



**Aalto University  
School of Chemical  
Engineering**

**Liis Västra**

**AMMONIA STRIPPING OF AMMONIFIED CHICKEN LITTER  
IN PILOT SCALE**

Master's Programme in Chemical, Biochemical and Materials Engineering  
Major in Biotechnology

Master's thesis for the degree of Master of Science in Technology  
submitted for inspection, Helsinki 14.3.2017.

Supervisor: Professor Katrina Nordström

Instructor: D.Sc. (Tech.) Ilkka Virkajärvi

---

**Tekijä** Liis Västra

---

**Työn nimi** Ammonifioidun kananpehkon ammoniakkipitoisuuden pilottimittakaavassa

---

**Laitos** Biotuotteiden ja biotekniikan laitos

---

**Pääaine** Biotekniikka ja elintarviketekniikka

---

**Työn valvoja** Professori Katrina Nordström

---

**Työn ohjaaja(t)/Työn tarkastaja(t)** Tekniikan tohtori Ilkka Virkajärvi

---

**Päivämäärä** 14.3.2017**Sivumäärä** 81 + 5**Kieli** Englanti

---

### Tiivistelmä

Kananpehku sisältä paljon typpeä, joka biokaasutusprosessissa muuttuu myrkylliseksi ammoniakiksi. Ammoniakki haittaa metaanin tuotantoa. Kananpehkulietteen ammoniakkipitoisuus kasvaa korkeassa lämpötilassa ja emäksisessä pH:ssa. Tutkimme pilottimittakaavassa, miten 70 % ammoniumtyyppistä saadaan poistettua huonontamatta biokaasun laatua.

Typpeä poistettiin kaksivaiheisessa esikäsitelyssä. Ensin ammonifikaatioprosessissa muodostettiin tyyppiyhdisteistä ammoniumtyyppiä ja tämän jälkeen ammoniakki strippattiin ilmapuhalluksen avulla yksinkertaisessa panosreaktorissa. Stripausmateriaalina käytettiin sekä ammonifioitua kananpehkulietettä, että ammonifioitua ja kierrätettyä rejektilietettä. Pyrimme löytämään tehokkaimmat parametrit ammoniakin poistolle muuttamalla strippauslämpötilaa, pH:ta, sekoitusta ja ilmastussyvyyttä. pH:n säätöön käytettiin erilaisia emäksiä (NaOH, KOH, CaO) sekä CO<sub>2</sub>-strippausta. Stripatun syötteen laatua valvottiin mittaamalla kiintoainepitoisuutta, orgaanisen aineen määrää, puskurikapasiteetta, haihtuvien rasvahappojen määrää ja hiili-typpisuhdetta sekä testaamalla stripattua lietettä biokaasureaktorissa. Stripauskustannuksia verrattiin vastaavan mittakaavan kolonnistripperin kustannuksiin.

Ammoniakkipitoisuuden seurasi ensimmäisen kerraluvun kinetiikkaa. Stripattu biokaasusyöte soveltui hyvin biokaasutukseen, eikä ongelmia metaanintuotannossa näyttänyt esiintyvän. Kolmetuntisissa kokeissa strippattiin kokonaisammoniakkipitoisuudesta 43-80 %. Lietteen pH:n säätöön sopi sekä KOH<sub>45wt%</sub>, että NaOH<sub>50%</sub>-liuos, mutta CaO jauhe ei liennut hyvin. Stripauslämpötilan oli oltava 74 °C - 80 °C, jotta 70 % ammoniumtyyppistä saatiin poistettua. Korkeammassa lämpötiloissa haihtuminen aiheutti laitteistossa ongelmia. Optimiolosuhteissa strippaus kesti 2.5 h ( $t_{-70\% \text{ TAN}}$ ), lämpötila oli 80 °C ja pH 10,0-10,2. Tavalliseen ammonifioituun lietteeseen kului lipeäliuosta vähintään 10.5 ml/l, kun taas rejektilietteeseen kului 15,8 ml/l. CO<sub>2</sub>-strippauksella nostettiin lietteen pH:ta 0,4-1,6 pH-yksikköä, jolloin lipeän tarve pieneni merkittävästi. Sekoitus tehosti prosessia huomattavasti. Myös ilmastussyvyuden lisääminen näytti edistävän ammoniakin poistoa. Laskelmiemme mukaan optimiolosuhteissa panosstrippaus maksoi 4,36 €/NH<sub>3</sub> kg ja se oli hieman edullisempi strippausmetodi, kuin kolonnistrippaus (4,84 €/NH<sub>3</sub> kg). Menetelmää on kuitenkin tutkittava ja kehitettävä edelleen, jotta se olisi taloudellisesti kannattava.

---

**Avainsanat** ammoniakki, strippaus, biokaasutus, kananpehku, ammonifikaatio

---

---

**Author** Liis Västra

---

**Title of thesis** Ammonia Stripping from Ammonified Chicken Litter in Pilot Scale

---

**Department** Department of Bioproducts and Biosystems

---

**Major** Biotechnology and food technology

---

**Thesis supervisor** Professor Katrina Nordström

---

**Thesis advisor/ Thesis examiner** D.Sc. (Tech.) Ilkka Virkajärvi

---

**Date** 14.3.2017**Number of pages** 81 + 5**Language** English

---

**Abstract**

Chicken litter contains high levels of nitrogen, which can form toxic ammonia and inhibit methane production in a biogasification process. Ammonia concentration of chicken litter slurry increases in high temperature and alkaline pH. We studied how 70 % of the ammonia nitrogen can be removed efficiently, in a pilot scale, without impairing the quality of the biogas feed.

Ammonia nitrogen was removed in a two phase pre-process: First ammonia nitrogen was formed from nitrogen compounds in an ammonification process. Then ammonia was stripped in a simple batch type reactor by aeration. The stripping material used was ammonified chicken litter slurry, as well as, ammonified and recycled reject slurry. We strived to find the most efficient parameters for ammonia removal by changing the stripping temperature, pH, stirring and aeration depth. Moreover, variable alkalis (NaOH, KOH and CaO) were used for pH adjustment as well CO<sub>2</sub>-stripping. The quality of stripped feed was monitored by measuring the concentration of total solids, volatile solids, volatile fatty acids, buffer capacity along with carbon-nitrogen fraction and by testing the slurry in a biogas reactor. The costs of the batch style ammonia stripping were compared to the costs of column stripping of a similar scale.

The ammonia stripping process followed first order kinetics. The stripped biogas feed was well suited to biogasification and no problems seemed to occur in methane production. In three-hour stripping experiments 43-80 % of total ammonia nitrogen (TAN) was removed. Both KOH<sub>45wt%</sub>, and NaOH<sub>50%</sub> solutions were suitable for pH adjustment. However, CaO powder did not dissolve well. For 70 % TAN removal, the required stripping temperature was 74 °C - 80 °C. Higher temperatures caused problems in the setup due to excessive evaporation. In optimized conditions stripping time was 2.5 h ( $t_{-70\% \text{ TAN}}$ ), temperature was 80 °C and pH 10.0-10.2. The lye requirement for regular ammonified chicken litter slurry was no less than 10.5 ml/l. Whereas, reject slurry required 15.8 ml/l. CO<sub>2</sub>-stripping raised the pH of reject slurry by 0.4-1.6 pH-units and lowered the lye requirement significantly. Stirring had a notable positive affect on the efficiency of the stripping process. Also, the increase of aeration depth seemed to promote ammonia removal. According to our calculations, in optimized conditions, batch stripping costs were 4.36 €/ NH<sub>3</sub> kg, a little less than column stripping costs, 4.84 €/ NH<sub>3</sub> kg. However, the stripping process needs to be studied and developed further, to make it profitable.

---

**Keywords** ammonia, stripping, biogasification, chicken litter, ammonification

---

## Preface

This master's thesis was conducted at Ductor Oy from June 2015 to November 2016. The aim of this project was to test new stripping equipment with ammonified chicken litter to determine if the stripping technology can be applied in industrial scale biogas plants. The goal was to create ammonia removal process to reduce ammonium inhibition in biogas fermentation and aim to improve biogas economics and nutrient recycling.

I want to thank my co-workers M.Sc. Minna Lahtinen, Ph.D. Kerttu Koskenniemi, M.Sc. Aili Möttönen, M.Sc. Essi Kangasaho and M.Sc. Jari Koponen who participated in this work and helped me out in the pilot plant and assisted me with lab analysis. Big thank you goes to my instructor D.Sc. (Tech.) Ilkka Virkajärvi and supervising Professor Katrina Nordström for support. I want to thank them for advising and patience.

This thesis would have been much more difficult without the peer support from my co-workers of "Kopituskerho". Thanks to Laura Euro, Ville Karhu, Simo Matias Linkola, Anu Patjas. Thanks the crew of Kansankoti, Juhani Paasonen, Mikael Nenonen, Malla Salminen and Veli-Matti Vikström. And my special friend Marcus Olsson.

## Abbreviations

TS	Total solids. m-%
VS	Volatile solids. m-%
TAN	Total ammonia nitrogen, g/l
VFA	Volatile fatty acids
FOS	Volatile fatty acids ( <i>germ. flüchtige organische Säuren</i> )
TAC	Total inorganic carbon ( <i>germ. Totales Anorganisches Carbonat</i> )
TIC	Total inorganic carbon, buffer capacity, CaCO <sub>3</sub> mg /L
C	Carbon fraction (%)
N	Nitrogen fraction (%)
C/N	Carbon-nitrogen ratio
Rpm	Revolutions per minute
VVM	Aeration rate, vessel volumes of gas per minute
G/L	Gas-liquid ratio ( $V_{\text{gas}}/V_{\text{slurry}}$ )
k	Rate constant for first order reactions

## Table of Contents

1 Introduction .....	1
2 Biogasification of chicken litter .....	3
2.1 Anaerobic digestion .....	3
2.2 Parameters of anaerobic digestion .....	5
2.3 Chicken manure as biogas feed .....	7
3 Prevention of nitrogen inhibition.....	10
3.1 pH control of biogas reactors.....	10
3.2 Ammonia stripping.....	10
3.3 Alternative nitrogen removal methods .....	12
4 Stripping theory.....	17
4.1 Thermodynamic equilibria .....	17
4.2 Henry's law.....	18
4.3 Mass transfer .....	20
5 Materials and methods .....	23
5.1 Aims of the study .....	23
5.2 Ammonia removal equipment .....	23
5.3 Chicken litter .....	25
5.4 Ammonification.....	26
5.5 Preliminary experiments.....	26
5.6 Stripping in pilot scale .....	27
5.6.1 Stripping ammonified slurry .....	27
5.6.2 pH adjustment.....	28
5.6.3 Stripping ammonified reject slurry and CO <sub>2</sub> -stripping.....	29
5.6.4 Cooling unit .....	29
5.6.1 The effect of stirring.....	29
5.6.2 The effect of aeration depth .....	30
5.6.3 Volume measurement .....	30

5.7 Laboratory analysis .....	31
5.7.1 Total ammonia nitrogen concentration.....	31
5.7.2 Total solids and volatile solids .....	31
5.7.3 Volatile fatty acids and alkalinity .....	32
5.7.4 Carbon and nitrogen content.....	33
6 Results .....	34
6.1 Ammonification.....	34
6.2 Preliminary experiments .....	34
6.3 Pilot experiments .....	35
6.3.1 pH adjustment.....	35
6.3.2 Aeration.....	36
6.3.3 Stripping slurry .....	38
6.3.4 CO <sub>2</sub> -stripping .....	40
6.3.5 Evaporation and foaming.....	41
6.4 Laboratory analysis .....	42
6.4.1 Ammonia removal.....	42
6.4.2 Total solids and volatile solids .....	48
6.4.3 Volatile fatty acids and buffer capacity .....	51
6.4.4 Carbon-nitrogen-ratio .....	53
6.5 The effect of stripped slurry on biogas reactors .....	55
6.6 Sources of errors .....	57
7 Cost calculation .....	59
7.1 Mass balance of ammonia stripping .....	59
7.2 Utility costs of stripping .....	62
7.3 Stripping costs in 500 MW biogas plant.....	66
8 Discussion and conclusions .....	68
References.....	73

## APPENDIX 1 Detailed stripping specifications

## 1 Introduction

Biogasification is an effective way to utilize a wide variety of agricultural waste such as chicken manure which is otherwise harmful to the environment (Ahring et al., 1992). Uncontrolled waste storage in manure piles leads to spontaneous methanogenic activity, foul odors and escape of greenhouse gases, which contribute to climate change. Agricultural waste also contains pathogens and nutrients that can contaminate waterbodies (Yetilmezsoy and Sakar, 2008). There is an increasing number of biogas plants in Germany which use manure and energy crops as feed (Belostotskiy et al., 2013). Biogas production can decrease the environmental impact of agriculture and add value to waste. However, the use of chicken manure as feed can lead to problems in anaerobic digestion due to ammonia formation (Belostotskiy et al., 2013).

In anaerobic digestion nitrogen is degraded into ammonium. At high temperature and high pH most ammonium ( $\text{NH}_4^+$ ) is converted to free ammonia ( $\text{NH}_3$ ) which is toxic to methane producing bacteria (Gangagni Rao et al., 2008; Chen et al., 2008). High nitrogen concentration limits the use of chicken litter as biogas feed, because it can cause low methane production. The nitrogen flux should be controlled in biogasification by monitoring the ammonia concentration and the carbon-nitrogen ratio in input and output (Ponsá et al., 2008).

Toxic ammonia can be removed prior to biogasification in a two step process. First the chicken slurry is ammonified, anaerobically predigested. A specific population of ammonification bacteria breaks down proteins and produces ammonium ions,  $\text{NH}_4^+$ . In the second step, stripping, the  $\text{NH}_4^+$  is converted into free ammonia,  $\text{NH}_3$ , by adjusting the pH of the slurry in a heated stripping vessel (Nishio and Naomichi, 2013). The temperature should be as high as



possible to shift the reaction balance from ammonium to ammonia. When the temperature is 80 °C and pH 10, most of the ammonium will be in free ammonia form which is volatile and can be removed with submerged aeration. Air is then washed with an acid solution and ammonia recovered as nitrogen fertilizer, ammonium sulphate  $(\text{NH}_4)_2\text{SO}_4$ , (Bonmati and Flotats, 2003).

In this thesis ammonia nitrogen batch stripping was studied in a pilot scale from ammonified chicken slurry (TS 9-8 %.  $[\text{NH}_4^+]$  ca. 2.1 g/l). The target was to remove 70 % of total ammonia nitrogen (TAN) and 50 % of total nitrogen. The effects of temperature, pH, alkali type, string and aeration submersion depth on the efficiency of TAN removal were studied. Additionally, ammonia stripping from recycled (ammonified reject) slurry was studied. In these experiments  $\text{CO}_2$  removal was conducted as a pre-process to find means for raising the pH without adding chemicals.

Batch stripping was compared to previous experiments with a column stripping unit by Nurmi (2015) by performing cost calculations. The goal was to determine the most economical method for ammonia nitrogen removal. This study was conducted to gain information on which stripping method could be recommended for a 500 MW biogas plant.

## 2 Biogasification of chicken litter

### 2.1 Anaerobic digestion

Biogas is a gas mixture of primarily methane (CH<sub>4</sub>, 55–70%) and carbon dioxide (CO<sub>2</sub>, 30-45%). The gas mixture includes also smaller amounts of other components such as water vapor (H<sub>2</sub>O, 1-5 % by vol.), hydrogen sulfide (H<sub>2</sub>S, 0-0.5 % by vol.), siloxanes (0–50 mg/Nm<sup>3</sup>), ammonia (NH<sub>3</sub>, 0-0,05 % by vol.), oxygen (O<sub>2</sub>, 0.01–2 % by vol.), carbon monoxide (CO, < 0.2 % by vol.), nitrogen (N<sub>2</sub>, 0–2% by vol.) and halogenated hydrocarbons (Deublein and Steinhauser, 2010). 1 kg of poultry litter can produce 99 liters of methane (Moody et al., 2011). 100 liters of methane produces roughly to 4 MJ or 1 kWh of energy (Anon., Electrigaz, 2016).

Methane production from biomass, biological anaerobic digestion, occurs in a 4 step process (Apples et al., 2011; Hamilton, 2009). Complex organic matter such as manure can be converted into gases in a CSTR reactor according to figure 1 (Lyberatos and Skidas, 1999; Zhang et al., 2014).

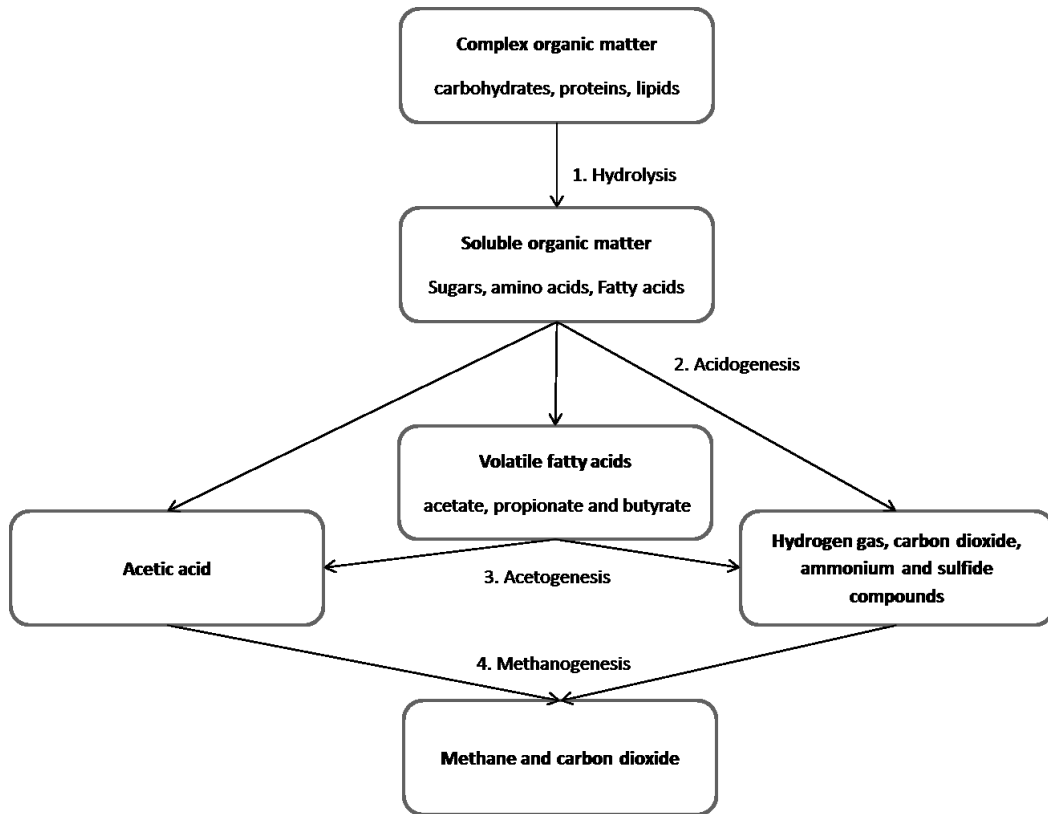


Figure 1. Anaerobic digestion of organic matter occurs in four steps: 1 hydrolysis, 2 acidogenesis, 3 acetogenesis and 4 methanogenesis. The figure is modified from (Hamilton, 2009; Zhang et al., 2014).

It can be seen from figure 1 that the first step in anaerobic digestion is hydrolysis. Hydrolytic bacteria break down and liquify complex organic matter such as lipids, carbohydrates and proteins and degrade them into soluble organic molecules such as fatty acids, sugars and amino acids (Hamilton, 2009). In the second step of the breakdown process, acetogenic bacteria degrade soluble organic molecules into short chain fatty acids (volatile fatty acids, VFA) such as acetate, propionate and butyrate. Acetogenesis produces also acetic acid, hydrogen, carbon dioxide, free ammonia, soluble ammonium and sulfide compounds such as dihydrogen sulfide. In the third step, acetogenesis, VFA are broken down to acetic acid, H<sub>2</sub>, CO<sub>2</sub>, NH<sub>3</sub>, NH<sub>4</sub>, and H<sub>2</sub>S by anaerobic bacteria (Zhang et al., 2014). In the last and slowest step of anaerobic digestion,

methane forming bacteria produce methane via 2 major pathways. Namely 30 % of methane is produced via carbon dioxide reduction, according to equation (1): carbon dioxide and hydrogen produce methane and water (Al Seadi et al., 2008; Hamilton, 2009). The rest, 70 % of methane, is produced through acetic acid cleavage according to equation (2). The end products of acetic acid cleavage are methane and carbon dioxide (Zhang et al., 2014; Hamilton 2009; Al Seadi et al., 2008).



## 2.2 Parameters of anaerobic digestion

Methanogenic bacteria are sensitive to changes in operating conditions and need stable environment to maintain high methane yield. Conditions such as temperature, pH, loading rate and composition of feedstock influence methanogenesis. Changes in temperature and pH, or the presence of oxygen, can severely inhibit methanogenic activity (Al Seadi et al., 2008). Methane yield depends also on factors such as the carbon-nitrogen (C/N) fraction, total solids (TS) and moisture. Thus it is important to consider what kind of feed is inserted into biogas reactors (Ponsá et al., 2008).

Anaerobic digestion can occur at various temperature ranges: psychrophilic digestion operates at less than 25 °C, the mesophilic process at 25-45 °C and the thermophilic process at 45-70 °C. As can be seen from table 1, the temperature range affects the production rate of methane. A thermophilic process has its advantages due to fast process, higher loading rate and high methane yield. On the other hand high temperature in a thermophilic process demands higher heating costs than mesophilic and psychophilic processes. However, these energy costs can be covered with more efficient methane production. Higher temperature increases ammonia formation, which can lead to ammonia

inhibition. Therefore, thermophilic processes should be operated at just over 50 °C to minimize ammonia inhibition and to ensure the growth of thermophilic bacteria. Thermophilic bacteria are very temperature sensitive and only tolerate a variation of  $\pm 1$  °C temperature fluctuation whereas mesophilic bacteria are more flexible and tolerate a variation of  $\pm 3$  °C (Al Seadi et al., 2008).

Table 1. Thermal stage and characteristic retention times of anaerobic digestion. Adapted from (Al Seadi et al., 2008).

