

**LAPPEENRANTA UNIVERSITY OF TECHNOLOGY**

School of Engineering Science

Degree Program in Chemical Engineering

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**PHOSPHATE FERTILIZERS FROM PIG MANURE - FEASIBILITY STUDY OF  
ALTERNATIVES FOR INCREASED PHOSPHORUS RECOVERY FROM PIG MANURE  
ASH AND CHAR**

Examiners: Professor Tuomas Koiranen  
Tech.Lic. Esko Lahdenperä

## **ABSTRACT**

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Keywords: phosphorus, manure, fertilizer, dicalcium phosphate, phosphate precipitation, manure surplus, combustion, gasification, acid leaching

The objective of this study was to examine the feasibility to treat manure further to recover phosphorus and at the same time utilize the energy content in manure and decrease the surplus manure in the Netherlands. First the possible methods to recover phosphorus and to produce energy from manure were indicated. Followed by the literature study a process comparison was made by comparing yields and concentrations of phosphorus and also energy consumption and production in different methods. Resulting process route included first treatment of manure in an anaerobic digestion followed by solid-liquid separation. Solid fraction would be dried and then combusted and formed ashes would be leached with sulfuric acid. Finally, phosphates would be precipitated from the extract as dicalcium phosphates (DCPD), which are comparable to the fertilizer products from phosphate rock. Best way to treat the liquid fraction would be to first separate organics by ultrafiltration and recycle them to the drying section of the solid manure and then purify water with reverse osmosis. The concentrate from reverse osmosis could be used as a mineral fertilizer, which is rich in nitrogen and potassium. Experiments were done for the solid fraction of pig manure, since there is no research done for this process route. Experiments were also done for pig manure char from a gasification plant. Results showed that it is possible to produce DCPD from the acid leached ash solution with highest yield of phosphate being 94.4 % in precipitation. Precipitation from char originated solutions gave calcium carbonate and amorphous DCPD as final products with lower phosphate yields. By combining results from literature and results from experiments, it was observed that 79.0 % of the phosphorus from initial manure could be recovered as DCPD via incineration process route. Based on energy balances the same route would produce 118 MJ/tonmanure energy. Economical evaluation showed that after 9 years the studied treatment process would be more feasible than the conventional way of applying manure on the fields. Gasification route resulted being unfeasible.

## TIIVISTELMÄ

Lappeenrannan Teknillinen yliopisto  
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Työn tarkoituksena oli tutkia, onko lantaa kannattavaa käsitellä pidemmälle, jotta lannassa oleva fosfori ja energia saataisiin talteen ja lisäksi Hollannissa ongelmaksi muodostunut lannan vuosittainen ylimäärä saataisiin pienennettyä. Ensin mahdolliset fosforin talteenottomenetelmät lannasta selvitettiin ja myös millä menetelmillä energiaa voidaan tuottaa lannasta. Kirjallisuuskatsauksen jälkeen eri menetelmiä vertailtiin keskenään fosforisaantojen, fosfori-konsentraatioiden ja energiakulutuksen ja – tuoton perusteella. Prosessivertailun tulosten perusteella lanta tulisi käsitellä ensin anaerobisella mädätyksellä tuottaen biokaasua, jonka jälkeen lanta erotettaisiin kiinto- ja nestevirtoihin. Kiintoaines kuivattaisiin ensin ja sen jälkeen se poltettaisiin täysin tuhkaksi. Tuhkissa oleva fosfori uutettaisiin rikkihapolla liuokseen, jonka jälkeen se voidaan kiteyttää kalsiumhydroksidin lisäyksellä. Kokeet sisälsivät kiinteän lannan kuivauksen, polton, happouuton ja kiteytyksen. Kaasutuksen jäljiltä oleva hiili, johon fosfori päätyy kaasutuksen jälkeen, sisällytettiin myös kokeelliseen osaan. Tulosten perusteella tuhkien uuton ja uuttoliuoksen kiteytyksen jälkeen lopputuote oli dikalsium fosfaatti (DCPD). Fosfaatin saannoksi saatiin 74.7 %. Hiilen uuttamisella ja kiteytyksellä saatiin lopputuotteiksi DCPD ja kalsiumkarbonaatti. Fosfaatin saanto hiilestä oli maksimissaan 60 %. Teknisen ja taloudellisen arvioinnin perusteella 9 vuoden jälkeen lannan käsittely käyttämällä polttoprosessia ja tuottamalla DCPD:tä olisi kannattavampaa kuin lannan levittäminen pelloille, mistä sikalan pitäjiä pitää maksaa tällä hetkellä. Jos lantaa käsiteltäisiin ehdotetulla prosessilla, fosfori saataisiin talteen lannoitetuotteena, prosessissa tuotettu energia voitaisiin myydä ja lopuksi Hollannin lannan ylimäärää saataisiin pienennettyä.

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## List of symbols

$C_0$	total initial investment costs, €/year
$c_{H_2SO_4}$	acid concentration, g/L
$c_{l,i}$	initial concentration of phosphate in aqueous solution after precipitation, g/L
$c_{l,e}$	final concentration of phosphate in aqueous solution after precipitation, g/L
$c_P$	concentration of phosphates in solution after leaching, g/L
$C_{p,90\%}$	specific heat capacity of manure with 90 % water content, MJ/tonC
$c_{s,i}$	initial concentration of component in ash, g/L
$c_{s,e}$	final concentration of component in ash, g/L
$C_t$	net cash flow during time period t, €/year
$E_e$	electrical energy, MJ/ton <sub>water</sub>
$E_{in}$	energy input, MJ/ton <sub>manure</sub>
$E_{out}$	energy output, MJ/ton <sub>manure</sub>
$E_{out,A}$	energy produced in anaerobic digestion, MJ/ton <sub>manure</sub>
$E_{out,c}$	energy produced in combustion, MJ/ton <sub>manure</sub>
$E_{th}$	thermal energy, MJ/ton <sub>water</sub>
$E_{u,A}$	energy required to reach 40 °C during digestion, MJ/ton <sub>manure</sub>
$E_{u,e}$	electrical energy required, MJ/ton <sub>manure</sub>
$H_c$	heat of combustion, MJ/ ton <sub>Org</sub>
$H_{c,CH_4}$	heat of combustion of methane, MJ/m <sup>3</sup> <sub>CH4</sub>
$H_L$	heat loss, -
$\dot{m}_{CH_4}$	the mass flowrate of methane, m <sup>3</sup> /year
$\dot{m}_{H_2O}$	mass flow rate of water, ton/year
$\dot{m}_m$	mass flowrate of manure, ton/year
$\dot{m}_{m,in}$	initial manure flowrate, ton <sub>manure</sub> /year
$\dot{m}_{Org}$	mass flowrate of organic matter in manure, ton/year
$\dot{m}_{P,in}$	initial phosphorus mass flowrate in the manure, ton/year
$\dot{m}_{P,out}$	outgoing phosphorus mass flowrate, ton/year
$\dot{m}_{tot}$	total mass flowrate, (ton <sub>manure</sub> /year)
$\dot{m}_x$	mass flow of a component in manure, ton/year
$r$	discount rate, -
$t_{NPV}$	number of time periods, -
$t_p$	precipitation time, min
$\Delta T$	temperature change, C

$V_{H_2SO_4}$	volume of acid, L
$V_L$	volume of calcium hydroxide, L
$V_P$	volume of leached solution, L
$x$	component concentration, kg/ton <sub>manure</sub>
$x_{CH_4}$	methane yield from organic matter, m <sup>3</sup> <sub>CH<sub>4</sub></sub> /ton <sub>Org</sub>
$x_{H_2SO_4}$	acid consumption, kg H <sub>2</sub> SO <sub>4</sub> /kg P
$\eta_a$	yield of component in acid leaching, %
$\eta_e$	energy efficiency, %
$\eta_p$	yield of phosphate in the precipitate, %
$\eta_{P,tot}$	total yield of phosphorus, %

### List of abbreviations

AD	Anaerobic digestion
DAP	Diammonium phosphate
DCP	Dicalcium phosphate
DCPA	Dicalcium phosphate anhydrate
DCPD	Dicalcium phosphate dihydrate
DM	Dry matter
HAP	Hydroxylapatite
IM	Inorganic matter
MAP	Monoammonium phosphate
MCP	Monocalcium phosphate
MF	Microfiltration
NPV	Net Present Value
OM	Organic matter
RO	Reverse osmosis
SSP	Singe superphosphate
TSP	Triple superphosphate
UF	Ultrafiltration
UV-VIS	Ultraviolet visible spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence



## 1. INTRODUCTION

Phosphorus is an important resource especially as a fertilizer in the agriculture. The most common source for phosphorus is phosphate rock, which is also the main feedstock for the phosphate fertilizer process. The amount of phosphorus rock is limited and it has been estimated to be enough only for the next 20 – 40 years. (Desmidt, Ghylselbrecht et al. 2015) Due to the fast growth of world population the food demand is increasing and it is urgent to find new sources for phosphorus to produce fertilizers. The increasing phosphorus demand is shown in Figure 1. Therefore, more focus has been put recently into the phosphorus recovery from different renewable sources. These alternative sources for phosphorus can be, for instance, sewage sludge and animal manure. (Schoumans, Rulkens et al. 2010)

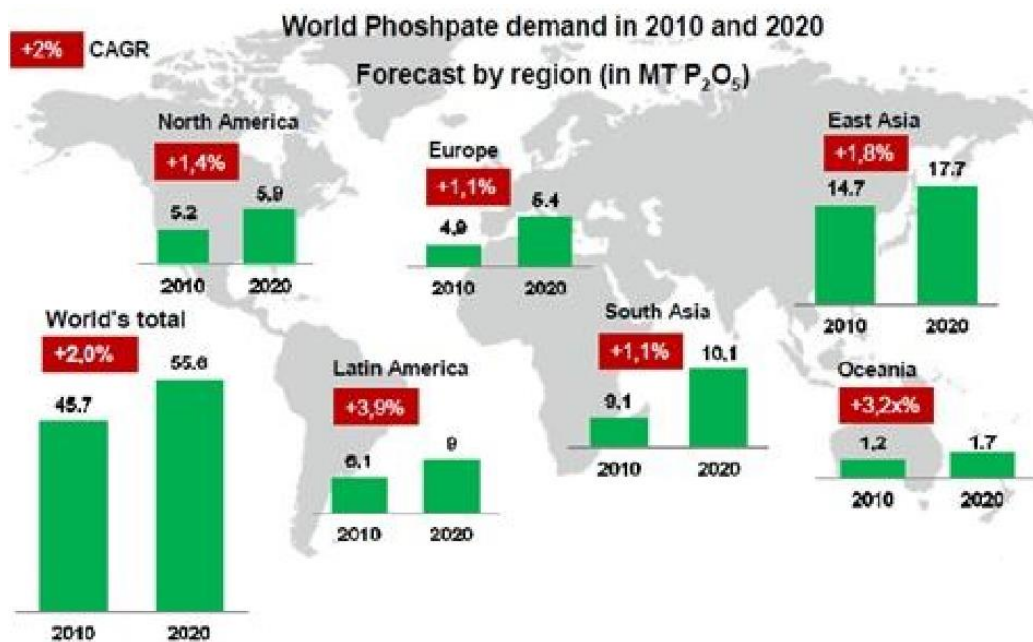


Figure 1 Worldwide demand for phosphorus in 2010 and expected demand in 2020. (d. Ridder, d. Jong et al. 2012)

Animal feed is imported to the Netherlands and this feed contains phosphorus. Animal manure has been applied as fertilizer on the fields in the Netherlands and it is not exported out from the Netherlands. Due to the stricter manure policy, it is not possible to apply all of the produced manure on the fields anymore. Manure has relatively high nutrient content and, when a large amount of nutrients is leached through the fields, it can cause eutrophication of surface and ground waters. (Desmidt, Ghylselbrecht et al. 2015, Statistiek 2016) This is why manure treatment and nutrient recovery are becoming more interesting and a lot of research has been done on this topic (Schoumans, Rulkens et al. 2010). Different manures vary in nutrient contents depending on the type of animal, age of the

animal and the feed material. For instance, pig manure is higher in phosphorus whereas cattle manure is higher in nitrogen. Poultry and horse manure are low in phosphorus and nitrogen. (Schick, Haneklaus et al. 2013) Application of manure also leads to unbalanced utilization of nutrients due to these differences.

