR	3.1	3.1	gVS/m^3/day
HRT	31	31	days
SGP	2.37 ± 0.12	1.97 ± 0.37	NL/m^3/day
SMP	1.37 ± 0.07	1.18 ± 0.07	NL/m^3/day
SGY	0.78 ± 0.04	0.65 ± 0.04	NL/gVS
SMY	0.45 ± 0.02	0.39 ± 0.02	NL/gVS
Gas flows			
Total	15.4 ± 0.8	12.9 ± 0.8	NL/day
CH_4	-	7.6 ± 0.5	NL/day
CO_2	-	5.2 ± 0.3	NL/day
N_2	-	0.04 ± 0.01	NL/day
Gas composition (Gas flows)			
CH_4	-	59.5	%
CO_2	-	40.2	%
N_2	-	0.4	%
Gas composition (GCM-MB1)			
CH_4	-	59.5 ± 0.1	%
CO_2	-	40.2 ± 0.1	%
N_2	-	0.4 ± 0.1	%
Gas composition (Clarus 400)			
CH_4	60.0 ± 4.7	62.1 ± 1.5	%
CO_2	36.1 ± 4.7	36.1 ± 1.2	%
Air	0.5 ± 0.1	0.8 ± 0.0	%
pH			
Digester	7.3 ± 0.2	7.3 ± 0.2	-
Before column	-	7.2 ± 0.1	-
After column	-	7.6 ± 0.1	-
Shift column	-	0.4 ± 0.0	-

The process parameters presented in Table 21 show that the process performed more normally compared to phase B1. The specific methane yields were 0.39±0.02 NL/gVS and 0.45±0.02 NL/gVS for *TestR* and *RefR*, respectively, which is quite close to the theoretical value of 0.49 NL/gVS. However, also here the treated process produced less methane compared to the untreated which suggests that the procedure may have a negative effect on the methane production. The methane content was almost the same with a slightly higher value for *TestR* (62.1±1.5%) compared to *RefR* (60.0±4.7%). Also the pH values were similar for the two digesters which confirm that the treatment did not have a significant impact on the process. A smaller increase in the column compared to B2 suggests, once again, that air stripping is a more potent method to desorb carbon dioxide compared to vacuum at 0.4 bar. However, the method was only evaluated for a period of four days and at the final day a bigger difference was observed (71.4% vs. 67.0%) in the methane content. The digesters were not fed during this day and therefore this data were not used when calculating the average values. It gives an indication that the treatment had an impact though. The lower methane yield for the treated process suggests that the process was either inhibited or a large amount of methane was stripped away together with the carbon dioxide the column. Since the pH increase was less compared to the air treatment, suggesting a lower removal force, it is more likely that the lower methane yield was due to some kind of inhibition.

3.2.6 B3. Vacuum with organic acids addition using a mixed substrate

The variations in gas flow and methane content of *TestR* and *RefR* during phase B3 can be seen in Figure 39. During this phase many more measurements compared to previous phases were taken. However, in order to avoid a cluttered look only one measurement per day from Clarus 400 is shown. For all the measurements the reader is referred to Appendix III. It should be pointed out that the treatment was first initiated on January 8 and prior to this, the milk and orange juice were added together, which generated the high peaks seen in the graph. During the treatment, on the other hand, the additions of the orange juice were spread out throughout the day, producing the shorter but wider peaks. As seen in the figure, the methane content for *TestR* was constantly higher compared to *RefR*. It is also clear that the methane content remained rather stable for *TestR* whereas it is slowly decreased for *RefR*. With regard to the gas production, there was a declining trend for both digesters, which, in combination with the constant or declining methane content, can be seen as a sign of inhibition.