<b>Thermal stage</b>	<b>Process temperatures</b>	<b>Minimum retention time</b>
psychrophilic	< 20 °C	70 to 80 days
mesophilic	30 to 42 °C	30 to 40 days
thermophilic	43 to 55 °C	15 to 20 days

The optimal pH range for most methanogens is between pH 7.0-8.0. However, acidogenic bacteria usually have lower optimum pH value. The operational pH for methane production is pH 5.5-8.5. The buffering capacity of the bicarbonate system in anaerobic digesters is important since it can keep the pH stable. The buffering system can counteract drastic changes in pH value if acid or base accumulates in the process (Al Seadi et al., 2008). Low C/N ratio will increase the pH due to production of harmful ammonia. Whereas, increase in carbon content (higher C/N ratio) will form more CO<sub>2</sub> and lower the pH (Dioha et al., 2013). According to Dioha and others (2013) the optimum yield of biogas from manure can be attained in the range of 20–30 C/N ratio (Dioha et al., 2013). In this range bacteria will have sufficient amount of nitrogen for cell growth and degeneration of carbon while maintaining a nontoxic ammonia level (Fricke et al., 2007).

VFA, the intermediate products of anaerobic digestion, can indicate the stability of a biogas reactor. The accumulation of VFA indicates instability of the process and can lead to drop in pH. The optimal level of VFA varies between biogas reactors and is highly individual. Thus, VFA concentration should not be used as sole process monitoring factor (Al Seadi et al., 2008).

In biogas production it is important that the feed that is added to biogas reactors is suitable feedstock for a balanced growth of microorganisms. The temperature, pH, nitrogen ratio and other parameters need to be carefully managed to keep the methane yield high (Al Seadi et al., 2008; Dioha et al., 2013).

### **2.3 Chicken manure as biogas feed**

Chicken manure or chicken litter has many advantages as biogas feedstock. According to Huang and Shih (1981) chicken litter has a high CH<sub>4</sub> potential, 270 m<sup>3</sup>/tn. It is also a low-cost substrate with good availability and it contains anaerobic bacteria (Al Seadi et al., 2008; Abouelenien et al., 2009). Additionally, poultry manure is composed of a more biodegradable organic matter than other livestock wastes (Hill, 1983). The problem with utilizing some of the agricultural by-products, such as manure in biogasification, is that they can have a high nitrogen content (Nie et al., 2015). In anaerobic digestion, nitrogen compounds such as proteins and urea are degraded into ammonium NH<sub>4</sub><sup>+</sup> (Kayhanian, 1999; Chen et al., 2008; Nahm, 2005).

Ammonia and ammonium ions are interchangeably dependent on temperature and pH (Liao et al., 1995; Patoczka and Wilson, 1984). Figure 2. illustrates that most ammonium (NH<sub>4</sub><sup>+</sup>) converts to free ammonia (NH<sub>3</sub>) at high temperature and a pH over 9 (Patoczka and Wilson, 1984). It can be seen from figure 2 that if a mesophilic anaerobic digester reaches pH 8 at 40 °C, the reactor will contain growth inhibiting ammonia.

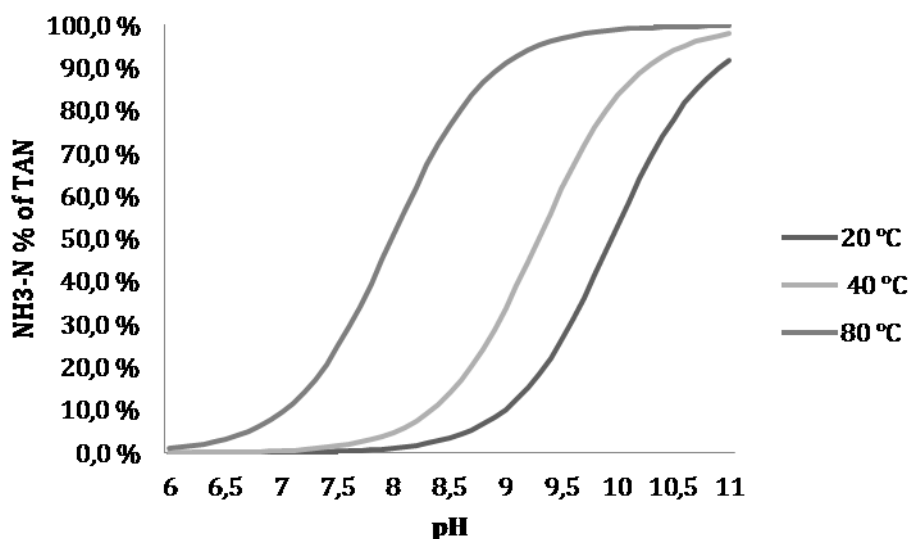


Figure 2. The percentage of free ammonia present in solution is greater at higher temperature and pH (Patoczka and Wilson, 1984).

It has been observed that biogas reactors fed with 8 % total solids (TS) of poultry waste give better biogas yield than higher solids levels. This is due to high ammonia concentration of the manure slurry (Shivraj and Seenayya, 1994). Different sources report that, in anaerobic digestion, free ammonia concentrations should be kept under 0.08 – 1.1 g/l (Al Seadi et al., 2008, Hansen et al., 1998). Calli and others (2005) report that ammonia inhibition occurs above pH 7.4 in the range of 1.5–3 g/l total ammonia nitrogen (TAN), whereas at concentrations above 3 g/l, ammonia is claimed to be toxic regardless of pH. Ammonia can be toxic in high concentrations to methanogenic bacteria because it can diffuse into the cell membrane and cause proton imbalance and potassium deficiency (Jarrell et al., 1987; Sprott and Patel, 1986; Gallert et al., 1998). Koster and Lettinga (1988) witnessed that ammonia concentration of 4051–5734 mg/l can lead to 56.5 % decrease in methanogenic activity. Thus it can be concluded, that ammonia limits the methane yield and for this reason high nitrogen concentration can restrict the use of chicken litter as biogas feed.

The buffer capacity, pH and other characteristics of manure can vary from season to season and it can depend on the animal feed. Chicken manure is high in alkalinity. High ammonia concentration is characteristic to anaerobically digested animal manure slurries. The ammonia originates from urea and proteins (Kayhanian, 1999; Chen et al., 2008; Nahm, 2005). Chicken manure can also include some sand which can cause clogging in process instruments and valves (Deublein and Steinhauser, 2010).



## **3 Prevention of nitrogen inhibition**

### **3.1 pH control of biogas reactors**

Ammonia concentration in biogas reactors can be controlled due to the fact that formation of free ammonia is pH and temperature dependent. From figure 2 it can be seen that the fraction of ammonia can be lowered by decreasing the pH of the biogas reactor to 7. The pH can be buffered with volatile fatty acids (Al Seadi et al., 2008). Strik and others (2006) found that it is possible to reduce the quantity of free ammonia in the biogas reactor by controlling the pH by adding lye and HCl. However, this had negative impact on biogas yield and was not recommended as an ammonia control technique. Instead Strik and others (2006) recommended removing the ammonia prior to biogasification.

### **3.2 Ammonia stripping**

A stable solution for preventing ammonium inhibition would be to optimise the C/N ratio because anaerobic bacteria require suitable nutrient balance for their growth. Moreover, a stable environment and C/N ratio controls the pH value of the slurry (Dioha et al., 2013). Thus, the nitrogen flux should be controlled in biogasification by monitoring the ammonia concentration and the C/N input and output.

Biogas production can be optimized with nitrogen removal in a two step process according to figure 3. First, the feed with high nitrogen content is ammonified, and anaerobically predigested for 3-5 days. The specific ammonification bacterial population breaks down proteins and produces ammonium ions,  $\text{NH}_4^+$ .

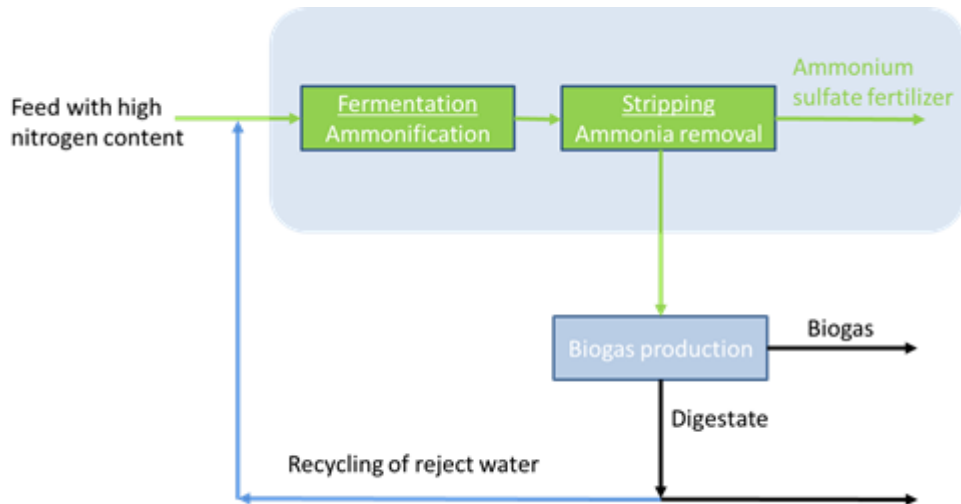
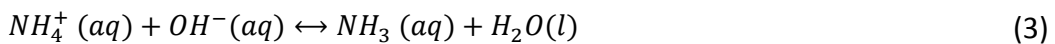


Figure 3. Flow sheet of nitrogen removal process in biogas production. Modified from source (Ductor Corporation, 2016).

In the second step, stripping, the  $\text{NH}_4^+$  is converted into free ammonia ( $\text{NH}_3$ ) according to equation (3) by adjusting the pH of the slurry up to 10 in a heated stripping vessel (Guštin and Marinšek-Logar 2011).



The temperature should be as high as 80 °C to shift the reaction balance from dissociated ammonium to free ammonia. When temperature is 80 °C and pH is 10, most of the ammonium will be converted into ammonia (see figure 2) which is volatile and can be removed by aeration under the liquid surface (Patoczka and Wilson, 1984). However, at room temperature, pH 10.5–11.5 is required for efficient ammonia removal (Bonmatí and Flotats, 2003).

Air is then scrubbed with acid solution and ammonia recovered as nitrogen fertilizer, ammonium sulphate  $(\text{NH}_4)_2\text{SO}_4$  (Patoczka and Wilson, 1984). Since the anaerobic digester is sensitive to rapid changes in pH, the pH of the feed should be adjusted to approximately pH 7, when adding stripped slurry to the biogas reactor. The pH can be achieved by addition of buffering feed such as corn or by

neutralizing the slurry with acid such as HCl (Al Seadi et al., 2008; Dioha et al., 2013).

### **3.3 Alternative nitrogen removal methods**

Possible techniques for nitrogen removal other than stripping are for example reverse osmosis, ion exchange, ammonia, electro dialysis, distillation and membrane filtration. However, suitable nitrogen removal methods are dependent on the type of use, feed type and costs of removal process. Some of the ammonia nitrogen removal techniques require pre-processing of feed such as solids separation step and pH adjustment prior to the ammonia removal process. Additional process steps commonly require higher installation and operation costs (Reeves, 1972).

Municipal waste water, landfill leachate and agricultural waste contain waste water with suspended solids. Water treatments and the process industry has widely utilized ammonia removal techniques, especially ammonia stripping. The most common ammonia removal methods in the water treatment industry are ammonia stripping in packed columns and holding ponds. Holding ponds may also utilize diffused aeration or surface agitation (Obaid-ur-Rehman and Beg, 1990). However, holding ponds pollute the air and the environment with ammonia gas and produce foul odors. It is vital to collect removed ammonia. This is usually done with ammonia scrubbing units which contain for example sulfuric acid solution.

The efficiency of the ammonia stripping from wastewater depends primarily on the way the gas and the liquid are brought into contact with each other. Cross flow and counter flow towers have been broadly used for ammonia stripping (Obaid-ur-Rehman and Beg, 1990). Alternative stripping methods include:

- Air or steam stripping
- Atmospheric pressure, high pressure or vacuum stripping
- Cross flow, counter flow or flow through medium
- Continuous or batch stripping
- Closed loop aeration or flow through aeration
- High or ambient temperature

Alternatively, stripping towers can utilize for example packed columns, spray columns or tray columns (Noyes, 1994). The column air stripping process is illustrated in figure 4 where stripping liquid flows through but air is circulated within the system. The main advantages of packed column stripping reactors are continuous process, high ammonia removal efficiency and speed. However, the feed must have low concentration (Reeves, 1972). Solids accumulate in the system leading to clogging of the packaging material and thus decreasing stripping efficiency. The column needs to be cleaned regularly. If manure slurry is used there needs to be a solids separation step prior to stripping. Separation can be done with a settling pond or a centrifuge (Jiang, et al., 2010). Additionally, foaming and flooding is a problem using high pH in stripping towers. Foaming can inhibit ammonia transfer and lower the efficiency, so antifoam needs to be mixed in the slurry (Jiang, et al., 2010; Nurmi, 2015). Advantages of column stripping are fast and efficient ammonia removal. Of all the stripping methods, packed towers give the highest efficiencies (Obaid-ur-Rehman and Beg, 1990).

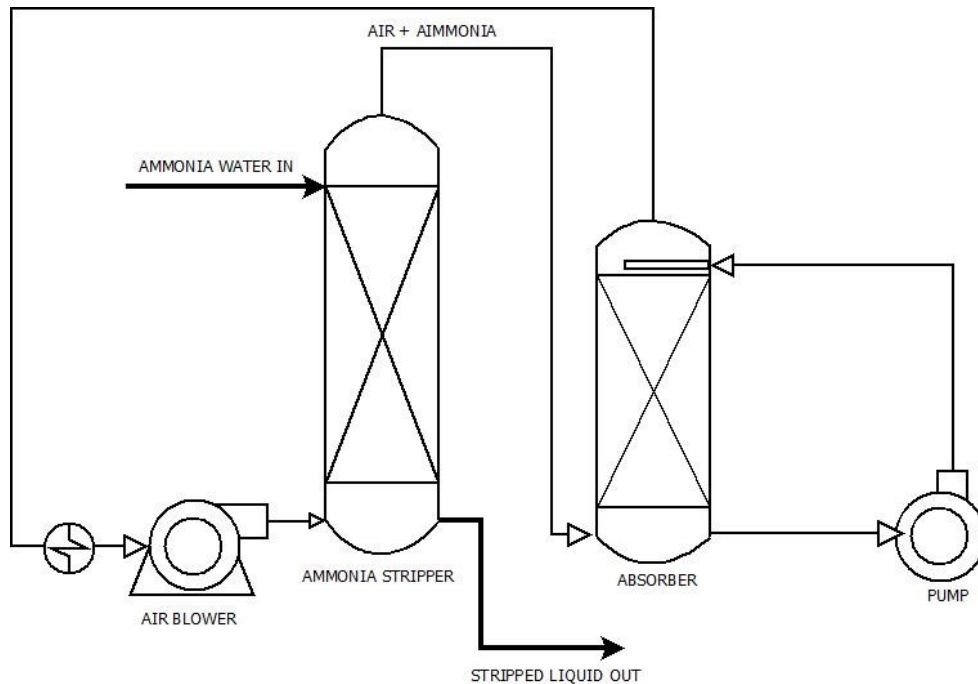


Figure 4. Diagram of ammonia stripping column and absorber unit with closed loop aeration. Modified from source (Anon., Branch Environmental Corp., 2016).

Air to water flow ratio and height of the stripping column are key parameters which control the removal rate of ammonia in air stripping columns (Huang and Shang, 2006). Larger air-to-water interfacial area can be achieved using packing material which affects the ammonia removal rate (Huang and Shang, 2006). It is vital to choose packing material which allows lowest possible operating costs. Common packing material types that are used are plastic Pall rings, Jaeger Tri-Pack and Rauschert Hifilow (Zhao et al., 2010; Anon., Branch Environmental Corp., 2016).

Steam stripping can utilize higher temperatures than air stripping. Since the dissolving of volatile compounds is dependent on temperature, raising the temperature above 100 °C can be an advantage compared to air stripping. High temperature makes ammonia more volatile than stripping below boiling point with air, thus making the process more efficient. However, this extra energy consumption has higher costs (Noyes, 1994). The Dutch company Xergi claims

45 % ammonia nitrogen removal from chicken litter using a pressurized steam stripping method and high temperature (145 °C). According to their studies, ammonia from slurry can be removed efficiently in one step using this batch process (Fink, 2014). Steam transfers ammonia efficiently from liquid to gas phase at 2-4 bar pressure. Gas is then directed to a scrubber where ammonia salts are collected. Burnt lime (CaO) is used for pH adjustment (pH up to 10.5). However, this technology has a high energy and chemical demand. Other disadvantages include fouling; lime residue collects on the inner surface of the batch cooker which needs to be cleaned in between batches (Fink, 2014).

Low pressure can also be utilized in ammonia stripping. A patent by Green Farm Energy AS describes a steam stripping system in which water is steamed in low pressure (less than 1 bar, temperature less than 100 °C) and the steam is released into a shunt vessel, which holds ammonia containing liquid, which is pH adjusted. The ammonia is removed from the wastewater to the gaseous phase and the gas is then directed to a condensation unit and an air scrubber. The condensed liquid is then re-stripped with steam in a stripping column with high pressure (up to 5 bars) (Bonde, 2003).

When designing a profitable industrial ammonia stripping unit, it is vital to try to minimize all operating costs while maintaining sufficient removal efficiency. Stripping in a diffused aeration batch reactor allows skipping the solids separation pre-process. There are many types of diffused aeration stripping systems, however, the ones suitable for ammonia stripping generally consist of a closed vessel with an air diffuser close to the bottom of the vessel, a heating jacket, an air outlet, stirring paddles and an air pump according to figure 5. Air diffuser creates bubbles that interact with the slurry, mixing turbulently as bubbles rise through the sludge (Noyes, 1994).

Another advantage of diffused aeration stripping is that prior to ammonia stripping, buffer capacity can be lowered and pH can be raised without adding chemicals. This can be obtained by air stripping CO<sub>2</sub>. Following this base is added and pH adjusted chemically. This lowers the chemical costs and chemical load in biogas production (Zhao et al., 2015; Liu et al., 2015). Liu and others (2015) experimented with ammonia removal from pig manure using an eight liter batch type diffused aeration stripping system with closed loop aeration and CO<sub>2</sub> stripping prior to ammonia stripping. They reached an ammonia removal efficiency of 96.78 %.

The advantages of closed air loop systems are energy conservation and no emissions to the environment. However, the disadvantages are higher manufacturing costs and higher operating costs compared to open an air system (Anon., Branch Environmental Corp., 2016).

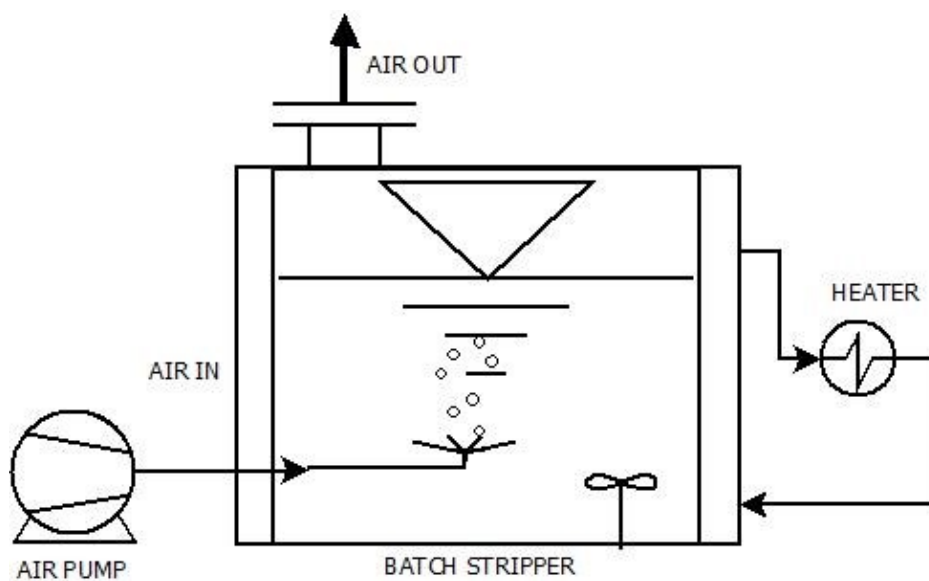


Figure 5. Batch type diffused aeration ammonia stripping system: Stripping vessel with heating jacket contains predigested slurry which is heated and stirred. The slurry is aerated and ammonia-air is removed through outlet. Modified from source (Walker et al., 2011; Liu et al., 2015)

## 4 Stripping theory

### 4.1 Thermodynamic equilibria

Ammonia stripping process is based on mass transfer of ammonia from liquid phase into gas phase according to figure 6. The ability to strip ammonia from solution is highly dependent on the thermodynamic equilibrium (ammonia gas/liquid equilibrium) and how much ammonia is available in gaseous form. As can be seen from figure 6 ammonia exists in the slurry as diffused gas,  $\text{NH}_3$  (l) and as the dissociated ammonium ion,  $\text{NH}_4^+$ . These two forms of ammonia are in thermodynamic equilibrium according to equation (3) and can be characterized as a function of pH and temperature according to equations (4) and (5) (Bonmatí and Flotats 2003).

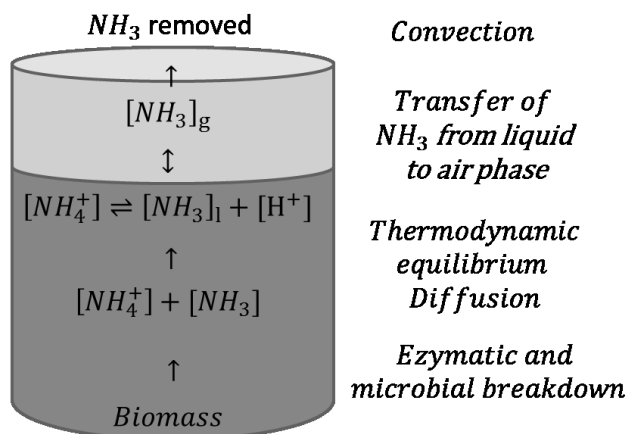


Figure 6. Schematic of ammonia stripping process. Modified from (Ni, 1999).

