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POTENTIAL ITILIZATION WAYS OF RECOVERED CHEMICAL PRODUCTS FROM DIGESTATE

Examiners: Professor Lassi Linnanen

Professor Mika Sillanpaa

Abstract

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Potential utilization ways of recovered chemical products from digestate

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The study evaluates the potential application of chemical substances, obtained from biogas plants` by-products. Through the anaerobic digestion process with biogas the large amount of digestate is produced. This digestate mainly consists on the organic matter with the high concentration of nutrients such as nitrogen and phosphorus. During ammonia stripping and phosphorus precipitation the products- ammonia water, ammonium sulfate, ammonium nitrate, ferrous phosphate, aluminum phosphate, calcium phosphate and struvite can be recovered. These chemicals have potential application in different industrial sectors. According to Finnish market and chemicals properties, the most perspective industrial applications were determined.

Based on the data, obtained through the literature review and market study, the ammonia water was recognized as a most perspective recovered substances. According to interview provided among Finnish companies, ammonia water is used for flue gas treatment in SNCR technology. This application has a large scale in the framework of Finnish industrial sectors. As well nitrogen with phosphorous can be used as a source of nutrients in the biological wastewater treatment plants of paper mills.

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This research was for me totally new field for studying. But in the process of research I got true enjoy and invaluable experience. Only with the help of my colleagues I obtained result which, I believe, will bring real benefit.

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As well I would like to thank my native university- Saint-Petersburg Mining University (now it is National Mineral Resources University). Only with assistance with my native university I got a chance to study in Lappeenranta University of Technology.

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List of symbols and abbreviations

AD	Anaerobic digestion
AOX	Adsorbable organic halogen
$CaHPO_4 \cdot 2H_2O$	Brushite, dicalcium phosphate dihydrate
$CaHPO_4 \cdot 2H_2O$	Monetite
$Ca_4H(PO_4)_3 \cdot 2.5H_2O$	Octacalcium
$Ca_3(PO_4)_2$	Amorphous calcium phosphate
$Ca_5H(PO_4)_3O$	Hydroxyapatite
$Ca_3H(PO_4)_2$	Tricalcium Phosphate (TCP)
DEHP	Di(2-ethylhexyl) phthalate
H_2	Hydrogen
LAS	Alkyl benzene sulfonate
MAP	Struvite
NH_4-N	Ammonium nitrogen
$NH_4\ MgPO_4 \cdot 6(H2O)$	Struvite
NP	Nonylphenol
P	Phosphorus
PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenyl
PCDD	Polychlorinated dibenzodioxins
PBDE	Polybrominated Diphenyl Ethers
P_{tot}	Phosphorus total
SCR	SCR - Selective catalic reduction
SNCR	SNCR - Selective non-catalic reduction
TKN	Total Kjeldahl nitrogen
TS	Total solids
VFA	Volatile fatty acids
VS	Volatile solids
VSS	Volatile suspended solids
Ww	Wet weight

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1. Introduction

The constant growth of human population and industrial activity undoubtedly leave the footprint on the environment situation all over the world. Scientific progress leads to provide life for more than seven billions of people, but at the same time the environment suffers from new technologies. Due to this fact, the humanity awareness of environmental situation is reaching a big scale. During the last few decades several theories and assessment of the current and future environment issues were put forward by different scientists.

Primarily works such as “The Limits to Growth” (Meadows & Randers, 1972) and “Tragedy of common” (Hardin, 1968) were the first impulse to understanding that the current pace of human development and in particular industrial activity lead to the deterioration of natural ecological environment. As consequences, the further existence of humanity may be jeopardized.

In 2009 Stockholm Resilience Centre in report examined the non-negotiable planetary conditions that humanity needs to respect and maintain in order to avoid catastrophic environmental changes. Scientists from around the world determined a “safe planetary operating space” described by nine planetary boundaries within which humanity must remain in order to continue to thrive and develop (Rockström, et al., 2009). Two of these planetary boundaries are nitrogen and phosphorus cycles. According to Rockström J., nitrogen cycle bondaries have been crossed, and currently humanity has approached close to phosphorus cycle boudaries.

Human activities convert around 120 million tons of naturally occurring nitrogen from the atmosphere into reactive nitrogen. Reactive nitrogen is a term used for a variety of nitrogen gases that are highly reactive, such as nitrogen oxides (NO_x), ammonia (NH_3), nitrous oxide (N_2O), nitrate (NO^{3-}), urea and organic-nitrogen compounds (Iovine, Pursnani, Voldman, Wasserman, Blaser, & Weinrauch, 2008). The nitrogen is main ingredient in synthetic fertilizers, which are produced with Haber-Bosch process. Haber-Bosch process is used to help feed the world. Synthetic fertilizer production, leguminous crops (soybeans, peanuts, alfalfa), different types of manufacturing, burning of fossil fuels and vehicles produce reactive nitrogen. The planetary boundary for the nitrogen cycle is measured in millions of tons per year removed from the atmosphere;

the background level is 0, the acceptable boundary is set at 35, and we are already at 121. (Cho, 2011; Rockström, 2009)

Phosphorus is a mineral that is mined for utilization in fertilizers, detergents, pesticides, steel production. It is measured in millions of tons of phosphorus containing compounds entering the ocean per year. The background level is -1, the sustainable boundary is 11, and currently the value is 8.5 to 9.5 million tones. According to different literature sources, the excess amount of phosphorus depletes oxygen level and harming marine life. (Cho, 2011)

Obviously, there are several problems on the way to sustainable development in this field. The first is the extraction of natural non-recoverable resources to meet human needs (e.g. extraction of limited phosphorus ore for the fertilizers production and natural gas using for Haber-Bosch process) and secondly, it is a pollution of environment by excessive nutrients (pollution of groundwater and surface water, soil, air).

One of the scientific communities, which has started to understand risks involved in the current nutrient situation and has looked for the ways to solve these problems is NUTs (Transition towards Sustainable Nutrient Economy) project. (NUTs:A nuts to crack, 2012) NUTS project was established in Finland three years ago to define the nutrient footprint for the production of food, energy, commodities and services. This project presents the co-operation between the scientific commodity with the stakeholders like farmers, producers, retailers, consumers, and decision-makers, for successful nutrient management.

Precisely in the framework of NUTs project was created research “Utilization of recovered chemical products from digesate” for biogas companies. Curently, Finland has several waste management companies, which utilizes organic waste through anaerobic digestion. Besides the biogas plants produce the fertilizers, which are sold to farmers.

As a result of anaerobic digestion, the digestate is produced in addition to the biogas. Digestate has high concentration of nutrients such as nitrogen and phosphorus. The chemical products produced from these nutrients can have potential application in different industrial fields.

1.1 Research objective

This study considers the anaerobic digestion process, which is used as a part of waste management system, with the goal of waste utilization and biogas obtaining. The research leads to show the digestion process with special consideration of by-product or co-called digestate formation. The by- product´s characteristics and properties should be evaluated with the further decision making of their utilization possibilities. The digestate form, amount and composition have significant influence on the chemicals production.

The main objectives of this work are to define the potential chemical products, which can be recovered from the digestate and determine the industrial application possibilities of these substances in Finnish market.

A number of methods have been developed to recover nutrients from the sludge. Most implemented in big scale are the crystallization or precipitation of phosphorus as calcium phosphate, aluminum phosphate, ferrous phosphate or struvite (Parsons, Wall, Doyle, Oldring, & Churchley, 2001) and ammonia stripping for nitrogen recovery (Evans, 2009). Final products of ammonia stripping process depend on which substances are used for absorption. Sulfuric or nitric acid can be used, resulting in ammonium sulfate or ammonium nitrate production. This study has to define all products that can be recovered, despite of the further utilization possibilities of these chemical. The most promising and not really perspective recovered substances as well should be identified on the way to effective digestate utilization.

Potentially, these chemical products can be applied in different industrial sectors. Chemical, textile, metallurgical, wood industries and it is not full list of potential customers of chemical substances which can be got from digestate. Through the market study the certain application of chemical products should be defined. The survey of companied, which belongs to different industrial sectors, will allow to create the common understanding of recovered products´ utilization possibilities. This market study allows identifying a niche for recovered chemicals utilization.

During the chemical products utilization, the Finish industries´ requirements such as purity, form and concentration of products should be observed. Due to industrial requirements the chemicals properties can be changes. For instance, the concentration (more or less concentrated ammonia water) and form (liquid or precipitated crystals of ammonium sulfate) can be regulated with using additional technologies.

The final objective of research is recommendation formulation towards to further digestate processing technology. These recommendations should leave open space for biogas plants to build their own scenario with chemicals recovery utilization being based on the results obtained from study.

1.2 Research boundaries

The research boundaries were set within the goal to define main directions of work conducting. Fig.1 shows the place of research boundaries in the digestate processing chain. The study deals with the liquid fraction of digestate which obtained from mechanical separation of digestate. The given study considers centrifuge as mechanical separation equipment.

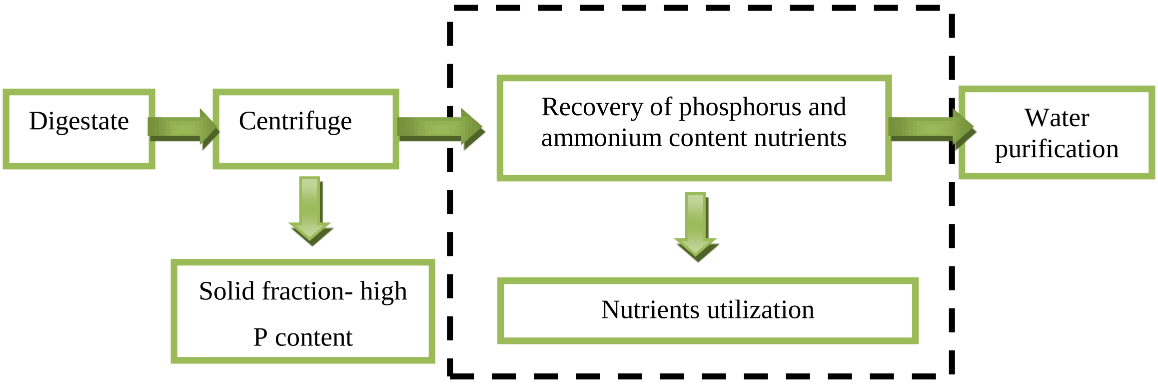

Figure 1. Research boundaries in digestate processing chain

The separated liquid fraction mainly contents elements such as nitrogen and phosphorus. The detailed description of nutrients recovery technologies is not included in this work. However the most commonly adapted technologies are briefly introduced with the goal to determine possible forms of recovered chemical products (Fig.2). Nitrogen can be recovered from digestate by the stripping with the further processes of condensate collection or ammonia absorption by acid. As a result, the products such as ammonia water, ammonium sulfate or nitrate can be obtained. Phosphorous can be removed by precipitation with the magnesium, calcium, aluminum or iron. In this case the products such as calcium phosphate, struvite, aluminum phosphate and iron phoshate can be produced.