Next to the nutrients animal manure contains organic matter, which can be utilized for energy production. Energy from manure is currently produced mainly by anaerobic digestion to produce biogas. (Jorgensen 2009) However, further treatment is still needed after digestion due to large volumes of water and some solids, which are not converted into biogas during anaerobic digestion. Conventional processing has included anaerobic digestion and solid-liquid separation of manure till the recent years. However, this way of processing is not sufficient enough to decrease the surplus of manure. (Schoumans, Rulkens et al. 2010)

### **1.1. Scope**

The goal of the study is to develop a process with increased phosphorus and energy recovery. An evaluation is done whether the chosen process is feasible compared to the conventional application of manure. First possible phosphorus process and products are studied. Then different manure treatment methods are compared find the solution for the stated problem. The comparison is based on phosphorus yields and concentrations in the process streams and energy production and consumption of the different methods. By this it can be concluded, which route is most interesting for the recovery of phosphorus, energy production from manure and for reducing the manure surplus in the Netherlands. Based on the results from the comparison, experiments are made for the chosen process route using animal manure as a feedstock. A model is then made in AspenPlus for part of the process to examine the experimental results whether they are comparable with the model and, if the model can predict the results. Finally, the process will be evaluated technically and economically using information from literature and results from the experiments.

## 2. THEORY AND BACKGROUND

In this theory section conventional process, feedstock and products for phosphorus will be studied in detail. After indicating possible ways to produce phosphorus, compositions of different animal manures and treatment methods of manure will be discussed in detail. Ways to recover phosphorus from manure are also included to the discussion.

### 2.1. Phosphorus

Phosphorus is usually found as orthophosphates in nature and the main source of phosphorus is phosphorus rock. Phosphorus is one of the main nutrients and is mainly used in agriculture as fertilizer and a smaller amount is used for animal feed production. (Kongshaug, Brentnall et al. 2000) Demand for phosphorus is increasing, because of the worldwide food demand is increasing especially in countries with fast growing population. Meantime, phosphorus rock is a diminishing natural resource and it has been estimated that within 20 – 40 years phosphorus rock cannot anymore fulfill the demand. This issue has become a driver for finding new resources for phosphorus. (Desmidt, Ghylselbrecht et al. 2015)

#### 2.1.1. Feedstock

Major part of phosphates is processed from phosphate rock, which is found mainly in Morocco. Igneous phosphate rocks are also important sources for phosphorus and besides the phosphate rocks some minor sources for phosphorus have been bone ash and basic slag. Phosphorus is found in the phosphorus rock mainly as fluorapatite  $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$ . Phosphates are also found in other minerals, mainly calcium apatites. Substituting ions for  $\text{F}^-$  can be  $\text{OH}^-$  and  $\text{Cl}^-$ . The composition of phosphate rock is given in Table 1. Half of the rock is calcium and the other main component is phosphorus having average content of 33 %. (Kongshaug, Brentnall et al. 2000)

*Table 1 Composition of the phosphate rock. (Kongshaug, Brentnall et al. 2000)*

Constituent	Range of content, %	Average content, %
P <sub>2</sub> O <sub>5</sub>	29–38	33
CaO	46–54	51
SiO <sub>2</sub>	0.2–8.7	2.0
Al <sub>2</sub> O <sub>3</sub> +Fe <sub>2</sub> O <sub>3</sub>	0.4–3.4	1.4
MgO	0.1–0.8	0.2
Na <sub>2</sub> O	0.1–0.8	0.5
CO <sub>2</sub>	0.2–7.5	4.5
F	2.2–4.0	3.7
Cl	0.0–0.5	<0.02
SO <sub>3</sub>	0.0–2.9	1.0
CaO:P <sub>2</sub> O <sub>5</sub> ratio	1.35–1.70	1.5

Plants uptake phosphorus as orthophosphates H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and HPO<sub>4</sub><sup>2-</sup>. To be available for plants the compounds should be water or citrate soluble, which can be produced at the roots. Therefore, the aim in processing phosphate rock is to produce water or citrate soluble compounds. The phosphorus content is usually given as P<sub>2</sub>O<sub>5</sub>, which contains all the forms of phosphorus. (Gard 2000, Kongshaug, Brentnall et al. 2000)

### 2.1.1. Phosphorus rock process and products

Figure 2 shows an overview of the different process routes and fertilizer products, which can be produced from the phosphate rock. The products can be divided into calcium phosphates, ammonium phosphates, for which the formulas and meanings are presented in Table 2, and compound and complex fertilizers. (Gard 2000, Kongshaug, Brentnall et al. 2000)

*Table 2 Phosphate products from the phosphorus rock process.*

Product	Product name	Process route	Phosphate compound	Side products
SSP	Single superphosphate	Phosphate rock + sulfuric acid	Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	CaSO <sub>4</sub> , HF
TSP	Triple superphosphate	Phosphate rock + phosphoric acid	Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	HF
MAP	Monoammonium phosphate	Phosphoric acid + ammonia	NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	-
DAP	Diammonium phosphate	Phosphoric acid + ammonia	(NH <sub>4</sub> ) <sub>2</sub> H <sub>2</sub> PO <sub>4</sub>	-

Most of the phosphoric acid (90 %) is produced by wet process (H<sub>2</sub>SO<sub>4</sub>) from the phosphate rock. It is then used further in the process to produce the fertilizers, but it is also applied in

production of animal feed. The other route is to produce it by a thermal process. When it is produced thermally, excess air is present while white phosphorus is burned. Phosphorus pentoxide is formed and then hydrated, which leads to phosphoric acid mist formation. Wet process is more common, because of the high combustion temperatures, corrosion problems and the separation of phosphoric acid, when it is mist. On the other hand phosphoric acid produced by thermal process is more pure than with the leaching of phosphate rock. (Gard 2000, Kongshaug, Brentnall et al. 2000, Schrödter, Bettermann et al. 2000)

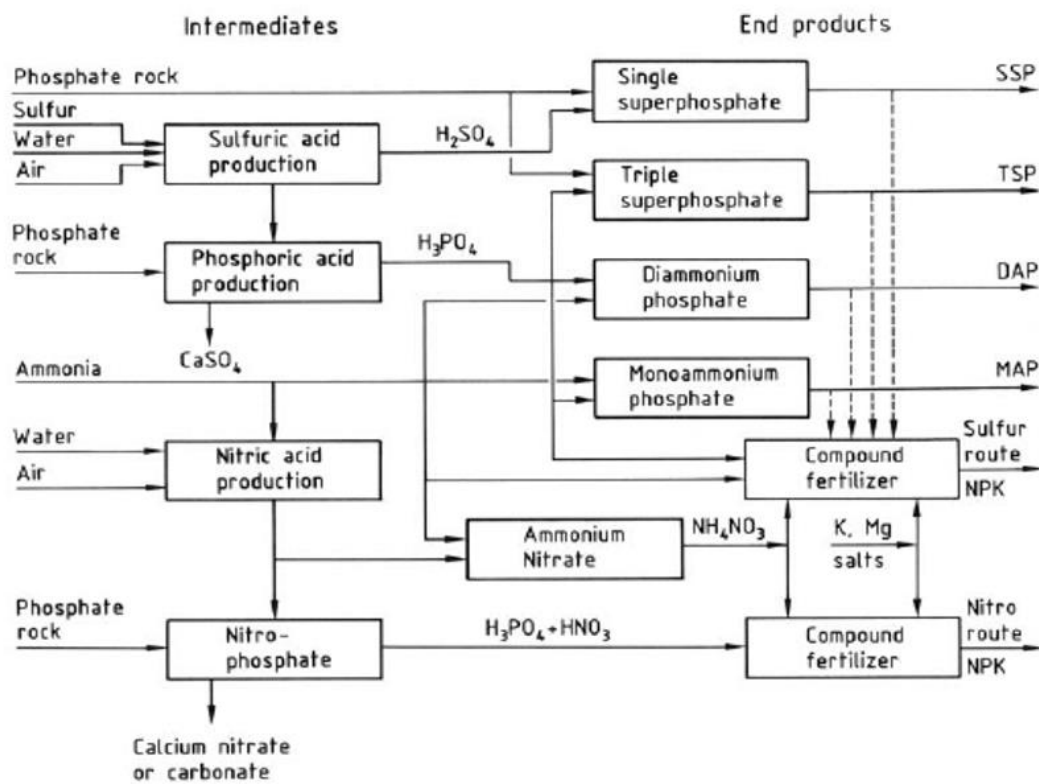
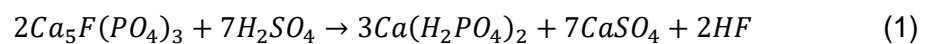


Figure 2 Fertilizer production from phosphorus rock by wet processing. (Kongshaug, Brentnall et al. 2000)

One of the original routes was to produce single superphosphate (SSP), which is a mixture of monocalcium phosphate (MCP) and gypsum ( $\text{CaSO}_4$ ). It is produced by leaching phosphorus rock with sulfuric acid (Eq. 1). Hydrogen fluoride HF is also formed. Gypsum is a byproduct and, if it is not separated from the fertilizer, it will remain as an inert solid. Hydrogen fluoride is usually used for the production of fluosilicic acid. (Kongshaug, Brentnall et al. 2000, Taylor 2000)



Triple superphosphate (TSP) is produced in a similar way as SSP, but leaching is done with phosphoric acid (Eq. 2). Phosphoric acid is first produced by the wet process route, where phosphate rock is leached with sulfuric acid. By using phosphoric acid to produce MCP no gypsum is formed and the only byproduct is hydrogen fluoride. (Kongshaug, Brentnall et al. 2000, Taylor 2000)



During the wet process dicalcium phosphates (DCP) can be formed (Eq. 3), when the phosphoric acid concentration is limited. The difference between MCP and DCP is that the anion  $H_2PO_4^-$  in MCP has formed with removal of one proton from phosphoric acid, whereas in the case of DCP two protons are removed from phosphoric acid to form  $HPO_4^{2-}$ . This is also the reason why DCP has the di- prefix. The difference between fertilizer properties of MCP and DCP is that MCP is water soluble and DCP is only citrate soluble. (Gard 2000, Kongshaug, Brentnall et al. 2000)



Other common fertilizers are the ammonium phosphates, which are produced by ammonia reacting with phosphoric acid (Eq. 4). This reaction is highly exothermic and the reaction heat is utilized to evaporate the water from the solution. Monoammonium phosphates (MAP) are used as fertilizers, but they are also blended or mixed with other fertilizers to produce compound fertilizers. Monoammonium phosphate is highly soluble in water and the solubility increases at increasing temperature. (Kongshaug, Brentnall et al. 2000)



Production of diammonium phosphates (DAP) is similar to the MAP production process. Only the N/P ratio is higher in DAP production process thus less phosphoric acid, but more ammonia is used in the neutralization (Eq. 5). Water solubility of DAP is even higher than the solubility of MAP. (Kongshaug, Brentnall et al. 2000)



Compound fertilizers are mixtures of N, P and K. Nitrogen and potassium are also essential nutrients and by producing mixtures of them, farmers do not need to apply several different

fertilizers. In the production of compound fertilizers, the single fertilizers are granulated and blended together and they do not react with each other. To produce complex fertilizers one way is to treat MCP with ammonia to form DCP and MAP (Eq. 6). Other common ways are the addition of ammonium nitrate  $NH_4NO_3$  or potassium chloride KCl (Eq. 7 and 8). (Kongshaug, Brentnall et al. 2000)



Main components of the commercial fertilizers are presented in Table 3.