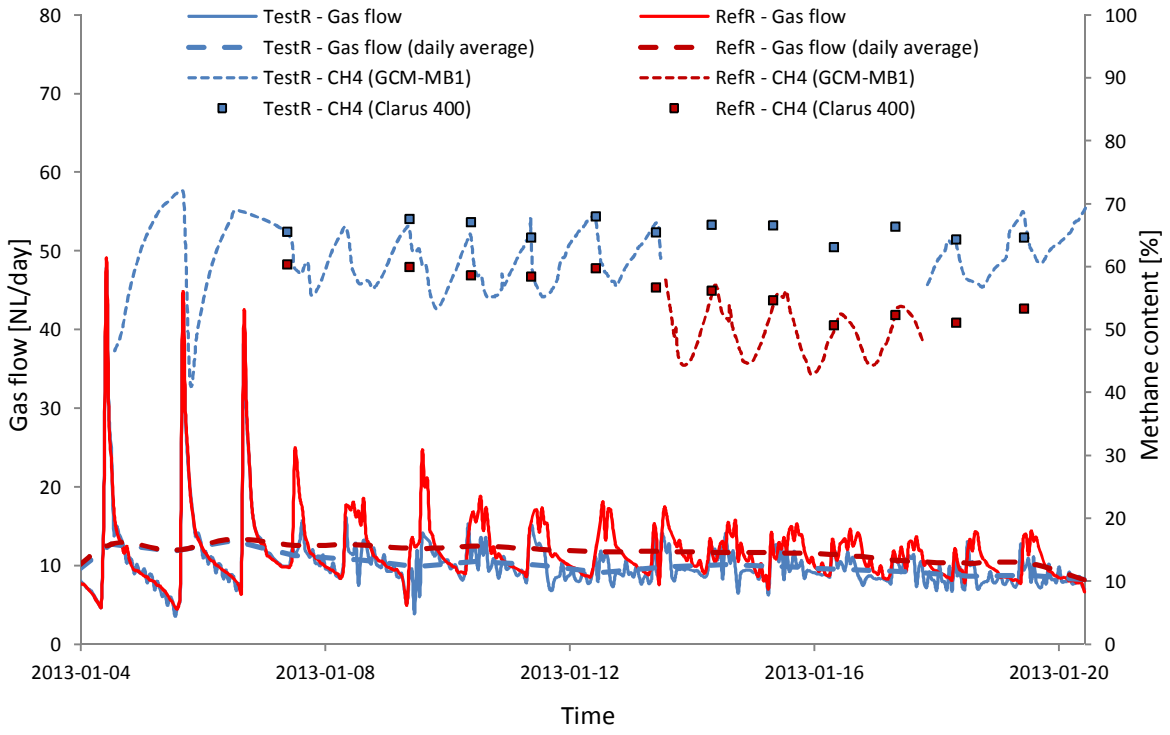

Figure 39: Gas flow rate and methane content of produced gas for TestR (blue) and RefR (red) during B3

The variation in digester pH (Figure 40,) indicates that *TestR* had a higher and more stable pH compared to *RefR*. As seen in Table 24, there was also a difference in the average value with *TestR* having a higher average of 7.2±0.1 compared to 7.0±0.1 for *RefR*. In the figure, the line drawn between each measurement point of a day shows that *RefR* had a declining trend due to the feeding whereas *TestR* only experienced a slight decline at the start but then stabilized around a value for the remaining part of the day. The daily average displays a declining pH throughout the period which is another sign of inhibition.

In order to study the pH profile in the column during this phase, the pH was measured four times throughout the procedure: before the treatment, after the initial vacuum period, after applying the orange juice and after the final vacuum period. As seen in Table 24, the pH was lower after the full treatment (7.2±0.1) compared to the start (7.2±0.1) which show that not enough carbon dioxide was stripped away to counteract the pH decrease caused by the organic acids. Another interesting point is that the pH was lower at the end of the process compared to after adding the orange juice (7.2±0.1) which much likely indicates that the juice was degraded inside the column producing even more acidic compounds. However, as orange juice contains a lot of sugar, the same effect might not be as apparent with an organic acid mixture from a hydrolysis reactor.

As seen in Figure 41 there was an increase in TS and VS for both *TestR* and *RefR* during the period. Considering the decrease in gas production, this is much likely due to accumulation of undigested substrate and not increase in bacterial mass.