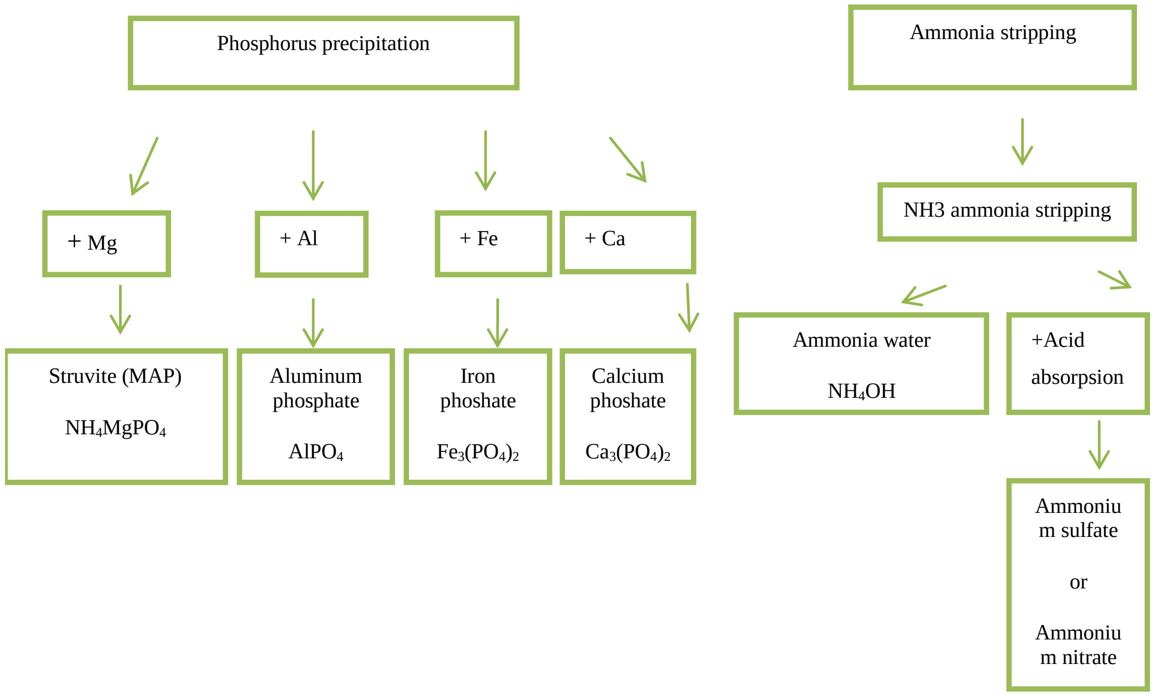

Figure 2. Chemicals recovery technologies and potential products

Thus, the main boundaries relatively the digestate processing, chemical products, recovery methods and chemicals form were set. In this framework, the study considers only liquid fraction of digestate. Chemicals– struvite, calcium phosphate, aluminum phosphate, iron phosphate, ammonia water, ammonium sulfate, ammonium nitrate are main recovered products.

The main objective of research is to determine industrial sectors where recovered chemical products can find application. Noticeably, industries such as food, beverage and pharmaceutical don´t include in work boundaries because of hygiene considerations. These industries consume only high purity chemical products.

Chemicals use in the agriculture sector has been widely studied by different researches. Large amount of data deal with this topic is available, in this case additional study conducting doesn´t need. Thus, the agriculture industry is out of study boundaries

1.3 Research methodology

Research methodology is a way to solve research problem systematically. Research methodology allows understand the path of study development. Generally, research methodology answers for questions as- how the research problem has been determined, in what way and why the hypothesis has been formulated, why particular technique of data analyzing has been used (Kumar, 2008).

To achieve the objectives of study the literature review and market study as research methodologies were applied. These methodologies logically supplement each other. The results obtained in literature review are a basis for market study conducting.

The literature review includes several steps. Firstly, the research questions or study objectives were selected. Making start from these selected objectives the suitable databases and web-resources were defined. The research data, obtained from different biogas companies, formed a basis for literature review. These data content information about biogas plants technologies and real digestate chemical analysis results. Through the databases analysis the descriptive review was produced (Kumar, 2008). In general literature review was carried out with the goal to ensure clear understanding of anaerobic digestion process. Process stages, conditions, requirements were clarified through the literature review. As a result, this methodology allows defining the forms of main recovered products and their potential application.

The second methodology was applied for research conducting is a market study. As a literature review, the market study consists on the several steps. The scheme of providing market study was accepted based on “Marketing management” by Kotler P. and Keller K.. The first steps of market study were the methodology objectives defining and research plan development. The practical part of methodology represents cooperation with industrial companies through interview conducting (Kotler & Keller, 2012). The essential goal of market research was to define industrial sectors and numbers of specific Finnish companies, which could utilize chemical products, obtained in the process of nutrients recovery from digestate. Furthermore, the market requirements toward chemicals properties should be identified.

2. Literature research (review)

Literature review was provided with the goal to describe anaerobic digestion process and to define what kind of chemical products can be recovered from process´s waste. Moreover, the chapter considers the potential chemicals application in different industries. The presented information is a starting point for further market study conducting and conclusion making.

2.1 Anaerobic digestion technology

This chapter describes the process of anaerobic digestion (AD) - its stages, parameters, raw material and residue. The technologies of some biogas plants are considered here as well. Because of keeping confidentiality, the biogas plants have names plant 1 and plant 2 in the study context.

2.1.1 AD process

Anaerobic digestion (AD) aims to utilize organic wastes sludge in oxygen absent conditions producing biogas. AD process uses naturally occurring microorganisms to destroy organic raw material and produce biogas. (National Non-Food Crops Centre, 2011). The main feedstock for AD can include the organic fractions of industrial wastes and by-products, sewage sludge, municipal solid waste and other organic materials such as animal manures, agricultural crops, agricultural processing residues, organic fraction of household waste.

The feedstock for anaerobic digestion process can be as a single input (e.g. animal manure) or as a mixture of two or more feedstock types (co-digestion). Most biogas plants use more than one substrate. When the dry matter content of inputs is below 15% the AD process is called „wet" digestion (or „wet" fermentation) and when feedstock is above this level it is „dry" digestion (Lukenhurst;Frost;& Seadi, 2010).

To reach high efficiency of anaerobic digestion process, it is important to create and support certain conditions inside digestion tank. The temperature is one of such sensitive parameters. AD with temperature 30-38 ^{O}C is called mesophilic, and with temperature 50- 57 ^{O}C- termophilic. Thermophilic digestion is four times more intense, has higher volatile suspended solids (VSS) removal efficiency and yields more biogas, than mesophilic. The only disadvantage of thermophilic type is that more energy is used for heating fermenters (Vindisa, Mursec, Janzekovi, & Cus, 2009).

As well parameters such as pH, alkalinity and retention time is essential. The average values of these parameters are introduced in the Table 1.

Table 1. Value of anaerobic digestion parameters (Vindisa, Mursec, Janzekovi, & Cus, 2009)

Parameter	Value (unit)
pH	7,0 - 7,2 (can be 6,2 - 8,0)
Total alkalinity	2000 to 5000 mg/l

The digestion tank has cylindrical or egg- shape form. Both of these design types have their own benefits and drawbacks. For instance, the cylindrical tank has low construction cost and possibility for large volume gas storage. But as a disadvantage, this tank form has died zones in the mixing process and high degree of foam formation. In its turn, egg- shape form allows to enhance mixing efficiency and to eliminate the need for cleaning. But it has quite expensive construction cost (Wes tech Engineering, 2005).

During AD process the organic matter undergoes different changes thereby forming methane (CH_4). Carbon dioxide, ammonia and hydrogen sulfide are produced with methane as well. The table 2 shows the proportion of the gases, which produced in the AD process. Majority of these gases is made up by methane (about 55-57 %). As well there is quite significant part of carbon dioxide (25- 57 %). Hydrogen sulfide and moisture form in minor amounts. The biogas can be combusted to produce electricity or further processed into compressed gas fuel.

Table 2. Biogas composition (Zhao, Leonhardt, MacConnell, Frear, & Chen, 2010)

Component	Percent (dry volume basis)
Methane CH4	55 – 75
Carbon dioxide CO2	25 – 45
Hydrogen sulfide H2S	< 1
Moisture H2O	4 – 7

Biogas plant #1 has mesophilic and wet co-digestion process of manure and industrial sludge in cylindrical tank. This plant co-digests annually approximately 50 000 t of pig slurry and 50 000 t of industrial byproducts e.g. from food and biotechnology industries. At the beginning of digestion process, all raw materials are sent to the tank (100 m3) and pumped into a larger pre-storage tank (900 m3) for load equalization. The mixed feed is hygienised in three parallel batches (30 m3 each; 1 hour, 70 °C) before the biogas reactor (6700 m3). Reactor of plant 1 has a temperature about 38 °C and hydraulic retention time - 25 days. The digestate is then pumped into a covered post-methanisation tank (1200 m3). All tanks are closed with separate off-gas treatment system. The produced biogas is collected into the gas storage and utilized by two CHP-units with a total energy output of 4 MW. The heat and electricity produced is used for own biogas plant purposes and the excess electricity is sold to the grid (Paavola, Ervasti, Luostarinen, & Kapuinen, 2011).