At room temperature and pH below 7 only ammonium ions are present in the ammonia solution. However, as pH and temperature increase, the equilibrium shifts and the proportion of the ammonia gas increases. At pH 11 almost all ammonia is in gas form as can be seen from figure 2 on page 8 (Patoczka and Wilson, 1984; Huang and Shang, 2006). The percent of ammonia present in



solution in undissociated form can be calculated with equation (4) (Bonmatí and Flotats 2003):

$$P = [NH_3] = \frac{[NH_3 + NH_4^+]}{1 + \frac{[H^+]}{K_a}} = \frac{[NH_3 + NH_4^+]}{1 + 10^{pK_a - pH}} \quad (4)$$

Where  $[NH_3]$  is the concentration of free ammonia  
 $[NH_4^+]$  is the concentration of ammonium ions  
 $[H^+]$  is the concentration on hydrogen ions  
 $K_a$  is the acid dissociation constant as a function of temperature T (°C)

Equation (5) is obtained by polynomial regression of data from Lide (1993) which goes up to 50 °C. However, Bonmatí and Flotats (2003) regarded the equation (5) sufficient enough for calculating the free ammonia present in aqueous solution, despite of the fact that higher temperature, 80 °C, since the equation is uniform with measured data.

$$pK_a = 4 * 10^{-8} T^3 + 9 * 10^{-5} T^2 + 0.0356 T + 10.072 \quad (5)$$

## 4.2 Henry's law

The driving force in the mass transfer is the difference in ammonium concentration difference between the liquid phase and gas phase. Ammonia gas is removed using aeration. As a large surface area of the air is exposed to water, contamination from the liquid phase is transported into the gaseous phase. Ammonia concentration of gas phase stays relatively low and maintains the ammonia transfer between liquid and gas as fresh air is constantly pumped into the reactor (Huang and Shang, 2006).

Ammonia release from the liquid phase depends on the ammonia concentration difference between the slurry and the air and the resistance of

ammonia transfer. There is transfer resistance between the liquid-gas interface. Henry's law states that the partial pressure of dissolved gas in gas phase in a given volume is proportional to the concentration of the dissolved gas in liquid. There are many methods to express this law. The release of NH<sub>3</sub> into the air phase can be described by using the Henry's constant, H<sub>C</sub>, which is a property of the solute/solvent system and the temperature according to equation (6) (Huang and Shang, 2006). For many volatile organic compounds Henry's constant increases three times for every 10 °C temperature rise (Kavanaugh and Trussell, 1980).

$$\log H_C = \frac{-H^\circ}{RT} + k \quad (6)$$

Where  $H_C$  is Henry's constant,  
 $H^\circ$  is enthalpy change resulting from dissolution of the compound in water  
 $R$  is the universal gas constant  
 $T$  is absolute temperature (K)  
 $k$  is compound dependent constant.

Henry's law, equation (7) describes the ability of the compound to be removed by air stripping through the ratio of ammonia concentration in gas phase at equilibrium to the ammonia concentration in liquid phase at equilibrium (Huang and Shang, 2006).

$$H_C = \frac{C_G}{C_L} \quad (7)$$

Where  $C_G$  is concentration of ammonia at equilibrium at gas phase and  
 $C_L$  is concentration of ammonia at equilibrium in liquid phase.

### 4.3 Mass transfer

Earlier it was stated that mass transfer is dependent on the concentration difference of ammonia gas in air and liquid phase. Thus, to keep the ammonia concentration of the gaseous phase low, it is vital to supply fresh air into the stripping vessel. Mass transfer is also dependent on air supply rate, area of liquid-gas interaction, pH and temperature (Zhang et al., 2012) Mass transfer rate can be calculated according to equation (8) (Arogo et al, 1999).

$$\frac{dM}{dt} = K A_0 (C_L - C_{air}) \quad (8)$$

Where

M	is the mass of the dissolved volatile compound (kg),
K	is the overall mass transfer coefficient for the dissolved volatile compound (m/s),
A <sub>0</sub>	is the interfacial surface area (m <sup>2</sup> ),
C <sub>L</sub>	is the concentration of the dissolved volatile compound in the liquid (g/l) and
C <sub>air</sub>	is concentration of the dissolved volatile compound found in the air (g/l).

However, the concentration of dissolved NH<sub>3</sub> cannot be directly measured from the stripping liquid. Thus equation (8) cannot be used as it is. Hence, the removal of ammonia is expressed as removal of total ammonia nitrogen. If the concentration of ammonia in the slurry can be assumed to be uniform, the equation (8) can be written to express mass transfer of total ammonia as in equation (9) (Arogo et al, 1999).

$$\frac{dM_{TAN}}{dt} = K_{OL} A_0 ([NH_3]_L - [NH_3]_{air}) \quad (9)$$

Where	$M_{TAN}$	Mass of total ammonia nitrogen (kg)
	$K_{OL}$	is the overall mass transfer of ammonia (m/s)
	$[NH_3]_L$	Ammonia concentration in liquid (g/l)
	$[NH_3]_{air}$	Ammonia concentration in air (g/l)

Since  $[NH_3]_L = P \times TAN$  where P is the percentage of free ammonia of the total ammonia nitrogen concentration in the liquid,  $M_{TAN} = V \times TAN$ , and due to continuous aeration, ammonia concentration in air is negligible ( $[NH_3]_{air} \approx 0$ ), equation (9) can be integrated and written in the form of equation (10) to express the concentration of total ammonia nitrogen in a given time, t (Huang and Shang, 2006):

$$TAN = TAN_0 e^{\left(\frac{K_{OL} P A_0}{V}\right)t} \quad (10)$$

Ammonia removal rate constant, -k can be used to replace  $\left(\frac{K_{OL} P A_0}{V}\right)$  in the equation (10). Ammonia removal rate resembles first order kinetics according to equation (11) (Walker *et al.* 2011; Zhang *et al.* 2012).

$$C_i = C_0 e^{-kt} \quad (11)$$

Where	$C_i$	is the concentration of removed compound (g/l) at given time, t
	$C_0$	is the initial concentration of removed compound (g, l)
	k	is the removal rate constant
	t	is stripping time

The minus sign in front of k, the removal rate constant, in equation(11) designates that the concentration of the compound which is reduced during the stripping process.

If it is assumed that the ammonia concentration of entering air and leaving liquid is zero, the theoretical requirement aeration (Gas volume/Liquid volume) can be calculated with equation (12). The air requirement equals the concentration fraction of  $x$ , inlet water-ammonia and  $y$ , outlet air ammonia (moles ammonia/mole air) (Huang and Shang, 2006).

$$\frac{G}{L} = \frac{x}{y} \quad (12)$$

However, the operating efficiency cannot be 100 % in the physical world. Huang and Shang (2006) recommend air supply of 1.5 times the theoretical value to remove more than 90 % of the ammonia.

## **5 Materials and methods**

### **5.1 Aims of the study**

The overall aim of the study was to determine the economic suitability of the ammonia stripping setup for large scale biogas production. The objective was to determine the parameters, where at least 70 % of total ammonia nitrogen could be stripped, using ammonified chicken litter slurry (TS ca. 8 %) as stripping material. Additionally recycled reject slurry was used to study how it would change the required stripping parameters. Specifically, we investigated the temperature range and the alkali requirements for sufficient ammonia removal as well as suitable alkali types (NaOH, CaO and KOH). In addition, CO<sub>2</sub>-stripping was explored as means to lower the alkali requirement in the reject slurry stripping experiments. Furthermore, we tried to determine if ammonia stripping would affect the quality of biogas feed.

### **5.2 Ammonia removal equipment**

A batch type pilot stripping vessel was used, illustrated in figure 7. It was designed by Ductor. The total volume of the stripping vessel was 130 l which was enough for stripping 60 l of slurry. The vessel had satisfactory headspace, adequate for possible foaming. The equipment setup can be seen in figure 8. For agitation, a propeller blade and a 55 W motor were used. The jacket of the stripping reactor was heated with circulating water which was heated with a 9 kW boiler.



Figure 7. Illustration of pilot stripping reactor used in experiments.

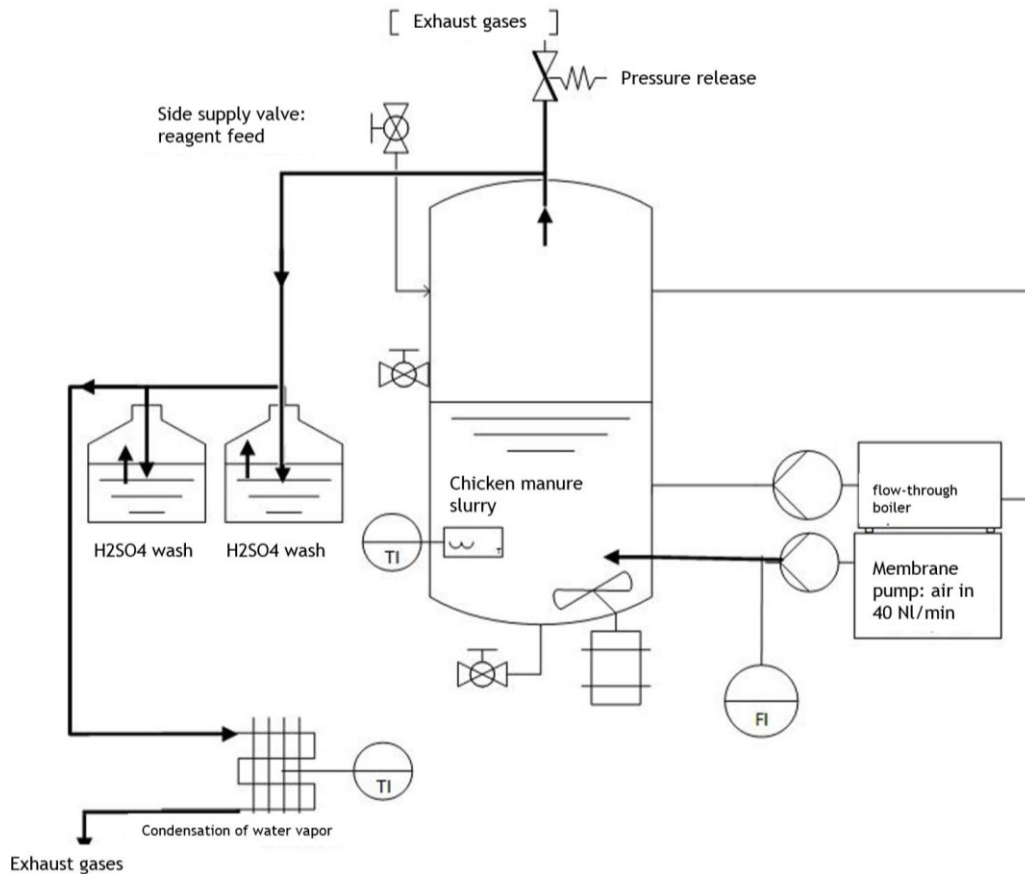


Figure 8. Ammonia stripping reactor and process equipment.

The temperature was measured inside the vessel with a digital thermometer. To pump 40 NI/min 60 °C air into the vessel below the surface of slurry a 240 W membrane pump was used. The air was directed through two acid scrubbers and a cooling unit. After cooling the air was let to an exhaust air vent. The vessel was equipped with pressure release valves in case of rapid pressure buildup and explosions.

### 5.3 Chicken litter

The chicken litter was obtained from Pälkäne, Finland (batch collected 29.4.2015) and stored in room temperature in closed plastic boxes. The chicken litter was somewhat clumped. To prevent clogging in valves, the litter needed



to be ground by hand and foreign objects such as twigs were removed. The chicken litter had an average total solids (TS) content of 70.3 % and volatile solids (VS) content of 60.9 %. TS and VS were measured according to standard SFS 3008. The moisture in chicken litter was 29.7 % on average and the proportion of dry matter was 70.3 %. The C/N proportion was 9.55. One kg of wet chicken litter contained 31.6 g of total nitrogen and 30.2 g of total carbon on average. Samples contained 9.5 % ash.

#### **5.4 Ammonification**

Chicken litter was pre-treated in ca. 50 l batches to release nitrogen as ammonia mostly from proteins. Slurry of ground chicken litter, tap water and (10 v-%) starter culture (S1) was made. The aim was to produce a slurry with 9 % TS. The slurry was stirred and anaerobically digested for 3-5 days in 55 °C in a closed, 70 l ammonification vessel.

To save water and recycle nutrients, reject water from biogas digesters was used in the second type of ammonification according to figure 3 on page 11. To make reject slurry and to dilute chicken litter (to 9 % TS) tap water and reject water were used in 1:1 ratio. Otherwise ammonification was completed as in the first case. All samples were stored in refrigerator.

#### **5.5 Preliminary experiments**

To estimate the necessary alkali requirements for raising the pH to a desired level, ammonified and hygienized chicken litter slurry was used. A volume of 1 l of pre-treated slurry was treated with 50 % sodium hydroxide solution (NaOH, Sigma Aldrich), 45 wt.-% potassium hydroxide solution (KOH, Sigma Aldrich) and quicklime powder (CaO, Sigma Aldrich) in laboratory scale to raise the pH from 6 to 11. The mixture was constantly stirred while the pH was adjusted.

The pilot stripping reactor was tested with ammonia-water-solution instead of ammonified slurry to gain understanding of possible flaws and kinetics of the stripping system. 37 l of (1.6 g/l) ammonia solution was stripped. The reactor was heated to 80 °C, stirred and aerated 40 NI/min for 2.5 h. The TAN concentration was measured.

## **5.6 Stripping in pilot scale**

### **5.6.1 Stripping ammonified slurry**

The objective was to test 3 different temperatures (80 °C, 74 °C and 68 °C) and 3 different pH-value combinations (pH 9, 9.6 and 10.2) in ammonia stripping using 50 % lye solution for pH adjusting. Additionally, based on the study by Zhang and Jahng (2010), 2 different alkali types were used for pH adjustment: KOH solution (45 wt. %) and solid CaO. In the case of adjustment with CaO and KOH, the goal was to raise the pH to 10 and 10.5 in 2 parallel experiments using the highest temperature, 80 °C.

The effect of stirring was studied with duplicate experiments with and without stirring. Also the effect of aeration depth on stripping kinetics was studied in duplicate experiments in which the volume of the slurry was raised by 50 % and other constants in the same ratio. To prevent the inhibiting effect of foaming on stripping, 0.2 % of rape seed oil was added to ammonified chicken litter prior to stripping.

The volume of stripped slurry in batch experiments was ca. 40 l. The ammonified slurry was diluted with 0.2 to 3 liters of water per batch to flush in most of the solids from the ammonification reactor and to keep the surface level high enough for aeration. The goal for the aeration level was VVM 1. Circa 40 NI/min of air was inserted into 40 liters of slurry. Theoretically a G/L ratio of

170 should be sufficient for removing 70 % of the TAN when initial concentration of TAN is 2.5 g/l and temperature is 80 °C. The standard stripping time was 3 h so the volumetric gas-liquid-ratio (G/L) was 180 (liters/liters) (Huang and Shang, 2006).

The scrubber units contained sulfuric acid solution which reacted with ammonium and formed ammonium sulphate. The diluted solution was recycled to the following experiments and additional sulfuric acid was added to ensure the scrubbing capability of the solution in the following experiments.

### **5.6.2 pH adjustment**

Firstly 1 l sample was taken from ammonified chicken slurry and the pH was preadjusted by adding alkali with an automatic pipette (100–1000 µl pipette). The slurry was stirred and pH measured with pH meter (ThermoScientific Orion Star A121, 9107BNMD Orion Triode gel-filled epoxy-body pH/ATC electrode). The pH of the whole reactor was adjusted by adding alkali straight to the reactor through side the input valve while stirring. The pipe was flushed with 1 l of preadjusted slurry. All the valves were closed to prevent ammonia from escaping and the slurry was stirred for 10 min. After this, a 200 ml starting sample was taken and stripping was started with aeration. Samples were taken every 30 min through the bottom valve.

It was noticed that the pH of the whole batch did not match with the preadjusted slurry due to heterogeneity of the sludge. It was decided that instead of trying to keep the adjusted pH level constant, the amount of base was kept constant. pH was adjusted by adding 8, 10.5 and 12 ml 50 % NaOH solution per 1 liter of slurry.

After stripping the final pH of the slurry was higher than the required optimal pH which is 7.0-8.0. Thus, the pH needed to be lowered to pH 8 using 37 % HCl solution.

### **5.6.3 Stripping ammonified reject slurry and CO<sub>2</sub>-stripping**

In CO<sub>2</sub>-stripping dissolved carbon dioxide is stripped before the actual NH<sub>3</sub> stripping with air which this leads to moderate rise in pH (Zhao et al., 2015). To save chemicals, ammonified slurry, which contained reject water, was stripped for 1 hour without adjusting the pH with lye. After 1 h of CO<sub>2</sub>-stripping the pH was adjusted using lye and normal stripping was continued for 3 h. The reject slurry was stripped in a similar way as in the normal stripping in 40 l batches, using VVM 1, 50 % NaOH solution to adjust pH and 70-80 °C temperature.

### **5.6.4 Cooling unit**

Due to heat induced evaporation of water in the stripper, the exhaust air needed to be cooled to less than 30 °C with a water and ice bath to retain the evaporated water. The temperature of the water bath was controlled with ice bricks which were changed if the temperature rose above 30 °C.

### **5.6.1 The effect of stirring**

It was investigated if stirring had any effect on the stripping kinetics in this setup. A regular stripping experiment without stirring was executed. Temperature was 80 °C, addition of lye was 10.5 ml/l and the the aeration level was VVM 1. While adjusting the pH, lye was distributed using stirring for 10 min. However, the slurry was not stirred with blades while stripping but the aeration caused some mixing and diffusion in the reactor.

### **5.6.2 The effect of aeration depth**

It was investigated if the submersion level of the aeration pipe had any effects on the stripping kinetics. Pazoka and Wilson (1984) stripped  $\text{CH}_4\text{Cl}$ -deionised water solution and altered the aeration submersion level from 1.6 to 47 cm. They witnessed that the submersion level of the aeration pipe did not have an effect on stripping kinetics as the air bubbles were saturated with ammonia (Pazoka and Wilson, 1984). However, in the present setup it was worthwhile to re-examine this effect since the ammonia concentration was low and air flow was high.

Since it was not possible to move the level of the aeration pipe, the effect of submersion level was studied by increasing the stripping volume from 40 l to 60 l. Thus the level of the slurry rose and the aeration pipe was submerged deeper. The constants of experiment were kept the same as in comparison experiment: Temperature was 80 °C, addition of lye was 10.5 ml/l and the the aeration VVM 1 level was preserved. Stirring was not used in the experiments.

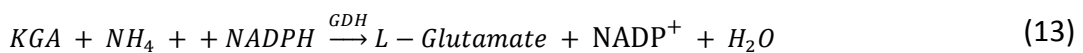
### **5.6.3 Volume measurement**

The total volume of the slurry was difficult to measure because neither the ammonification reactor nor the stripping reactor had a volume meter. The floor under the stripping reactor was slightly slanted. First the volume was measured by measuring the surface level of the slurry with a measuring stick. However, it was noticed that this method gave variable and too high values. The measuring stick method was replaced with measuring the slurry with 5 l plastic pitchers which gave much more accurate values (accuracy was  $\pm 250$  ml which was within the 5 % error margin). The earlier volume measurements with the measuring stick were corrected to match pitcher measurements.

## 5.7 Laboratory analysis

### 5.7.1 Total ammonia nitrogen concentration

Ammonium and ammonia concentration analysis was performed by using two methods. Ammonium strip test (MQuant™ Ammonium Test, Merck KGaA) was used for rough estimate. For more accurate quantitative estimation Ammonia Assay Kit (Sigma-Aldrich) was used. According to equation (13), in the presence of GDH (L-glutamate dehydrogenase), ammonia reacts with KGA (Alpha-ketoglutaric acid) and NADPH (Reduced nicotinamide adenine dinucleotide phosphate) to form L-glutamate, NADP<sup>+</sup> (Oxidized nicotinamide adenine dinucleotide phosphate) and water. The decrease in absorbance at 340 nm is proportional to the ammonia concentration due to the oxidation of NADPH.



### 5.7.2 Total solids and volatile solids

According to Kim and others (2003) it can be beneficial to pretreat slurry with heat and alkali before anaerobic fermentation because this will cause hydrolysis and disruption of cells and flocks. This disintegration of organic matter should be done in the heating range of 70-200 °C (Athanasoulia et al., 2007). As the process was done at 68-80 °C some changes in volatile solids should be detected.

The stripped chicken litter slurry samples were stored in a refrigerator and analyzed within a few days. Sample bottles were well shaken so that uniform samples could be obtained. The samples were weighed in dry crucibles. Samples were dried in 105 °C for 22-24 h. The samples were weighed again and total solids could be calculated according to equation (14).

$$TS \% = \frac{m_{dried\ sample\ 105\ ^\circ C}}{m_{wet\ sample}} * 100 \% \quad (14)$$

The samples were combusted in 550 °C for 2 h and weighed after cooling. Only inorganic ash remained in the crucible. Organic volatile solids were calculated from the evaporated mass according to equation (15).

$$VS \% = \frac{m_{dried\ sample\ 105\ ^\circ C} - m_{dried\ sample\ 550\ ^\circ C}}{m_{wet\ sample}} * 100 \% \quad (15)$$

### 5.7.3 Volatile fatty acids and alkalinity

To keep the pH of the anaerobic digester stable it was important to monitor the fraction of volatile fatty acids (VFAs) and the alkalinity i.e. buffer capacity of total inorganic carbon (TIC) in the biogas feed. As the organic material was digested by anaerobic bacteria, VFAs such as propionate, butyrate, lactate and acetate are produced. As these compounds dissociate they release hydrogen ions which can lower the pH of biogas reactor. The effect can be buffered with dissolved inorganic carbon, which neutralizes the hydrogen ions. Bicarbonate can buffer the effects of VFAs and keep the pH constant. However, the bicarbonate can become exhausted and as a result, the pH of the reactor starts to lower rapidly resulting in the inhibition of digestion.

VFA's were analyzed corresponding to acetic acid (mg CH<sub>3</sub>COOH/l) and alkalinity as bicarbonate (mg CaO<sub>3</sub> /l) equivalent using Biogas Titration Manager (Hach Kange GmbH). Hach uses terms such FOS (*germ. flüchtige organische Säuren*) for VFA and TAC (*germ. Totales Anorganisches Carbonat*) for TIC. According to Hach (2016) the stable FOS/TAC ratio for biogas plants is 0.3-0.6.

To remove solid particles the samples were centrifuged and three parallel samples were analyzed. 1ml samples were pipetted into 50 ml of distilled water. The diluted samples were constantly stirred and titrated with 0.05 M sulfuric acid to pH 5. VFA mass concentration,  $\gamma$  (mg CH<sub>3</sub>COOH/l) was calculated from the consumption of H<sub>2</sub>SO<sub>4</sub> according to equation (16) as the concentration of sulfuric acid was known.

$$\gamma_{\text{acetic acid}} = (V_1 N_{\text{sulphuric acid}} * 20 * 1.66 - 0.15) * 500 \quad (16)$$

The diluted samples were further titrated to pH 4.4 using 0.05 M sulfuric acid. The mass concentration,  $\gamma$  of total inorganic carbon (mg CaO<sub>3</sub>/l) was calculated according to equation (17).

$$\gamma_{\text{bicarbonate}} = V_2 N_{\text{sulphuric acid}} * 20 * 250 \quad (17)$$

#### 5.7.4 Carbon and nitrogen content

The carbon-nitrogen fraction needs to be adjusted before biogasification since excess nitrogen inhibits methanogens. The C/N fraction was measured with Vario MACRO Cube Elemental Analyzer (Elementar Analysensysteme GmbH) which combusted and reduced the samples. The samples were frozen and defrosted in a water bath at room temperature. The samples were centrifuged at 15000 rpm for 10 minutes at 4 °C. The liquid and solid fractions were wrapped in tinfoil and tungsten (VI) oxide (Elementar) compound. The samples were analyzed with Vario MACRO Cube Elemental Analyzer.