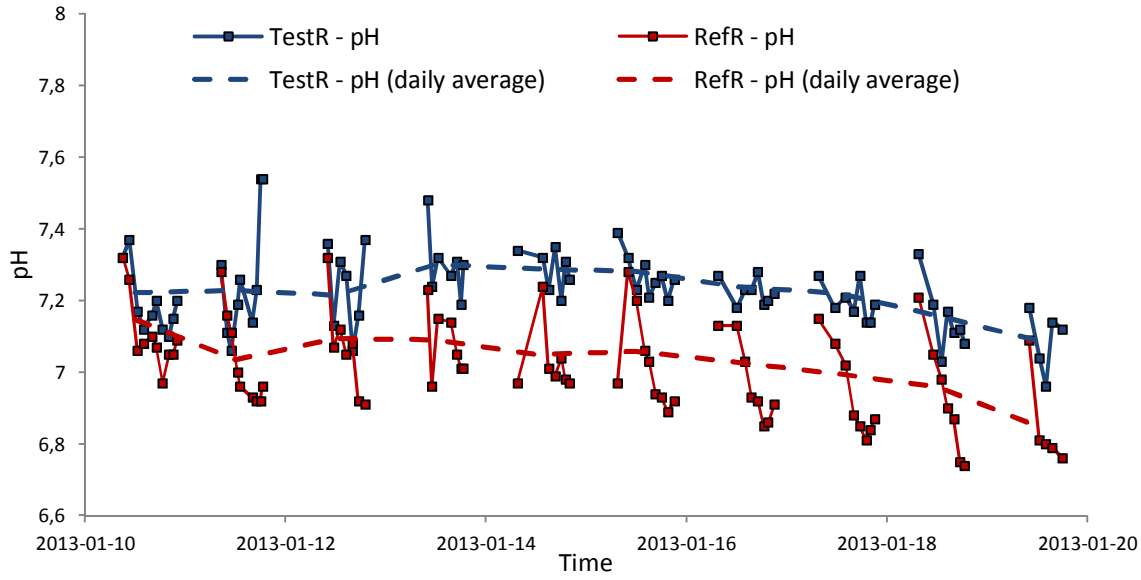

Figure 40: Digester pH of TestR (blue) and RefR (red) during B3

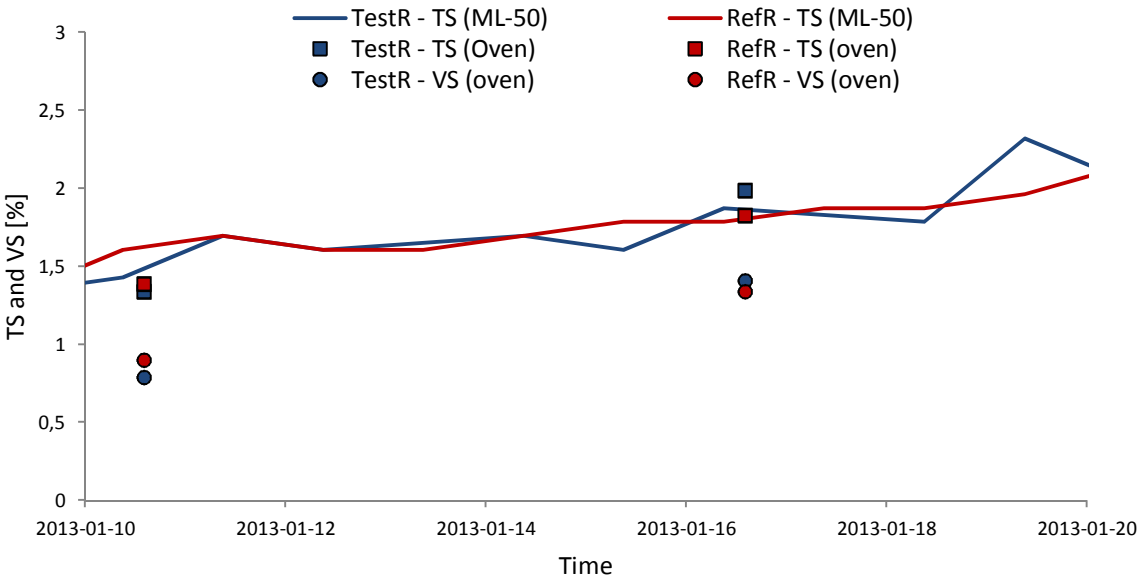

Figure 41. TS and VS of TestR (blue) and RefR (red) during B3

The process parameters presented in Table 22 show that there are strong indications of an inhibition during this period. The specific methane yields were only 0.31±0.02 and 0.29±0.01NL/gVS for *TestR* and *RefR* respectively which are much lower values compared to the theoretical value of 0.49 NL/gVS. Clearly, having an organic loading rate of 3.0 gVS/L/day, with a high strength substrate as orange juice, was too much for the anaerobic sludge used in this phase. However, the higher methane content for *TestR* (61.4%) compared to *RefR* (49.6%) show that the vacuum and organic acids treatment had a significant impact on the process. During B3, *RefR* was connected to GCM-MB1 for 4 days (Jan 13 to 17) which allowed continuous measurement of the gas composition for this digester as well. Therefore, the values during this period were used for the calculation of the methane content and gas flow for *RefR*. An interesting outcome was that the

difference from the manually sampled measurements with Clarus 400 was much smaller compared to the continuous ones with GCM-MB1. This indicates a larger difference during the night, when no feeding or treatment was applied, compared to during the day.

Table 22: Summary of results from B3

Parameter	RefR	TestR	Unit
Process parameters			
OLR	3.1	3.1	gVS/m^3/day
HRT	31	31	days
SGP	1.77 ± 0.07	1.53 ± 0.08	NL/m^3/day
SMP	0.88 ± 0.03	0.94 ± 0.05	NL/m^3/day
SGY	0.58 ± 0.02	0.50 ± 0.03	NL/gVS
SMY	0.29 ± 0.01	0.31 ± 0.02	NL/gVS
Gas flows			
Total	11.5 ± 0.4	9.9 ± 0.5	NL/day
CH_4	5.7 ± 0.3	6.1 ± 0.3	NL/day
CO_2	5.8 ± 0.2	3.8 ± 0.3	NL/day
N_2	0.04 ± 0.02	0.04 ± 0.01	NL/day
Gas composition (Gas flows)			
CH_4	49.6	61.4	%
CO_2	50.0	38.2	%
N_2	0.3	0.4	%
Gas composition (GCM-MB1)			
CH_4	49.6 ± 0.1	61.4 ± 1.7	%
CO_2	50.0 ± 1.1	38.2 ± 1.7	%
N_2	0.3 ± 0.2	0.4 ± 0.1	%
Gas composition (Clarus 400)			
CH_4	53.5 ± 1.8	59.4 ± 0.6	%
CO_2	45.8 ± 1.9	40.3 ± 0.8	%
Air	0.6 ± 0.1	0.6 ± 0.1	%
pH			
Digester	7.03 ± 0.08	7.22 ± 0.06	-
Before column	-	7.24 ± 0.05	-
Before organic acids	-	7.37 ± 0.08	-
After organic acids	-	7.24 ± 0.09	-
After column	-	7.17 ± 0.06	-
Shift column	-	-0.07 ± 0.06	-

The results observed in B3 show that treatment with vacuum and organic acids has a positive effect compared to a process without any treatment. The treatment generated a higher and more stable methane content and pH as well as a slightly higher specific methane yield. However, due to the suspected inhibition during this phase, it is difficult to determine how well the actual procedure work. As with the

air treatment in A1, the vacuum and organic acids seem to make the process more robust towards reactor imbalance and inhibition.

Most likely the driving force from a vacuum at 0.4 bar was not strong enough to remove enough of the carbon dioxide inside the column since the pH actually decreased during the treatment after the addition of the organic acid. In order to benefit more, the pH should increase before the sludge is returned to the digester. This would allow the maximal removal of the bicarbonate that is converted to carbon dioxide . Thus, longer exposure time or smaller dosages of the organic acid should have been made in order for the procedure to be more successful.

3.2.7 Summary and final discussion

The different evaluated methods to increase the methane content was unsuccessful when a substrate rich in nitrogen was used. Both air and vacuum at 0.4 bar decreased the gas production as well as the methane content. High pH values and methane contents suggest a high alkalinity level, probably due to great amounts of ammonium ions. Low specific methane yields implies an inhibition, most likely due to the high content of free ammonia which effects were further amplified by the increase in pH coming from removal of carbon dioxide. This indicates that, even at pH levels above 8 with suspected high content of ammonium nitrogen, the stripping of ammonia is less compared to carbon dioxide and therefore the synergetic effect coming from the removal of these two components cannot be utilized. As a result it can be concluded that *in-situ* methane enrichment by carbon dioxide removal with nitrogen rich substrates is not feasible with a standard approach.