Biogas plant # 2 provides termophilic and wet co-digestion of 120 000 ton manure and industrial sludge annually. In this plant retention time makes up 16- 20 days that less than in plant #1 (Paavola, Ervasti, Luostarinen, & Kapuinen, 2011).

2.1.2 AD residue

In the process of AD together with biogas the large amount of digestate is produced. Digestate consists on the non-biodegradable matter such a lignin, with high nutrients and water content (Fig.3). Mainly, nutrients are presented by nitrogen (N) and phosphorus (P).

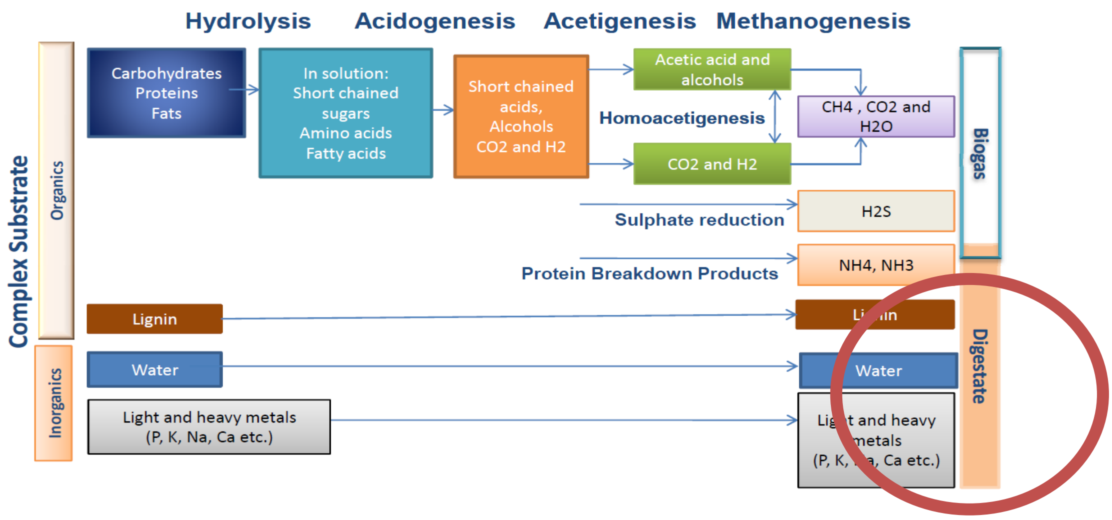

Figure 3. AD process and digestate content (Esteves, 2011)

The operation of the Plant #1 started in 2004 with the feed consisting mainly of pig slurry. However through the years, the amount of industrial by-products has been increased to more than 50% of feed. Currently, the feed of the plant consists from ten different sources at least and the proportions of these may vary few during the year. According to Paavola T., during 2009-2010, the feed in the equalisation tank was on average the following: TS 10.6%, VS 5.5%, TKN 7.4 g/l and NH4-N 4.2 g/l (Fig.4). The chemical composition of digestate can vary according to raw material and conditions in the tank.

Table 3. Main characteristics of the feed and digestate (Paavola;Ervasti;Luostarinen;& Kapuinen, 2011)

Parameter	Feed Equalisation tank	After hygienisation	Digestate
TS (%)	10.6	10.6	8.9
VS (%)	5.5	5.5	3.3
TKN (g/l)	7.4	7.4	7.6
NH4-N (g/l)	4.2	4.2	5.8

For the further nutrients recovery and utilization, it is necessary to separate solid and liquid fraction of digestate. The technologies such as gravity or mechanical separation can be used for this stage. The digestate presents a low dry material, usually solid fraction makes up about 20% of digestate wet weight (ww). The solid fraction contains most of the phosphorous.

The liquid fraction (80% of ww) contains most of the ammonium and it can be further subjected to nitrogen recovery through filtration and ammonia stripping. In practice, after increasing the temperature, ammonia is absorbed with a vacuum and condensed as ammonium water, which includes 51% of initial nitrogen. According to Paavola T. -

> “The surplus liquid from stripping is directed to evaporation process in which the pH is firstly decreased to approximatly. 5.2 by sulphuric acid to retain the remaining ammonia and then fed to the evaporator”. During the evaporation with a vacuum, the TS content of the liquid is increased from 2-3% to 15-17%. Thus, the evaporation residue concentrates the remaining nutrients (so-called NP-concentrate). As a last stage, the evaporated

condensate goes through ion exchange to wastewater treatment plant (30-50 mgN/l remaining).” (Paavola;Ervasti;Luostarinen;& Kapuinen, 2011)

Important that digesate may content potential toxic elements (PTEs) such as heavy metals. For instance, zinc and copper additives are used for pig feeds. This fact can be reason for relatively high concentration of these metals in pig slurry (WRAP, 2011). In this case the preliminary chemical analysis should be conducted before digestate utilization.

2.1.3 Mass balance of nitrogen and phosphorous in digestate processing

The possibility for nutrient recovery is presented by figure 4. As a result of the digestate processing, incoming nutrients are concentrated into several different products. After mechanical separation with centrifuge, more than 60 % of phosphorus recovered with solid fraction and the rest (34%) goes into the NP-concentrate. Over 50% of the initial nitrogen is recovered as ammonium water. Simultaneously, more than half of the initial material volume is directed to a wastewater treatment plant as a very dilute reject water (Paavola;Ervasti;Luostarinen;& Kapuinen, 2011).

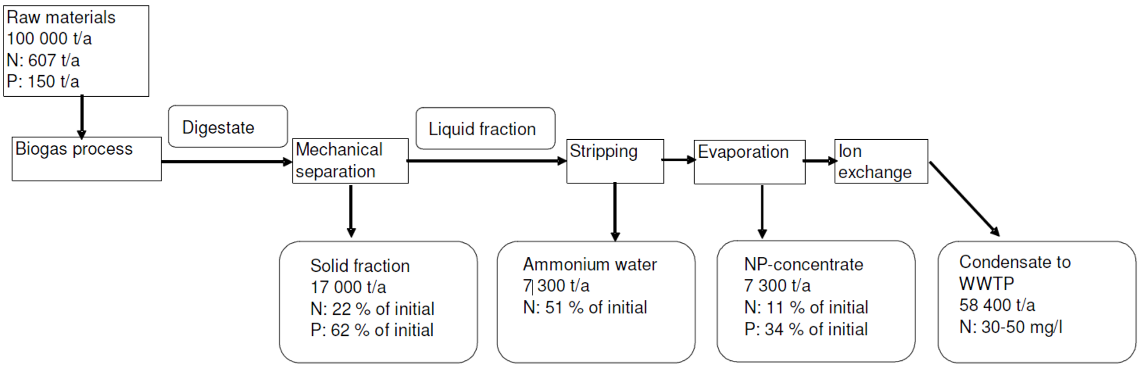

Figure 4. The mass and flow of N and P nutrients during digestate processing (Paavola, Ervasti, Luostarinen, & Kapuinen, 2011)

On the Fig. 5 the combined scheme of nitrogen and phosphorus is presented. (Jiang, Frear, Zhang, & Chen, 2008) Differ from digestate processing scheme proposed by Paavola, Jiang included phosphorous precipitation with lime (CaOH) and ammonium absorption with sulfuric acid. As a result, chemicals such as calcium phosphate and ammonium sulfate are produced during implementation of this scheme. Author mainly oriented these products for using as the fertilizers, but the purpose can be changed according to industrial requirements.

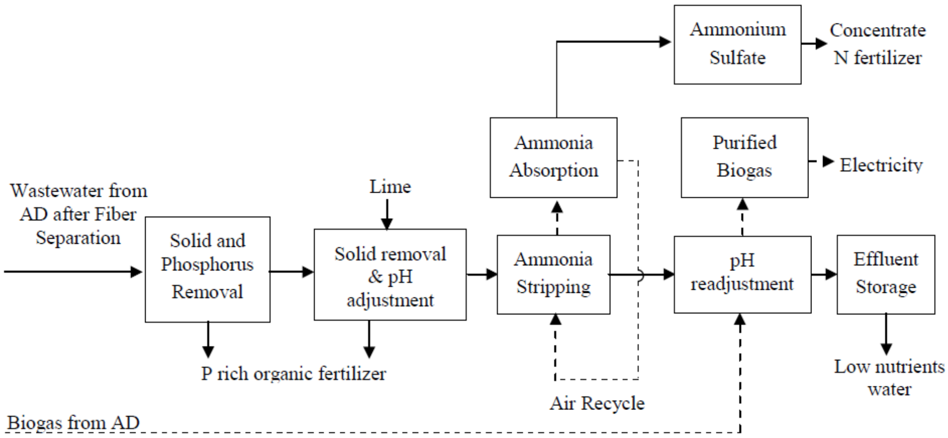

Figure 5. Schematic flowchart of digestate processing (Jiang;Frear;Zhang;& Chen, 2008)

In the process of phosphours precipitation the replacement of lime by magnium leads to struvite formation instead of calcium phoshate (Evans, 2009). Struvite presents a substance, which consists both ammonium and phoshate, and has main application as a fertilizer. As well, aluminum or ferrous substances can be used for phosphorous precipitation. In this case the aluminum phosphate and iron phosphate are formed.

According to literature review, apart from sulfuric acid as well nutric or some organic acids can be used for ammonium absorption. Hovewer, evaluating the acid price and chemical products importance, the only sulfuric and nutric acids are included in study (Frear, 2012).

Summarizing all technologies which can be used for nutrients recovery, the next potential chemicals are produced- calcium phoshate, struvite, aluminum phosphate, iron phosphate, ammonia water, ammonium sulfate, ammonium nitrate.

2.2 Recovery technology

In this chapter different nutrient recovery technology is presented. A significant number of methods have existed for nitrogen and phosphorus recovery from sludge liquor. Mainly the choice of certain technologies bases on the desired chemical product type.