Table 3 Main components of commercial phosphorus fertilizers. (Kongshaug, Brentnall et al. 2000)

Chemical composition	Type of fertilizer					
	Single super-phosphate (SSP) <sup>a</sup>	Triple super-phosphate (TSP) <sup>a</sup>	MAP	DAP	S-route NPK <sup>b</sup>	N-route NPK <sup>c</sup>
P <sub>2</sub> O <sub>5</sub> <sup>e</sup> , wt %	21	48	53	46	15	12
P <sub>2</sub> O <sub>5</sub> , % (min.-max.)	18–22	46–50	48–61	46–53	5–30	5–23
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> , MAP, P:P <sup>f</sup> (total)	0	0	0.80–0.89	0.01	0–0.89	0.74
(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> , DAP, P:P (total)	0	0	0.05	0.84–0.93	0–0.93	0.01
Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> , MCP, P:P (total)	0.81–0.91	0.81–0.91	0	0	0–0.71	0
CaHPO <sub>4</sub> , DCP, P:P (total)	0	0	0.01	0.01	0–0.2	0.2
Fluorapatite, P:P (total)	0.04	0.04	0	0	0–0.04	0
Calcium silicophosphate, P:P (total)	0	0	0	0	0	0
Metal phosphates (mainly Al, Fe, Mg), P:P (total)	0.05–0.15	0.05–0.15	0.05–0.2	0.05–0.2	0.05–0.2	0.05
CaO, wt %	32	22	0.7	0.7	0.7–15	1.5–7
CaO:P <sub>2</sub> O <sub>5</sub> , weight ratio	1.52	0.46	0.01	0.01	0.01–0.5	0.3
N, wt %	0	0	10–12	16–21	0–30	12–30
NO <sub>3</sub> :NH <sub>4</sub> , molar ratio			0	0	0–0.9	0.7–0.9
K <sub>2</sub> O, wt %	0–30	0–30	0	0	0–21	0–21

## 2.2. Manure

In this study the focus is on the phosphorus recovery from animal manure. A lot of animal feed (containing phosphorus) is imported and animal manure production has been increasing over the years in the Netherlands. Manure contains nutrients and due to the application of manure on fields, agricultural soil has been enriched with nutrients. Eutrophication of lakes has become an issue due to the nutrients ending up in the surface and ground waters. Therefore the policy on direct manure use has become stricter, which has decreased the application room for manure. This has led to a situation, where there is

a surplus of manure in the Netherlands. Besides nutrients manure also consists of organics, which can be used for energy production. (Schröder, Cordell et al. 2010, d. Ridder, d. Jong et al. 2012)

### 2.2.1. Manure and phosphorus production

In the Netherlands the greatest animal manure feedstocks for phosphorus production are cattle, pig and poultry. This can be seen in Figure 3, where the phosphorus production from the various animals and the phosphorus limit are presented. (Statistiek 2016) Phosphorus limit is determined by the European Sustainable Phosphorus Platform (ESPP), where they aim to optimize the phosphorus cycle. If the phosphorus production is below the platform, the nutrient cycle can be closed in the Netherlands. Based on the limits required amount for recovery of nutrients can be estimated. Recovered nutrients can be then exported outside the Netherlands to decrease the nutrient surplus. (ESPP 2011)

It can be seen that the platform was crossed in 2010, but during the following years the phosphorus production was within limits. However, since 2012 the phosphorus production from animal manure has been increasing and in 2015 the platform has been crossed again by 7.1 million kg. Main increase has been for the cattle manure, but also amounts of pig and poultry manures have been increasing. (Statistiek 2016)

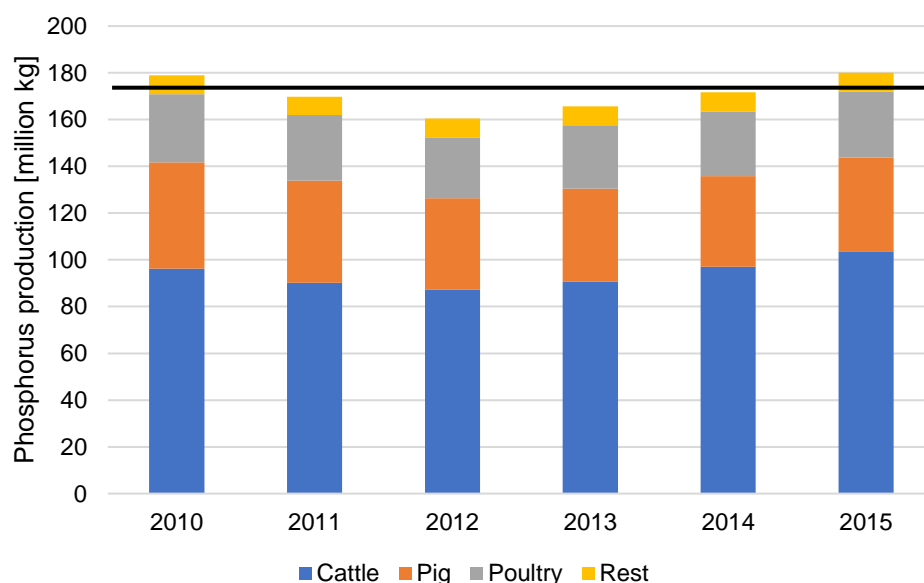


Figure 3 Phosphorus production from animal manure in the Netherlands during the years 2010 – 2015 and the phosphorus limit at 172.9 million kg. (Statistiek 2016)



Manure production, nitrogen and phosphorus production and use via manure treatment are shown in Table 4 in more detail for the overall manure production. As it was seen in Figure 3 the manure production has been increasing during the recent years. Due to the increased manure production, also the amount of nutrients from animal excretion has been increasing recently. On the other hand, use of animal manure as a fertilizer has been decreasing due to the stricter legislation. Exporting of phosphorus is currently not in balance with the increasing amount of phosphorus produced. (Statistiek 2017)

*Table 4 Manure, phosphorus and nitrogen production, discharge, export and use from animals in the Netherlands. (Statistiek 2017)*

	1950	1960	1970	1980	1990	2000	2002	2013	2014	2015
	[1000 ton]									
<b>Manure production</b>	49019	60696	68192	85634	87445	75560	71529	73155	74089	76326
<b>Nitrogen (N) secretion</b>	-	-	-	565,1	691,2	549,1	504,4	472,7	486,7	497,5
<b>Phosphate (P<sub>2</sub>O<sub>5</sub>) secretion</b>	117,1	143,4	181,3	231,6	229,1	190,9	172,9	165,6	171,7	180,1
<b>Manure discharged from farms</b>										
<b>Phosphate discharged</b>	-	-	-	-	-	65	63,6	81,5	82,3	-
<b>Manure taken to farms</b>										
<b>Phosphate in used manure</b>	-	-	-	-	-	47	43,2	41	37,5	-
<b>Manure processing</b>										
<b>Used phosphate</b>	-	-	-	-	-	1,8	2,5	10	9,7	-
<b>Net export of livestock manure</b>										
<b>Phosphate export</b>	-	-	-	-	3,2	13,1	16,5	26,1	27,5	-
<b>Manure placement</b>										
<b>Phosphate placement</b>	-	-	-	-	432	208	194	135	137	134
<b>Use of animal manure</b>										
<b>Phosphate to agriculture</b>	-	-	-	-	-	173	153	125	127	-

There are some differences in animal livestock numbers between the provinces in the Netherlands, which is shown in Table 5. The greatest number of animals is in the Eastern and Southern part of the Netherlands. Cattle is found more both in the South and in the Eastern part of the Netherlands (Overijssel, Gelderland and Noord-Brabant) and pigs in the Southern part (Noord-Brabant). Poultry manure is also from the same areas, but the amount of manure produced is less compared to pig and cattle. (Lesschen, v.d. Kolk et al. 2013)

Table 5 Animal livestock x 1000 in different provinces in the Netherlands. (Lesschen, v.d. Kolk et al. 2013)

Province	Dairy cattle*	Beef cattle	Beef calves	Pigs	Poultry	Other animals
Groningen	166	11	19	111	5392	61
Friesland	486	19	38	56	8785	153
Drenthe	175	18	29	164	6437	54
Overijssel	446	53	137	966	10460	111
Flevoland	51	2	10	41	2284	18
Gelderland	431	75	405	1313	18620	314
Utrecht	147	16	42	187	1944	60
Noord-Holland	140	17	2	12	1061	114
Zuid-Holland	166	20	6	88	698	112
Zeeland	33	15	3	48	1819	58
Noord-Brabant	404	67	189	3175	27296	652
Limburg	92	31	21	991	16446	205
Total	2738	344	901	7153	101241	1912

\* Incl. young cattle

### 2.2.2. Composition

Manure contains nutrients, which are valuable for plants. Although the over enrichment of soil with nutrients is not desired. Depending on the type of the animal, different manures have varying contents of nutrients and metals. Pig and broiler manures have the highest contents of phosphates, which can be seen in Table 6. Total nitrogen content is relatively high in manure, which also makes it a valuable nutrient to be recovered. Depending on the end use of the recovered nutrients potassium can be found also in relatively high concentrations in manure. (Ylivainio K. 2013)

Table 6 Mean nutrient content in cattle, pig and broiler manures. (Ylivainio K. 2013)

Animal type	Manure	DM (%)	Content [g/kg DM]						
			P	K	Ca	Mg	S	Cu	Zn
<b>Cattle</b>	slurry	5 - 10	8	59	17	7	0,6	0,05	0,23
<b>Pig</b>	slurry	5 - 10	24	63	33	12	0,8	0,23	0,86
<b>Cattle</b>	solid	25	9	26	22	7	0,5	0,03	0,14
<b>Pig</b>	solid	25	28	46	39	15	0,6	0,21	0,49
<b>Broiler</b>	solid	45	47	26	24	7	0,6	0,11	0,38

Depending on the animal the phosphorus is found mostly in inorganic form in manure. Pig and poultry manures have the highest inorganic contents of phosphorus and in the solid pig manure 25 – 67 % of the total phosphorus is water soluble. Only 15 – 42 % of the total phosphorus in solid cattle manure is water soluble. (Schick, Haneklaus et al. 2013) The rest of the phosphorus in manure is in nucleic acids, phytic acids and a small amount is in lipids. In fertilizers, the solubility of P is given as water soluble, citrate soluble and citrate insoluble phosphorus (Kongshaug, Brentnall et al. 2000). Water soluble phosphorus has been

indicated to be in the range of 15 – 75 % for different animal manures. Phosphorus in pig slurry is almost totally citrate soluble. This means also almost all phosphorus in pig manure is plant available. (Schick, Haneklaus et al. 2013)

### 2.2.3. Treatment

There are several ways to treat manure and these are presented in Figure 4. Manure is often first digested to produce biogas from the organic matter of manure. The digestate will be then separated into solid and liquid fractions. These fractions have been mainly applied directly on the field and in this study different ways to further treat these fractions are studied. (Schoumans, Rulkens et al. 2010)

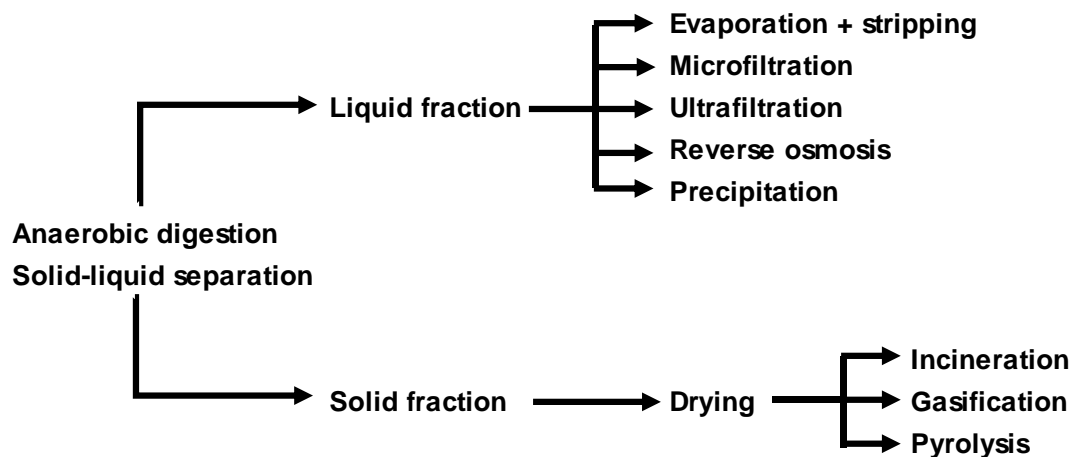


Figure 4 Possible methods to treat manure.