During the second part of the experiment, where a substrate with lower content of nitrogen was used, differences in the methane content coming from the treatments could be observed. However, the increases in methane content were small and both the air and vacuum treatment experienced lower methane productions compared to the reference. The largest difference in methane content (61.4% vs. 49.6%) was observed when vacuum at 0.4 bar together with organic acids was applied. During this procedure, the total methane production was also similar to the reference. However, the specific methane yields were much smaller compared to the theoretical value, which suggests an inhibition of the process. In this case, it was most likely due to an overloading of the process. Normally an organic loading rate of 3.1 gVS/L/day presents no problem for an AD process, but with a poorly adapted sludge and a high strength substrate as orange juice, it appear to have been too much. Both in the case with air stripping and vacuum + organic acids, the procedures seem to have reduced the effect of a reactor imbalance. In both cases, the trend for the treated digesters were more positive compared to the reference which were experiencing more severe drops in gas production, methane content and pH level. This suggests that an *in-situ* methane enrichment procedure might actually partly protect the process from the effects of overloading. The most likely explanation for this is the increase in pH which should be beneficial for the methanogenic population.

In contrast with all other procedures, the pH decreased after column treatment when orange juice was added. This suggests that the driving force from the acidic feed were not utilized enough and most likely an increased exposure time together with smaller addition of the acids would have made the process more efficient.

However, as orange juice contains large amounts of sugar, this effect might not be as obvious when an acidic feed from a hydrolysis reactor are used. One drawback with supplementing organic acids is the reduced alkalinity of the system, which can lead to an unstable system in the end. Another drawback is their contribution of inorganic carbon as they are degraded. A way to minimize this could be to supplement an inorganic acid instead. However, as this will deplete the alkalinity permanently and could be quite expensive to add on a continuous basis in large scale, the required amount has to be determined.

In comparison with previous studies, the results obtained in the present one are much less significant. However, as most of the studies have been carried out under different conditions, it is difficult to compare them directly. One thing in common for all previous studies was that they were working with a lower organic loading rate and performed the procedure continuously. Another important factor is that they used nozzles to increase the contact area of the air inside the column.

Further testing is needed to evaluate the concept of *in-situ* methane enrichment in detail. The results obtained in this study suggest that air treatment is a more powerful approach in stripping carbon dioxide compared to vacuum at 0.4 bar without being more toxic. Therefore, organic acids should be added in combination with air stripping in order to achieve the best results. The next step would thus be to apply a continuous air stripping procedure with small dosages of organic acid inside the column. Since a continuous approach allows a constant and gentler stripping of carbon dioxide compared to the manual batch alternative, it is believed that a much more effective process will be observed. Furthermore, a lower organic loading rate should be applied to avoid the inhibition problems observed in this study.

One drawback with the experimental setup was the direct addition of digester sludge to and from the column which means that sludge rich in methane enters the column whereas sludge rich in oxygen and nitrogen enters the digester. (Nordberg *et al*. 2012) did not experience any significant problems running the process with direct connection between the two operational units, whereas (O'Keefe *et al*. 2000) could show of a significantly lower methanogenic activity of the sludge after the column treatment. In this study, the results were inconclusive but the indication was that the gas production was decreased every time the sludge from the column was added to the digester. In a continuous operation this would not be as obvious but might still exert some effect. Therefore, it would be interesting to compare a system with and without this feature.

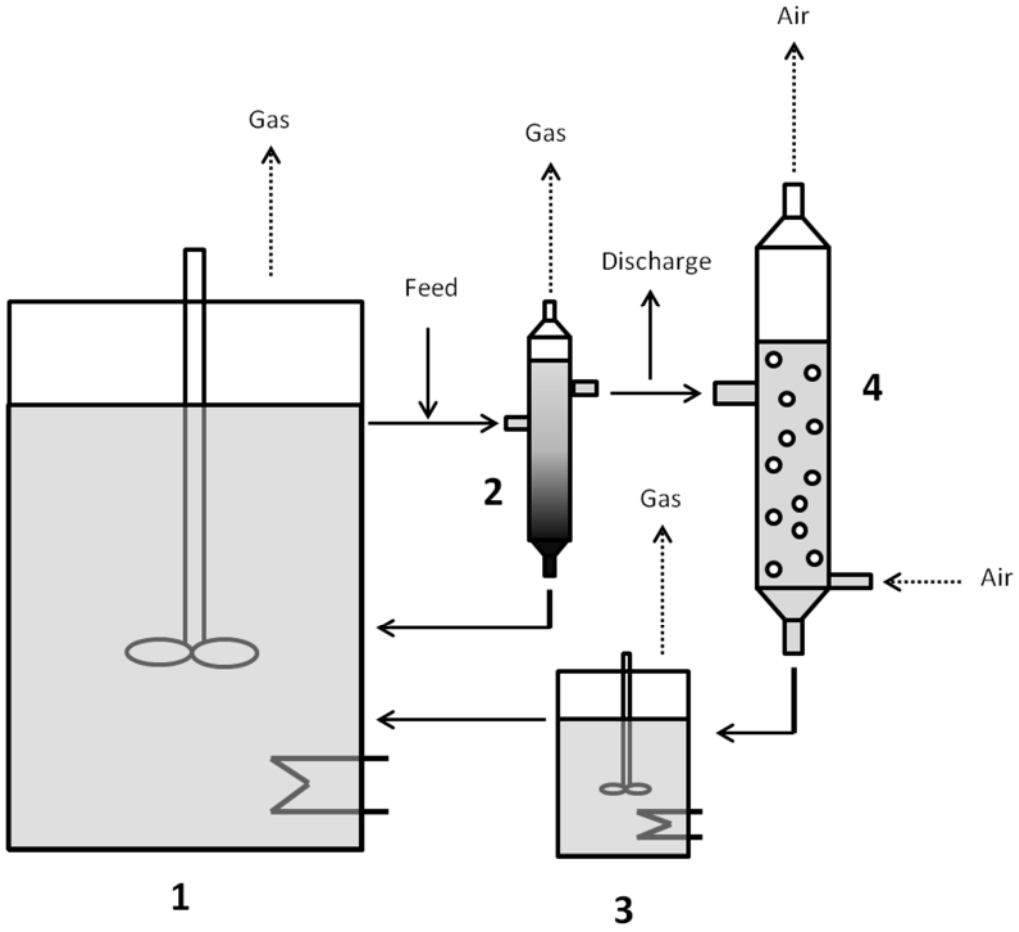

Figure 42: Suggestion for an improved process configuration with (1) digester, (2) settler, (3) holding tank and (4) air stripping column.