## 6 Results

### 6.1 Ammonification

While the formula for all ammonification batches were the same, the characteristics such as pH, total solids, volatile solids, total nitrogen and total ammonia nitrogen concentration of ammonified slurry varied from batch to batch. In ammonification the TAN concentration of plain chicken slurry increased from ca. 1.3 g/l to 2.1 g/l on average. While TAN concentration of ammonified normal slurry ranged from 2.0 g/l to 2.6 g/l, the TAN concentration of ammonified reject slurry ranged from 1.9 to 2.8 g/l (table 2) and on average it was 2.4 g/l, which was somewhat higher than in the case of normal slurry. However, the total nitrogen ratio was the same in both cases.

Table 2. Characteristics of two different types of ammonified slurry

	Normal slurry	Reject slurry
$[\text{NH}_4^+]$ (g/l)	2.0-2.6	1.9-2.8
Total nitrogen %	0.4-0.5	0.4-0.5
TS %	6.3-10.1	8.2-8.9
VS %	4.3-7.2	5.2-6.4
Initial pH	6.0-8.2	7.5-8.9

Overall, it can be assumed that the ammonification process was modest since the inhibition level, 4 g/l of total ammonia nitrogen, was not exceeded. Nonetheless, the TAN concentration was high enough for detecting changes in TAN concentration during the stripping experiments.

### 6.2 Preliminary experiments

The preliminary test for the pilot stripping reactor was a success and this experiment was a baseline for other stripping experiments. 76 % of TAN was removed during 2.5 h of ammonia stripping from ammonia solution (initial TAN

concentration was 1.6 g/l). The ammonia removal rate,  $-k$  was 0.010. The pH of the solution decreased from 10.8 to 9.7 which indicated decrease of ammonia in solution. No gas leakages were detected. The stripping system seemed to be adequate for stripping slurry.

## **6.3 Pilot experiments**

### **6.3.1 pH adjustment**

The initial pH of ammonified slurry varied in experiments. For example from figure 9 it can be seen that initial pH of ammonified slurry was 6.0 to 8.2 in experiments done with NaOH. The amount of added lye did not directly correlate with adjusted pH in different experiments due to buffering capacity. For example, when the experiments "80 °C /12.5 ml" and "74 °C /12.5 ml" were compared it was evident that the final pHs were different (9.8 and 10.9) even though the initial pHs were approximately the same and a similar amount of lye was added. However, most of the experiments had a gradient in adjusted pH which can be seen as steps of "adjusted pH" of the figure below (figure 9). Thus pH adjustment was successful for comparing the nitrogen removal at variable pHs.

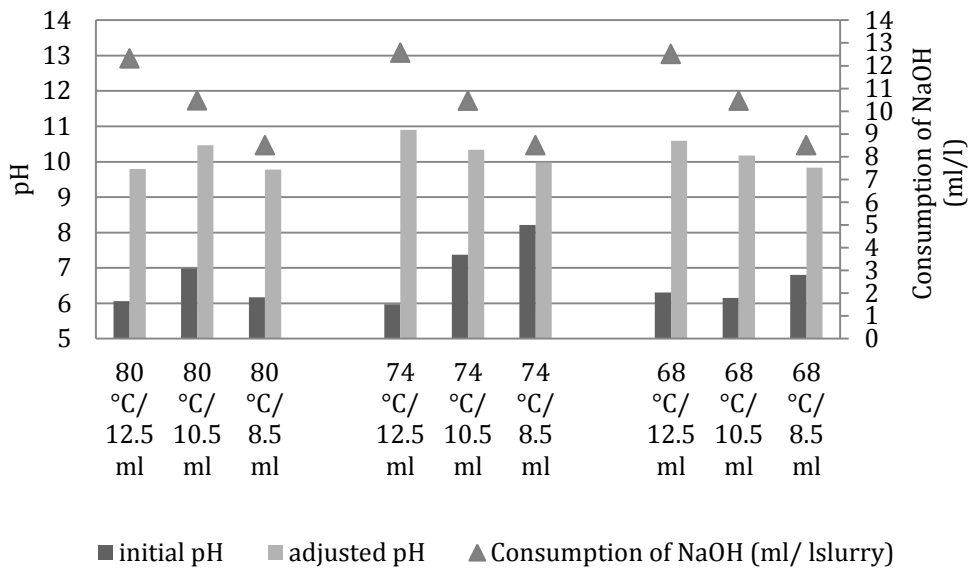


Figure 9. pH adjustment using 50 % NaOH solution in 9 stripping experiments.

Similar to NaOH also KOH worked well for pH adjustment since it reacted rapidly. With addition of 19.5 ml of KOH per liter of slurry the pH increased from 7.7 to 10.7 (3.0 pH units) and with 17.5 ml/l addition pH increased from 6.2 to 10.0 (3.8 pH units). When CaO was used for pH adjustment, the change in pH was very slow and some of the alkali floated on top of the slurry and did not mix in at all. Thus, CaO powder cannot be recommended for use as it is.

The lime should have been mixed in to a small amount of liquid to dissolve the powder. However, dissolving CaO is an exothermic reaction, which releases a lot of heat. Therefore, using CaO can be hazardous in pilot scale and difficult to control. Moreover, the additional water would have significantly diluted the slurry and made interpretation of the results difficult because the results could not have been directly compared to other experiments.

### 6.3.2 Aeration

The aeration pump was quite inefficient since it heated the input air from room temperature to 60 °C. It can be assumed that the majority of the energy was

wasted on heating. The aeration pump was also challenging to adjust and thus it was kept on full force. In most of the experiments it was possible to maintain 1 VVM and G/L ratio above the theoretical minimum, 170, which can be seen from table 3. However, in the experiment PM-5 (“80 °C/ 12.5 ml”) the aeration average was 0.8 VVM which was lower than the desired VVM of 1. Nonetheless, this did not affect the ammonia removal rate in a significant manner since the G/L ratio was 190. However, as can be seen from table 3 in experiment PM-11, done with KOH, the G/L ratio was only 114. This was due to the shorter stripping time of 120 min, since the ammonia removal was so rapid (ammonia removal rate was 0.009).

Table 3. Aeration parameters in pilot stripping experiments carried out with ammonified chicken litter, also including reject slurry.

PM-	VVM	G/L	F <sub>aeration</sub> (N l/min)	Quantity of air pumps
3	1,0	180	34.4	1
4	0.8	192	32.0	1
5	0.8	190	33.5	1
6	1.0	211	40.2	1
7	1.0	242	39.9	1
8	1.0	196	40.3	1
9	1.0	177	39.8	1
10	1.0	178	40.6	1
11	1.0	114	38.8	1
12	0.9	170	38.4	1
13	1.0	282	40.0	1
14	1.0	182	39.0	1
15	1.0	183	39.0	1
16	1.0	187	40.0	1
17	1.0	243	39.1	1
18	1.0	186	40.3	1
19	1.0	182	39.8	1
20	1.0	187	40.5	1
21	1.0	236	38.1	1
22	1.0	179	39.4	1
23	1.0	179	60.4	2

*PM-* indicates the pilot stripping experiment number, *VVM* indicates the vessel volumes of airflow per minute, *G/L* indicates the gas to slurry ratio during stripping (l/l) and *F* indicates the air flow (normal liters /minute).

One aeration pump was able to pump air ca. 40 NL/min. It should be noted that to achieve air flow of 60 NL/min, another pump was added in experiment PM-23. It can be concluded that aeration was successful since the aeration gas-liquid-ratio could be maintained above theoretical minimum.

### **6.3.3 Stripping slurry**

The conditions in the pilot stripping experiments are summarized in Table 4 which includes the achieved ammonia removal percentages. The Experiments PM-13, PM-17 and PM-17 which utilized reject slurry included a 60 minute CO<sub>2</sub>-removal prior to stripping. Table 4 does not include the solids content or VFA concentration, which substantially affect the alkali demand. More detailed information about the stripping conditions and results are summarized in Appendix 1 table 1. The experiments PM-1 and PM-8 were discarded due to inconsistencies in stripping procedures thus they are marked with grey text in table 4.

It is imperative to note that experiment PM-5 was overly long, 224 min, instead of the standard 180 min stripping. The experiment PM-5 was however, evaluated as 180 min stripping. This was based on the ammonia removal rate of 0.007 which allowed the experiment to be examined along with other 180 min experiments. In other words, it was necessary to make this experiment comparable with other experiments done with NaOH. Accordingly, in experiment PM-5, when stripping time was 224 min, 82 % of ammonia was removed, whereas when PM-5 was cut to 180 min, 77 % of ammonia was removed.

It should also be noted that the stripping time varied in experiments done with reject slurry due to slow reaction and in some cases due to 1 h CO<sub>2</sub> stripping.

Table 4. Conditions in pilot stripping experiments.

Experiment (PM-)	Slurry type: (Reject/ Normal/ Amm.-water)	Alkali type	Added alkali (ml/g per l)	CO <sub>2</sub> strip. (y/n)	Stirring (y/n)	T (°C)	Aeration (Nl/min)	Volume (l)	adjusted pH	Strip. time (min)	TAN in (mg/l)	TAN removal (%)	TAN removal rate (-k)
1	A	(NH <sub>3</sub> ) <sub>4</sub> OH	-	n	y	69	38	60	11.0	120	3127	44 %	0.005
2	A	(NH <sub>3</sub> ) <sub>4</sub> OH	-	n	y	74	38	37	10.8	150	1574	76 %	0.010
3	N	NaOH	12.6 ml	n	y	74	34	36	10.9	180	2400	75 %	0.008
4	R	NaOH	15.8 ml	n	y	80	32	42	10.0	250	2842	85 %	0.007
5	N	NaOH	12.3 ml	n	y	80	34	40	9.8	224	2601	82 %	0.007
6	N	(NH <sub>3</sub> ) <sub>4</sub> OH	10.2 ml	n	y	80	40	40	10.0	210	2469	70 %	0.005
7	N	CaO	6.9 g	n	y	77	40	40	9.8	240	2302	53 %	0.003
8	N	CaO	10.3 ml NH <sub>4</sub> OH	n	y	61	40	40	10.2	195	3108	44 %	0.003
9	N	NaOH	10.5 ml	n	n	79	40	40	10.0	180	1944	54 %	0.004
10	R	NaOH	15.9 ml	n	y	70	41	41	11.5	180	1900	51 %	0.004
11	N	KOH	19.5 ml	n	y	81	39	41	10.7	120	2010	71 %	0.009
12	N	KOH	17.2 ml	n	y	80	38	41	10.0	180	2151	70 %	0.006
13	R	NaOH	6.3 ml	y	y	71	40	38	10.0	270	2405	82 %	0.007
14	N	NaOH	10.5 ml	n	y	80	39	39	10.5	180	2118	80 %	0.008
15	N	NaOH	8.5 ml	n	y	80	39	38	9.8	180	2447	60 %	0.005
16	N	NaOH	8.5 ml	n	y	73	40	38	10.0	180	2059	58 %	0.005
17	R	NaOH	5.0 ml	y	y	81	39	39	9.6	240	2792	63 %	0.003
18	N	NaOH	8.5 ml	n	y	67	40	39	9.8	180	2288	43 %	0.003
19	N	NaOH	10.5 ml	n	y	74	40	39	10.3	180	2339	67 %	0.006
20	N	NaOH	10.5 ml	n	y	68	41	39	10.2	180	2195	56 %	0.004
21	R	NaOH	5.0 ml	y	y	80	38	39	9.8	240	2299	70 %	0.006
22	N	NaOH	12.5 ml	n	y	69	39	40	10.6	180	2030	54 %	0.004
23	N	NaOH	10.5 ml	n	n	81	60	61	10.5	180	2572	78 %	0.008

*PM-* indicates the pilot stripping experiment number. The slurry type indicates the nature of stripping medium (N = normal slurry, R = reject slurry, A = ammonia water mixture). The alkali type indicates the base used for pH adjustment (NaOH, KOH, CaO or (NH<sub>3</sub>)<sub>4</sub>OH). The added alkali indicates the volume of base used per liter of stripping medium. CO<sub>2</sub>-stripping indicates if carbon dioxide stripping was conducted before ammonia stripping (y = yes and n = no). The stirring indicates if the vessel was agitated during stripping experiment (y = yes and n = no). T indicates the average measured temperature (°C) in stripping vessel during the stripping experiment. TAN<sub>in</sub> indicates the initial concentration of total ammonia nitrogen.

### 6.3.4 CO<sub>2</sub>-stripping

Carbon dioxide stripping step (60 min) was done prior to ammonia stripping in the experiments PM-13, PM-17 and PM-21 where only reject slurry was used. These experiments were compared to ammonia the stripping experiments PM-4 and PM-10 which also used reject slurry as stripping material. CO<sub>2</sub>-stripping significantly reduced the alkali requirement. It can be seen from table 5 that 1 h of CO<sub>2</sub>-stripping increased the pH from ca. 8.0 to ca. 8.8, specifically 0.4-1.6 units.

Table 5. Comparison of ammonia stripping parameters with and without CO<sub>2</sub>-stripping. Due to operational errors, pH of PM-17 was adjusted in two phases.

Experiment #	PM-4	PM-10	PM-13	PM-17	PM-21
CO <sub>2</sub> -stripping	no	no	yes	yes	yes
T (°C)	80	70	71	81	80
Initial pH	7.5	7.5	8.5	7.18	8.2
pH post CO <sub>2</sub> -stripping	-	-	8.9	8.8	8.9
adjusted pH	10	11.5	10	9.5/ 9.6	9.8
V <sub>NaOH</sub> (ml/l)	15.8	15.9	6.3	5 / +2.5	5
ammonia removal rate, -k	0.007	0.004	0.007	0.003/ 0.005	0.006
Corrected TAN removal (%)	85 %	51 %	82 %	63 %	70 %

*PM-* is the number of pilot stripping experiment. *T* (°C) is the average measured temperature in stripping vessel during the stripping experiment. The measured pH indicates the pH of the ammonified reject slurry before and after CO<sub>2</sub>-stripping. The Adjusted pH indicates the pH level attained lye. The V<sub>NaOH</sub> is the volume of lye (ml) used per liter of slurry. Ammonia removal rate, -k, describes the decreasing of the TAN according to first order kinetics. Corrected TAN removal (%) is the total ammonia nitrogen removal percentage taking into account the evaporation rate.

This increase in pH reduced the alkali requirement. We can see from table 5 that after CO<sub>2</sub>-removal in the experiments PM-13 and PM-21 only 5.0-6.3 ml/l of lye was required to achieve pH ca. 10, whereas, in other experiments where CO<sub>2</sub>-removal was not done, (PM-4 and PM-10) the lye requirement was over 15 ml/l to achieve pH 10-11.5.

The experiment PM-17 had operational errors due to higher temperature and extraordinary evaporation. After one hour of CO<sub>2</sub>-stripping and one hour of ammonia stripping the aeration pipes became visible in PM-17. The slow ammonia removal rate (0.003) can be explained by this error because the air was not properly in contact with the slurry. Thus, the experiment was re-established by adding water (1.9 l) and lye (85.5 ml), increasing the surface level above the aeration pipes and pH from 8.2 to 9.1. After this change the ammonia removal rate, -k increased from 0.003 to 0.005.

### **6.3.5 Evaporation and foaming**

The rate of evaporation was greater in stripping experiments with higher temperature. The evaporation rate varied greatly as can be seen in figure 10. Some 10 % of the volume of slurry evaporated during 3 h stripping when the temperature was 80 °C. Due to evaporation, the slurry was concentrated and thus the final batch stripping sample analysis needed volume correction when comparing the results to initial sample analysis. All final concentrations were corrected with volume change based on evaporation rate. The evaporated water accumulated in scrubbers diluting sulfuric acid solution and part of the evaporated water was lost in the exhaust pipe. The detailed evaporation rates are listed in appendix 1, table 1.



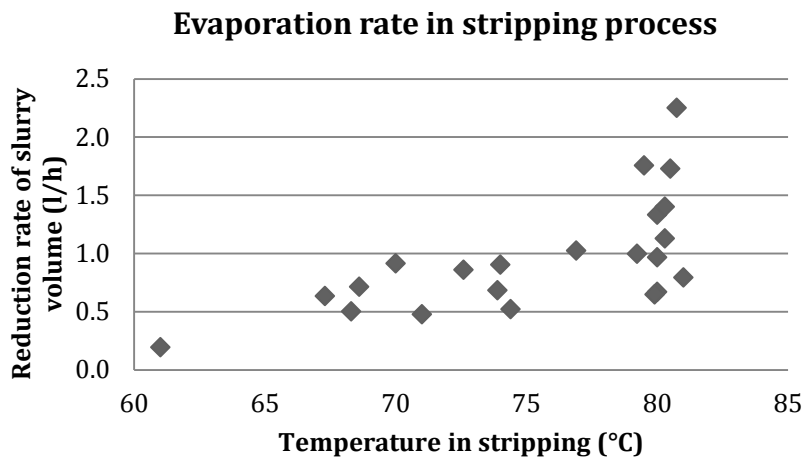


Figure 10. Evaporation rate in ammonia stripping experiments varied greatly, particularly in experiments done in 80 °C.

Some foaming was detected in batch stripping. However, rapeseed oil prevented it in most cases. The foaming was intense mainly, when ammonified reject slurry was stripped.

## 6.4 Laboratory analysis

### 6.4.1 Ammonia removal

Ammonia removal appeared to follow first order kinetics as can be seen from figure 11, where concentration of TAN is expressed over stripping time. In this figure the stripping experiments were done in 80 °C and the TAN concentration dropped from ca. 2.4 g/l to 0.5-1.0 g/l (60-82 % TAN removal). The initial pH of the ammonified slurry was rather low 6.0-8.2 and thus lye consumption was high to attain a pH around 10. Experiment PM-5 used 12.3 ml of lye per liter of slurry, PM-14 used 10.5 ml/l and PM-15 used 8.5 ml/l of lye. The corresponding ammonia removal rates,  $-k$ , were 0.007, 0.008 and 0.005. The ammonia removal rate was not directly proportional to the volume of added lye due to difference in initial pH of ammonified chicken litter slurry. Comparatively more ammonia was possible to remove in the experiment PM-14 because it had a

slightly higher initial pH (pH 7) than PM-5 (initial pH 6.1) and PM-15 (initial pH 6.2).

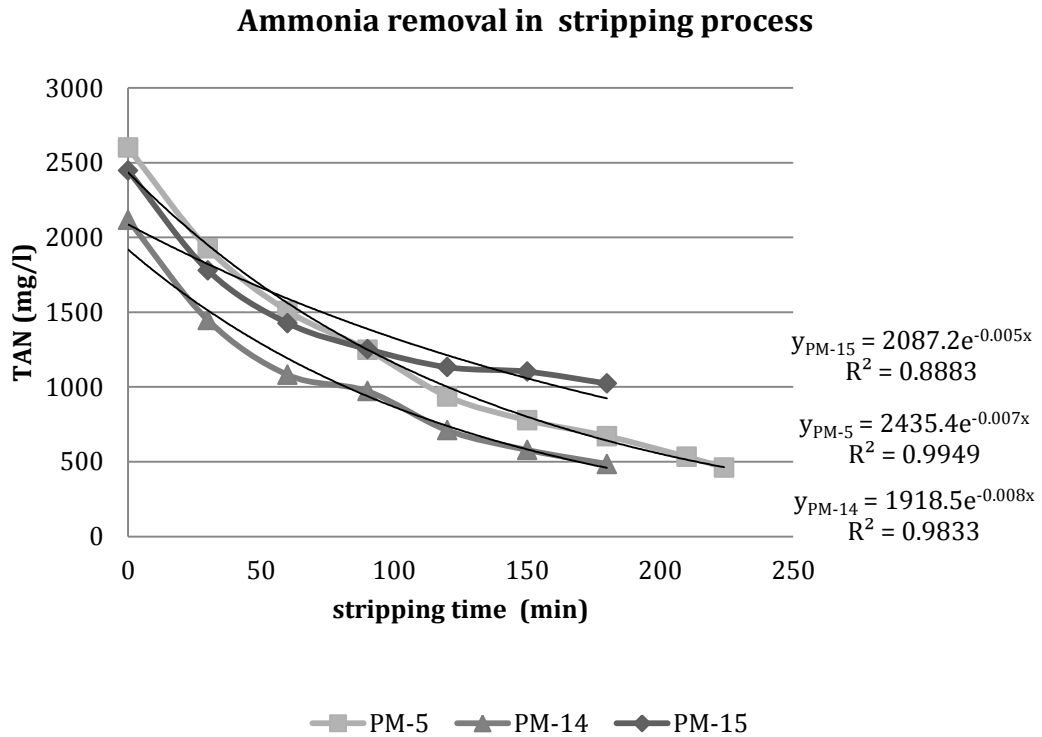


Figure 11. Change in TAN concentration in ammonia stripping. Experiments were executed in 80 °C using different volumes of 50 % lye for pH adjustment. PM-5, 12.3 ml/l; PM-14, 10.5 ml/l; PM-15 ,8.5 ml/l.

Ammonia removal rate was directly dependent on temperature which can be seen from figure 12. The higher the temperature, the higher the ammonia removal was. The ammonia removal rate was also to some extent dependent on the pH. This can similarly be seen from the figure 12. The highest ammonia removal percentage, 83 %, was achieved at 80 °C and pH 10 (3 h stripping). The pH raise above pH 10 did not contribute to increase in ammonia removal rate at this temperature (80 °C). However, surprisingly at a lower temperature, 74 °C, the pH raise above 10 did promote ammonia removal. On the contrary, at even lower temperature, 68 °C , pH raise above 10.2 did not lead to additional ammonia removal. However, there was some variance in the ammonia removal

in experiments done at 80 °C. So it can be concluded that variance in other temperatures is expected as well, if further experiments were to be conducted in future. Thus, the exact pH point where ammonia removal plateaus cannot be concluded from these experiments.