2.2.1 Nitrogen -recovery technology

There are several successful and widely used methods for nitrogen recovery from sludge. Biological treatment and conventional nitrification (denitrification) technology (Fux, Huber, Brunner, & Siegrist, 2002) allow to quite efficiently reduce the nitrogen concentration in the sludge, but only in the process of ammonia stripping the nitrogen can be caught as valuable chemical product- ammonium.

Ammonia stripping

Ammonia stripping presents a desorption process which used for the ammonia content decreasing in wastewater sludge. Usually wastewaters contain significant amounts of ammonia and nitrogen compounds that can form ammonia. It is simpler and less expensive to remove nitrogen in the form of ammonia than to convert it to nitrate-nitrogen (Culp, Wesner, & Culp, 1978).

According to Paavola T., the liquid fraction of digestate, which makes up approximately 80 % of the waste weight, contains most of the ammonium and it can be further subjected to nitrogen recovery through filtration and subsequent ammonia stripping (75 °C, pH 8). In this case the ammonia water with concentration of 51 % initial nitrogen is absorbed with a vacuum technology (Paavola, Ervasti, Luostarinen, & Kapuinen, 2011).

As well air-stripped ammonia can be captured in acid scrubbing tower. This technology is applied in the wastewater treatment plant in Oslo, Norway. The alkaline filtrate (1200-1500 mgN/litre) is pumped (via an in-line filter cartridge to remove large sludge solids) to the top of a stripping tower that is packed with plastic media. It is sprayed down the tower against an air flow, which is then blown up a second packed tower against a rain of acid (Figure 5) (Evans, 2009). Sulfuric and nitric acid can be used for ammonia absorption.

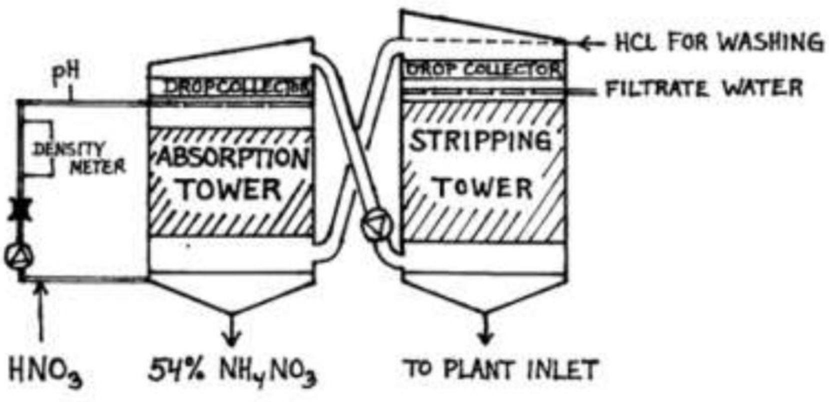

Figure 6. Ammonia absorption by nitric acid (Evans, 2009)

The most common method for ammonium nitrate formation is injection of gaseous ammonia into 40-60% nitric acid at 150 ^{o}C according to reaction 1 (Akhavan, 2004) The similar technology is used for ammonium sulfate producing; only the sulfuric acid is used instead of nitric.

$$NH_3 + HNO_3 \rightarrow NH_4NO_3 \qquad (1)$$

For solid ammonium sulfate and ammonium nitrate the evaporation and granulation processes are required. Evaporation allows reduce the water amount in solution to 1-8%, for the further granules production (Kent & Riengel, 2007).

2.2.2 Phosphorus-recovery technology

Phosphorus is one more component which high concentrated in digestate. Mainly phosphorus is contened in solid fraction of slurry. Because of the research boundaries, the only liquid fraction which contains Phosphorus Total (P tot) = 1 g/kg and Soluble P = 0,53 (g/kg) (Paavola;Ervasti;Luostarinen;& Kapuinen, 2011) is entered in research consideration.

The main technology of phosphorus recovery from digestate liquor is precipitation. Liquid aluminum, iron compounds, lime and magnesium are the most common coagulants for phosphorus settle out (Young, 2003).

MAP-struvite precipitation

One of the technologies can be applied for nutrient recovery is struvite (MAP) precipitation. Struvite ($(NH_4MgPO_4 \cdot 6(H_2O))$) is an ammonium magnesium phosphate mineral. The chemical precipitation of magnesium-ammonium-phosphate (MAP) or struvite is effective for both- nitrogen and phosphorus removal from digestate water. Struvite precipitation is more efficient with increasing pH. Struvite precipitation is going in the presence of Mg^{2+}, NH_4^+ (N) and PO_4^{3-} (P) ions according to following reaction (Eq.2):

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O \qquad (2)$$

According to different scientific researches, the appropriate pH for phosphorus recovery is 8 – 9 (Çelen, 2001). Maximum total phosphorus recovery was occurred at the pH= 8.8 and magnesium concentration 120 ppm that made up 26,5 % (Table 4).

Table 4. Removal efficiency of phosphorus in different conditions (Sheffield, 2005)

pH	Mg (ppm)	% PO_4 removed	% total P removed
8.4	60	69.8	18.5
8.8	60	81.4	14.7
8.4	120	46.0	18.3
8.8	120	64.6	26.5

Calcium phosphate (HAP) crystallization

The phosphorus can be recovered through the calcium phosphate (HAP) crystallization. Calcium is typically added to the water as calcium hydroxide $Ca(OH)_2$. The amount of calcium needed to precipitate phosphorus is dependent on the total alkalinity, because calcium reacts first with bicarbonates in water, forming calcium carbonate. According to Vesilind P.:

> "Only above pH 10, the excess calcium reacts with phosphorus with precipitating of hydroxyapatite (HAP). The molar ratio Ca: PO_4 may vary between 1.3 and 2.0 because of the changes in the composition of the precipitated HAP. This is because the final product- calcium phosphate can precipitate in different forms. The flocks contain calcium carbonate formed in calcium reaction with bicarbonates. $CaCO_3$ is dense, and enhances the settling of the flock. Low alkalinity in wastewater results in small amount of calcium carbonate, thus decreasing the settleability of the flock. If alkalinity is high, excellent rates of phosphorus removal can be achieved in pH 9.5 to 10". (Vesilind, 1998)

Due to literature review, the removal efficiency of SP at the low calcium dosage (1.3 g/L) is about 39% SP in one hour, and at the high calcium dosage (6.6 g/L) – 78 % SP in one hour (Young, 2003).

The difference between MAP (struvite) and HAP (hydroxyapatite) precipitation technologies is the value of calcium ion (Ca^{2+}) concentration for HAP crystallization and magnesium (Mg^{2+}) and ammonium (NH_4^+) concentrations for struvite crystallization. Noticeably, the products are removed in precipitation form have tendency to clog the equipment and may cause temporal breakdown of the systems.

Aluminium phosphate

Aluminum- content coagulants are wide used for phosphorus precipitation from sludge streams. These coagulants can be presented by aluminum chloride, aluminum sulfate and liquid sodium aluminate (LSA, 38 % solids) (Usalco, Alumina chemical solution, 2011). However, during the process together with precipitated aluminum phosphate the hydrous aluminum floc particles are formed (Eq.3 and Eq.4). The formation of aluminum hydroxide floc makes aluminum ineffective material for phosphate precipitation. In this case the additional mixing is required.

$$Al^{3+} + PO_4^{3-} \rightarrow Al(PO_4) \quad (3)$$

$$Al^{3+} + 3(OH^-) \rightarrow Al(OH)_3 \quad (4)$$

Iron phosphate

Both ferrous Fe(II) and ferrous Fe(III) ions can be used as iron salts for phosphorus precipitation from wastewater. The precipitation process bases on the following reactions (Eq.5 and Eq.6):

$$3FeCl_2 + 2PO_4^{3-} \rightarrow Fe_3(PO_4)_2 \downarrow + 6Cl^- \quad (5)$$

$$3FeSO_4 + 2PO_4^{3-} \rightarrow Fe_3(PO_4)_2 \downarrow + 3SO_4^{3-} \quad (6)$$

2.3 Product characteristics

On the result of nutrient`s recovery technologies evaluation the next list of possible chemical products is created (Fig. 7). This list includes ammonia water, anhydrous ammonia, ammonium sulfate, ammonium nitrate, struvite, aluminum phosphate, iron phosphate and calcium phosphate.

NH4OH Ammonia water
Anhydrous ammonia
(NH4)2SO2Ammonium sulfate
NH4NO3Ammonium nitrate
Ca3(PO4)2 Calcium phosphate
Aluminum phosphate
Iron phosphate
Struvite

Figure 7. Potential chemical products obtained from digestate.

The chapter 2.3 considers chemical products` characteristics and quality. However, worth take into account that laboratory researches and pilot trials should be provided before chemical products introduction in industry. Only additional chemical studies can give the accurate information and guarantees of successful product application.

2.3.1 Ammonia water

Ammonia water (aqueous or aqua ammonia, ammonium hydroxide), NH_4OH is presented by ammonia gas dissolved in water. Ammonia water recovered from considered biogas digestate has quite low concentration approximately 5 %. The concentration of the studied organic harmful substances (PAH, PCB, PBDE, NP and NPE, LAS, DEHP, AOX, PCDD/F, pharmaceuticals and hormones) in ammonia water is very low - under detection limit (Biovirta-project, 2010). As well, next assumption was made, that ammonia water is quite pure because the stripping process doesn´t allow metals and other impurities to pass. However, if ammonium hydroxide will be used in sensitive industrial processes, the purity test must be conducted in co-operation with end-user. The reaction of dissolving ammonia in water is presented by reaction.7.

$$NH_3 + H_2O \rightarrow NH_4OH \qquad (7)$$

The reaction 7 is reversible and ammonia gas could release. According to this, the ammonia water can be used as a source of ammonia gas in some industries.

2.3.2 Anhydrous ammonia

Chevron company proposes the scheme for ammonia recovery (Fig. 8). The ammonia vapour from the stripping process can be handled in a range of ways. One of them is anhydrous ammonia. Anhydrous ammonia is high concentrated ammonia solution (more than 99% NH_3). Anhydrous ammonia is a main raw material for ammonia derivatives producing. Noticeably that compressor and cooler presence are essential for this chemical production (Chervon company, 2013).