In Figure 42, a suggestion for an experimental setup that will maximize the methane content but limit the methane loss is given. In this setup, the digester content is pumped into a settler where a liquid and solid separation can take place. The solids can then be recirculated back to the digester whereas the liquid is pumped further on to the column. The settler has three purposes: 1) minimize the bacteria's and solid organic material's exposure to the column, 2) collect some of the methane trapped in the solution, as methane releases faster compared to carbon dioxide under standard conditions (Lindberg et al 2012) and, finally, 3) cool down the liquid so that the risk of methane production inside the column is minimized since the methanogenic activity decreases severely at lower temperatures. In the column, more liquid solution is stripped with air in order to desorb the carbon dioxide. Here additions of inorganic acids could also be applied in order to lower the pH. Before entering the digester, the liquid solution is fed to a heated holding tank where it is reheated back to the digester temperature and stripped of most of the solubilized oxygen. If a liquid feed or a hydrolysis reactor were to be used, the feed should be added just before the settler to utilize its acidity. Feeding at this point will also induce a pseudo-continuous operation as the substrate would gradually enter the digester leading to a more stable process with smaller fluctuations. Discharging should be made of the liquid part after the settler in order to minimize the removal of biomass. Important here would be to discharge

before feeding the system in order to avoid removing the substrate. Even though an experimental setup like this would have many benefits it would also add a lot of complexity, including several pumps and a quite sophisticated control system to avoid overflow in any of the operational units. As a result, this would lead to larger investments and higher energy and maintenance costs. However, considering the limitations seen in this study with a simpler setup, it might be needed in order to accomplish methane contents of 80-90% without losing in productivity.

Another interesting improvement could be to run the procedure at a higher temperature as this would decrease the solubility of carbon dioxide. (Richards, et al. 1994) were able to increase their methane content up to 98% running the process at 55 °C. A higher temperature in the column would be especially effective if the liquid and the solids could be separated in order to avoid exposure of the biomass to the higher temperature.

4 Conclusions

The simulation results show that a methane slip below 2 % can be obtained simultaneously as a significant increase in the digester methane concentration. As an example, simulation of a 2000 m^3 digester (active volume) and a desorption column of 30 m^3 with a sludge flow of 600 m^3/d and an air flow of 11 000 m^3/d gave an increase in the methane concentration from 58 % to 69 % with a methane loss of 1.3 %.

To minimize the methane slip and to maximize the digester methane concentration the results show that:

- The sludge flow rate should be low. At low sludge flow rate all methane in the sludge passing through the desorption column is desorbed, but the flow limits the overall methane slip.
- The air flow rate should be high. A higher gas flow rate will significantly increase the biogas methane concentration, but have a minor negative effect on the methane slip when the sludge flow rate is low.
- The influence of the volume of the desorption column is fairly week within the range studied, especially at low sludge flow rates.
- An increasing column diameter leads to less desorption of carbon dioxide, (and of methane unless the sludge flow rate is low).
- An increasing column height increases the desorption of carbon dioxide, and of methane unless the sludge flow rate is low.

Suggestions for further work:

- The weak influence of the desorption column volume needs to be further investigated to be fully understood.
- The hydrodynamics of the bubble column will switch from homogeneous flow into heterogeneous, less efficient flow at a linear gas velocity exceeding about 5 cm/s. However, if it would be favorable to increase the gas flow beyond this point remains to be investigated.
- The rate of conversion of bicarbonate to carbon dioxide decreases at increasing pH. Since the pH will increase over the desorption column as a result of the desorption of carbon dioxide this may set a limit to the achievable biogas methane concentration at low methane slip.

The experience from the second part of the project was that applying *in-situ* methane enrichment is a very complex and difficult task that surely requires optimization of all operational parameters. As there were many uncertain factors and problems during the study, further research should be carried out before any definitive conclusions can be drawn. However, some interesting observations were made:

- *In-situ* methane enrichment with *ex-situ* stripping seems to function poorly when using a substrate rich in nitrogen.
- Stripping with air seems more efficient compared to a vacuum force at 0.4 bar without being more toxic.
- Addition of organic acids seems to aid the removal of dioxide removal. However, it has long term effects and needs to be added carefully as it decreases the alkalinity.

- *In-situ* methane enrichment seems to have a stabilizing effect on an overloaded process. Most likely due to the increased pH level which will be beneficial for the sensitive methanogenic population.
- In order to achieve high methane content, the stripping procedure should be performed continuously with an organic loading rate below 2 gVS/L/day.

5 Acknowledgements

The authors acknowledge the financial support provided by the Swedish Energy Agency and the gas industry via SGC (Swedish Gas Technology Centre), Göteborg energy AB, Kristianstad Biogas AB, EON Sverige AB, Avfall Sverige AB and LRF.