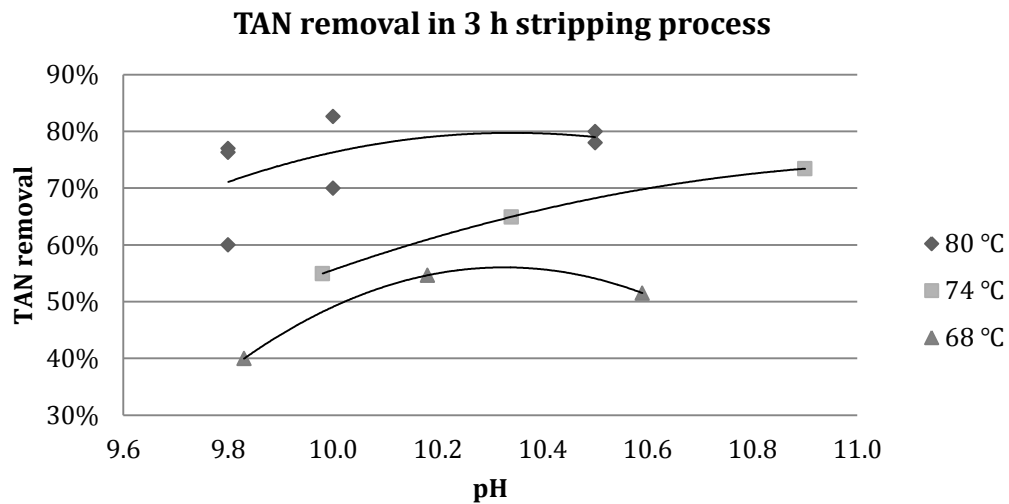


Figure 12. Total ammonia nitrogen removal percentage in 3 h ammonia stripping experiments as a function of pH in three different temperatures (80 °C, 74 °C and 68 °C). The stripping material used in these experiments was pH adjusted ammonified chicken slurry. pH adjustment was done using lye.

The optimal ammonia stripping parameters for regular ammonified chicken litter were:

- 80 °C
- at least 10.5 ml/l lye (50 %) addition
- adjusted pH at least 10

In these optimal conditions, when the ammonia removal rate,  $-k$  was 0.008, theoretically 70 % of TAN was removed in only 2.5 h of stripping..

When ammonified reject slurry was stripped, the TAN removal rate was much lower and it took 2.9-3.3 hours to remove 70 % of ammonia nitrogen. However,

due to the CO<sub>2</sub>-stripping the initial pH of the slurry was higher (pH 7.5-8.5) than in the case of regular slurry and thus it required less alkali to adjust the pH. Only about 5 ml/l of NaOH was needed. The figure 13 below illustrates how some of the ammonia was removed during the CO<sub>2</sub>-stripping process. In the experiment PM-13 the ammonia removal rate, -k, was 0.003 during CO<sub>2</sub>-stripping whereas, after the pH adjustment the rate increased to 0.007. Hence, ammonia can be removed without chemical pH adjustment. However, this process was relatively slow; 3 hours of CO<sub>2</sub>-stripping would have hypothetically lead to only 42 % ammonia removal.

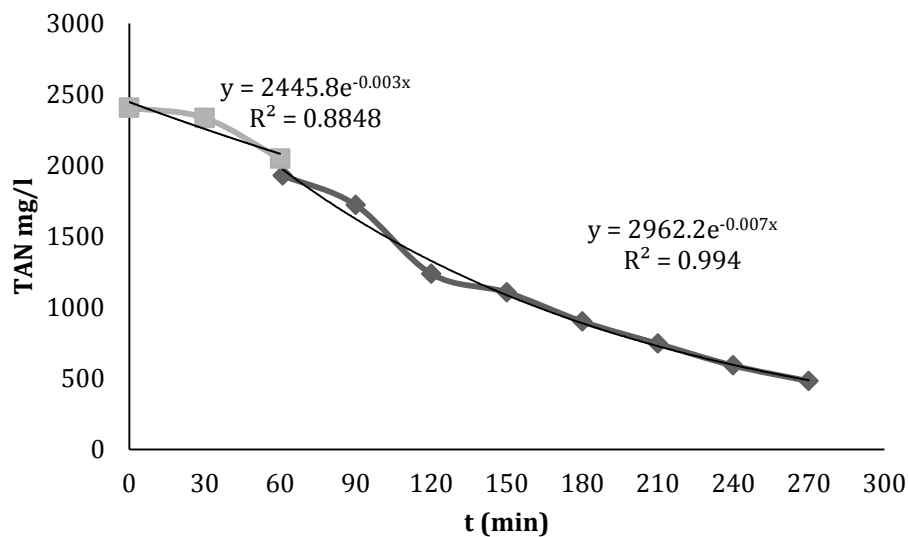


Figure 13. TAN removal rate in experiment utilizing CO<sub>2</sub>-stripping and ammonia stripping (PM-13)

To attain 70 % TAN removal, the consumption of base and stripping time are dependent on the stripping material. Figure 14 illustrates how these differences affect the lye consumption and the stripping time. Furthermore, the CO<sub>2</sub>-stripping was also taken into account in this block diagram. If the stripping material was regular ammonified CL, only ammonia stripping process was conducted at 80 °C, using 10.5 ml/l of lye and 2.5 h for 70 % ammonia removal. On the other hand if the ammonified CL slurry contained reject, either the

material was pre-processed or not. If there was only ammonia stripping process, the lye consumption was higher, 15.8 ml/l and 70 % ammonia removal took slightly more time, 2.9 h, than in the first case. Otherwise if the reject containing CL was pre-processed with 1 h of CO<sub>2</sub>-stripping, the lye consumption was much lower than in both cases, 5 ml/l. However the ammonia stripping time was much longer, 3.3h.

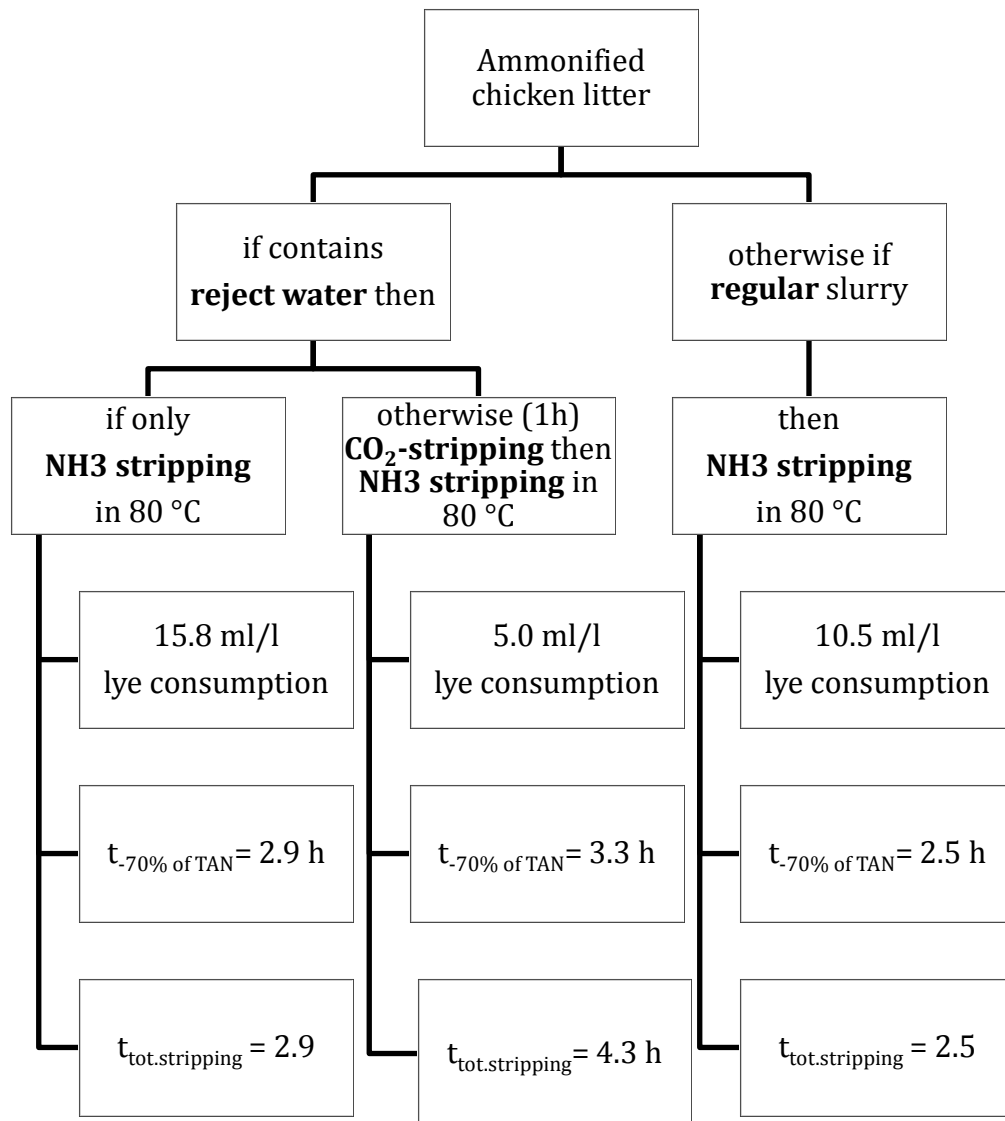


Figure 14. The block diagram illustrates the optimal stripping parameters used for 70 % TAN removal, when slurry type and stripping methods varied. T<sub>tot.stripping</sub> indicates the combined stripping time of ammonia stripping and CO<sub>2</sub>-stripping.

Additionally, when the CO<sub>2</sub>-stripping time was added to the ammonia stripping time, the  $t_{\text{tot.stripping}}$  was 4.3 h, which was much higher than in both other cases.

Changing the slurry volume from 40 to 60 liters lead to change in aeration depth from 3 to 22 cm. These changes appeared to double the ammonia removal rate. From appendix 1 table 1 it can be seen that in the experiment done with 40 l volume, (PM-9) ammonia removal rate,  $-k$  was only 0.004 and in the experiment where the volume was 60 l, (PM-23) the ammonia removal rate,  $-k$  was double, 0.008. However, it should be pointed out that some of the effect can be due to the fact that the experiment with larger volume had 2 degrees higher temperature (81 °C) and also 0.5 units higher adjusted pH level (pH 10.5). Thus this result should be interpreted with caution.

Stirring increased the ammonia removal rate, halving the required stripping time. The ammonia removal rates were compared in figure 15. To remove 70 % of TAN, the experiment without stirring (PM-9) took twice as much time, 5.0 h whereas with the experiment with stirring (PM-14), took only 2.5 h. However, it should be noted that even though the lye addition was same in both experiments, the adjusted pH was not the same. The adjusted pH in PM-14 was 10.5 due to higher initial pH, whereas in PM-9 adjusted pH was only 10.0. To boot the experiment without stirring (PM-9) had 1 degree lower average stripping temperature (79 °C). The differences in adjusted pH and stripping temperature can explain the drastically distinctive ammonia removal rates. If we consider the experiment PM-15 where the parameters were the same as in PM-14 with the exception that only 8.5 ml of lye was used and the adjusted pH was 9.8, which was closer to the adjusted pH of the experiment PM-9, we can see that the ammonia removal rate  $-k$  was 0.005 which was still higher than in the experiment without stirring. It can be concluded, that within these stripping parameters, stirring increased ammonia removal, which can potentially decrease the energy consumption as the stripping can be done in shorter time.

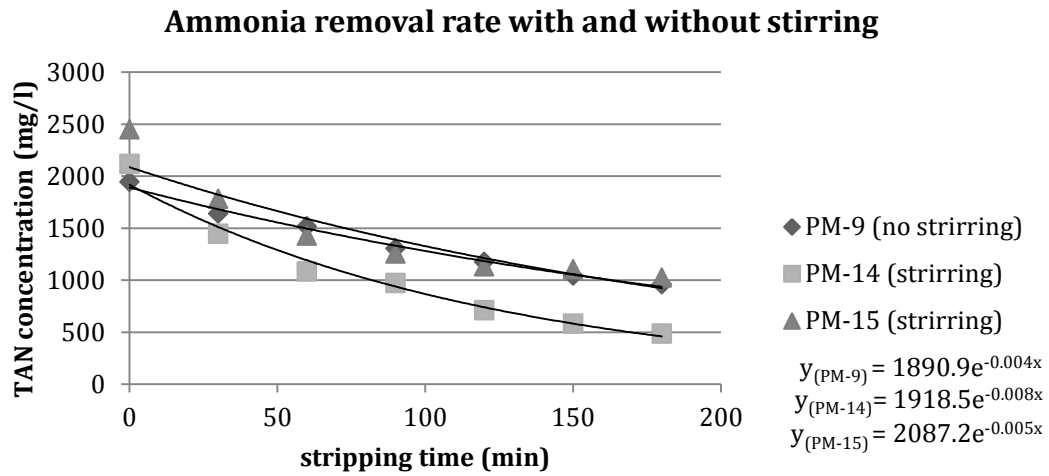


Figure 15 Total ammonia nitrogen (TAN) removal in stripping experiments PM-9, PM-14 and PM-15 done in 3 h and ca. 80 °C.

70 % TAN removal took longer time with 45 wt. % KOH, 3.3 h, than with NaOH. Solid CaO dissolved and adjusted pH very slowly. The experiments with CaO did not succeed as they were intended and further experiments were not carried out.

#### 6.4.2 Total solids and volatile solids

Initial total solids percentage in ammonified and pH adjusted chicken litter slurry was roughly between 10 to 6 %. Volatile solids and total solids were concentrated due to water evaporation. All final concentrations were corrected to match the initial volume using evaporation rates. Some decrease in TS was detected which can be seen from figure 16 (first 4 bars) where experiments done at 80 °C using 12.5 and 10.5 ml/l NaOH showed a decrease of 14 % and 12 % in total solids respectively. This was due to the fact that evaporation in the case of experiment “80 °C /12.5 ml” was so extreme that the surface level of the slurry dropped during stripping and 2 liters of water needed to be added during the stripping process and thus the slurry was diluted. In the case of

experiment “80 °C / 10.5 ml” the drop in TS concentration can be due to the fact that an unknown amount of concentrated slurry splattered and was lost due to clogging of the sample valve when samples were taken. Otherwise there was no significant change in TS in the experiments.

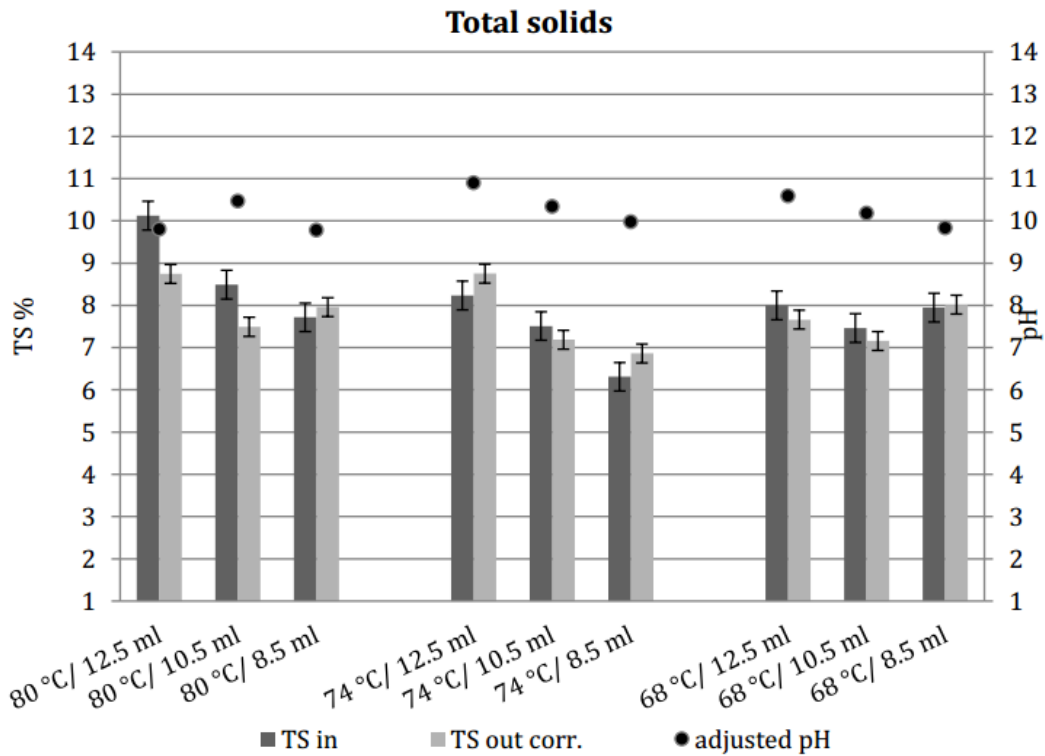


Figure 16. Change in total solids (TS) before ( $TS_{in}$ ) and after ( $TS_{out\ corrected}$ ) stripping experiments using lye. The total solids measurements post stripping were corrected taking into account the volume change in medium due to evaporation.

The ammonified chicken litter was lumpy and clearly not homogeneous. It was evident that the TS measurement had some sampling errors due to uneven sample material, which could not be stirred thoroughly due to the closed reactor. This can be deduced from the fact that, for example in one of the experiments (74 °C /8.5), the total solids increased by 9.5 %, from 6.3 % to 6.9 % (corrected value), which should not be possible as solids were not added during stripping process and evaporation was accounted for in the final TS



value. Also the evaporation rate was in line with other experiments in the series. In addition, the ammonified chicken litter, which was used in the experiment, had initial TS value of 7.2 % which was much higher, indicating that the starting sample of stripping was unevenly mixed.

Initial volatile solids percentage ranged between 7.2 % and 5.2 %. Roughly 70 % of the solids were volatile. During stripping, the slurry was further degraded at high pH and temperature due to hydrolysis (Kim et al., 2003; Athanasoulia et al., 2007). The degradation was observed as the slurry material turned smoother. However, the proportion of volatile solids did not increase. Similarly, as in the case of total solids, small decrease (14 % and 13 %) in volatile solids was detected in two experiments. The decrease can be seen in figure 17, experiment “80 °C /12.5 ml”, which was diluted and experiment “80 °C/ 10.5 ml” where sampling problems were encountered. In other experiments significant changes in VS-% were not detected.

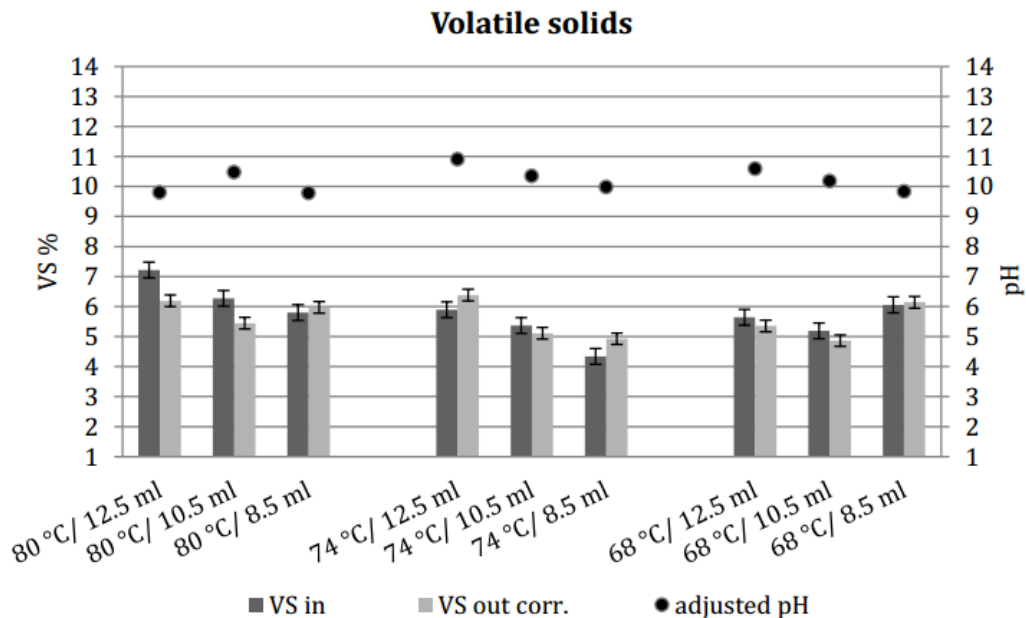


Figure 17. Change in volatile solids before ( $VS_{in}$ ) and after ( $VS_{out}$  corrected) stripping experiments using lye. The volatile solids measurements were

corrected taking into account the volume change in stripping due to evaporation.

### 6.4.3 Volatile fatty acids and buffer capacity

Volatile fatty acids (VFAs) did not change significantly. The VFA concentration varied between 5000 and 16000 mg/l as can be seen from figure below, figure 18.

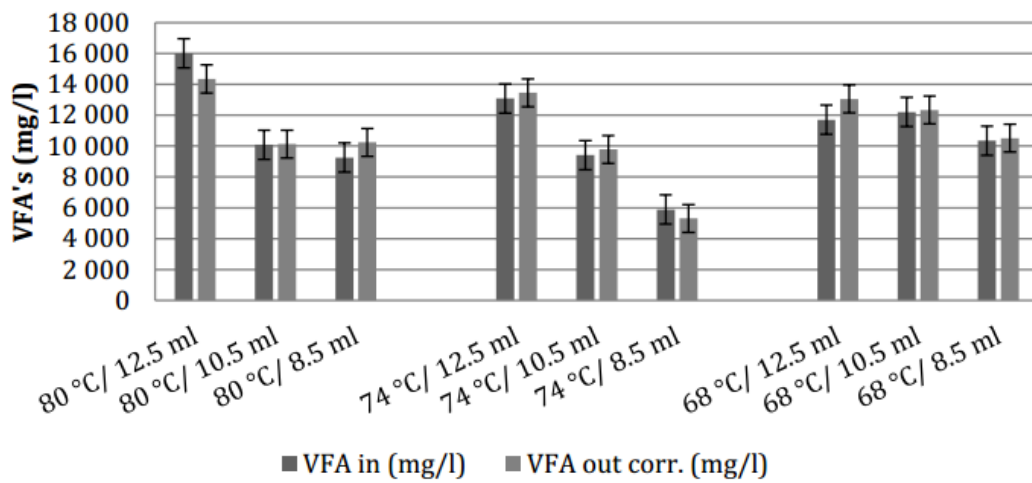


Figure 18. The concentration changes of volatile fatty acids in normal stripping experiments.

Initial total inorganic carbon ranged between 14 000-9 000 mg/l. Total inorganic carbon was reduced by 44 % on average. Final buffer capacity ranged between 9000-4000 mg/l of TIC as can be seen from figure 19.