### **Anaerobic digestion**

Anaerobic digestion (AD) is a process, where the organic matter is broken down by anaerobic microbes producing biogas. It can be applied for wastewater, manure and food processing waste, for instance. Formed gas is a mixture of carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>), which can be further utilized for energy production. After the treatment biogas is usually taken up for the energy use and digestate will be taken for further treatment. Sludge will remain for a certain time in the AD reactor and then it will be separated. Benefits from using AD can be odor reduction, energy production and decreasing organic content in the manure. (Schoumans, Rulkens et al. 2010, Lin, Gan et al. 2015)

Biogas production during AD has relatively low CO<sub>2</sub> emissions. This is because of the released CO<sub>2</sub> is again used for the formation of organic matter by the plants. 35 – 40 % of the biogas can be converted into electrical energy. During biogas production gases, such as methane and nitrous oxide are formed, and these gases are considered as greenhouse gases. By treating manure with AD these greenhouse gases can be released and, when applied on land, the gases will not be released into the atmosphere. Manure has a strong odour, which is due to several compounds present in manure. Some of these compounds are decomposed during AD, but also new odour causing compounds are formed. It has been indicated that the odour of AD treated manure is equal to the odour of the untreated manure. Due to the faster discharge of manure fertilizer to the land the odour effect is less. The AD plant itself can still have a strong odour, which may be an issue. Phenomena and reactions during the AD are relatively complex and this can be seen in Figure 5. (Schoumans, Rulkens et al. 2010, Möller and Müller 2012)

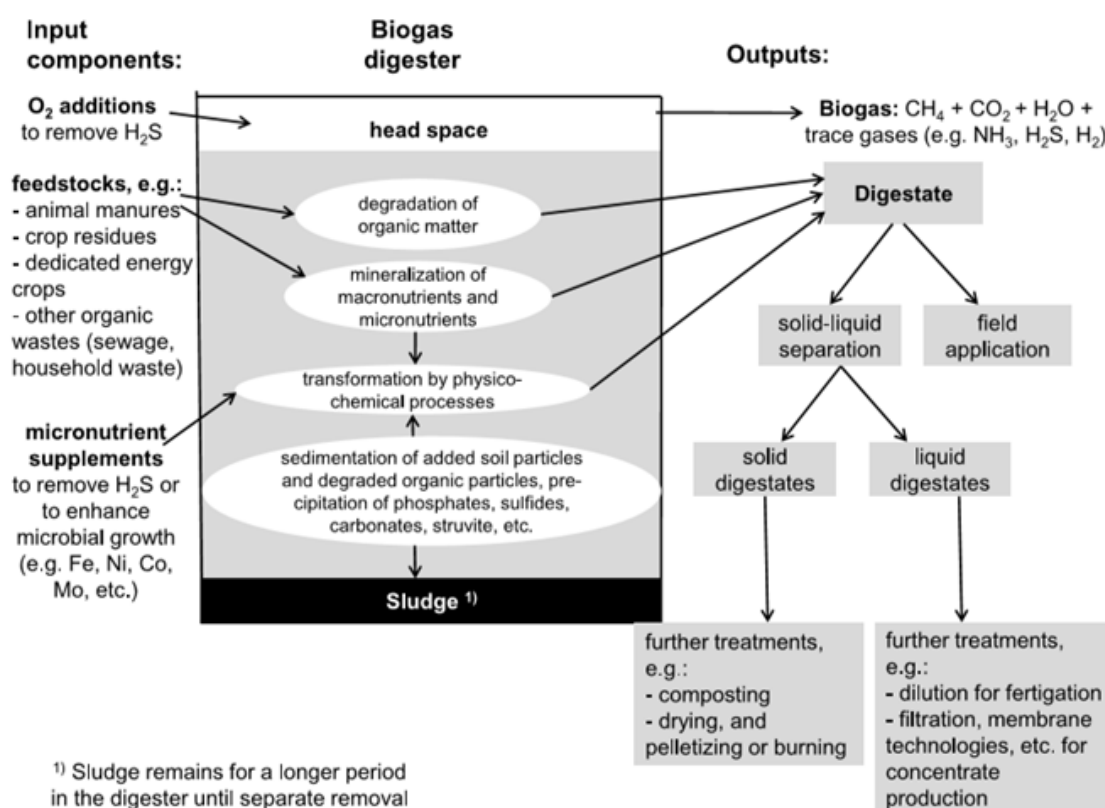


Figure 5 Possible phenomena occurring during anaerobic digestion. (Möller and Müller 2012)

Depending on the pH during the AD phosphates can precipitate and end up in the sludge, which is shown in Figure 6. If magnesium and ammonium are present in equimolar amounts with phosphates and the pH is high, they will precipitate as struvite. If calcium is present, phosphates will also precipitate. Phosphates can also react with metals such as iron and

aluminum, which will lead to a formation of insoluble compounds. Precipitation with metal ions will then also influence the phosphate plant availability. These compounds will be found in the sludge and not in the digestate. The plant availability would be expected to be enhanced after AD due to the mineralization, but it is not always the case. pH has a great effect on the products in digestate. For instance, if pH increases, chemical equilibrium from  $\text{HPO}_4^{2-}$  will shift to  $\text{PO}_4^{3-}$ . Retention of phosphates in AD is most probably due to the precipitation processes. Due to the different nutrient contents in animal manures, usually on a biogas plant manures have been mixed together with organic waste in order to reach balance. (Möller and Müller 2012)

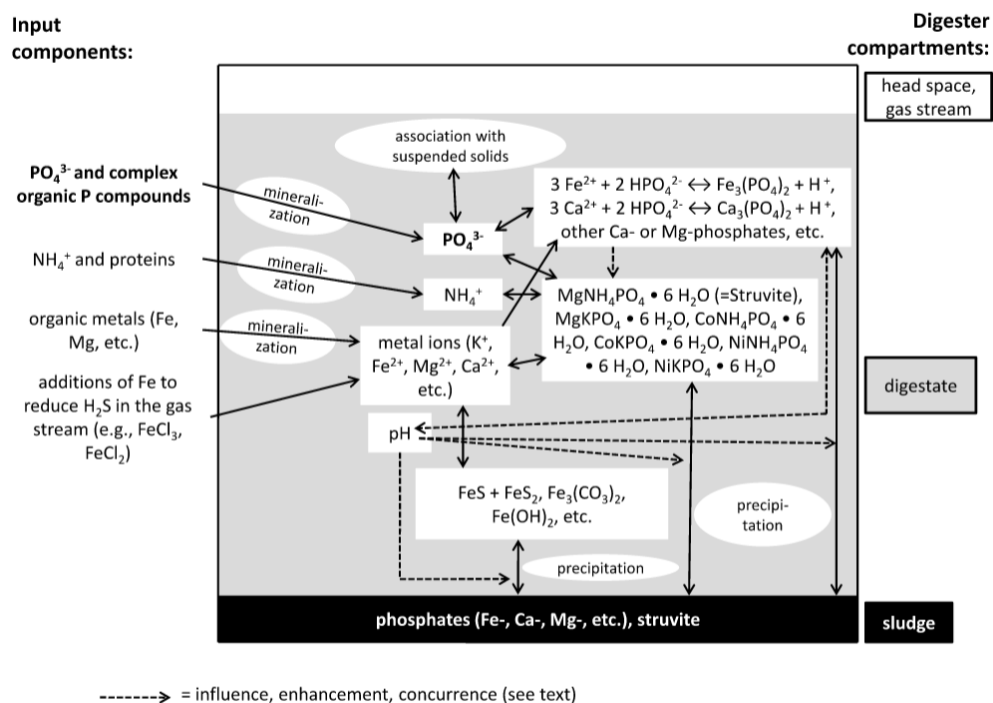


Figure 6 Possible reactions of phosphates during anaerobic digestion. (Möller and Müller 2012)

### Solid-liquid separation

After AD the digestate has a significant water content (90 %), which has to be separated in order to ease the storage, transportation and further treatment of the manure. Separation is usually done by simple solid-liquid mechanical separation such as centrifugation, sedimentation, screening or filtration. The water content in the solid fraction after the separation will be 70 %, respectively. Depending on the separation method and used flocculants or coagulants after solid-liquid separation most of the phosphates can be found in the solid fraction. When using centrifugation, 20 % of phosphates will end up into the liquid fraction. On the other hand, when using screw press, up to 30 % of phosphates can

end up into the liquid fraction. Usually centrifuge is most efficient in removing dry matter (DM), P and N. Inorganic N and both inorganic and organic K will end up in the liquid fraction, whereas remaining nutrients and metals usually end up in the solid fraction. (Hjorth, Christensen et al. 2010)

### ***Drying***

Drying of the solid manure cake is necessary due to the remaining water content (approximately 70%) in the cake. By removing water from solid manure storage, transportation and further treatment will become easier. Simple drying can be applied, for instance, by blowing air on the cake. With direct or indirect driers, the remaining water will be evaporated. Drum dryer is a direct dryer, whereas belt dryers and fluidized bed dryers are convective dryers where the solid fraction is in direct contact with the hot gas. Drum dryers, paddle dryers and fluidized bed dryers can be equipped with an internal heat exchanger, which makes them indirect dryers. In this way, the heating gas will not need additional purification. More advanced driers are also available, but they are usually more complex and expensive. (Schoumans, Rulkens et al. 2010)

Phosphates remain in the solids after drying. The gas phase leaving the drier contains air, water vapor, ammonia, some organic pollutants and dust particles. Manure pellets can be produced for fertilizer use after drying the wet manure cake. Usually solid manure is dried from 70 % moisture content to 40 % or 10 % moisture content depending on the further use or treatment. If the manure will be combusted, 90 % DM content is preferred to decrease energy consumption for evaporation during combustion. (Schoumans, Rulkens et al. 2010)

Energy consumption of drying greatly depends on the technology used. This is shown in Table 7 for several different dryer types, which can be used to dry the solid fraction of manure. The thermal and electrical energy consumption for direct and indirect drying are shown in Table 8.

Table 7 Energy consumption of the different dryer types for drying of the manure solid fraction. (Lemmens B. 2007)

Dryer type	Energy source	Electrical energy [kJ/kg <sub>water</sub> ]	Dry matter content of the input [%]	Total energy consumption [kJ/kg <sub>water</sub> ]
Pipe bundle	Steam	35	> 65	4100
Disk dryer	Steam	35	30	3850
Paddle dryer	Steam	38	>60	5600
Drum dryer	Gas	200	50-65	4000
Fluidized bed dryer	Gas	100-200	20-50	5050-7000
Mechanical vapor compression		470		1200
Multi-stage evaporator	Steam	700-900	20	2900

Table 8 Thermal and electrical energy consumption of direct and indirect dryers for drying the solid fraction of manure. (Lemmens B. 2007)

Dryer type	Thermal energy [MJ/ton <sub>water</sub> ]	Electrical energy [kWh/ton <sub>water</sub> ]	Total energy consumption [MJ/ton <sub>water</sub> ]
Direct drying	2800-3300	25-100	3025-4200
Indirect drying	3250	60	3790

### **Combustion processes of dried solid pig manure**

The dried solid pig manure can be further treated by incineration, pyrolysis or gasification. All of them are done at high temperatures to decompose the organic matter in the solids. In incineration, organic matter will be combusted entirely in the presence of oxygen. After incineration of manure cake the phosphates will be found in the formed ashes. Other inorganics will be also found in the ashes. Phosphorus is not in a plant available form in the ashes thus ashes should be further treated. Exhaust gases from the incineration of manure can be utilized for energy use in the manure treatment for example in drying, which has a high heating duty. (Schoumans, Rulkens et al. 2010)

In pyrolysis, the dried manure cake is heated up to 300 – 550 C in the absence of oxygen. At these conditions the solids will be thermally cracked to vapors, which are condensed to obtain oil. The end products from pyrolysis are char, pyrolysis oil and gases. Most of the carbon (60 – 70 %) is obtained in the char together with the phosphates. In addition, most of the heavy metals will also end up in the char. Organic acids and aromatics will end up in the pyrolysis oil. Gas phase can contain several components, such as, water vapor, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub> and CO. The produced gases can be used for energy production. Composition of the gas phase depends on the initial composition of manure cake, but also on the pyrolysis

temperature and duration. It has been determined that application of phosphate rich char on soil increases the phosphate availability, but the drawback is possible negative effect on the roots. (Schoumans, Rulkens et al. 2010) This means char should be also further treated in order to produce more plant available phosphates (Azuara, Kersten et al. 2013). Gasification is done in higher temperatures than pyrolysis, but also in the absence of oxygen. More carbon is degraded than in pyrolysis, but the compositions of the formed char and gases are similar to the char and gases formed in pyrolysis. (Schoumans, Rulkens et al. 2010)