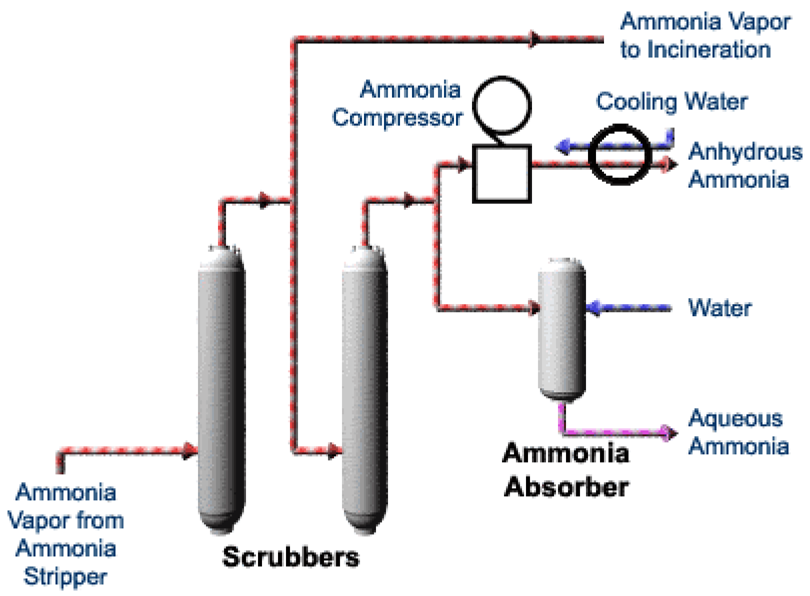

Figure 8. Ammonia recovery options (Chervon company, 2013)

2.3.3 Ammonium sulfate and ammonium nitrate

Ammonium sulfate and ammonium nitrate can be produced in liquid and solid (crystal) forms. Liquid ammonium sulfate contents more than 50 % water. The concentration of typical ammonium nitrate solution is about 75-85 % at 40-75 ^oC. For solid form of ammonium nitrate production, the solution must be concentrated in low water content (about 1-2%) and then fed to prilling of granulation equipment. As a result the solid products have size 2-4 mm (Roy, 2010). The products´ quality mainly depends on the acid characteristics (concentration, purity, etc.). The figure 9 shows the 35% solution of ammonium sulfate.

Figure 9. The 35% solution of ammonium sulfate (Dvorak & Frear, 2011)

2.3.4 Calcium phosphate characteristics

Calcium phosphate is comparable to phosphate rock that makes it valuable recovered chemical, which can be utilized in phosphate industry (Schipper;Klapwijk;Potjer;Rulkens;& Temmink, 2001). The calcium phosphate pellets is presented by Fig.10.

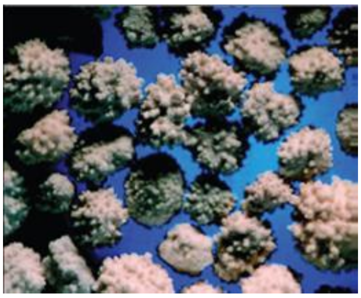

Figure 10. Calcium phosphate pellets (Giesen, 2009)

Calcium phosphate precipitates in different forms depends on the solution pH and composition (Table 5). However the most stable is hydroxyapatite. Other calcium phosphates that formed faster eventually turn into HAP (CEEP, 2001).

Table 5. Possible calcium phosphate form and formula

Calcium phosphate form	**Chemical formula**	**Molar ratio of calcium : phosphate.**
Brushite, dicalcium phosphate dihydrate	$CaHPO_4$ *$2H_2O$	1
Monetite	$CaHPO_4$ *$2H_2O$	1
Octacalcium	$Ca_4H(PO_4)_3$ *2.5 H_2O	1,33
Amorphous calcium phosphate	$Ca_3(PO_4)_2$	1,5
Hydroxyapatite	$Ca_5H(PO_4)_3O$	1,67
Tricalcium Phosphate (TCP)	$Ca_3H(PO_4)_2$	undefined

2.3.5 Ferrous phosphate and aluminum phosphate

Ferrous phosphate and aluminum phoshate are formed on the result of precipitation with appropriate metal (iron of aluminum). There is no exact data relates to chemical substances´ quality and properties.

2.3.6 Struvite

Differ from others chemical products obtained on the result of nutrients recovery, struvite contains both valuable recovered elements- nitrogen and phosphorus. This fact determinates the struvite as a high- quality fertilizer. At the same time, because of the so complicated chemical composition struvite doesn´t have another industrial application.

2.4 Haber-Bosch process

Currently Haber-Bosch process is a main commercial way for ammonia production. It uses the hydrogen and nitrogen as the main components for ammonia synthesis (Eq.8).

$$3H_2 + N_2 \rightarrow 2NH_3 \qquad (8)$$

Nitrogen for Haber-Bosch process is separated from air and hydrogen is produced from natural gas. Because of the high prices for natural gas the ammonia production by Haber-Bosch process is quite expensive. The end-product of Haber Bosch process is anhydrous liquid ammonia. At normal temperatures and pressures anhydrous ammonia (>99 percent NH_3) is a gas. But usually anhydrous ammonia is kept under high pressure, thereby acquires liquid form.

In USA the 80 % of all produced ammonia is used for fertilizers making. Chemical industry consumes about 19 % of ammonia and the rest (about 1%) is used in pulp and paper, metals treatment and refrigeration application (Kent & Riengel, 2007).

Fig. 11 presents the ammonia application in chemical industry. Ammonia is a basic for production important organic and inorganic substances such as amines, hydrazine, nitric acid, etc. Given study considers the possibilities to replace ammonia produced with Haber Bosch process to chemicals recovered from digestate. To reach this, the several conditions should be observed. Firstly, the form of required chemicals should be determined- ammonia water, anhydrous ammonia or ammonia salts could be used. As well special attention has to be direct to chemicals properties, qualities and industry sensitivity.

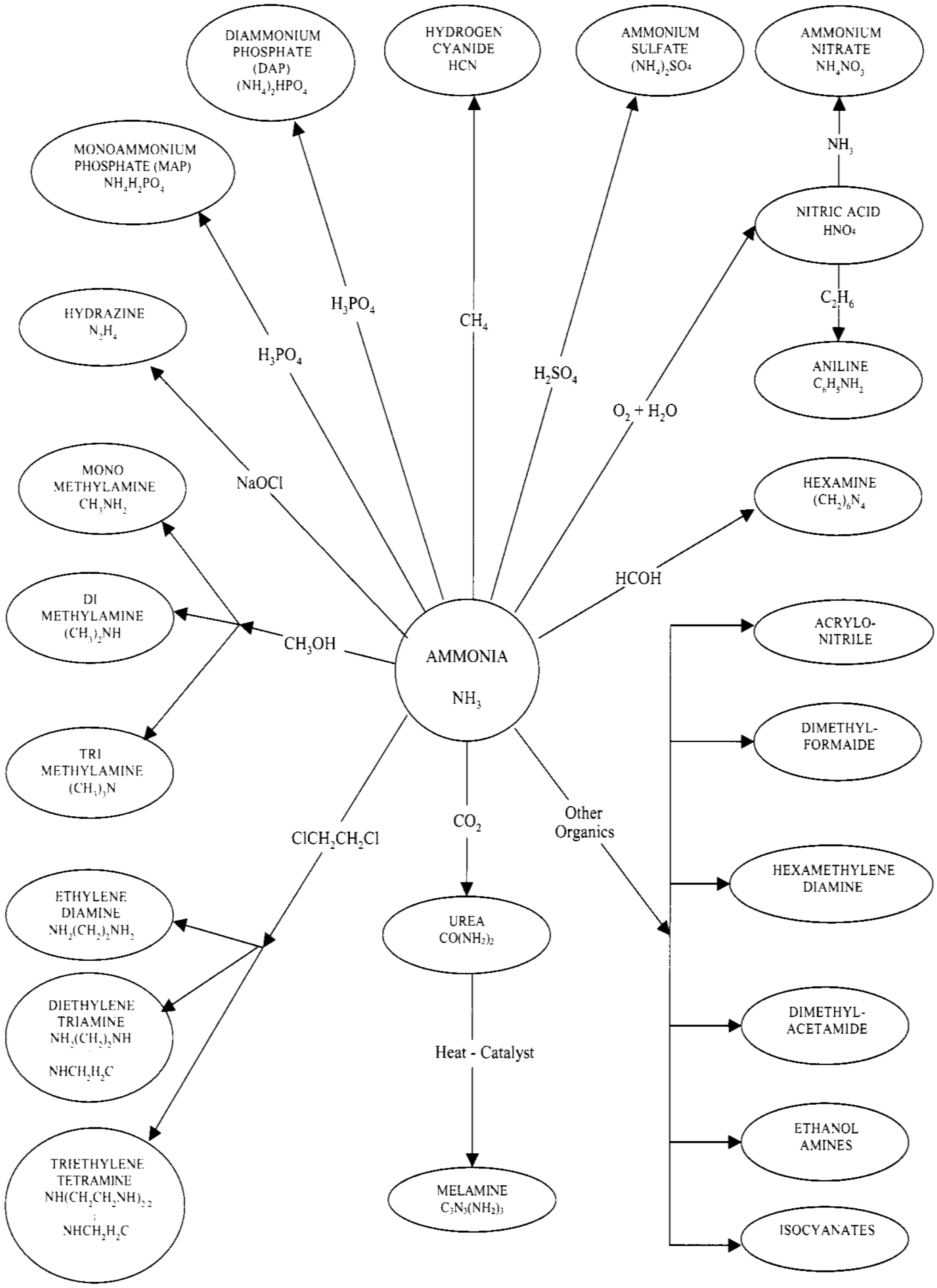

Figure 11. Synthetic nitrogen products (Kent & Riengel, 2007)

2.5 Industrial processes using chemicals

The chapter considers application of recovered chemical products. These applications were set through the literature review. Different industrial sectors can be potential consumers of chemicals recovered from digestate.