6 References

Angelidaki, I. and Sanders, W. (2004). Assesment of anaerobic biodegradabilityu of macropollutants. *Reviews in Environmental Science and Biotechnology* 3, 117-129

Batstone, D.J., Keller, J., Angelidaki, R.I., Kalyuzhnyi, S.V., Pavlostathis, S.G., Rozzi, A., Sanders, W.T.M., Siegrist, H. and Vavilin, V.A. (2002). *Anaerobic Digestion Model No.1*. STR No. 13, IWA Publishing, London, UK.

Bonmatí, A and Flotats, X. (2003). Air stripping of ammonia from pig slurry: characterisation and feasibility of a pre- or post treatment to mesophilic anaerobic digestion. *Waste management* 23, 261-272

Chen, Y., Cheng, J.J. and Creamer, K.S. (2008). Inhibition of anaerobic digestion process: A review. *Bioresource Technology* 99, 4044-4064

Deckwer W.-D., Burckhart R. and Zoll G. 1974. Mixing and mass transfer in tall bubble columns, *Chem. Eng. Sci.* 29(11), 2177-88

Deckwer W.-D., Schumpe A. 1993. Improved tools for bubble column reactor design and scale-up, *Chem. Eng. Sci.* 48(5), 889-911.

Guštin S. and Marinšek-Logar, R. (2011) Effect of pH, temperature and air flow on the continuous ammonia stripping of the anaerobic digestion effluent. Process *safety and Environmental Protection* 89, 61-66

Hansen, K.H., Angelidake, I. and Ahring, B.K. (1998). Anaerobic digestion of swine manure: Inhibtion by ammonia. *Water Research* 32 (1), 5-12.

Hayes TD, Isaacson HR, Pfeffer JT, Liu YM. (1990). In situ methane enrichment in anaerobic digestion. *Biotechnology and Bioengineering,* 35(1),73-86.

Hebrard G., Bastoul D., Roustan M. 1996. Influence of the gas sparger on the hydrodynamic behaviour of bubble columns, Chem. Eng. Res. Des., Vol. 74(A3), Part A, 406 – 414.

Holmström, H. 1981, Rötning av kommunalt avloppslam – Teknik med möjligheter, Publikation VAV P42, *The Swedish water & Wastewater Association*, feb (in Swedish)

Joshi J. B. 1980. Axial mixing in multiphase contactors – a unified correlation. *Transaction of the Institution of Chemical Engineers* 58 (3), 155-165.

Jarvis, Å. and Schnürer, A. 2009. Mikrobiologisk handbok för biogasanläggningar, *Rapport SGC 207.*

Liao, P.H., Chen, A. and Lo, K.V. (1995). Removal of nitrogen from swine manure wastewaters by ammonia stripping. *Bioresource Technology* 54. 17-20.

Lindberg A. (2003). *Development of in-situ methane enrichment as a method for upgrading of biogas to vehicle fuel standard – selective desorption of carbon dioxide from sewage sludge,* Licentiate Thesis, Department of Chemical Engineering, Royal Institute of Technology, Sweden.

Lindberg, A. and Å. C. Rasmuson (2006). Selective desorption of carbon dioxide from sewage sludge for *in-situ* methane enrichment – part I: pilot-plant experiments, *Biotechnology and Bioengineering*, 95(5),794-803.

Lindberg, A. and Å. C. Rasmuson (2007). Selective desorption of carbon dioxide from sewage sludge for *in-situ* methane enrichment – part II: modelling and evaluation of experiments, *Biotechnology and Bioengineering* 97(5),1039-1052.

Martens, H. and Naes, T (1989), Multivariate calibration, Wiley, New York

Nordberg, Å., Edström, M., Uusi-Penttilä, M. & Rasmuson, Å. (2005). Processintern metananrikning. JTI-rapport 33, Kretslopp & Avfall. JTI- Institutet för jordbruks- och miljöteknik, Uppsala

Nordberg, Å., Edström, M., Uusi-Penttilä, M. and Rasmuson, Å.C. (2012). Selective desorption of carbon dioxide from sewage sludge for *in-situ* methane enrichment: Enrichment experiments in pilot scale. *Biomass and Bioenering* 37 (February 2012), 196-204. doi:10.1016/j.biombioe.2011.12.012

O'Keefe, D.M., Brigmon, R.L. and Chyoweth, D.P. (2000) Influence of methane enrichment by aeration of recirculated supernatant on microbial activities during anaerobic digestion. *Bioresource Technology* 71, 217-224.

Petersson, A. and Wellinger, A. (2010). Biogas upgrading technologies – developments and innovations. IEA Bioenergy Task 37. 19 pages http://www.iea-biogas.net/Dokumente/upgrading_rz_low_final.pdf

Quan, X., Ye, C., Xiong, Y., Xiang, J. and Wang, F. (2010). Simultaneous removal of ammonia, P and COD from anaerobically digested piggery wastewater using an integrated process of chemical precipitation and air stripping. *Journal of Hazardous Materials* 178, 326-332.

Richards BK, Herndon FG, Jewell WJ, Cummings RJ, White TE. (1994) *In situ* methane enrichment in methanogenic energy crop digesters. *Biomass and Bioenering* 6(4),275-282.

Srivastava VJ, Hill AH. (1993) Methane enrichment digestion experiments at the anaerobic experimental test unit at Walt Disney World. Chicago, IL: Institute of Gas Technology; 1993 Jun. Report No: GRI- 92/0498.

Stumm, W. & Morgan, J.J., 1996. Aquatic chemistry: chemical equilibria and rates in natural waters 3rd ed., New York: Wiley.

Towell G. D. and Ackermann G. H. 1972. Proc. 2nd Int. Symp. Chem. React. Eng., B 3-1, Amsterdam.

Westerholm, M. (2012). Biogas production through the syntrophic acetate-oxidising pathway. Doctoral thesis, Swedish University of Agricultural Sciences, Uppsala.