It has been determined that application of phosphate rich char on soil increases the phosphate availability, but the drawback is possible negative effect on the roots. (Schoumans, Rulkens et al. 2010) This means char could be also further treated in order to produce more plant available phosphates. (Azuara, Kersten et al. 2013) Gasification is done in higher temperatures than pyrolysis, but also in the absence of oxygen. More carbon is degraded than in pyrolysis, but the compositions of the formed char and gases are similar to the char and gases formed in pyrolysis. (Schoumans, Rulkens et al. 2010)

### ***Treatment of ashes***

Low metal content with Fe/P molar ratio of 0.2 in ashes is required, if incineration ashes are used as elemental phosphorus. The molar ratio is important for phosphorus to be easily separated from the ashes. In addition, copper content should be low, because if ferrophosphorus is desired, copper will have negative impact on the properties. Other metals, such as, volatile ones should be also in small amounts to prevent dust formation. If the ashes from pig manure, for instance, are compared to the phosphate rock, the ashes contain less  $P_2O_5$ , but on the other hand more metals. There are some propositions for combining sewage sludge incineration with manure cake incineration. If this was applied, the volumes could be increased. Benefit from using manure instead of sewage sludge for incineration is the lower Fe content. (Schoumans, Rulkens et al. 2010)

Ashes can be treated either by wet chemical extraction or by thermo-chemical treatment. Treatment using both of these methods has been done for sewage sludge ash and several commercial processes are available, which are shown in Table 9. (Violtje, Accoe et al. 2013) Treatment of animal manure ashes has not been done on such a large scale as the treatment of sewage sludge ashes. Chicken manure ashes are the only animal manure originated ashes, which have been treated by wet chemical extraction and by further



precipitation. Some studies also include chemical extraction of pig manure ashes, but not further recovery from leached solutions. (Kaikake, Sekito et al. 2009, Azuara, Kersten et al. 2013)

*Table 9 Available processes for recovery of phosphorus from sewage sludge. (Viooltje, Accoe et al. 2013)*

<b>Process name</b>	<b>Process type</b>	<b>Product</b>	<b>Country</b>
<b>Sephos</b>	wet chemical extraction	Aluminium phosphate	Germany
<b>Advanced Sephos</b>		Calcium phosphate	Germany
<b>PASH</b>		Calcium phosphate	Germany
<b>ECOPHOS</b>		Phosphoric acid	Belgium
<b>Leachphos</b>		Struvite or calcium phosphate	Germany
<b>RecoPhos</b>	thermo-chemical	Phosphate fertilizer	Denmark, France, Belgium, Austria, Switzerland
<b>SUSAN/ASH DEC</b>		Sodium calcium phosphate or magnesium calcium phosphate	Denmark, Finland, The Netherlands, Austria
<b>Mephrec</b>		Thomas phosphate	Germany

The principle of one of the thermo-chemical treatment methods called Mephrec is shown in Figure 7. Separated sewage sludge is first dried and then combined with the sewage sludge ashes by briquetting. Then the briquettes are combusted in a furnace, from where the gases are led to be further treated to produce heat and electricity. The different ways to treat the gas is to lead it to an Organic Rankine Cycle (ORC) process or to a municipal waste incineration plant (RDF). The gas can be also lead to a combined heat and power plant (CHP) to produce heat and electricity. The slag and the iron alloy, where phosphorus can be found are then separated by phase separation. Product of this process is silica phosphate, which is also known as Thomas phosphate. (P-REX 2015)

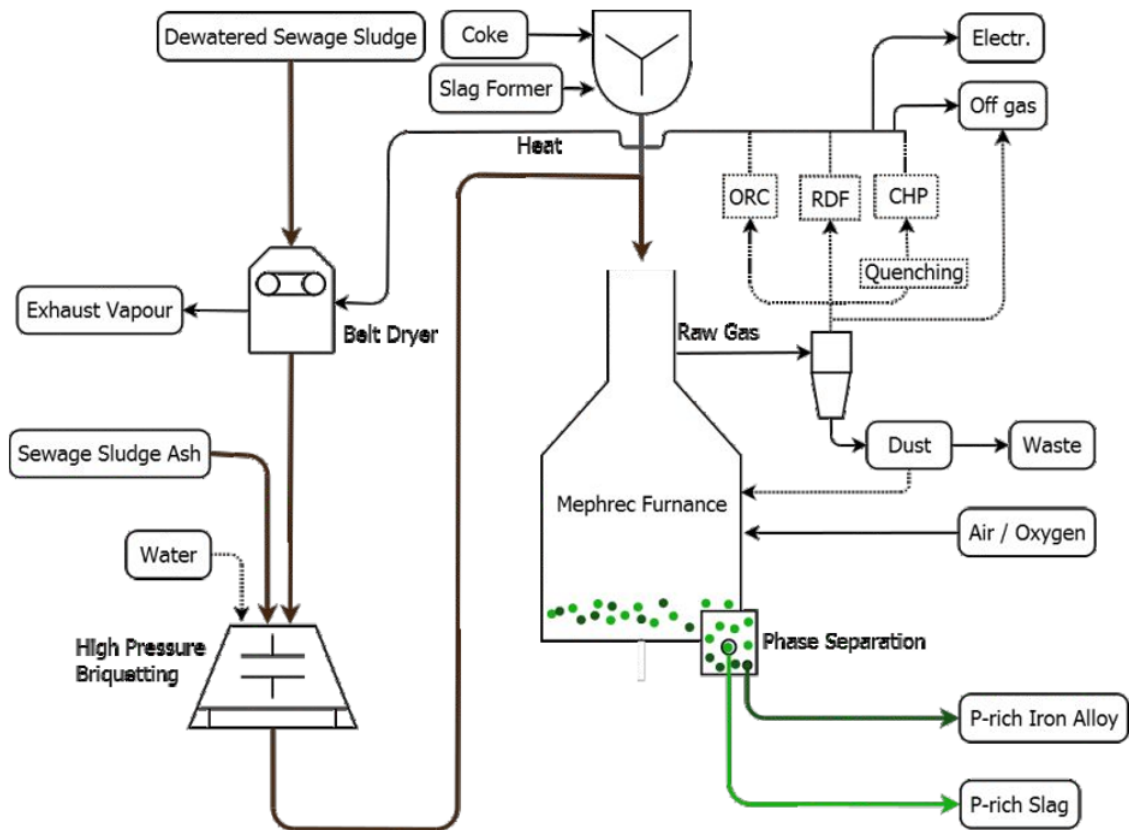
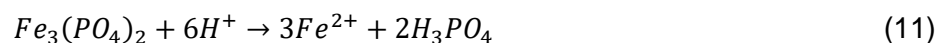
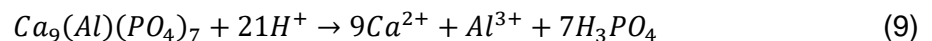


Figure 7 MEPHREC thermo-chemical treatment of sewage sludge and sewage sludge ash. (P-REX 2015)

Principle of the wet chemical extraction is shown in Figure 8. First the ash is leached with sulfuric acid followed by a filtration unit, where the solid residual from the leaching is separated for further treatment. The aqueous phase is then pumped into a precipitation unit, where phosphates are precipitated as calcium phosphates by the addition of lime slurry. pH adjustments are done by addition of sodium hydroxide (NaOH). Because the sewage sludge ash contains more heavy metals, these heavy metals need separate treatment units, which are both seen in the MEPHREC and in the LEACHPHOS process. (P-REX 2015)

Possible reactions occurring during the acid leaching of sewage sludge ashes are shown in the following equations (Eq. 9 – Eq. 12). When the pH is below 2, nearly all of the phosphates are leached into the aqueous solution as phosphoric acid. Metal ions, such as, Ca, Fe and Al will precipitate and can be separated together with the solid residual. Some of them can be still leached and found in the aqueous solution depending on the concentrations. (Petzet, Peplinski et al. 2012)



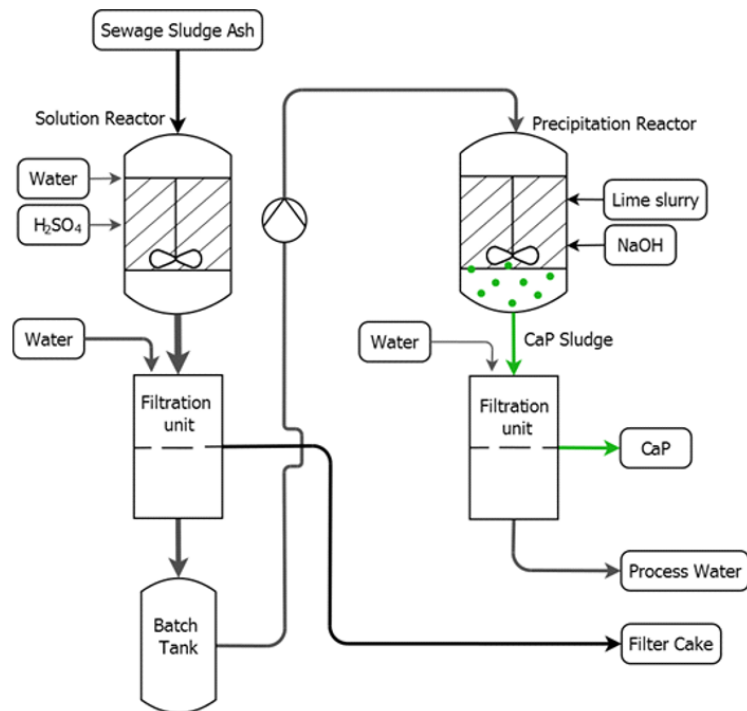


Figure 8 LEACHPHOS process for sewage sludge ash. (P-REX 2015)

After phosphates have been leached into the solution, they can be precipitated from the aqueous solution. Precipitation of phosphates is pH, Ca/P ratio and temperature dependent. Temperature dependency of calcium phosphate precipitation is shown in Figure 9. Dicalcium phosphates (DPC) are formed with smaller amounts of  $P_2O_5$  at lower temperatures whereas hydroxyapatite (HAP) is formed at higher temperatures and lower amounts of  $P_2O_5$ . The lines with percentage values represent the required minimum amount of CaO in the liquid, which is required for the different calcium phosphate forms to precipitate. Monocalcium phosphates (MCP) are only formed at higher amounts of  $P_2O_5$ . (Kongshaug, Brentnall et al. 2000)

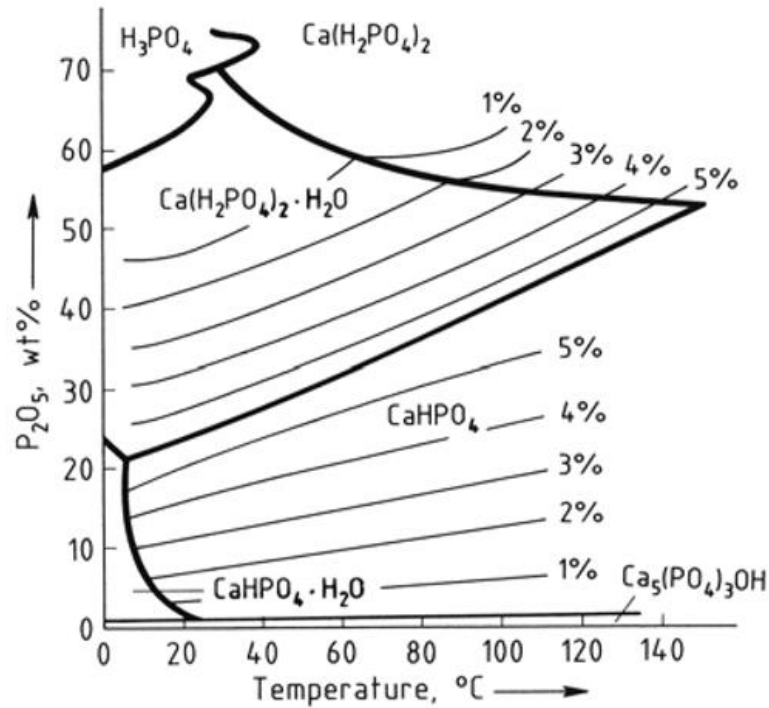
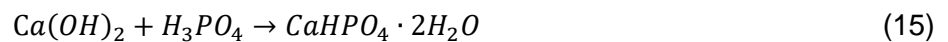
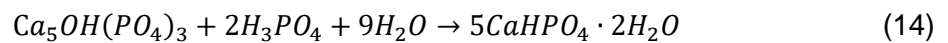
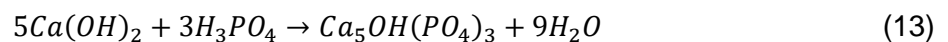