2.5.5 Ammonia water (NH4OH)+Anhydrous ammonia

Ammonium hydroxide or co-called ammonia water (NH_4OH) has varying application in different industrial fields. The next list of ammonia water and anhydrous ammonia utilization possibilities was created based on the industrial sectors` needs. It is quite difficult to distinguish the ammonia water from anhydrous ammonia application because usually the anhydrous ammonia is used for ammonium hydroxide preparation. As well the form (gas or liquid) of chemicals has to be accurate through the cooperation with appropriate industrial sector where the chemical substances are used.

1. The petroleum industry utilizes ammonia for neutralizing the acid constituents of crude oil and for protection of equipment from corrosion (General Monitors, 2012).
2. Ammonia used in air pollution control systems to neutralize sulfur oxides and nitrogen oxides from combustion processes (Yara, 2012).
3. Ammonia is used in the rubber industry for the stabilization of natural and synthetic latex to prevent premature coagulation (R.M. Technologies Inc., 2003).
4. The pulp and paper industry uses ammonia for pulping wood and as a casein dispersant in the coating of paper (R.M. Technologies Inc., 2003).
5. In the textile industry, ammonia is used in the manufacture of synthetic fibres, such as nylon and rayon (Ammonia is component of acrylonitrite and caprolactam, which are used for syntetic fibers manufactufing) (Environment Canada, 1997) (Kent & Riengel, 2007).
6. Some water treatment plants uses ammonium hydroxide for water purification (Crittenden;Trussel;& Hand, 2005).
7. Waste treatment enterprises consume small amount ammonia for several purposes. Ammonia can be used as a nitrogen source for the bacteria in industrial and municipal biological waste treatment systems. As well ammonia can be used for acid neutralizing in plant wastes (Kent & Riengel, 2007).
8. Ammonia water can be employed in the dyeing and scouring of cotton, wool, and silk (R.M. Technologies Inc., 2003).

9. Ammonia serves as a catalyst in the production of some synthetic resins (amination agent, as a catalyst for manufacturing thermosetting phenolic resin) (R.M. Technologies Inc., 2003).
10. Chemical industry uses ammonia for nitric acid (Ostwald process) and soda ash (ammonia-soda or Solvay process) production. As well, ammonia is a basic ingredient for chemicals such as urea, hydrazine, amines, ammonia acetate, ammonium chloride (Kent & Riengel, 2007).
11. Metallurgical industry used ammonia for nitriding of alloy sheets to harden their surfaces. By this industry ammonia is cracked for "dissociated ammonia" production, which consists of 75% hydrogen and 25% nitrogen. This dissociated ammonia is used in varying metal treatment processes (R.M. Technologies Inc., 2003) (Kent & Riengel, 2007).
12. Detergent industry makes minor use of ammonia water for household cleaning agents (R.M. Technologies Inc., 2003).
13. Anhydrous ammonia is consumed by different industries as a refrigerant (Kent & Riengel, 2007).
14. Furniture making industry requires ammonium hydroxide for darken or stain wood containing tannic acid. After being sealed inside a container with the wood, fumes from the ammonium hydroxide react with the tannic acid and iron salts naturally found in wood, creating a rich, dark stained look to the wood. This was commonly used during the arts and crafts movement in furniture- a furniture style which was primarily constructed of oak and stained using these methods (Rigers & Umney, 2007).
15. Mining industry uses ammonia water for extracting such metals as copper, nickel, molybdenum from their ore (US Environmental Protection Agency, 1994) (R.M. Technologies Inc., 2003).
16. Ammonia water can be used as solution for making mirrors.
17. Ammonia can be used for ammonia sulfite production by the reaction of ammonia with sulfur dioxide in aqueous solution (Eq.9):

$$2NH_3 + SO_2 + H_2O \rightarrow (NH_4)_2SO_3 \qquad (9)$$

On the result, obtained ammonium sulfite can be used for:

- Pulp and paper industry, as a pulping reagent;

- Making of bricks. The bricks made using ammonium sulfite are mainly used for blast furnace linings (Maryadele, 2001);
- Ammonium sulfite can be included in lubricants for cold metal working. The lubricants are intended to reduce friction to keep heat production down and keep impurities out of the metals (Maryadele, 2001).

18. Semiconductor industry consumes high purity ammonia (99,99995%) for gallium nitride (GaN) manufacturing to ensure high brightness blue and white LEDs (light emitting diodes), in high performance optoelectronics (liquid crystal displays and flat panel displays), and in high-power electronic devices (such as lasers and laser diodes).

Based on the Finnish industries, the most promising applications of anhydrous ammonia and ammonia water are next sectors:

a. Energy sector (Air pollution control)
b. Water treatment
c. Chemical industry sector

Utilization in air pollution control systems

The exhausted gases treatment is an acute problem. One of the major flue gas pollution components is nitrogen oxides – NO_x. NO_x is a margin term for NO and NO_2 oxides (nitric oxide and nitrogen dioxide). NO_x control systems are required for most industrial and manufacturing power plants.

Selective non-catalic reduction (SNCR) and selective catalic reduction (SCR) systems use ammonia or urea for NOx emission reduction in the combustion gases. According to Yara company, ammonia solution is used in larger scale than urea because of efficiency.

SNCR system involves the injection of a reagent (ammonia solution or urea), into flue gas in the upper furnace. Effectiveness of SNCR systems depends on the temperature where the reagent is injected, mixing of the reagent in flue gas, reagent residence time, reagent to NO_x ratio. Primary by-products of SNCR systems are NH_3 and N_2O (Nalbandian & Carpenter, 2000).

In SCR systems, a reagent, ammonia or urea, is entered to flue gas in a reactor in the presence of a catalyst. System products are nitrogen and water. Flue gas temperature, fuel sulphur content, ammonia to NOx ratio, inlet NOx concentrations, space velocity and catalyst condition influence on the performance of SCR system (Nalbandian & Carpenter, 2000).

Fig.12 shows the basic scheme of SCR system for NOx reduction. In this case the aqueous ammonia is used as a reagent. Usually ammonia water in concentration 19% is applied in SNCR and SCR systems (Yara, 2012).

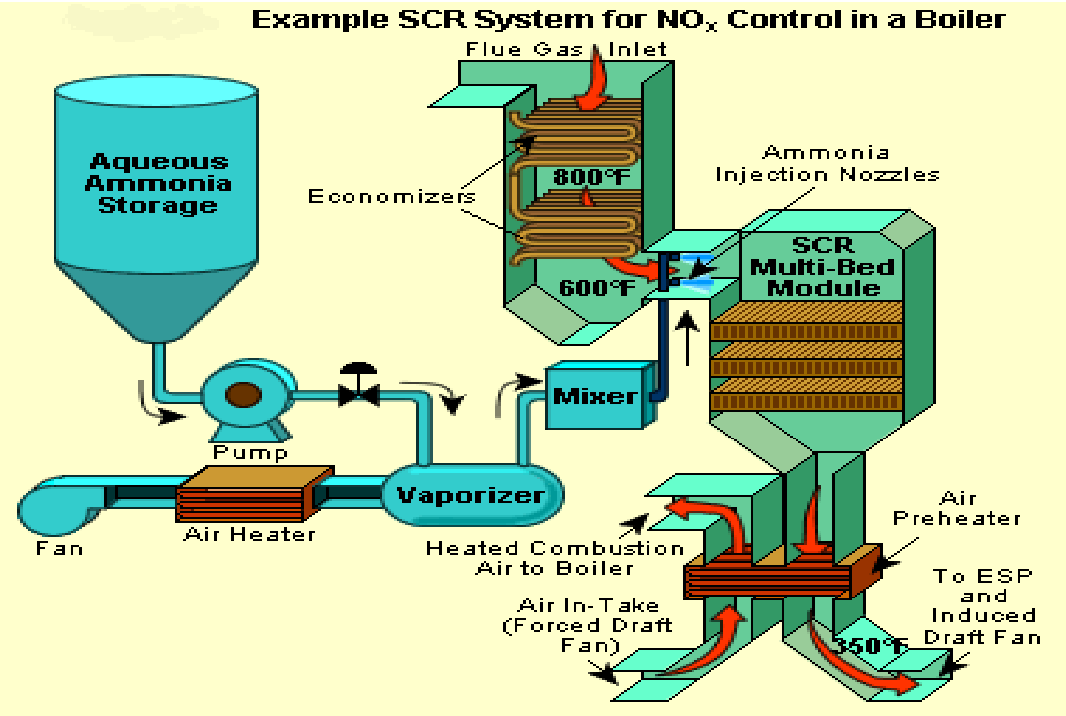

Figure 12. SCR system for NOx control (Hamada Boiler, 2013)

Water treatment technology

The ammonia is supplied the water treatment technology together with chlorine (of chloramines). Ammonia additives in the chlorination process allow converting free-chlorine residual to a combined chlorine residual that makes the treatment process safer. Ammonia can be used for water treatment facility in three forms: as pure liquid anhydrous ammonia, dissolved ammonia in water (ammonium hydroxide) or as a dry ammonium salt (usually ammonium sulfate). Aqueous ammonia form is most commonly used because of the price and convenience form. However ammonium sulfate has advantage that it does not increase the pH as much as ammonium hydroxide and anhydrous ammonia (Crittenden;Trussel;& Hand, 2005).

Chemical industry

Ammonium water can be used for several chemicals production. In this case, ammonia mainly consumes as a gas. The anhydrous ammonia can serve as a source of ammonia gas.