Yu, Z, Rasmuson, Å.C. (2008). Selective desorption of carbon dioxide from sewage sludge for *in-situ* methane enrichment – a comprehensive model; Report to FUTURA, January 2008

Zhang, L. Jahng D. (2010) Enhanced anaerobic digestion of piggery wastewater by ammonia stripping: Effects of alkali types. *Journal of Hazardous Materials* 182, 536-543

Zhang, L., Lee, Y.W. and Jahng D. (2012). Ammonia stripping for enhanced biomethanization of piggery wastewater. *Journal of Hazardous Materials* 199-200, 36-42.

7 Appendix

7.1 Appendix I. Top level of Simulink model

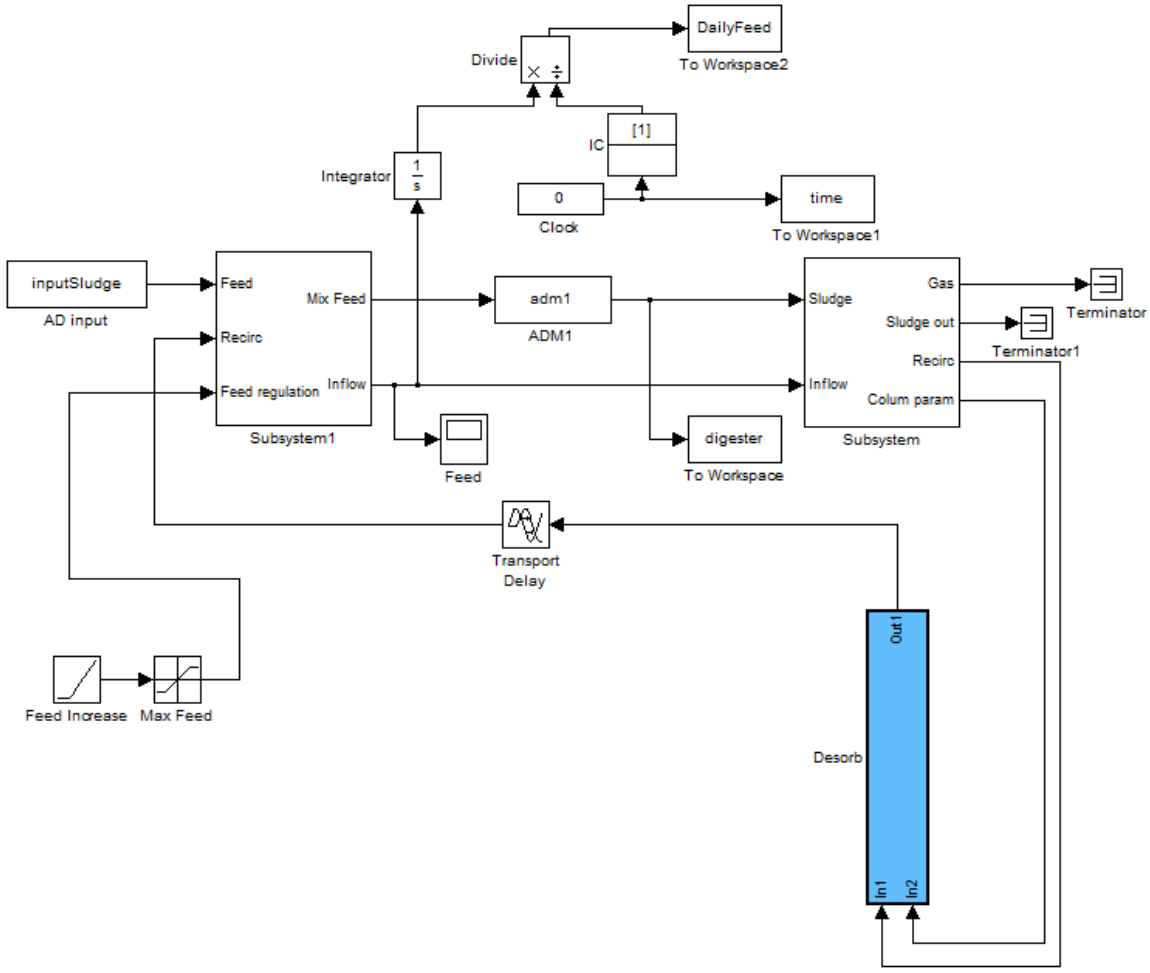

Figure 43: Toplevel of simulink model

Figure 43 shows the toplevel of the combined ADM1 and Desorption column models in the Simulink© interface. Each one of the boxes contains further graphical programing steps. The programming interface is very easy to learn and is intuitive. It also allows access to the powerful calculation functions of Matlab©.