Figure 9 Phase diagram for different calcium phosphate formation with different amounts of  $P_2O_5$  at different temperatures. The lines represent the minimum amount of calcium oxide (CaO) in the liquid, which is required for precipitation of a certain calcium phosphate. (Kongshaug, Brentnall et al. 2000)

When lime is reacted with phosphoric acid in the aqueous solution, dicalcium dihydrate (DCPD) and HAP are formed. This is shown in the reactions below (Eq. 13 – Eq. 15). First HAP is formed, when phosphoric acid is neutralized with lime (Eq. 13). When calcium hydroxide dissolves more, HAP further reacts together with phosphoric acid to form DCPD (Eq. 14). The overall reaction to DCPD is shown in Eq. 15. (Ferreira, Oliveira et al. 2003)



The formation of the different calcium phosphate is also depending on the pH. The equilibria of phosphoric acid at different pH values is shown in Figure 10. Phosphoric acid is the main compound at pH below 2. (Kongshaug, Brentnall et al. 2000) For instance, hydroxyapatite, which has the  $PO_4^{3-}$  anion, is formed at higher pH range of 7 and above and DPCD, which has the  $HPO_4^{2-}$  anion, is formed at pH between 5-6. (Ferreira, Oliveira et al. 2003)

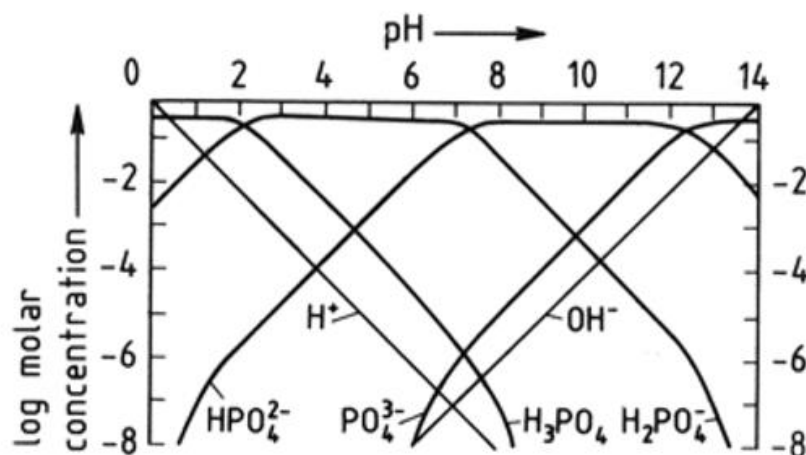


Figure 10 Phosphoric acid equilibria at different pH values. (Kongshaug, Brentnall et al. 2000)

Kaikake et al. have studied a similar process as LEACHPHOS to recover phosphates from chicken manure incineration ashes. Method with acid dissolution – alkali precipitation was used to recover the phosphates as DCPD. Different from LEACHPHOS they used hydrochloric acid to leach the phosphates and then adding only sodium hydroxide to increase the pH up to the desired value. DCPD was reported to be formed at pH of 4 whereas, at higher pH values HAP was formed. They reported high product purity, for DCPD up to 92 %. (Kaikake, Sekito et al. 2009)

Acid leaching of pig manure char has been done with using sulfuric and oxalic acid. High P yields have been reported for both acids. However, unlike the final product has been produced already from the chicken manure ashes, the recovery of phosphates from the leached solutions of pig manure ash has not yet been studied. (Azura, Kersten et al. 2013)

### ***Treatment of the liquid fraction***

Only 5 – 30 % of the initial phosphate will be found in the liquid fraction. Liquid fraction contains almost all of the ammonium, which has a great plant uptake. The liquid could be also then applied directly on land as N-K fertilizers. AD treatment prior to the separation would have a positive effect in this case, because more plant available  $\text{NH}_4^+$  would end up in the liquid fraction. Most of the metals will end up in the solid fraction together with phosphorus, which is better for the final liquid fertilizer use. However, the problem is the same as with the solid fraction, that the manure surplus has to be decreased. Applying the liquid on the fields will not decrease the surplus significantly. (Schoumans, Rulkens et al. 2010)

Several studies indicate that it is possible to recover the phosphates by precipitation from the liquid fraction. Depending on, which components will be added in the liquid either calcium phosphates or struvite can be precipitated. For production of calcium phosphates, calcium hydroxide is added, and in case of struvite magnesium hydroxide is added. Struvite contains also ammonium, which will also then be recovered partly. (Doyle and Parsons 2002, Bauer, Szogi et al. 2007) If magnesium, ammonium and phosphates are present in alkaline conditions with certain ratios, they will precipitate as struvite. Struvite has been described to be a slow release fertilizer, from which most is only acid soluble. Many studies have been done on the struvite precipitation especially in wastewater, where struvite precipitation is a problem in pipes, for instance. Struvite can be sold as N-P-Mg compound fertilizer (5.7-28.9-9.9). Usually the amount of forming struvite is limited by the amount of phosphate ions. Phosphorus must be in its inorganic form in order to recover it by precipitation. If phosphorus is present mainly in phytins and lipids, an additional hydrolysis step is required. (Schoumans, Rulkens et al. 2010)

Struvite precipitation can be already occurring during the anaerobic digestion, where Mg, P and  $\text{NH}_4^+$  are already present. Suspended solid though have a negative impact on the struvite precipitation, which means S-L separation is preferred to be done prior to the precipitation. Because struvite precipitation requires alkaline conditions, base needs to be added together with the addition of Mg. If a lot of competing ions, which are not struvite ions, are present, they will inhibit the crystal growth of struvite. Competing ions can be potassium, which can replace ammonium, and cobalt or nickel, which can replace magnesium. According to earlier done experiments K-struvite will precipitate only, when ammonium content is low. Usually ammonium content in manures is relatively high, which leads to higher yield of struvite. (Schoumans, Rulkens et al. 2010, Song, Qiu et al. 2011)

Fertilizer properties of struvite differ from the commercial ones, such as TSP, DAP and MAP. Solubility of struvite increases in the presence of organic acids. This means plants, which contain organic acids, can utilize nutrients in struvite easier than other plants. Struvite is a slow release fertilizer and this has been seen, for instance, when struvite granules dissolve slower than DAP granules. If the struvite is combined with commercial fertilizer like DAP, this fertilizer will act as fast and slow releasing fertilizer. This will ensure more stable P release and overall P efficiency will be increased. (Rahman, Salleh et al. 2014, Talboys, Heppell et al. 2016)

### ***Microfiltration and ultrafiltration***

In microfiltration (MF) most of the organic matter can be recovered in the retentate. Usually MF can achieve 75 % removal efficiency. Most of the phosphorus, which has particle size between 0.45 and 10  $\mu\text{m}$  can be removed into concentrate but inorganic phosphorus will remain dissolved in water by MF. This is also the case for ultrafiltration (UF), but higher separation efficiencies can be obtained by UF. All of the organic matter can be removed and up to 87 % of total phosphorus can be removed by UF. UF and MF cannot remove dissolved components, such as, dissolved N and K. (Hjorth, Christensen et al. 2010)

### ***Reverse osmosis***

After ultrafiltration or microfiltration, the liquid still contains dissolved components. Inorganic components usually inorganic potassium and nitrogen can be removed by nanofiltration (NF) and reverse osmosis (RO). Most of the  $\text{NH}_4^+$  up to 90 % and up to 93 % of  $\text{K}^+$  can be removed by RO, but  $\text{NH}_3$  is not removed as much.  $\text{K}^+$  separation is not pH dependent but separation of  $\text{NH}_4^+$  and  $\text{NH}_3$  is highly pH dependent. Nanofiltration does not purify the water as efficiently as RO. 52 % of the  $\text{NH}_4^+$  and 78 % of the  $\text{K}^+$  can be removed by NF. All of the soluble DM can be removed in most cases with NF. NF and RO cannot be applied directly after S-L separation, because otherwise the membrane will be fouling. UF or MF has to be applied prior to the RO. After RO water can be discharged to surface and ground waters. (Hjorth, Christensen et al. 2010)

### ***Evaporation and stripping***

If evaporation is applied, it is efficient in removing water and volatile components from the liquid fraction. Ammonia will evaporate together with the water and usually the applied temperature is around 100 °C. Evaporated components will then be condensed to recover some of the used energy. Phosphates and remaining organics will be found in the concentrate from evaporation. It is possible then to strip ammonia, for instance, as ammonium sulfate and apply it for fertilizer use. (Al-Sahali and Ettouney 2007, Hoeksma, Buissonjé et al. 2014)

### ***Treatment projects in the Netherlands***

Due to the current issues with manure surplus some projects already exist. All the processes include the transportation of the manure to the treatment plants. This makes it more feasible for the treatment plant itself, but the farmers need to pay not only for manure treatment, but also for transportation, if they cannot bring the manure themselves to the treatment plant. Reason for centralized treatment can be, that the equipment, which would be placed on a farm might be too expensive to treat the relatively small amount of manure produced. In addition, it may be unfeasible to process the manure on farm, if a lot of additives are required for the treatment process. (Hoeksma, Buisonjé et al. 2014, Greencrowd 2015, TwenceB.V. 2016)

Raps-Muhle-Seligenstadt (RMS) is developing manure treatment plant, which is shown in Figure 11. 450,000 tons of pig manure together with 150,000 tons roadside grass is treated first by co-fermentation. Digestate coming from the fermentation is separated into solid and liquid fractions. They indicate that most of the N will end up in the liquid fraction whereas most of the P and K will end up in the solid fraction. They produce fertilizer pellets from the solid fraction by drying the solid with steam to reach 90 % solid content. Solid content of the manure cake after solid-liquid separation is still relatively low (30 %), which requires further water removal. N containing liquid fraction is treated with evaporation to evaporate water and ammonia. Ammonia is separated from water by distillation and then removed from the evaporated air by adding sulfuric acid to produce ammonium sulfate. Ammonium sulfate is then sold as fertilizer. The concentrate from evaporation will be added to the separated solid fraction, which was separated in the first solid-liquid separation. They are then dried together. (Hoeksma, Buisonjé et al. 2014)

Biogas produced in the anaerobic digestion is processed into green gas using membrane filtration. Methane and carbon dioxide will be separated from each other. Ammonia is removed prior to the filtration by a gas scrubber and H<sub>2</sub>S is removed using activated carbon filter. Remaining biogas will be pressed through a membrane in a high pressure. Methane will remain in the retentate and CO<sub>2</sub> will go through the membrane. Green gas is then obtained in a high pressure (40 bar) and led to the natural gas network. 90 - 95 % of the available nitrogen ends up into the water vapor from drying and evaporation. (Hoeksma, Buisonjé et al. 2014)



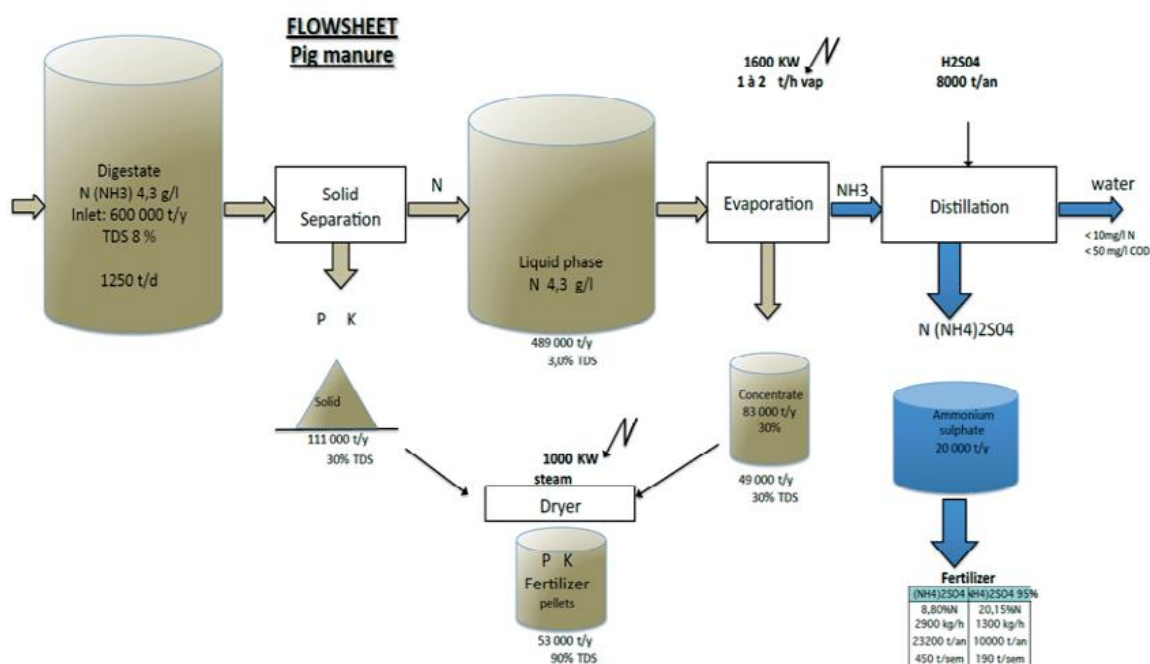


Figure 11 Process scheme for digestate treatment in RMS concept. (Hoeksma, Buissonjé et al. 2014)