Nitric acid manufacturing (Ostwald process)

Ostwald process is main commercial technology for making nitric acid (HNO_3). Usually ammonia from Haber Bosch process serves as a raw substance for nitric acid production. Ammonia is converted to nitric acid in 2 stages. Firstly, ammonia is oxidized by air over platinum gauze at 900 C^o and nitric oxide is produced on the result (Eq.10). Whereupon, nitric oxide is oxidized to nitric acid by air and liquid water in a “nitrous gas absorber” (Eq.11 and Eq.12) (Swaddle, 1997) .

$$NH_3 + \frac{5}{4} O_2 \rightarrow NO + \frac{3}{2} H_2O \qquad (10)$$

$$NO + \frac{1}{2} O_2 \rightarrow NO_2 \qquad (11)$$

$$NO_2 + H_2O \rightarrow 2\,HNO_3 + NO \qquad (12)$$

In the framework of this study the possibilities to replace anhydrous ammonia from Haber-Bosch process by recovered chemicals is considered. The nitric acid production is one of the possible industrial applications of anhydrous ammonia or ammonia water obtained from digestate processing.

Urea manufacturing

The main raw materials for urea production are ammonia and carbon dioxide. These chemicals are fed into reactor where under high pressure and temperature urea is formed in a two steps reaction. Firstly the ammonium carbamate is produced according to reaction 13. Afterwards, ammonium carbamate decomposes to urea and water. (reaction 14) (Beyer, 1997).

$$NH_3 + CO_2 \rightarrow NH_2COONH_4 \qquad (13)$$

$$NH_2COONH_4 \rightarrow H_2O + NH_2CONH_2 \qquad (14)$$

Urea is widely used for manufacturing important chemicals such as:

- Different plastics, especially for urea formaldehyde resins (Fink, 2012).
- Different adhesives, such as urea-formaldehyde or the urea-melamine-formaldehyde used in marine plywood.
- Potassium cyanate, widely used industrial feedstock (Chemicalland21, 2013).
- Urea can be used in air pollution control systems such as SNCR and SCR (Nalbandian & Carpenter, 2000).
- Urea is a component of dish soap.
- Along with ammonium phosphate, urea is used as a yeast nutrient, for fermentation of sugars into ethanol.

Hydrazine manufacturing

Hydrazine, NH_2-NH_2, is the simplest diamine. There are several processes for hydrazine production (the Raschig process, Bayer ketazine process, the Raschig/Olin process, the Hoffmann (urea) process). Main of them base on the reaction of ammonia (or urea) with Hypochlorite (Eq. 15-17)

$$NaOH + \bullet Cl_2 \rightarrow NaOCl + H\ Cl \quad (15)$$

$$NH_3 + NaOCl \rightarrow NH_2Cl + NaOH \quad (16)$$

$$NH_4Cl + NH_3 + NaOH \rightarrow NH_2 - NH_2 \cdot H_2O + NaCl \quad (17)$$

Hydrazine is applied as: blowing agents (33%), pesticides (32%), water treatment (18%) and miscellaneous (17%) (Kent & Riengel, 2007).

Pulp and paper industry.

Pulp and paper industry can be promising area for ammonia water utilization because of the significant amount of these type industrial enterprises in Finland.

Ammonium hydroxide can be used for sulfite liquor production for further pulping process. In the sulfite pulping process a liquor of sulfurous acid (H_2SO_3) and bisulfate (HSO_3) is produced on site. Elemental sulfur is burned to produce sulfur dioxide (SO_2). The sulfur dioxide is sent to an absorption tower and treated with one of four alkaline substances, calcium carbonate (CaCO3), magnesium hydroxide (Mg(OH)2), ammonium hydroxide (NH4OH), or the original sulfite base to the liquor (Hamilton & Phillips, 2003).

As well ammonia water can be used for casein formation which is used for paper coating. Usually paper with casein coat is used in food industry (Academic.ru, 2013).

2.5.6 Ammonium sulfate

Ammonium sulfate is quite widely used chemical. In 2001 his demand reached 17,3 million tons worldwide among them the 2,8 million tons in Western Europe. But 90 % of ammonium sulfate was used directly as a fertilizer and only 10 % were used in the chemical industries or for metal producing (OECD SIDS, 2004). Ammonium sulfate can be used in next industries:

1. Chemical industry consumes $(NH_4)_2SO_4$ for manufacturing chemicals such as ammonium aluminium sulfate, ammonium persulfate (Helmboldt, и др., 2007).
2. Metallurgical industry uses $(NH_4)_2SO_4$ as a welding flux and for galvanizing iron.
3. Textile and wood industry make $(NH_4)_2SO_4$ uses as a flame retardant (White & Dietenberger, 1999).
4. Ammonium sulfate utilizes in dyeing industry as a dyeing auxiliaries of acid dyes (OECD SIDS, 2004).
5. Leather industry uses $(NH_4)_2SO_4$ as a deliming agent (Kustula, Salo, Witick, Kaunisma, Kalliala, & Talvenmaa, 2000).
6. Textile industry consumes $(NH_4)_2SO_4$ for nylon production (OECD SIDS, 2004).
7. Wood industry uses ammonium sulfate for plywood and venneer production. Besides in woodworking industry $(NH_4)_2SO_4$ can be used for the production of curing agents for urea-formaldehyde and melamine-formaldehyde resins which used in the chipboard manufacturing (Chemicalland21, 2012).
8. In the mining industry, ammonium sulfate can be used as flotation reagent for copper-lead-zinc ores (Bulatovi, 2007).
9. Ammonium sulfate has application as additives fire-extinguishing materials (OECD SIDS, 2004).
10. Pulp and paper industry consume $(NH_4)_2SO_4$ in the production of yeast and sulfite liquor (OECD SIDS, 2004).
11. Detergent industry uses $(NH_4)_2SO_4$ in the manufacturing of, wash- and cleaning agents and disinfectants.
12. In electroplating industry, ammonium sulfate is a plating bath additive (Tianjin Dongri Animal By-Product Co., 2013).

13. Ammonium sulfate is used in biological treatment plants as nutrient for bacterial cultures (EuroChem, 2013).
14. Ammonium sulfate is used in the production of lead acid batteries (EuroChem, 2013).

The most perspective industrial sectors for ammonium sulfate utilization according to current Finnish market state are:

a) Chemical industry
b) Wood industry

Ammonium sulfate for chemical industry

Chemical industry is one of the biggest industrial sectors in Finland. Every day chemical enterprises produce tons of chemical substances. Two of them, which can be produced base on the ammonium sulfate are ammonium aluminium sulfate and ammonium persulate.

Ammonium aluminum sulfate production

Ammonium aluminum sulfate (ammonium alum) is a white crystalline double sulfate salt with formula $(NH_4)Al(SO_4)_2 \cdot 12H_2O$. It has minor application in a variety of industrial niches. Main raw materials for ammonium alum production are aluminum hydroxide, sulfuric acid and ammonium sulfate. (Weast, 1981) Ammonium alum is used for water purification, in vegetable glues, in porcelain cements, in deodorants and in tanning, dyeing and in fireproofing textiles. (The Columbia Encyclopedia, 2004)

Ammonium persulfate production

Ammonium persulfate (Ammonium peroxydisulfate APS) is a white salt with formula $(NH_4)_2S_2O_8$. This substance has a strong oxidizing properties. Usually APS is produced by the electrolysis of ammonium sulfate solution and sulfuric acid.

Ammonium persulfate is the main component of Nochromix. This product is used for cleaning laboratory glassware as a metal-free alternative to chromic acid baths. It is also a popular ingredient in western blot gels and hair bleach (Goodguide, 2013).

Ammonium Sulphate as a flame retardant in textile industry and wood industry.

Most widely used flame retardence for wood are inorganic salts which have been known to humanity for more than 50 years. These inorganic salts include such as monoammonium and diammonium phosphate, ammonium sulfate, zinc chloride, sodium tetraborate, and boric acid. (White & Dietenberger, 1999) As well many cellulose companies use a blend of ammonium sulfate and borate for fire retardation.

2.5.7 Ammonium nitrate

One of the common applications of ammonium nitrate is mining explosive. The substitution of nitroglycerin by ammonium nitrate leads to give safer and less expensive product. However, because of mining industry has small scale in Finland, this ammonium nitrate application can`t be perspective.

Another use ammonium nitrate can find in instant cold packs. Instant cold packs consist on two packs, one with water and other with ammonium nitrate, and when broken these mix to create an endothermic reaction (absorbs heat from the surroundings to become cool). These packs are commonly used as a first aid in situations where ice is not available. However, this application of ammonium nitrate hasn`t a big scale. (Bortoli, 2013)

2.5.8 Calcium phosphate

Calcium phosphate is obtained in the process of phosphorus precipitation from liquid fraction of digestate. This chemical can be used for phosphoric acid preparation. Phosphoric acid is prepared commercially by heating calcium phosphate rock with sulfuric acid; purer grades may be prepared by treating red phosphorus with nitric acid. Because of recovered calcium phosphate presents as a phosphorus mineral analog, it can replace this mineral in commercial technology of phoshroric acid preparation.

2.5.9 Aluminum phosphate and Iron phosphate

The industrial application of aluminum phosphate and iron phosphate were not determinate through literature review. Only data were found that aluminum phosphate can be used as a basis of many adhesive, binders and cements (Greenwood & Earnshaw, 1997).

3. Market study in Finland

To reach objectives of study, the research of Finnish market state should be provided. This research will allow get real understanding of current chemicals` needs and requirements. Market study follows after literature review, where main recovered chemicals and their potential application have been defined. Moreover, the probability of finding new application of recovered chemicals still exists.

The strategy comprising of six steps was applied for market study conducting (Fig.13) (Kotler & Keller, 2012). Defining problem and research objectives, research plan developing, contacting with target group, analyzing and information presenting, decision making- are steps of market study. This clear structure of plan will allow provide fair market study relatively each industrial sector, because of the similar approach to different enterprises.