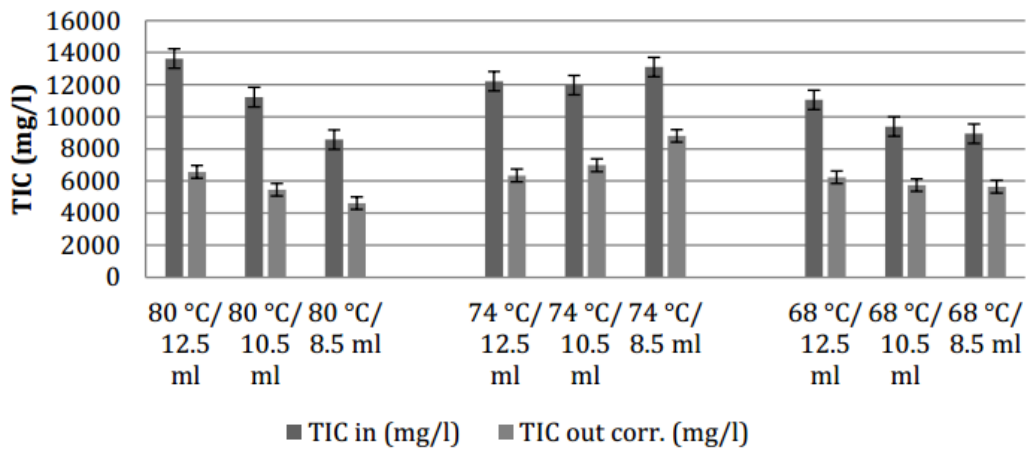


Figure 19. Concentration of total inorganic carbon (mg/l) in ammonia stripping with lye. The buffer capacity of total inorganic carbon is described as (mg CaO<sub>3</sub>/l). The final TIC concentration measurements were corrected to take into account slurry volume change. The decreasing of volume was due to evaporation during ammonia stripping.

Reduction in TIC was directly proportional to stripping temperature and as can be seen from figure 20. The removal rate of TIC was also proportional to adjusted pH. The higher the pH, the higher was the reduction in buffer capacity.

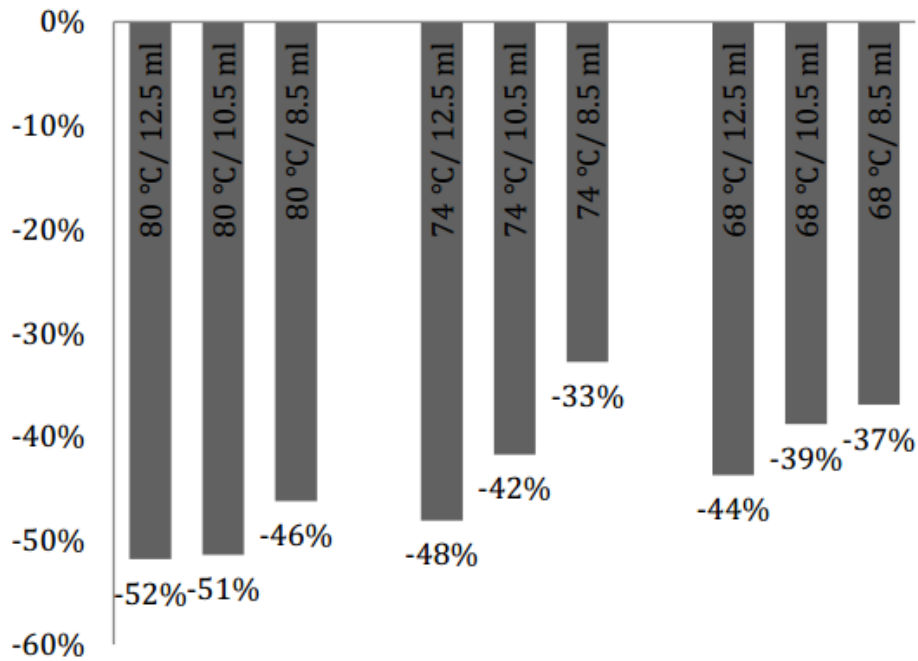


Figure 20. Reduction rates in buffer capacity (TIC) in ammonia stripping.

#### 6.4.4 Carbon-nitrogen-ratio

It can be seen from figure 21 that the total nitrogen removal was not directly proportional to the total ammonia removal. Some of the nitrogen was bound to the organic matter as inert form and would not be released into the slurry as ammonia or ammonium. Thus, all nitrogen cannot be stripped. Additionally, the nitrogen removal was not uniformly dependent on stripping parameters due to variance in nitrogen concentration between slurry batches. For example, when 77 % of TAN was stripped, only 41 % total nitrogen was removed (in experiment “80°C/12.5ml”). Whereas, when 80 % of TAN was stripped, only 28 % of nitrogen was removed (in experiment “80°C/10.5ml”). It can be concluded from the figure below (figure 21) that when ca. 70 % of TAN was stripped, on average ca. 30-40 % of total nitrogen was removed.

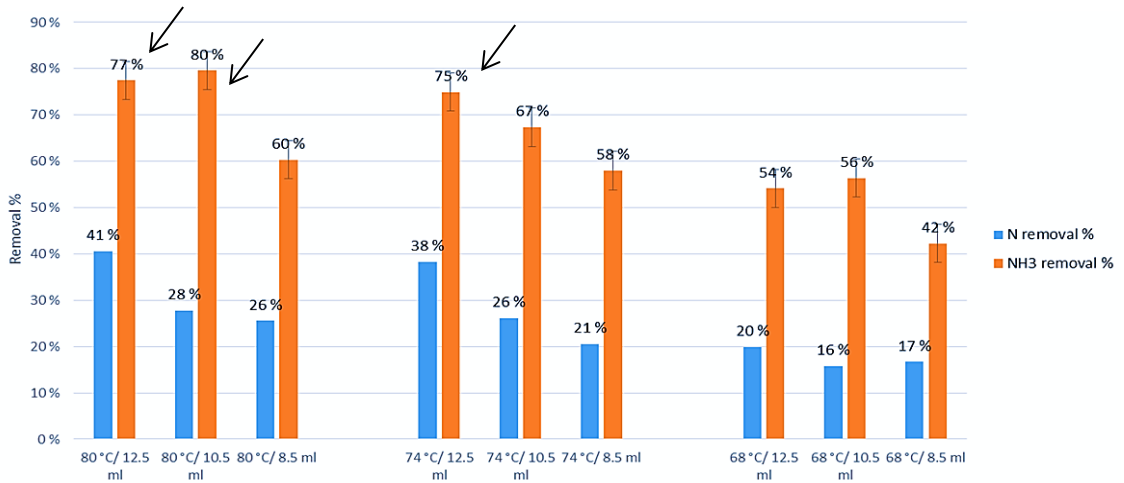


Figure 21. Total nitrogen removal in ammonia stripping experiments compared to TAN removal. The ideal stripping experiments, which exceeded 70 % TAN removal, are marked with an arrow.

According to the laboratory results, the C/N ratio in the predigested feed was ca. 7.1, and at the optimal stripping conditions (experiments PM-3, PM-5 and PM-14, where temperature 80 °C and 10.5 ml of lye was added,) the C/N ratio increased at best to 10.5-12.4, after nitrogen removal. This can be seen from the figure 22 below.

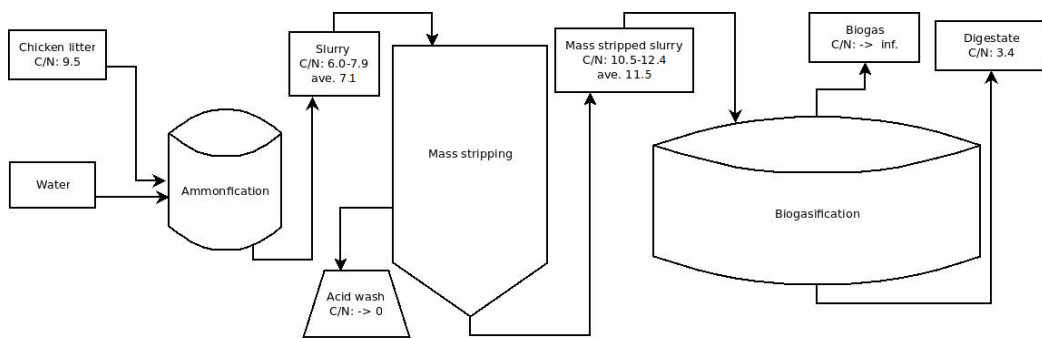


Figure 22. Carbon-nitrogen ratio of chicken litter slurry in different stages of biogas production. Not steady state.

Finally after the biogasification step the final C/N decreased to 3.4 due to conversion of carbon to CO<sub>2</sub> and CH<sub>4</sub> which evaporate from the slurry and leave

the system. Without the nitrogen removal step, the C/N ratio of biogas reactor would most likely steadily increase.

Detailed information about C/N fractions before and after stripping experiments can be found in appendix 1, table 1.

## **6.5 The effect of stripped slurry on biogas reactors**

Stripping or ammonification should not deteriorate the quality of biogas feed, because otherwise the methane production would suffer. Thus, it was important that the VS concentration remained the same as in the untreated chicken slurry, so that the anaerobic bacteria would have sufficient amount of substrate. It was also imperative that the C/N-ratio increased as nitrogen was removed from the system to ensure stable conditions for anaerobic activity.

Even though some VS content was lost in the ammonification process, the produced methane can be captured and utilized during the ammonification process. Thus, ammonification does not negatively affect methane yield. In the figure 23, it can be seen that the quality of preprocessed (ammonified and stripped) biogas feed was adequate for biogas production. In the long run the biogas reactor utilizing stripped chicken slurry (Bior7) produced more methane per gram of VS than the biogas reactor that utilized unprocessed chicken slurry (Bior6). The figure 23 indicates methane inhibition from day 233 onwards in Bior6. However, this might have been a temporary anomaly which needs to be studied further. Also, it should be pointed out that during the last days of data collection (days 329-337) both reactors did not seem to produce any methane which can be explained by operational anomalies.

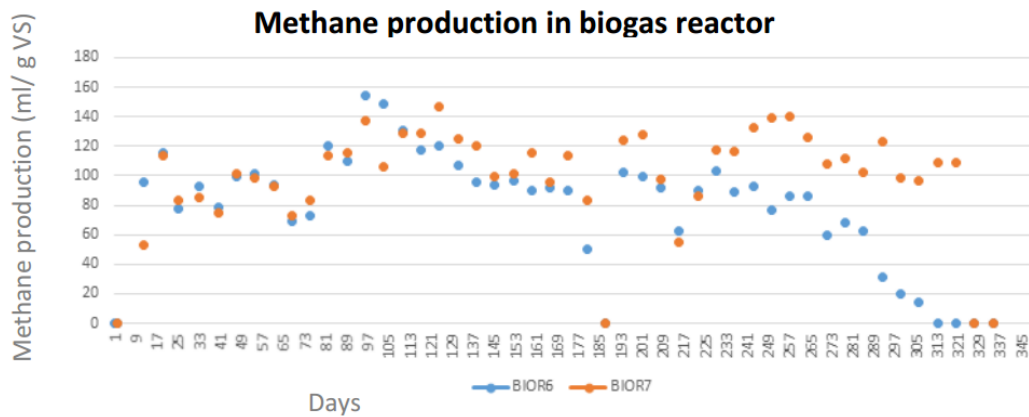


Figure 23. Methane production (ml CH<sub>4</sub>/ g VS) in biogas reactors utilizing unprocessed chicken slurry (Bior6) and stripped chicken slurry (BIOR7).

Some of the deviation in the methane production rates can be explained by changes in process conditions such as disruptions in stirring since the blades got stuck time to time. The ammonia accumulation effect can be seen in figure 24. According to Calli and others (2005), ammonia concentration above 3 g/l is toxic regardless of pH. The ammonia concentration of Bior7 (bioreactor using stripped feed) was kept steady (ca. 1 g/l) whereas in the Bior6 (bioreactor utilizing unprocessed chicken slurry), the ammonia inhibition level was clearly exceeded. It can be seen from figure 24 that the TAN concentration reached 8 g/l in Bior6. On the other hand, the ammonia accumulation level was dependent on loading rate and outflow of digestate which are not deliberated.

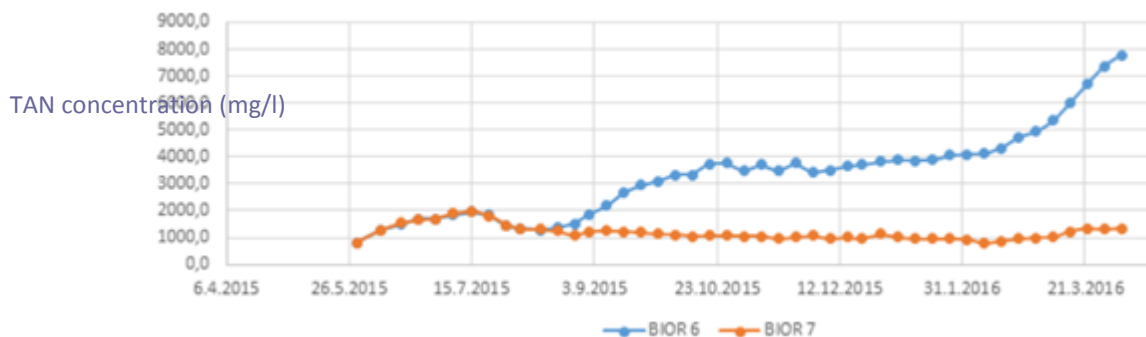


Figure 24. Total ammonia nitrogen concentration in bioreactors utilizing untreated (BIOR6) and stripped (BIOR7) chicken litter.

## 6.6 Sources of errors

There were some problems in the experiments regarding clogging, slurry volume, evaporation, aeration and pH adjustment. Some variations in stripping conditions altered the parameters and made the comparison of experiments difficult. These variations were assessed and accounted for in the result interpretations.

Some variations in slurry volume and slurry waste occurred due to clogged valves, when samples were drawn. Major contributors to the clogging were uneven, lumpy slurry and sand, which piled on the bottom of the stripping reactor. When a block was opened, usually some slurry was lost as it was squirted out of the valve with a high pressure and it flowed into a drain. However, the lost slurry was within the error margin and usually no more than 2 l of the slurry was lost. However, this volume loss did affect the initial evaporation calculations listed in appendix 1 table 1, as the volume of evaporated water was assumed to be the difference between the volume of (pH adjusted) slurry in and volume of slurry out of the stripping reactor. As all of the corrected values, in appendix 1 table 1, were dependent on the assumed evaporation rate, they were affected by the slurry loss. These corrected values were:  $C_{out,corr.}$ ,  $N_{out,corr.}$ ,  $VFA_{out,corr.}$ ,  $TIC_{out,corr.}$ ,  $VS_{out,corr.}$ ,  $TS_{out,corr.}$ , and ammonia removal (%). The frequency of clogging increased as the experiments proceeded. For example experiment PM-14 had a lot of sampling problems due to clogging.

There were problems with slurry volume measurements, as the stripping reactor did not have a scale. Originally, the slurry volume was calculated using measuring stick which was calibrated using water. However, the floor of the pilot hall was lightly slanted and gave somewhat varying results, so the method was replaced by measuring the slurry in batches using 5 l pitchers. The error margin in the pitchers was  $\pm 250$  ml (within 5 % error margin). The



measurements done using a measuring stick were approximated to match the pitcher volumes.

Due to high evaporation rate in the experiment PM-5, the aeration pipes emerged as the slurry level dropped. Additional water (2 l) was added to the stripping reactor. This altered the stripping conditions and diluted all concentrations (TAN, TIC, VFA, VS, TS) compared to other experiments. Additionally, in the experiment PM-5 ("80 °C/ 12.5 ml"), the aeration was 0.8 VVM which was lower than the desired VVM of 1. This was due to difficulties in aeration control, because the air pump setup didn't allow fine tuning of air flow. Thus, in this experiment, PM-5, the aeration was below the desired level.

The ammonified slurry batches were not totally uniform and for example the pH of ammonified slurry had some variations which affected the pH adjustment. Due to high buffer capacity the pH of the slurry batch was difficult to adjust on a predetermined level. The solids seemed to contribute to the buffering affect, since Nurmi (2015) did not have the same pH controlling problems, when solids were separated from similar ammonified slurry. As discussed on page 41, experiment PM-17 had operational errors and the pH of slurry needed to be readjusted by adding lye and water to the reactor as the initial pH adjustment was too weak for sufficient ammonia removal. Furthermore, the experiments PM-1 and PM-8 were rejected due to inconsistencies in pH adjustment. Therefore, they are marked with grey text in table 4 and appendix 1 table1.

Overall, the variations in stripping conditions made the result interpretations difficult. This could have been avoided by doing additional duplicate experiments. Nonetheless, the errors and problems gave valuable information about vulnerabilities of this type of ammonia stripping processes.

## 7 Cost calculation

### 7.1 Mass balance of ammonia stripping

To assess the costs of batch type ammonia stripping and make the results comparable with other stripping methods the mass balance for batch stripping was calculated. The mass balance over the stripping process could be estimated using optimal stripping conditions. In this example mass balance for stripping 1000 l of ammonified chicken litter (average TS 8.0 %) was assessed based on the experiment done in 40 l scale (stripping experiment PM-14). In this experiment, the temperature was 80 C° and 10.5 ml lye (50 % NaOH solution) was added to a liter of ammonified chicken litter slurry. It was assumed that the TAN concentration in predigested chicken litter was 2300 mg/l and that 70 % of it was removed.

As can be seen from figure 25, 1000 l predigested chicken litter (in stream 2. ) is added to the stripping reactor and 10.5 l of NaOH is also added (stream 1). Adding lye to the slurry increased total solids from 8.0 % to 8.2 %. It can be seen from table 6 that the total amount of water in the mixture is 930.7 kg and total amount of solids was 85.3 kg. 70 % (1.4 kg) of the ammonia was removed during the stripping process, which lasted for 2.5 h.

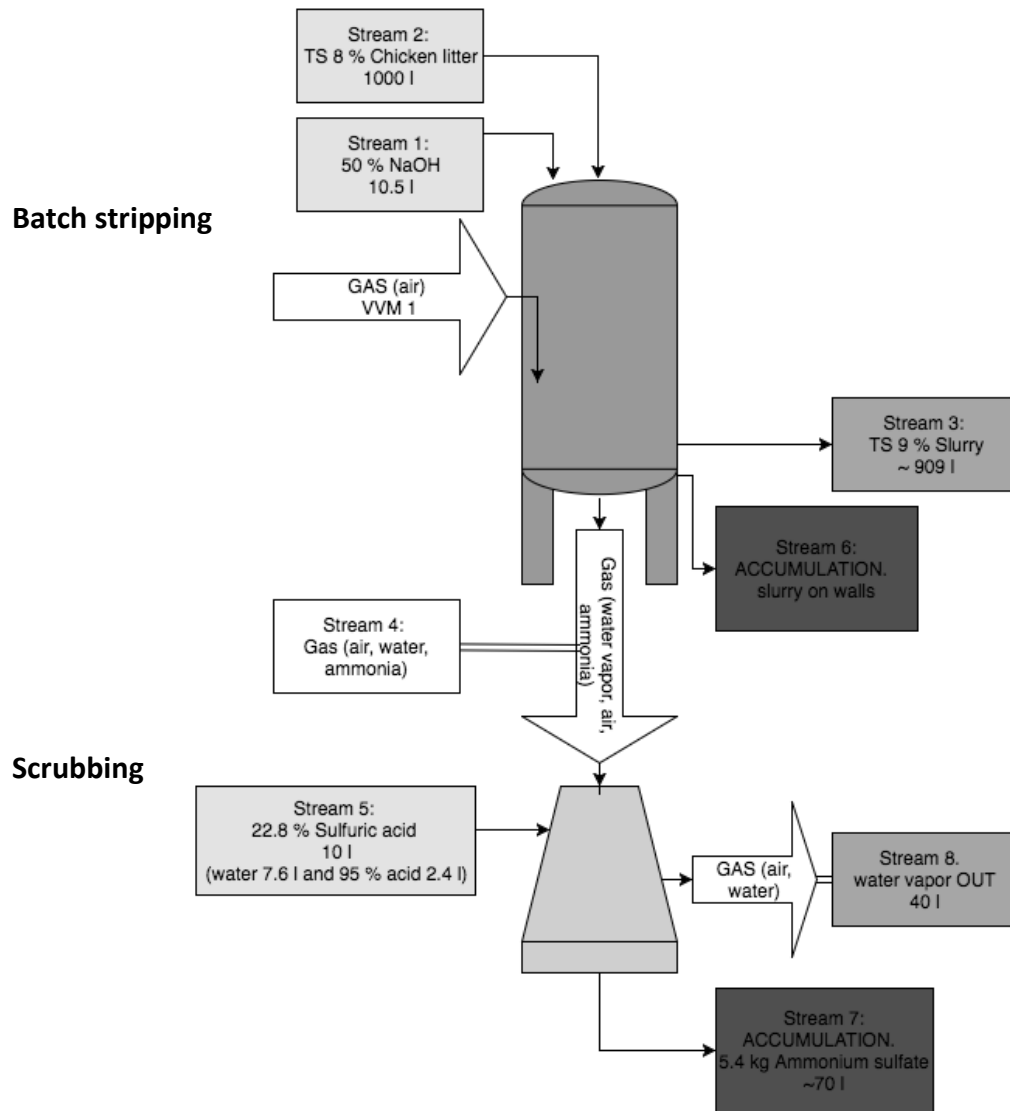


Figure 25. Process streams calculated for 1000 l ammonified chicken litter in batch type ammonia stripping and scrubbing process.

Table 6. Mass balance of 2.5 h ammonia stripping for 1000 l of predigested chicken litter based on experiment PM-14.

Batch stripping							
	Stream	IN	-	Stream	OUT	=	Stream ACC.
Water	1.	10.7 kg	3.	829.0 kg	6.	1.7 kg	
	2.	920.0 kg	4.	100.0 kg	-	-	
<b>Total</b>	-	<b>930.7 kg</b>	-	<b>930.0 kg</b>	-	<b>1.7 kg</b>	
Solids	1.	5.3 kg	3.	1.4 kg	6.	1.9 kg	
	2.	80.0 kg	4.	82.0 kg	-	-	
<b>Total</b>	-	<b>85.3 kg</b>	-	<b>83.4 kg</b>	--	<b>1.9 kg</b>	

From table 7 it can be seen that in stream number 4, 100 kg of water evaporated (9.9 V-%) from the stripping vessel. Most of the evaporated water was condensed and captured in the cooled scrubbers. Table 6 demonstrates that in the end 5.4 kg of ammonium sulfate was produced and along with ca. 909 liters of (TS 9.0 %) stripped slurry which had a TAN concentration of 660 mg/l.

Table 7. Mass balance of 2.5 h scrubbing for 1000 l of batch stripping based on experiment PM-14 .