In the province of Overijssel in the Netherlands a project has been started to treat manure on a centralized plant, which is shown in Figure 12. Farmers can bring their manure or the manure can be picked up for certain price to the treatment plant. Manure will be treated on the plant, where they produce fertilizers from the solid fraction, water is purified and then led to the surface waters and ammonia is utilized as a feedstock for another process. First the manure is treated in the anaerobic digester (monomest vergister), where they produce biogas, which can be further utilized for energy for local housing. Digestate is then led to flotation (flotatie scheider) from where the solid fraction is led to a belt press (zeefband pers). Solid fraction is then treated in a hygienisation process (hygienisatie). Calcium oxide or hydroxide (kalk) is added to the solid and finally a phosphate fertilizer is obtained (exportwaardige fosfaatmeststof). The separated liquid fractions are combined and purified by reverse osmosis membranes (omgekeerde osmose, membraan filters). After the membrane process evaporation is used to strip ammonia and recover potassium for fertilizer use. Water containing ammonia will be used in the waste incinerator of Twente. Separated water from the membrane process will be discharged via a control filter to the surrounding land. (TwenceB.V. 2016)





### 3. PROCESS COMPARISON

The process comparison has been made based on the found manure treatment methods from the literature. The aim is to compare different methods based on phosphorus recovery, phosphorus concentrations in the streams and energy efficiency, which is either required or produced in each method. The balances will be based on the required amount of phosphorus, which has to be removed in order to close the nutrient cycle in the Netherlands. Concentrations of the components in the process streams and the phosphorus yields in each stream have been compared to the amount of original pig manure, which needs to be treated.

#### 3.1. Theoretical considerations

##### 3.1.1. Mass balance

Table 10 shows the initial composition of pig manure, which is used in the process comparison. The calculations are based on the manure flow, which is equal to the amount of phosphate surplus above the phosphorus limit. This is presented in Table 11, where also component flows are presented based on the composition presented in Table 10. (Schoumans, Rulkens et al. 2010, Hoeksma, Buissonjé et al. 2014) Component flows are calculated as follows

$$\dot{m}_x = x \cdot \dot{m}_{tot} \cdot \frac{1 \text{ ton}}{1000 \text{ kg}} \quad (16)$$

where  $\dot{m}_x$  (ton/year) is the mass flow of a component,  $x$  (kg/ton<sub>manure</sub>) is the concentration of the component in the total flow and  $\dot{m}_{tot}$  (ton<sub>manure</sub>/year) is the total mass flow.

Table 10 Initial composition of pig manure, which is applied in the balances. (Schoumans, Rulkens et al. 2010, Hoeksma, Buissonjé et al. 2014)

Manure composition [kg/ton]							
Water	Dry matter	Inorganic matter	Organic matter	Total P	Inorganic P	Organic P	
907	93	43	50	4,6	3,2	1,4	
Total K	Total N	Oranic N	Inorganic N	Mg	Ca	Fe	Zn
5,8	7,1	4,6	2,5	1,8	4,0	0,04	0,07

Table 11 Surplus manure flow, which needs to be treated to not cross the phosphorus platform. (Schoumans, Rulkens et al. 2010, Hoeksma, Buissonjé et al. 2014)

Flow [ton/year]							
Total manure	Water	Dry matter	Inorganic matter	Organic matter	Total P	Inorganic P	Organic P
1420000	1287940	132060	71000	61060	6532	4572	1960
Total K	Total N	Oranic N	Inorganic N	Mg	Ca	Fe	Zn
8236	10082	6532	3550	2556	5680	61	99

The distribution of the components for the different processing methods is presented in Appendix I all coefficients are obtained from literature. Results are shown for each method containing stream flow, dry matter content, organic matter content, P content and finally the P yield in each stream. P yield is the yield from original P in the initial manure.

$$\eta_{P,tot} = \frac{\dot{m}_{P,out}}{\dot{m}_{P,in}} \cdot 100\% \quad (17)$$

where  $\eta_{P,tot}$  (%) is the total yield of phosphorus,  $\dot{m}_{P,out}$  (ton/year) is the outgoing phosphorus mass flow rate from the system and  $\dot{m}_{P,in}$  (ton/year) is the initial phosphorus in the manure.

These values are compared to the initial manure flow, which needs to be treated. Results for the remaining components are shown in Appendix I.

### 3.1.1. Energy balance

The energy balance is based on the energy going into the system, energy produced by CH<sub>4</sub> and energy needed by utilities. Energy input is calculated based on the organic matter content of the ingoing feed as follows

$$E_{in} = \frac{\dot{m}_{Org} H_c}{\dot{m}_{m,in}} \quad (18)$$

where  $E_{in}$  (MJ/ton<sub>manure</sub>) is the energy, which is brought into the system per ton of manure,  $\dot{m}_{Org}$  (ton<sub>Org</sub>/year) is the mass flowrate of organic matter in manure,  $H_c$  (MJ/ton<sub>Org</sub>) is the heat of combustion and  $\dot{m}_{m,in}$  (ton<sub>manure</sub>/year) is the initial manure flow into the whole system. Heat of combustion of dried manure was used as 19 MJ/kg<sub>Org</sub>. (Schoumans, Rulkens et al. 2010)

Energy consumption in anaerobic digestion is calculated by

$$E_{u,A} = \frac{\dot{m}_m C_{p,90\%} \Delta T}{\dot{m}_{m,in}} \quad (19)$$

where  $E_{u,A}$  (MJ/ton<sub>manure</sub>) is the heat required to reach 40 °C during digestion,  $\dot{m}_m$  is the mass flowrate of manure (ton/year),  $C_{p,90\%}$  (MJ/ton°C) is the specific heat capacity of manure with 90 % water content and  $\Delta T$  (°C) is the temperature change. Specific heat capacity of 4 MJ/ton°C was used for 90% water containing manure (Sutitarnnontr, Hu et al. 2014).

Energy production in anaerobic digestion is calculated based on methane formation from the organic matter

$$\dot{m}_{CH_4} = \dot{m}_{Org} x_{CH_4} \quad (20)$$

where  $\dot{m}_{CH_4}$  is (m<sup>3</sup><sub>CH<sub>4</sub></sub>/year) the mass flowrate of methane and  $x_{CH_4}$  (m<sup>3</sup><sub>CH<sub>4</sub></sub>/ton<sub>Org</sub>) is the methane yield from organic matter.

Based on the amount how much methane is formed the amount of produced energy can be calculated

$$E_{out,A} = \frac{\dot{m}_{CH_4} H_{c,CH_4} (1 - H_{L,A})}{\dot{m}_{m,in}} \quad (21)$$

where  $E_{out,A}$  (MJ/ton<sub>manure</sub>) is the heat produced in anaerobic digestion,  $H_{c,CH_4}$  (MJ/m<sup>3</sup><sub>CH<sub>4</sub></sub>) is the heat of combustion of methane and  $H_L$  is the heat loss (-). It is assumed that 40 % of the formed methane can produce electric energy and 50 % of the formed methane can produce thermal energy (Schoumans, Rulkens et al. 2010).

To calculate methane formation in anaerobic digestion following numbers were used, which are in Table 12.

Table 12 Properties of methane. (Jorgensen 2009, Haynes 2014)

	Heat of combustion $H_{c,CH_4}$ [MJ/kg]	Molecular weight $M_{CH_4}$ [kg/kmol]	Density $\rho$ [kg/m <sup>3</sup> ]	Methane yield from organic matter $x_{CH_4}$ [m <sup>3</sup> <sub>CH<sub>4</sub></sub> /ton <sub>Org</sub> ]
CH <sub>4</sub>	55,5	16,04	0,83	0,32

Energy, which is produced in combustion processes, is as following

$$E_{out,c} = \frac{\dot{m}_{org} H_c (1 - H_L)}{\dot{m}_{m,in}} \quad (22)$$

where  $E_{out,c}$  (MJ/ton<sub>manure</sub>) is the energy produced. It is assumed that 35 % of the formed energy is electric energy (Schoumans, Rulkens et al. 2010).

Energy efficiency for each process was calculated as follows

$$\eta_e = \frac{E_{out}}{E_{in}} \quad (23)$$

where  $\eta_e$  (%) is the energy efficiency,  $E_{out}$  (MJ/ton<sub>manure</sub>) is the energy, which is produced in the system and  $E_{in}$  (MJ/ton<sub>manure</sub>) is the energy, which is brought into the system.

Energy use for drying was based on energy consumption of an indirect dryer. With this assumption made the dryer consumes 180 MJ/ton<sub>water</sub> electrical energy and 3000 MJ/ton<sub>water</sub>. These numbers are based on the water, which needs to be evaporated in drying. (Lemmens B. 2007, Hoeksma, Buisonjé et al. 2014)

Energy consumptions of precipitation, reverse osmosis and ultrafiltration are taken from literature, these values are presented in Table 13.

*Table 13 Electrical energy consumption in precipitation, reverse osmosis and ultrafiltration.*

	<b>Energy use <math>E_e</math> [MJ/ton<sub>water</sub>]</b>	<b>Reference</b>
<b>Precipitation</b>	0,47	(Doyle and Parsons 2002)
<b>Reverse osmosis</b>	23,40	(Johnson, Culkin et al. 2004)
<b>Ultrafiltration</b>	0,47	(Fugère, Mameri et al. 2005)

This leads to the following calculation of energy use in drying and the treatments of liquid fractions

$$E_{u,e} = \frac{\dot{m}_{H_2O} E_e}{\dot{m}_{m,in}} \quad (24)$$

$$E_{u,th} = \frac{\dot{m}_{H_2O} E_{th}}{\dot{m}_{m,in}} \quad (25)$$

where  $E_{u,e}$  (MJ/ton<sub>manure</sub>) is the electrical energy required,  $\dot{m}_{H_2O}$  (ton/year) is the mass flow rate of water,  $E_e$  is the electrical energy needed and  $E_{th}$  (MJ/ton<sub>water</sub>) is the thermal energy needed to evaporate the water.

Usually more stages are used for evaporation to decrease the amount of energy required for evaporation, which is for water 67 kWh/ton. If single stage evaporators are used, recompressed steam is applied to decrease the energy costs. For multistage evaporators, the vapor from the first evaporator is utilized for heating in the next one. Mechanical vapor compression is relatively new evaporation technology, which uses a lot less energy than the conventional evaporator with stages. MVC alone is able to use only 40 MJ<sub>th</sub>/ton<sub>manure</sub> thermal energy. If MVC is combined with ammonia stripping, they use together 73 MJ<sub>e</sub>/ton<sub>manure</sub> electrical energy and 73 MJ<sub>th</sub>/ton<sub>manure</sub> thermal energy. These values will be used in the energy balances. (Al-Sahali and Ettouney 2007, Hoeksma, Buissonjé et al. 2014)

### 3.2. Anaerobic digestion and solid-liquid separation

The process scheme for anaerobic digestion and solid-liquid separation is shown in Figure 14 with process streams. Dry matter, organic and phosphorus contents and phosphorus yields for each stream for this process are shown in Table 14. This is the conventional process, from where the treated manure has been usually applied on the fields. This part of the process will be used as the conventional method in the final evaluation and will be compared with the examined process routes.