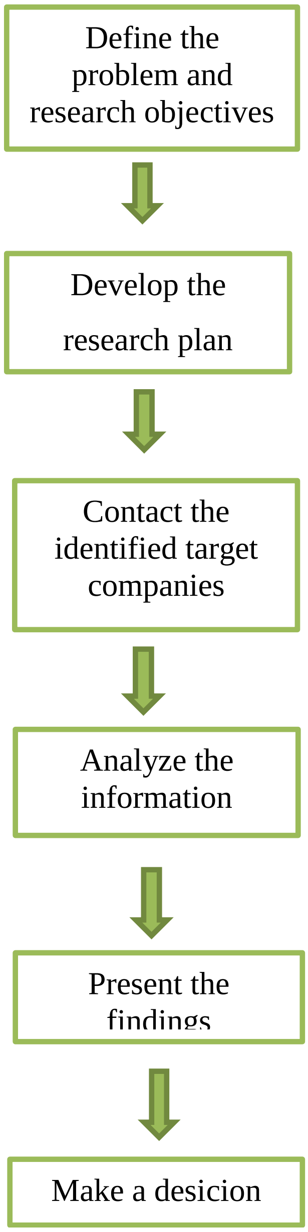

Figure 13. Market study scheme (Kotler & Keller, 2012)

3.1 Define the problem and research objectives

Market study is directed to define the range of potential industrial companies, which are interested in recovered chemical products utilization. It is important to identify the most appropriative for industrial enterprises chemicals` form, properties and quality. This identification will help biogas plants to produce actual chemicals and, as a result, to have successful marketing politics. As well, the definition of chemicals properties will allow finding suitable technologies for product recovery and assessing the expenses for new technology implementation. Despite of the different quality requirements they could be margined in one set of chemicals` properties for production process simplification and satisfying needs by several industrial enterprises simultaneously.

3.2 Research plan development

The detailed and effective plan for market study should be made up for getting successful results. In this case the plan was divided into several steps:

a) Determination of potential products and their characteristics.
b) Possible ways of product utilization.
c) Potential industrial sectors for product utilization.

These steps have been done through the literature review. The potential recovered products were defined in chapter 2.3. The next chemicals were considered as possible products: ammonia water, anhydrous ammonia ammonium sulfate, ammonium nitrate, ferrous phosphate, aluminum phosphate, calcium phosphate and struvite. Through the literature review the possible applications and industrial sectors, where chemicals can be utilized, were found.

d) Determination of the certain Finnish companies (their names) in the every sector.

Based on the possible chemicals` application the list of industrial sectors with the names of finnish companies was created. This list contents 11 industrial sectors (table 6). Because of interview confidentiality, the companies' names are kept in secret.

Table 6. Industrial sectors and finnish companies as a potential customers of recovered chemicals

Industrial sector	**Company in Finland**
Energy	Company 1, Company 2
Waste treatment	Company 3, Company 4
Pulp and paper	Company 5, Company 6
Chemical	Company 7, Company 8
Textile	Company 9
Metal treatment	Company 10, Company 11
Detergent industry	Company 12,
Petroleum industry	Company 13, Company 14
Furniture making industry	Company 15, Company 15
Polymer industry	Company 16, Company 17
Mining industry	Company 18, Company 19

e) Interview with the company, asking about current and possible ways of our chemicals utilization. Asking about properties and purity. The proposition of our products to company.
f) Decision making.

3.3 Contacts with target companies

The questionnaires were used as a main tool for contacting with Finnish companies. This tool was chose for several reasons. Firstly, the questionnaire allows conducting research in big scale. Because the quite large amount of companies participated in survey and the limit of time for study, the questionnaire presented the best option. As well this type of cooperation allows obtain comparable results from different industrial sectors. This fact can be essential for decision making.

The questionnaire includes several sub-levels. At the beginning the information from literature review, according to recovered chemicals application, is introduced. Based on this sub-level the companies confirm of reject literature research's data. The next questions have general character for all contacted enterprises. Here there are common questions such as: "What chemicals from our list do you use? What are the properties of chemicals? What amount of chemicals do you use annually?" As well some questions required more individual approach from industrial sector were included. These questions ask companies to propose some industrial processes of procedure, where recovered chemicals can be used or they can substitute current used ones. The last question asks companies about their interest in buying recovered chemicals and further cooperation.

These interviews will help to understand better the real application possibilities and the situation on the market, as well as to determine whether there is interest in the industry to use such chemicals at all.

3.4 Analyze the information and present findings

This step leads to discuss answers obtained from target companies. The answers from eight finnish companies from mining, energy, water treatment, pulp and paper, metal processing and furniture making sectors were received in the process of interview.

Mining company:

According to literature review it has been set, that ammonia water can be used for leaching metals such as copper, nickel and molybdenum. However, mining company reported, that currently mining companies all over the world are trying to escape ammonia water utilization due to environmental and safety reasons.

In mining industry, ammonia can be used as gas or saturated solution for pH-control. The excess of water in solution should be avoided because of the technological and economical purposes. Based on the company answer, this sector consumes several tons per day of this product. However this scale includes not only Finnish mining enterprises, but also other international. In this case is quite difficult to define real consumption level but probably it will be low because of the small amount of mining enterprises in Finland.

Energy sector

The answers from two energy producing companies were recieved. Because of the confidinciality keeping, the interviewing companies calles as company 1 and company 2.

Company 1

Energy producing company uses ammonia water for exhaust gases treatment via SNCR technology. This enterprise consumes 24,5% ammonia water in amount approximately 290 ton/year. Noticeably, that technology, where ammonia water is utilized, is almost not sensitive to impurities. This fact can simplify recovered ammonia water utilization process because the additional chemical analyses are not required. Interviewing company said that it is interested in ammonia water purchase.

Company 2

Another energy producing company reported, that it utilizes high quality ammonia only in gas-form for flue gas treatment in SNCR technology. This fact creates difficulties for recovered from digestate chemical utilization. However, if anhydrous ammonia will be produced from recovered ammonia water, it can be used as a source of gaseous ammonia.

Pulp and paper sector

Company from pulp and paper sector utilizes ammonia water for flue gas treatment technology. The concentration of solution is below 25 %. The nutrients (both-nitrogen and phosphorous) are required in wastewater treatment plant at paper mills. In the pulp mills these nutrients are used as well but wood contains enough phosphorous, that is why company doesn't interested in this nutrient. Some pulp and paper mills use urea, bur according to company answer urea easily can be replaced by ammonia water. Integrated pulp and paper mills consume about 1 ton ammonia water per day.

Waste management sector

Company, which utilizes waste trought incineration process,uses ammonia water for NOx removing by applying SNCR system. The concentration of ammonia water in container is about 25%, however the additional water is used for dilution till 5 %. This 5% ammonia water is used in sprays. Because of the block the sprayers the any impurities can be accepted. The company said, that it is not interested in products, if any equipment changes will be necessary of there are any quality risks during the testing and changing phase. Otherwise, company can consider this chemical in their utilization facilities.

Metal processing sector

Metal processing company didn`t conform any application of considered chemicals in their technological process.

Furniture making sector

The both interviewing furniture making companies reported that they are not use chemicals, which biogas companies could produces from digestate.

3.5 Make the decision

The market study reveals that ammonia water is a most promising recovered chemical, which can be obtained from digestate. Mainly this product is used for flue gas treatment technology. Worth to say, that exhausted gas treatment technologies are quite no sensitive to impurities in ammonia water. In this case, some additional chemical analysis and researches can be omitted. The consumption amount of this chemical product is quite high and, basically, companies open for cooperation in the case of appropriate cost. As well nitrogen together with phosphorus can serve as a nutrient source at paper mills for biological wastewater treatment technology.

4. Conclusion

Globally the waste utilization topic is getting new approach. If recently, the wastes were considered as an absolutely useless stack of materials, which pollutes environment and required large space for landfilling, but nowadays mankind recognized that wastes can serve as a second raw material. The waste utilization can replace the use of natural resources and reduce the speed of their depletion. Recovered materials employment is more sustainable and sometimes even more economically profitable than first raw material.

Given study confirms that recovered from digestate chemicals have applications in different industrial sectors. The first parts of research allowed define the form of recovered substances and their potential applications. Through the ammonia stripping with further material processing as an acid absorption, and phosphorous precipitation the next chemicals can be obtained: ammonia water, anhydrous ammonia, ammonium sulfate, ammonium nitrate, struvite, aluminum phosphate, iron phosphate and calcium phosphate. However provided market study bases on the Finnish companies interview set, that ammonia water is a most promising chemical.

Because of high industrialized structure of Finland`s economy, country has large amount of industrial and manufacturing enterprises. The energy, pulp and paper sectors are the most developed in Finland. Exactly in these sectors the ammonia water application was found in largest scale. These industrial enterprises consume ammonia water for flue gas treatment. Ammonia water allows remove NO_x pollutants from exhausted gases in SNCR technology. Some amount of nutrient, both nitrogen and phosphorus can be used for wastewater treatment at paper mills.

However, before recovered ammonia water utilization in the industrial enterprises is worth to think about concentration of this chemical. Currently the ammonia water producing by some biogas plants has quite low concentration- about 5% (Paavola, Ervasti, Luostarinen, & Kapuinen, 2011), whereas the minimum required by companies is 25%. Possibly, stripping process from some biogas plant can be changes on the way to obtain ammonia water with higher concentration. For instance, “Ammongas engineering company” proposed vacuum-stripping technology with steam, which allows to produce 25 % ammonia water solution from 0,2% ammonia industrial wastewater

(Ammongas, 2013). The initial concentration of ammonia in digestate of biogas plant described by Paavola T. is 0,6%, higher than in “Ammongas” case.

The considered biogas plant produces 7100 t/a of ammonia water with concentration 5 % (Paavola, Ervasti, Luostarinen, & Kapuinen, 2011). If ammonium hydroxide would be produced with 25% concentration, the total amount of recovered ammonia water will make up approximately 1420 t/a. The several companies – power plant and pulp, paper enterprise reported that they consume about 1 ton per day of ammonia water for technological purpose. In this case, considered biogas plant has to cooperate along with as minimum five companies within such chemical`s consumption level.

The ammonia water produced by biogas company could have economic benefits compare with aqueous ammonia produced with conventional Haber-Bosch process, which consumes expensive natural gas and high temperatures. In this case, industrial companies will agree to utilize recovered ammonia water with the condition of observing quality characteristics.

The answers were received not from all interviewing sectors. This fact narrowed down the total number of finding possible applications of recovered chemicals. However, the applications, which were found trough the literature review and which have largest utilization scale are confirmed by market study. In this case the mistake can be minimized.

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