Scrubbing									
	Stream	IN	-	Stream	OUT	=	Stream	ACC.	
Water	4.	100.0	kg	8.	40	kg	7.	67.7	kg
	5.	7.7	kg	-	-	kg	-		
<b>Total</b>	-	<b>107.7</b>	<b>kg</b>	-	<b>40</b>	<b>kg</b>	-	<b>67.7</b>	<b>kg</b>
Solids & acid	4.	1.4	kg	-	-	kg	7.	5.6	kg
	5.	4.2	kg	-	-	kg	-		
<b>Total</b>	-	<b>5.6</b>	<b>kg</b>	-	-	<b>kg</b>	-	<b>5.6</b>	<b>kg</b>

These calculations allowed for the approximation of the heating and chemical requirements. For instance, heating costs consisted of heating the ammonified slurry from ca. 50 C° to 80 C° and heat that was lost in evaporating water. The chemical costs consisted of added lye, sulfuric acid and hydrochloric acid used for neutralization. However, the ammonium sulfate that was produced can be sold for profit.

## 7.2 Utility costs of stripping

There were differences in the cost profiles of column stripping used by Nurmi (2015) based on experiment PS-13 and batch stripping used in this thesis. It should be noted that column stripping required decanting for solids separation and pumping slurry from decanter to stripper, while batch type stripping did not. Furthermore, stirring was limited to batch stripping.

Utility costs of ammonia stripping included electricity (for aeration, stirring, pumping and decanting), heating and chemicals (for pH adjustment, nitrogen recovery and neutralization of slurry). The expenditures that were used as the basis of the cost calculations are specified in table 8. Earnings on ammonium sulfate were approximated to be in the range of 60 % of the market price of 125 €/tn, which is 75 €/tn (Anon., Alibaba, 2015).

Table 8: Utility expenses of ammonia stripping

Utility	Cost	Source
Electricity	15 cents/kWh	(Virkajärvi, 2015)
Heating	3 cents/kWh	(Virkajärvi, 2015)
NaOH 50 %	100 €/ton	(Anon., Alibaba, 2015)
H <sub>2</sub> SO <sub>4</sub> 95 %	195.8 €/ton	(Anon., Alibaba, 2015)
HCl 37 %	237 €/ton	(Anon., Alibaba, 2015)

It is apparent that the heating costs are higher in column stripping because decanted slurry was heated from 22.5 C° to 59 C° and thus the temperature difference was higher. Namely,  $-\Delta T_{\text{column stripping}}$  was 36.5 C° whereas in batch stripping the difference was only 30 C°. There were other differences as well, which are listed in table 9. For instance the stripping time in column stripping was only 60 minutes while in batch stripping it was 180 min and the ammonia concentrations as well as ammonia removal efficiencies differed.

Table 9. Comparison of optimal ammonia stripping parameters of column stripping (based on PS-13) and batch type stripping (PM-14).

<b>Parameter</b>	<b>Batch stripping</b>	<b>Column stripping</b>
V slurry (l)	40	30
T <sub>i</sub> slurry (C°)	50.0	22.5
T <sub>f</sub> slurry (C°)	80.0	52.0
T <sub>IN</sub> air (C°)	60	unknown
TAN <sub>in</sub> (g/l)	2.3	1.4
TAN removed (g)	64.4	29.1
TAN <sub>removal</sub> (%)	80 %	87.9 %
TS <sub>in</sub> (%)	8.5	1.5
NaOH 50 % consumption (ml/l)	10.5	6.0
HCl 37 % consumption (ml/l)	5.0	2.4
t <sub>stripping</sub> (min)	180	60
P <sub>aeration pump</sub> (W)	240	370
P <sub>agitation motor</sub> (W)	55	-
P <sub>boiler</sub> (W)	9000	9000
P <sub>decanter, 40 % power</sub> (W)	-	4400
P <sub>decanter pumps 1 &amp; 2, 10 % power</sub> (W)	-	520

Cost of stripping 1000 l of ammonified slurry was calculated and the breakdown of costs can be seen in table 10. It must be pointed out that the inlet and outlet temperatures of air in column stripping were unknown and thus they were not assessed. It can be assumed that heating costs would be slightly higher in reality. In addition, column stripping costs did not include pumping costs of combining liquid slurry with solid fraction.

The cost of stripping 1000 liters of slurry with batch stripping method (7.32 €/m<sup>3</sup>) was slightly higher than the cost of column stripping (6.32 €/m<sup>3</sup>) which can be seen from table 10. This was due to slower process, which used more energy on aeration, more lye and hydrochloric acid. The biggest expenditures of batch stripping were aeration (2.70 €/m<sup>3</sup>), neutralization (1.28 €/m<sup>3</sup>) and heating (1.08 €/m<sup>3</sup>).

Table 10. Breakdown of costs and comparison of 2 different ammonia stripping methods for 1000 l of ammonified slurry.

Type of expense	Batch stripping of 1000 l	Column stripping of 1000 l *
Air	2.70 €	1.31 €
Stirring	0.65 €	0.00 €
Pumping	0.00 €	0.78 €
Heating	1.08 €	1.43 €
Decanting	0.00 €	1.54 €
Adjustment of pH	1.05 €	0.42 €
Recovery of Nitrogen	0.56 €	0.50 €
Neutralization	1.28 €	0.34 €
<b>In total</b>	<b>7.32 €</b>	<b>6.32 €</b>
*Costs do not include pumping costs of combining solids with liquid fraction.		

The greatest cost of column stripping was decanting, which made up 24 % of the processing expenses which can be seen from figure 26. In batch stripping the greatest cost was aeration which makes up ca. 37 % of expenses. Most of the energy used in aeration transformed into heat since the pump heated inlet air from room temperature to 60 C°. This heat was expensive since according to table 8 (on page 62) the price of electricity was 5 times the cost of heating. However, heating costs can be lowered by closed loop aeration in which the incoming air would not cool the reactor. In the presented experiments, air was not circulated and thus incoming air (60 C°) cooled the reactor (80 C°).

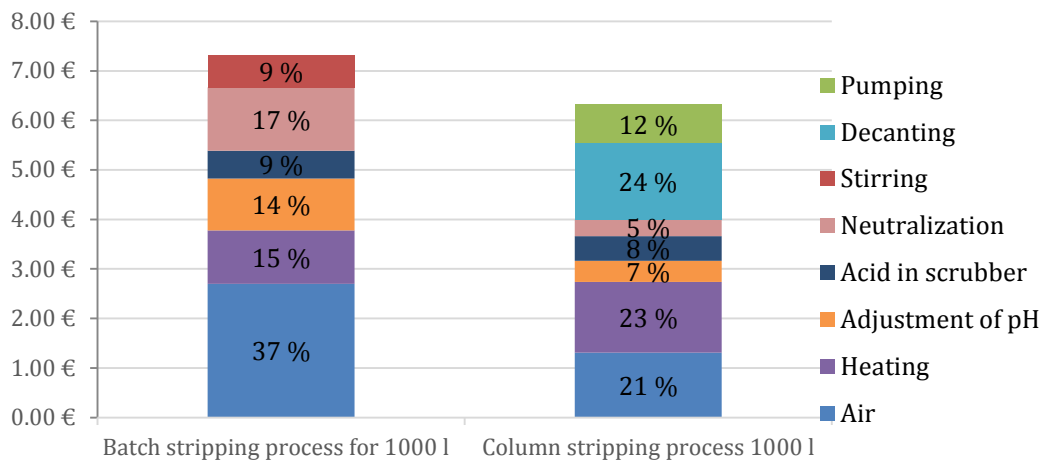


Figure 26. Cost comparison of 2 different stripping procedures for 1000 l of ammonified slurry (TS ca. 8 %).

Despite the fact that batch stripping seemed to be a more costly option, it should be taken under consideration that it was a more effective stripping method (80 % TAN removal) than column stripping. This was so because in column stripping only the liquid fraction of the slurry was stripped (87.9 % TAN removal). The liquid fraction needed to be reunited with the untreated solid fraction and this lowered the total ammonia removal of column stripping to 62.2 %. According to calculations, batch stripping removed ca. 1.7 kg TAN whereas column stripping removed only 1.3 kg TAN per 1000 l of ammonified slurry. Thus, when batch stripping is compared with column stripping to achieve 62.2 % ammonia removal, only 77.7 % of ammonified slurry needed to be treated with batch stripping method and the rest 22.3 % of the slurry could have gone untreated to the biogasification reactor. This lowered the batch stripping price to 5.69 €/m<sup>3</sup> which made it a more affordable stripping option. In batch, stripping a kilo of ammonia cost 4.36 €/NH<sub>3</sub> kg and in column stripping it was slightly more costly, 4.84 €/ NH<sub>3</sub>kg. Originally the aim was to remove 70 % of total ammonia nitrogen. This could have been achieved through batch stripping 87.5 % of ammonified slurry with a cost of 6.41 €/m<sup>3</sup>.



### 7.3 Stripping costs in 500 MW biogas plant

According to Luke (Luonnonvarakeskus, eng. *Natural Resources Institute Finland*) their smaller biogas plant, which produced electricity only 4 600–6 100 MWh/a, had 35 % electricity efficiency rate and 50 % heat efficiency rate (Marttinen et al., 2015).

A supposed 500 MW biogas plant produces annually 435 million m<sup>3</sup> of methane, which converts into 4.4 million MWh. It was approximated that if the plant operated at 30 % efficiency rate, the electricity produced, 1.3 million MWh, could have been sold for 287 million €/a, when government subsidized electricity price (in Germany) was 22 cents/kWh (Virkajärvi, 2015). According to figure 27, if the waste heat was 15 % of total energy, then the heat production was 55 % of total energy. This heat (2.4 million MWh) could have been utilized within the plant or sold for 0.03 €/kWh (Virkajärvi, 2015), which would have returned extra 72 million €/a. Total sales would have been 358 million €/a as illustrated in figure 28.

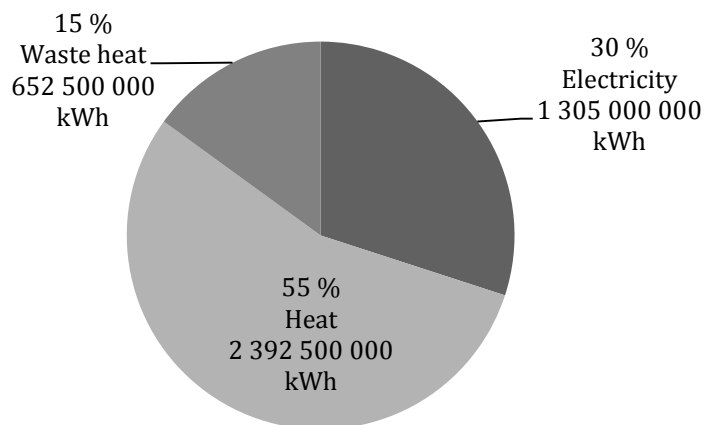


Figure 27. Distribution of heat and electricity production in a 500 MW biogas plant.

Such a plant needed to process approximately 4 million tons of chicken litter. Based on this study, theoretically the annual stripping costs for batch stripping

would have been 157 million €/a, when all the ammonified slurry was stripped with 80 % efficacy. This would have been 44 % of the revenue, as can be seen from figure 28. However, we wanted to compare the annual operating costs of batch and column stripping. Thus, we needed to take into account that column stripping removed only 62.2 % of total ammonia because, the solids were separated and only liquid fraction was stripped. Thus, we needed to limit the ammonia removal in batch stripping to 62.2 % as well. This was done by treating only fraction of the slurry (87.5 %) with the same setup as above, then the annual operating costs for batch stripping were only 137 million €/a (38 % of revenue). In contrast, the column stripping costs were still more costly, 141 million €/a (39 % of revenue), when 62.2 % of ammonia was removed.

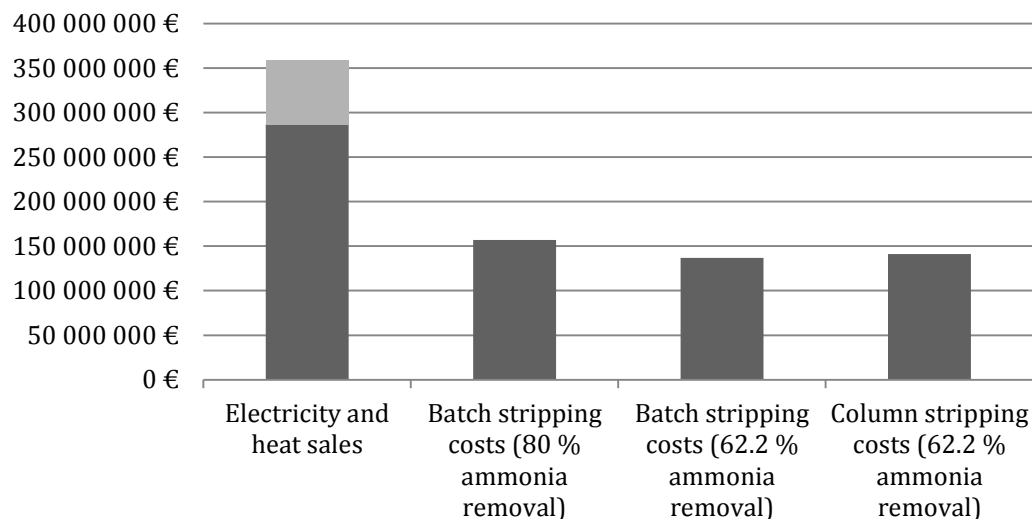


Figure 28. Electricity and heat sales revenue of a 500 MW biogas plant compared to operating costs of batch stripping and column stripping in the same plant.

After all the other costs, such as biogasification, operating and investment costs, profit would have been marginal and would have relied merely on government support. In conclusion, these two stripping methods were not yet sufficiently cost effective to be implemented and they should be optimized.

## 8 Discussion and conclusions

Due to high nitrogen content, untreated chicken manure is not suitable for industrial scale biogas production. We studied how nitrogen can be stripped from biogas feed to prevent ammonia inhibition in biogasification process. The goal was to pre-process chicken litter, which contains nitrogen, in a manner that the litter could be utilized in biogas production in an effective way. It was imperative to produce biogas feed, which would not inhibit the methane production in order to establish a functioning industrial scale biogas plant.

Specifically, we aimed for 70 % ammonia removal from the chicken litter by a two-step preprocess. First we used ammonification to break down nitrogen compounds into ammonium/ammonia and then a simple batch type stripping method, to remove excess ammonia from the slurry. As a main product we produced chicken litter slurry and as a side product we produced ammonia fertilizer (ammonium sulfate). Both regular ammonified chicken litter slurry, as well as, ammonified reject slurry was used in the experiments.

To find the most effective stripping parameters for 70 % total ammonia removal, we altered the amount of added lye, pH level of the slurry, stripping temperature, stirring and aeration depth. We also utilized various alkali types (NaOH, KOH, CaO) and CO<sub>2</sub>-stripping to adjust the pH of the slurry. We used the optimized ammonia removal parameters for calculating the costs of the batch stripping process. Batch stripping costs were compared to the costs of a similar scale column stripping.

The quality of stripped slurry was observed by measuring pH, TS, VS, VFA, buffer capacity and C/N of the stripped slurry. Finally the stripped chicken litter was used in biogas reactors to observe the response of the methanogenic bacteria to the pre-processed feed.

We learned that compared to regular feed, the quality of stripped slurry did not decrease significantly in the ammonia stripping process. Even though we did not reach the desired C/N level of 20, the stripped chicken litter slurry was suitable as biogas feed as the VFA's were not reduced. Additionally, in the bioreactor utilizing stripped chicken litter slurry, the total ammonia nitrogen level remained under the inhibition level of 3000 mg/l, whereas, the reactor, which was fed with non-treated slurry, clearly exceeded the inhibition level and produced less methane. Thus, ammonia stripping can be a beneficial pre-process for biogas plants that utilize chicken litter. However, to keep the bioreactor in balance, the pH of the stripped slurry needed to be readjusted closer to 8 before feeding it to the biogas reactor. Since the buffer capacity decreased 33-52 % in the stripping process, the pH adjustment was straightforward.

We managed to remove 43-80 % of TAN in 3 h ammonia stripping experiments. The ammonia stripping followed first order kinetics and in these experiments the ammonia removal rate constant,  $k$ , ranged from -0.003 to -0.008. The highest removal rate (-0.008) was attained in the highest stripping temperatures, close to 80 °C and pH 10.5 or above. However, no more than 80 °C can be recommended as a stripping temperature, because evaporation caused operational problems with aeration.

For pH adjustment, the liquid bases, NaOH and KOH solutions, were suitable because they adjusted the pH quickly, whereas, CaO powder cannot be recommended for use, because it did not dissolve well into the slurry. Stirring had a notable positive affect on the efficiency of the stripping process and reduced the stripping time of 70 % TAN removal from 5 h to 2.5 h. The increase of aeration depth from 3 cm to 22 cm also increased ammonia removal rate and reduced stripping time of from 5 h to 2.5 h. On the other hand, it should be

taken into consideration that the aeration depth experiments were done without mixing and deeper aeration promoted agitation, which in turn indirectly supported greater ammonia removal. Thus, we cannot determine if the aeration depth had an effect on the ammonia saturation in the air bubbles or if the mixing was responsible of the greater ammonia removal rate.

For 70 % TAN removal, the required stripping temperature was 74 °C - 80 °C. Parameters for optimized 70 % TAN removal were: t (2.5 h), T (80 °C) and pH (10.0-10.2). The lye (NaOH 50 %) requirement for regular ammonified chicken litter slurry was no less than 10.5 ml/l. Yet, reject slurry required much more, 15.8 ml/l of lye. However, CO<sub>2</sub>-stripping raised the pH of reject slurry by 0.4-1.6 pH-units and lowered the lye requirement significantly to ca. 6.3 ml/l.

When the costs of optimized batch stripping conditions were calculated, the biggest cost factors of batch stripping were aeration, neutralization and heating. Compared to column stripping, batch stripping was more affordable pre-process since solids were not separated and the overall ammonia removal process was more efficient. In optimized batch stripping the overall TAN removal was 80 % (3 h) while, the overall TAN removal was only 62 % in column stripping (1 h). In optimized conditions, batch stripping costs were 4.36 € per removed kg of NH<sub>3</sub>, whereas, removal of ammonia with column stripping method cost 4.84 €/kg.

Hypothetically, in a 500 MW biogas plant 4 million tons of chicken litter would be processed annually. Thus, when all of the chicken litter would be stripped with 80 % efficacy, in a batch type stripping reactor, the ammonia stripping costs would be 157 million €/a, which would be 44 % of sales revenue. 44 % is a disproportionately large cost. Though, the costs can be cut through treating only part of the feed and removing less ammonia with the same optimized stripping efficiency. Additionally the untreated chicken litter would buffer the

pH of the reactor and decrease the demand of neutralizers. In conclusion, the ammonia stripping process needs to be further developed and optimized to make it economical.

There were clearly many problems with batch type ammonia stripping setup. It was difficult to adjust and set the pH level of ammonified slurry batch based on pre-adjusted smaller batch because apparently, the slurry was heterogeneous. In addition, the ammonified slurry also had quite a high solids content which buffered the pH and this too made the pH adjustment very challenging.

To make the experiments more comparable, ideally the stripping material would have been from the same ammonification batch and thus, uniform. However, it should be noted that in the biogas industry, the feed material varies quite a lot and the experiment results should also reflect variation in the concentrations of solids, pH, etc.

In high enough concentrations, cumulating  $\text{Na}^+$  or  $\text{K}^+$  can inhibit the growth of anaerobic bacteria and methane production. In the ammonia stripping process, ammonia was basically swapped with NaOH or KOH. Thus, in further studies, the risk of cation toxicity should be assessed in this context. In addition, further studies could try to shed light on the possibility of base mixtures and alternative alkalis such as birch ash, to optimize the chemical and environmental costs.

The alkali consumption was very high so the  $\text{CO}_2$ -removal should be optimized to lower the alkali demand. Other ways to reduce alkali demand would be to separate solids, which buffer the pH. However, this additional process step has been used in column stripping process. Decanting is a costly process, which was observed in the cost calculation. However, if further studies are to be conducted, it should be taken into account that solids contributed to clogging

of sample valves and posed a threat on operators. It would have been much safer to draw samples if the valves had not clogged often. Thus, solid separation could be an option for achieving more homogenous slurry and safer working environment.

It can be concluded that batch stripping is a time consuming and a rather economically inefficient way to remove ammonia due to high energy and chemical demand. It would be recommended that the solids should be separated from the slurry. It should be taken into account that the prices of electricity and chemicals have a major impact on stripping costs. Even a small increase in the prices can elevate the processing costs in a significant way. Thus, sensitivity analysis would be advisable in further investigations into the matter. Furthermore, installation, maintenance and stripping equipment costs should also be evaluated when building an industrial scale plant.

## References

Abouelenien, F., Fujiwara, W., Namba, Y., Kosseva, M., Nishio, N. and Nakashimada, Y., Improved methane fermentation of chicken manure via ammonia removal by biogas recycle, *Bioresour.Technol.* **101** (16) (2010) 6368-6373.

Abouelenien, F., Nakashimada, Y. and Nishio, N., Dry mesophilic fermentation of chicken manure for production of methane by repeated batch culture, **107** (3) (2009) 293-295.

Ahring, B. K., Angelidaki, I. and Johansen, K., Anaerobic treatment of manure together with industrial waste, *Water Sci.Technol.* **25** (7) (1992) 311-318.

Al Seadi, T., Rutz, D., Prassl, H., Köttner, M., Finsterwalder, T., Volk, S. and Janssen, R., *Biogas handbook*, University of Southern Denmark, Esbjerg 2008, p. 23-27. ISBN 978-87-992962-0-0.

Anonymous, Alibaba, Retrieved 16.11.15 from <https://www.alibaba.com/?spm=a2700.7724838.0.0.Aydfc6>.

Anonymous, Ductor Corporation, Retrieved 20.4.2016 from <http://news.cision.com/ductor/r/ductor-is-revolutionizing-the-biogas-industry,c9959511>.



Anonymous, Electrigaz, Retrieved 11.08.2016, from [http://www.electrigaz.com/faq\\_en.htm](http://www.electrigaz.com/faq_en.htm).

Anonymous. Branch Environmental Corp., Retrieved 11.08.2016, from [http://www.branchenv.com/air\\_strippers/Ammonia%20Stripping.pdf](http://www.branchenv.com/air_strippers/Ammonia%20Stripping.pdf).

Athanasoulia, E., Melidis, P., and Aivasidis, A., Characterization of enhanced anaerobic degradation of digested sludge mixture after thermo-chemical and enzymatic treatment, *Proceedings 10th International Conferences Environmental Sciences and Technology*, Greece, Kos island 2007. pp. A-101-108.