7.2 Appendix II. Period with liquid/solid separation

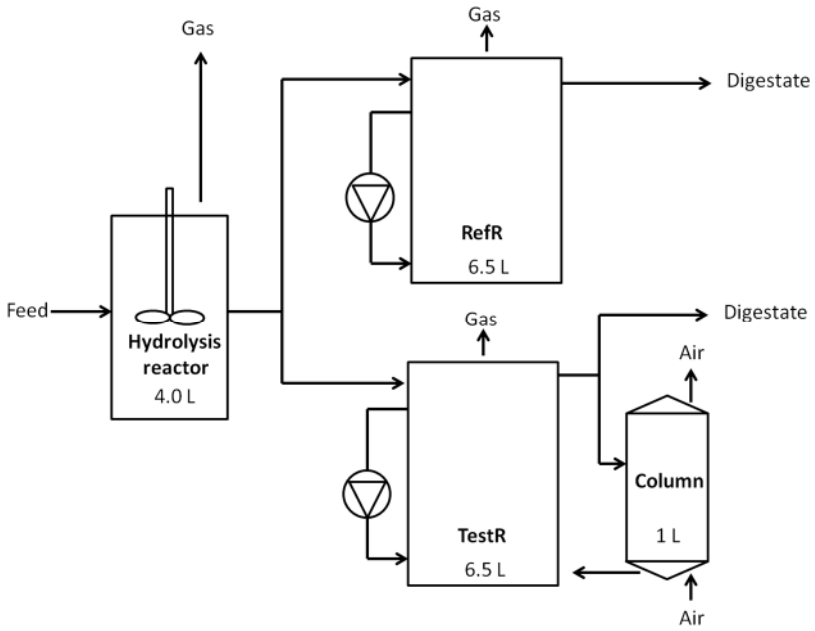

Figure 44: Process configuration during period with liquid/solid separation

Due to suspected ammonia inhibition when a using nitrogen-rich substrate as feedstock, as well as inhibition from oxygen exposure in the column during carbon dioxide stripping with air, a new type of substrate and new procedure with a different sludge was tested. The idea was to separate the solid biomass from the liquid containing the dissolved carbon dioxide before entering the column in order to avoid the bacteria's exposure to oxygen. Therefore, the mixing in the digester was carried out through recirculation of the liquid in order to let the biomass settle at the bottom of the digester. As in phase B1, the feedstock was changed to a mixture of milk, water and potato flour in order to decrease the viscosity and reduce the nitrogen content of the substrate. Two parallel digesters of 6.5 L were also used: giving a shorter retention time in the column (1 day). A schematic drawing of the setup can be seen in Figure 44 and in Table 23 the process operation details are given.

Table 23: Process operation parameters in B1

General	Substrate	Milk + potato flour
	Anaerobic sludge	WWTP
	Reference in parallel	Yes
Digester	Organic loading rate	3
	Hydraulic retention time	10 days
	Volume	6.5 L
	Fed from Hydrolysis	Yes
Hydrolysis reactor	Organic loading rate	10 gVS/L/day
	Hydraulic retention time	1.2 days
	Volume	4 L
Column	Treatment	Air
	Retention time	1 day
	Air flow rate	day

Due to a number of technical problems, the results from phase period with liquid/solid separation were not reportable. The separation of liquid and solids inside the reactor created a very unsteady gas flow and the poor settling properties of the sludge produced big challenges in upholding the separation properly and at the same time maintain a reasonable mixing inside the digester. The control digester could be operated rather well but, due to the constant liquid transfers with the column, the digester where the treatment was applied experienced much bigger problem with the separation. The poor visibility of the stainless steel digesters also made it difficult to know the status of the separation. After running the process for three weeks with constant problems it was decided that this was not a feasible approach and the process configuration was returned to a standard CSTR version for phase B.

7.3 Appendix III. Methane content from Clarus 400 during B3

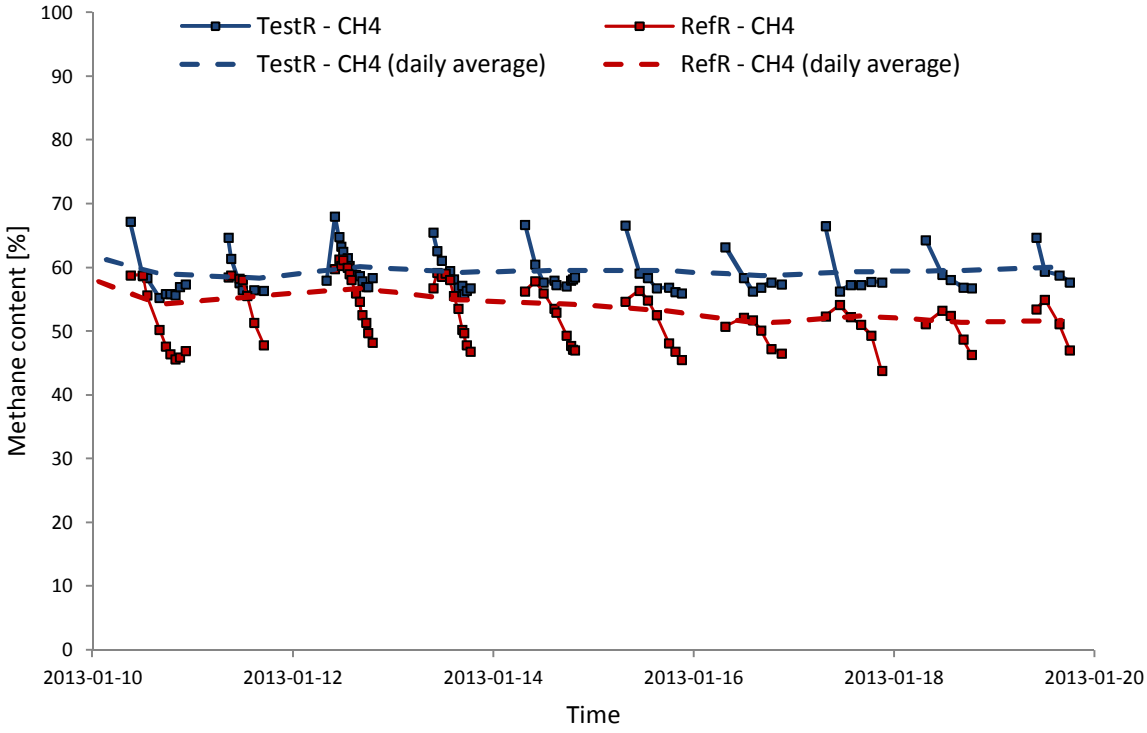

Figure 45: All GC measurement after gas bag with Clarus 400 during phase B3

Figure 45 shows the methane content from all GC measurements with Clarus 400 during phase B3. A line is drawn between each data point within the same day.