Belostotskiy, D., Jacobi, H., Strach, K. and Liebetrau, J. (2013) Anaerobic digestion of chicken manure as a single substrate by control of ammonia concentration, AD13 Recovering (bio) Resources for the World, Retrieved 11.8.2016 from <http://www.redbiogas.cl/wp-content/uploads/2013/07/IWA-11342.pdf>.

Bonde, T., Method and device for stripping ammonia from liquids, US 20060006055 A1, 2003.

Bonmati, A. and Flotats, X., Air stripping of ammonia from pig slurry: Characterisation and feasibility as a pre-or post-treatment to mesophilic anaerobic digestion, *Waste Manage.* **23** (3) (2003) 261-272.

Calli, B., Mertoglu, B., Inanc, B. and Yenigun, O., Effects of high free ammonia concentrations on the performances of anaerobic bioreactors, *Process Biochem.* **40** (3-4) (2005) 1285-1292.

Chen, Y., Cheng, J. J. and Creamer, K. S., Inhibition of anaerobic digestion process: A review, *Bioresour. Technol.* **99** (10) (2008) 4044-4064.

Deublein, D. and Steinhauser, A., *Biogas*, Biogas from Waste and Renewable Resources, Edited by Anonymous, Wiley-VCH Verlag GmbH & Co. KGaA, 2010, 85-95. ISBN 9783527632794.

Dioha, I., Ikeme, C., Nafi'u, T., Soba, N. and Yusuf, M., Effect of carbon to nitrogen ratio on biogas production, **1** (3) (2013) 1-10.

Fink, J. (2014) *Nix nitrogen extraction*, Retrieved 8.11.2016, from <http://www.rushlightevents.com/wp-content/uploads/2014/03/BioBriefing-12-3-14-Xergi.pdf>.

Fricke, K., Santen, H., Wallmann, R., Hüttner, A. and Dichtl, N., Operating problems in anaerobic digestion plants resulting from nitrogen in MSW, *Waste Manage.* **27** (1) (2007) 30-43.

Gallert, C., Bauer, S. and Winter, J., Effect of ammonia on the anaerobic degradation of protein by a mesophilic and thermophilic biowaste population, *Appl. Microbiol. Biotechnol.* **50** (4) (1998) 495-501.

Gangagni Rao, A., Sasi Kanth Reddy, T., Surya Prakash, S., Vanajakshi, J., Joseph, J., Jetty, A., Rajashekhara Reddy, A. and Sarma, P. N., Biomethanation of poultry litter leachate in UASB reactor coupled with ammonia stripper for enhancement of overall performance, *Bioresour.Technol.* **99** (18) (2008) 8679-8684.

Guštin, S. and Marinšek-Logar, R., Effect of pH, temperature and air flow rate on the continuous ammonia stripping of the anaerobic digestion effluent, *Process Saf.Environ.Prot.* **89** (1) (2011) 61-66.

Hamilton, D. W., *Anaerobic digestion of animal manures: Understanding the basic processes*, Division of Agricultural Sciences and Natural Resources, Oklahoma State University, 2009, Retrieved 1.10.2015 from <http://dasnr22.dasnr.okstate.edu/docushare/dsweb/Get/Document-6278/BAE-1747web2014.pdf>.

Hill, D. T., Simplified monod kinetics of methane fermentation of animal wastes, **5** (1) (1983) 1-16.

Huang, J. and Shang, C., *Air stripping*, Advanced physicochemical treatment processes, Edited by Wang, L., K., Hung, Y., Shamas, N., K., 4<sup>th</sup> volume, Springer, 2006, pp. 47-79.

Huang, J. J. H. and Shih, J. C. H., The potential of biological methane generation from chicken manure, *Biotechnol.Bioeng.* **23** (10) (1981) 2307-2314.

Jarrell, K. F., Saulnier, M. and Ley, A., Inhibition of methanogenesis in pure cultures by ammonia, fatty acids, and heavy metals, and protection against heavy metal toxicity by sewage sludge, *Can.J.Microbiol.* **33** (6) (1987) 551-554.

Jiang, A., Zhang, T., Zhao, Q., Frear, C. and Chen, S., Integrated ammonia recovery technology in conjunction with dairy anaerobic digestion, (2010) 19 p.

Kavanaugh, M. C. and Trussell, R. R., Design of aeration towers to strip volatile contaminants from drinking water, **72** (12) (1980) 684-692.

Kayhanian, M., Ammonia inhibition in high-solids biogasification: An overview and practical solutions, *Environ.Technol.* **20** (4) (1999) 355-365.

Kim, J., Park, C., Kim, T., Lee, M., Kim, S., Kim, S. and Lee, J., Effects of various pretreatments for enhanced anaerobic digestion with waste activated sludge, **95** (3) (2003) 271-275.

Koster, I. W. and Lettinga, G., Anaerobic digestion at extreme ammonia concentrations, **25** (1) (1988) 51-59.

Liao, P., Chen, A. and Lo, K., Removal of nitrogen from swine manure wastewaters by ammonia stripping, *Bioresour.Technol.* **54** (1) (1995) 17-20.

Lide, David R., Frederikse, Hans Pieter Roeter, CRC Press., *CRC handbook of chemistry and physics : A ready-reference book of chemical and physical data*, CRC Press, Boca Raton Taylor & Francis Group, Florida 1993, ISBN 0849304741 9780849304743.

Liu, L., Pang, C., Wu, S. and Dong, R., Optimization and evaluation of an air-recirculated stripping for ammonia removal from the anaerobic digestate of pig manure, *Process Saf. Environ. Prot.* **94** (2015) 350-357.

Lyberatos, G. and Skiadas, I., Modelling of anaerobic digestion—a review, *Global Nest Int J.* **1** (2) (1999) 63-76.

Moody, L., Burns, R., Bishop, G., Sell, S. and Spajic, R., Using biochemical methane potential assays to aid in co-substrate selection for co-digestion, *Appl. Eng. Agric.* **27** (3) (2011) 433-439.

Nahm, K. H., Factors influencing nitrogen mineralization during poultry litter composting and calculations for available nitrogen, *World's Poult. Sci. J.* **61** (2) (2005) 238-255.

Ni, J., Mechanistic models of ammonia release from liquid manure: A review, *J. Agric. Eng. Res.* **72** (1) (1999) 1-17.

Nie, H., Jacobi, H. F., Strach, K., Xu, C., Zhou, H. and Liebetrau, J., Mono-fermentation of chicken manure: Ammonia inhibition and recirculation of the digestate, *Bioresour. Technol.* **178** (2015) 238-246.

Nishio, N. and Nakashimada, Y., *Chapter 7 - manufacture of biogas and fertilizer from solid food wastes by means of anaerobic digestion*, Food Industry Wastes, Edited by Kosseva, M. R. and Webb, C., Academic Press, San Diego 2013, pp. 121-133. ISBN 9780123919212.

Noyes, R., *Unit operations in environmental engineering*, William Andrew Publishing/Noyes, 1994, p. 349 and 354. ISBN 978-0-8155-1343-8.

Nurmi, J., *Removal and recovery of ammonia with an air stripping process prior to biogas production in pilot scale*, Master's Thesis, University of Oulu, Environmental Engineering, 2015, 84 p.

Obaid-ur-Rehman, S. and Beg, S. A., Ammonia removal by air stripping—from origin to present state of technology, *J. Environ. Sci. Health, Part A.* **25** (4) (1990) 343-365.

Patoczka, J. and Wilson, D. J., Kinetics of the desorption of ammonia from water by diffused aeration, *Sep.Sci.Technol.* **19** (1) (1984) 77-93.

Ponsá, S., Ferrer, I., Vázquez, F. and Font, X., Optimization of the hydrolytic–acidogenic anaerobic digestion stage (55 C) of sewage sludge: Influence of pH and solid content, *Water Res.* **42** (14) (2008) 3972-3980.

Reeves, T. G., Nitrogen removal: A literature review, *J. - Water Pollut. Control Fed.* **44** (10) (1972) 1895-1908.

Shivraj, D. and Seenayya, G., Optimum total solids content for the generation of biogas from poultry litter waste, *Indian J.Environ.Health.* **36** (2) (1994) 115-118.

Sprott, G. D. and Patel, G. B., Ammonia toxicity in pure cultures of methanogenic bacteria, *Syst.Appl.Microbiol.* **7** (2) (1986) 358-363.

Strik, D. P. B. T. B., Domnanovich, A. M. and Holubar, P., A pH-based control of ammonia in biogas during anaerobic digestion of artificial pig manure and maize silage, *Process Biochem.* **41** (6) (2006) 1235-1238.

Virkajärvi, I., *Personal communication*, 16.9.2015.

Walker, M., Iyer, K., Heaven, S. and Banks, C. J., Ammonia removal in anaerobic digestion by biogas stripping: An evaluation of process alternatives using a first order rate model based on experimental findings, *Chem.Eng.J.* **178** (2011) 138-145.

Yetilmezsoy, K. and Sakar, S., Development of empirical models for performance evaluation of UASB reactors treating poultry manure wastewater under different operational conditions, *J.Hazard.Mater.* **153** (1–2) (2008) 532-543.

Zhang, L. and Jahng, D., Enhanced anaerobic digestion of piggery wastewater by ammonia stripping: Effects of alkali types, *J.Hazard.Mater.* **182** (1) (2010) 536-543.

Zhang, L., Lee, Y. and Jahng, D., Ammonia stripping for enhanced biomethanization of piggery wastewater, *J.Hazard.Mater.* **199** (2012) 36-42.

Zhang, C., Su, H., Baeyens, J. and Tan, T., Reviewing the anaerobic digestion of food waste for biogas production, **38** (2014) 383-392.

Zhao, Q., Ma, J., Zeb, I., Yu, L., Chen, S., Zheng, Y. and Frear, C., Ammonia recovery from anaerobic digester effluent through direct aeration, *Chem.Eng.J.* **279** (2015) 31-37.



## Detailed stripping specifications

Table 1. Detailed parameters of ammonia stripping experiments in pilot scale.

Experiment (PM-)	1	2	3	4	5	6
Feed	Ammonia water	Ammonia water	AMF. CL	Amf. CL with reject	Amf. CL	Amf. CL + NH <sub>4</sub> OH
Ammonia removal (%)	44 %	76 %	75 %	85 %	82 %	70 %
V in (l)	60	37	36	42	40	40
V out (l)	60	36	34	34	35	38
V feed (l)	0	0	35	40	40	~ 33
Base V/m (ml/g)	-	-	0.45	0.65	0.53	0.41
V added water (l)	60	37	0	1	3	7
Evaporation (V-%)	-	4 %	6 %	18 %	13 %	6 %
TAN in (mg/l)	3127	1574	2400	2842	2601	2469
TAN out (mg/l)	1748	393	638	522	532	785
Antifoam (y/n)	n	y	n	n	y	n
T reactor (C)	69	74	74	80	80	80
Time (min)	120	150	180	250	224	210
Initial pH of feed	7.0	10.8	6.0	7.5	6.1	9.0
pH after adjustment	11.0	10.8	10.9	10.0	9.8	10.0
Final pH	9.8	9.7	9.0	9.5	8.9	9.6
Consumption of base (ml/l or g/l)			12.6	15.8	12.3	10.2/ NH <sub>4</sub> OH
Aeration (N l/min)	38	38	34	32	34	40
Stirring (yes/no)	yes	yes	yes	yes	yes	yes
VVM	1	1	1	1	1	1
G/L	76	154	180	192	190	211
Ammonia removal rate (-k)	0.005	0.010	0.008	0.007	0.007	0.005
Initial aeration depth (- cm)	21	2	1	6	4	4
TS in	-	-	8.24	8.59	10.13	
TS out corr.	-	-	8.75	7.81	8.74	
TS change ( %)			-6 %	9 %	14 %	
VS in	-	-	5.90	5.43	7.22	
VS out corr.	-	-	6.38	4.73	6.19	
VS change ( %)			-8 %	13 %	14 %	
VS/TS in	-	-	0.72	0.63	0.71	
VS/TS out			0.73	0.61	0.71	
VS/TS change			-0.02	0.04	0.01	
FOS in (mg/l)	-	-	13075	6553	16005	
FOS out corr. (mg/l)	-	-	13451	6188	14344	
FOS change ( %)			-3 %	6 %	10 %	
TIC in (mg/l)	-	-	12207	24647	13620	
TIC out corr. (mg/l)			6342	14463	6387	

## APPENDIX 1 (2/5)

Experiment (PM-)	1	2	3	4	5	6
TIC change ( % )			48 %	41 %	53 %	
C/N fraction in			8.5	6.0	7.9	
C/N fraction corr.out			11.8	8.5	12.4	
C in (%)			4.2 %	3.1 %	3.9 %	
C out (%)			3.6 %	2.8 %	3.6 %	
N in (%)			0.49 %	0.52 %	0.50 %	-
N out (%)			0.30 %	0.33 %	0.29 %	-
Removal of total N (%)			38 %	37 %	42 %	

APPENDIX 1 (3/5)

Experiment (PM-)	7	8	9	10	11	12
Feed	Amf. CL	Amf. KP+ NH <sub>4</sub> OH	Amf. CL	Amf. CL with reject	Amf. CL	Amf. CL
Ammonia removal (%)	53 %	44 %	54 %	51 %	71 %	70 %
V in (l)	40	40	40	41	41	41
V out (l)	35	39	37	38	36	37
V feed (l)	39	~ 35	40	40	39	39
Base V/m (ml/g)	273 g CaO	0.411 NH <sub>4</sub> OH	0.42	0.65	0.78	0.69
V added water (l)	1	5	0	1	2	1
Evaporation (V-%)	10 %	2 %	7 %	7 %	11 %	8 %
TAN in (mg/l)	2302	3108	1944	1900	2010	2151
TAN out (mg/l)	1219	1756	958	991	665	704
Antifoam (y/n)	y	n	n	n	n	y
T reactor (C)	77	61	79	70	81	80
Time (min)	240	195	180	180	120	180
Initial pH of feed	6.3	9.7	6.2	7.5	7.7	6.2
pH after adjustment	9.8	10.2	10.0	11.5	10.7	10.0
Final pH	9.0	9.7	9.5	10.9	10.1	9.8
Consumption of base (ml/l or g/l)	6.9 g/l CaO	10.3 ml/l NH <sub>4</sub> OH	10.5	15.9	19.5 ml KOH	17.2 ml KOH
Aeration (N l/min)	40	40	40	41	39	38
Stirring (yes/no)	yes	yes	no	yes	yes	yes
VVM	1	1	1	1	1	1
G/L	242	196	177	178	114	170
Ammonia removal rate (-k)	0.003	0.003	0.004	0.004	0.009	0.006
Initial aeration depth (- cm)	4	4	5	5	5	5
TS in	7.71	7.68	7.36	8.94	6.48	8.43
TS out corr.	7.61	7.63	7.22	8.57	6.00	8.05
TS change ( % )	1 %	1 %	2 %	4 %	7 %	5 %
VS in	5.77	5.47	5.23	5.81	3.88	5.75
VS out corr.	5.61	5.44	5.17	5.57	3.20	5.47
VS change ( % )	3 %	1 %	1 %	4 %	17 %	5 %
VS/TS in	0.75	0.71	0.71	0.65	0.60	0.68
VS/TS out	0.74	0.71	0.72	0.65	0.53	0.68
VS/TS change	0.01	0.00	-0.01	0.00	0.11	0.00
FOS in (mg/l)	12397	10340	11922	9331	5009	13810
FOS out corr. (mg/l)	12324	10517	11422	8914	5268	12511
FOS change ( % )	1 %	-2 %	4 %	4 %	-5 %	9 %
TiC in (mg/l)	8138	12267	9083	16800	17207	10393
TiC out corr. (mg/l)	4745	7136	5553	12251	10659	5261
TiC change ( % )	42 %	42 %	39 %	27 %	38 %	49 %
C/N fraction in	-	-	6.8	7.1		
C/N fraction corr.out			8.7	8.2		
C in (%)			3.1 %	3.2 %		
C out (%)			3.0 %	3.1 %		
N in (%)			0.45 %	0.45 %		
N out (%)			0.34 %	0.37 %		
Removal of total N (%)	-	-	25 %	17 %		

APPENDIX 1 (4/5)

Experiment (PM-)	13	14	15	16	17	18
Feed	Amf. CL with reject	Amf. CL	Amf. CL	Amf. CL	Amf. CL with reject	Amf. CL
Ammonia removal (%)	82 %	80 %	60 %	58 %	63 %	43 %
V in (l)	38	39	38	38	39	39
V out (l)	35	34	37	36	35	37
V feed (l)	38	37	37	37	37	37
Base V/m (ml/g)	0.24	0.42	0.34	0.32	0.28	0.33
V added water (l)	1	1	1	1	3	1
Evaporation (V-%)	8 %	11 %	5 %	7 %	8 %	5 %
TAN in (mg/l)	2405	2118	2447	2059	2792	2288
TAN out (mg/l)	480	485	1023	927	1132	1374
Antifoam (y/n)	y	y	y	y	y	y
T reactor (C)	71	80	80	73	81	67
Time (min)	270	180	180	180	240	180
Initial pH of feed	8.9	7.0	6.2	8.2	8.1	6.8
pH after adjustment	10.0	10.5	9.8	10.0	9.5 / 9.6	9.8
Final pH	9.7	9.9	9.2	9.8	9.4	9.6
Consumption of base (ml/l or g/l)	6.3	10.5	8.5	8.5	5 ml/l + 2.5 ml/l	8.5
Aeration (N l/min)	40	39	39	40	39	40
Stirring (yes/no)	yes	yes	yes	yes	yes	yes
VVM	1	1	1	1	1	1
G/L	282	182	183	187	243	186
Ammonia removal rate (-k)	0.007	0.008	0.005	0.005	0.003 / 0.005	0.003
Initial aeration depth (- cm)	3	3	3	3	3	3
TS in	8.21	8.49	7.72	6.31	8.37	7.95
TS out corr.	8.08	7.49	7.96	6.86	7.98	8.02
TS change ( %)	2 %	12 %	-3 %	-9 %	5 %	-1 %
VS in	5.86	6.27	5.80	4.34	6.44	6.06
VS out corr.	5.66	5.45	5.97	4.93	5.56	6.14
VS change ( %)	3 %	13 %	-3 %	-14 %	14 %	-1 %
VS/TS in	0.71	0.74	0.75	0.69	0.77	0.76
VS/TS out	0.70	0.73	0.75	0.72	0.70	0.77
VS/TS change	0.02	0.02	0.00	-0.04	0.09	0.00
FOS in (mg/l)	9503	10088	9247	5884	14898	10349
FOS out corr. (mg/l)	9244	10132	10240	5312	14288	10507
FOS change ( %)	3 %	0 %	-11 %	10 %	4 %	-2 %
TIC in (mg/l)	12283	11223	8580	13102	-	8952
TIC out corr. (mg/l)	6801	5458	4617	8809	-	5586
TIC change ( %)	45 %	51 %	46 %	33 %	-	38 %
C/N fraction in	7.0	7.7	7.3	6.0	6.8	7.7
C/N fraction corr.out	9.0	10.2	9.6	8.4	7.7	9.7
C in (%)	3.4 %	3.2 %	3.3 %	2.5 %	3.7 %	3.4 %
C out (%)	3.3 %	3.0 %	3.2 %	2.7 %	3.2 %	3.5 %
N in (%)	0.49 %	0.41 %	0.45 %	0.41 %	0.54 %	0.43 %
N out (%)	0.37 %	0.30 %	0.33 %	0.33 %	0.41 %	0.36 %
Removal of total N (%)	25 %	28 %	26 %	21 %	23 %	18 %

APPENDIX 1 (5/5)

Experiment (PM-)	19	20	21	22	23
Feed	Amf. CL	Amf. CL	Amf. CL with reject	Amf. CL	Amf. CL
Ammonia removal (%)	67 %	56 %	70 %	54 %	78 %
V in (l)	39	39	39	40	61
V out (l)	37	38	35	38	55
V feed (l)	38	38	38	38	60
Base V/m (ml/g)	0.41	0.40	0.19	0.49	0.63
V added water (l)	1	1	1	1	2
Evaporation (V-%)	7 %	4 %	10 %	5 %	9 %
TAN in (mg/l)	2339	2195	2299	2030	2572
TAN out (mg/l)	820	996	763	984	606
Antifoam (y/n)	y	y	y	y	y
T reactor (C)	74	68	80	69	81
Time (min)	180	180	240	180	180
Initial pH of feed	7.4	6.2	8.2	6.3	6.6
pH after adjustment	10.3	10.2	9.8	10.6	10.5
Final pH	10.0	9.8	9.6	10.1	9.8
Consumption of base (ml/l or g/l)	10.5	10.5	5.0	12.5	10.5
Aeration (N l/min)	40	41	38	39	60
stirring (yes/no)	yes	yes	yes	yes	no
VVM	1	1	1	1	1
G/L	182	187	236	179	179
Ammonia removal rate (-k)	0.006	0.004	0.006	0.004	0.008
Initial aeration depth (- cm)	4	3	3	4	22
TS in	7.51	7.47	8.24	8.00	7.41
TS out corr.	7.19	7.16	7.98	7.66	7.05
TS change ( %)	4 %	4 %	3 %	4 %	5 %
VS in	5.37	5.19	5.79	5.64	5.26
VS out corr.	5.11	4.86	5.57	5.35	4.98
VS change ( %)	5 %	6 %	4 %	5 %	5 %
VS/TS in	0.71	0.70	0.70	0.70	0.71
VS/TS out	0.71	0.68	0.70	0.70	0.71
VS/TS change	0.01	0.02	0.01	0.01	0.01
FOS in (mg/l)	9412	12207	8918	11704	12338
FOS out corr. (mg/l)	9782	12333	9997	13049	11334
FOS change ( %)	-4 %	-1 %	-12 %	-11 %	8 %
TiC in (mg/l)	11978	9383	11605	11057	10310
TiC out corr. (mg/l)	6982	5745	5647	6226	4768
TiC change ( %)	42 %	39 %	51 %	44 %	54 %
C/N fraction in	7.5	6.9	6.4	7.2	6.9
C/N fraction corr.out	9.3	8.3	8.2	8.9	9.7
C in (%)	3.1 %	3.0 %	3.4 %	3.2 %	3.0 %
C out (%)	2.8 %	2.9 %	3.2 %	3.1 %	2.9 %
N in (%)	0.41 %	0.43 %	0.53 %	0.44 %	0.43 %
N out (%)	0.30 %	0.36 %	0.39 %	0.35 %	0.30 %
Removal of total N (%)	26 %	16 %	27 %	20 %	31 %