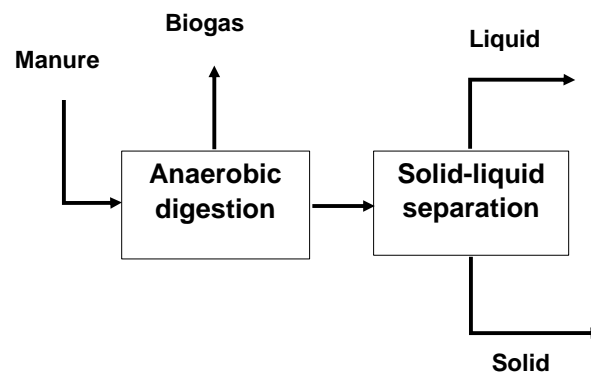


Figure 14 Process scheme of anaerobic digestion and solid-liquid separation of manure.

As indicated in the previous chapter a large part of organic matter will be degraded in anaerobic digestion. Most of phosphorus remains in the digestate and phosphorus



concentration is increased in the solid fraction of manure. In this comparison phosphorus yield has been calculated based on the use of centrifuge in solid-liquid separation, because it has the highest separation efficiency of phosphorus into the solid fraction (Hjorth, Christensen et al. 2010).

*Table 14 Dry matter, organic and phosphorus contents and phosphorus yield for streams in anaerobic digestion and solid-liquid separation pig manure.*

	Anaerobic digestion		Solid-liquid separation	
	Digestate	Biogas	Solid	Liquid
<b>Flow <math>\dot{m}</math> [kton/year]</b>	1383	37	221	1162
<b>Dry matter <math>x_{IM}</math> [kg/ ton<sub>manure</sub>]</b>	69	1000	302	25
<b>Organic matter <math>x_{OM}</math> [kg/ ton<sub>manure</sub>]</b>	18	1000	77	6
<b>P <math>x_P</math> [kg/ ton<sub>manure</sub>]</b>	5	0	24	1
<b>P yield <math>\eta_{P,tot}</math> [%]</b>	100	0	80	20

The energy consumption in the solid-liquid separation is based on average electrical energy usage based on values from literature (Ford and Fleming 2002). Results for energy balance of anaerobic digestion and solid-liquid separation are presented in Table 15. Relatively high amounts of energy can be produced by anaerobic digestion of manure, whereas the digestion itself does not consume a significant amount. Solid-liquid separation requires even less energy.

*Table 15 Energy input and production in anaerobic digestion and solid-liquid separation of pig manure.*

	Anaerobic digestion	Solid-liquid separation
<b>Energy input <math>E_{in}</math> [MJ/ton<sub>manure</sub>]</b>	817 (manure)	327 (digestate)
<b>Energy use by utilities <math>E_U</math></b>		
Thermal [MJ/ ton <sub>manure</sub> ]	38	0
Electric [MJ/ ton <sub>manure</sub> ]	12	5
<b>Energy production <math>E_{out}</math></b>		
Thermal [MJ/ ton <sub>manure</sub> ]	171 (biogas)	0
Electric [MJ/ ton <sub>manure</sub> ]	137 (biogas)	0
<b>Energy efficiency <math>\eta_e</math> [%]</b>	42 (biogas)	0

### 3.3. Solid fraction

The process scheme of treatment of the solid fraction from the solid-liquid separation is shown in Figure 15 and the results for dry matter, organic matter and phosphorus contents and phosphorus yields in drying up to 90 % dry content are shown in Table 16.

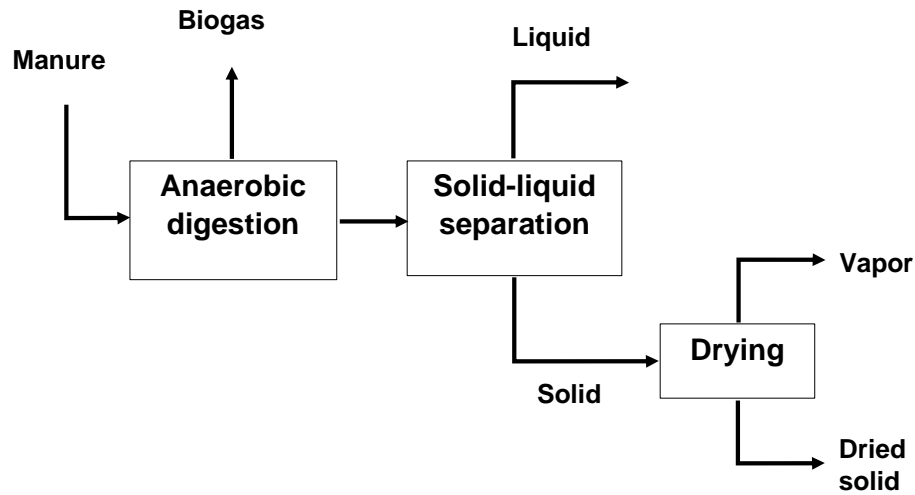


Figure 15 Process scheme for the processing of manure solid fraction with drying.

The dried solid manure can be applied on to the fields and it is more concentrated in phosphorus than the solid fraction with higher water content prior to drying. Another advantage is that dried material can be transported economically over large distance. However, the dried solid fraction contains high amount of organic matter, which can be further treated. By treating it further not only the organic matter is decomposed, but also the great volume manure can be decreased.

Table 16 Dry matter, organic and phosphorus contents and phosphorus yield for streams in drying of solid pig manure.

	Drying	
	Dried solid	Vapor
<b>Flow <math>\dot{m}</math> [kton/year]</b>	75	147
<b>Dry matter <math>x_{IM}</math> [kg/ ton<sub>manure</sub>]</b>	896	0
<b>Organic matter <math>x_{OM}</math> [kg/ ton<sub>manure</sub>]</b>	229	0
<b>P <math>x_P</math> [kg/ ton<sub>manure</sub>]</b>	70	0
<b>P yield <math>\eta_{P,tot}</math> [%]</b>	80	0

The energy required for drying and the energy produced via drying are shown in Table 17. Drying is the most energy requiring step of the process due to high amount of water, which needs to be evaporated. However, it is necessary to dry manure before the steps following drying. The organic matter can be further degraded in order to produce energy. This energy can be then recycled back for drying.

Table 17 Energy input and production for drying of the solid pig manure.

Drying	
Energy input $E_{in}$ [MJ/ton <sub>manure</sub> ]	229 (solid)
Energy use by utilities $E_U$	
Thermal [MJ/ ton <sub>manure</sub> ]	326,5
Electric [MJ/ ton <sub>manure</sub> ]	19,6
Energy production $E_{out}$	
Thermal [MJ/ ton <sub>manure</sub> ]	0,0
Electric [MJ/ ton <sub>manure</sub> ]	0,0
Energy efficiency $\eta_e$ [%]	0

The process schemes for pyrolysis, gasification and incineration of the dried solids are presented in Figure 16, Figure 17 and Figure 18. The dry matter, organic matter and phosphorus contents and the phosphorus yields are found in Table 18.

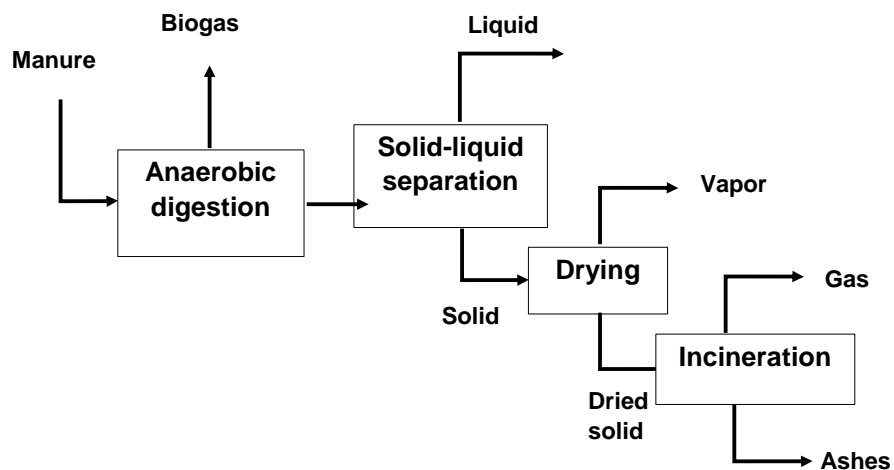


Figure 16 Process scheme for pig manure treatment with incineration.

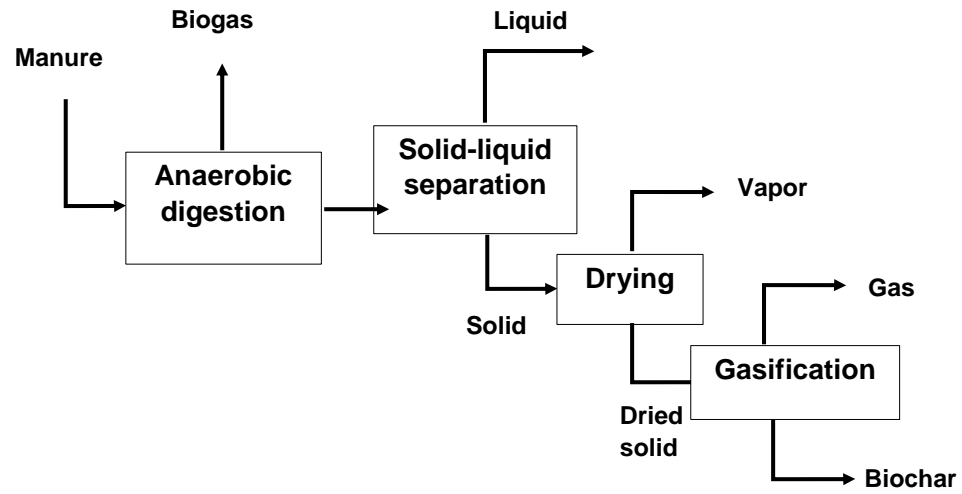


Figure 17 Process scheme for pig manure treatment with gasification.

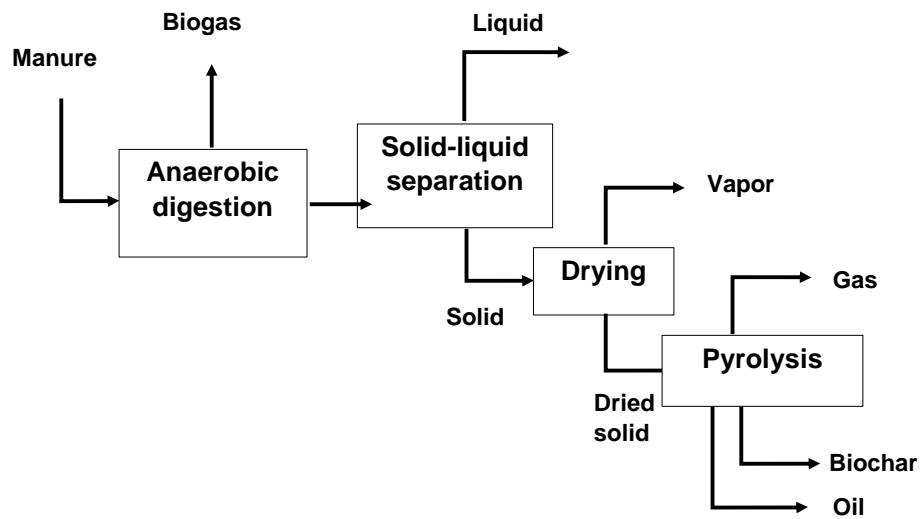


Figure 18 Process scheme for pig manure treatment with pyrolysis.

The highest phosphorus yield and concentration of phosphorus is in the ash stream from incineration of the dried solid manure. Although, the differences in yield are quite comparable. In pyrolysis and gasification, more phosphorus is lost to other outgoing streams, such as, gases and pyrolysis oil.

Table 18 Dry matter, organic and phosphorus contents and phosphorus yield for streams in incineration, combustion and pyrolysis of pig manure.

	Incineration		Gasification		Pyrolysis		
	Ash	Gas	Biochar	Gas	Biochar	Oil	Gas
<b>Flow <math>\dot{m}</math> [kton/year]</b>	50	25	53	21	56	13	6
<b>Dry matter <math>x_{DM}</math> [kg/ ton<sub>manure</sub>]</b>	1000	689	1000	639	1000	399	1000
<b>Organic matter <math>x_{OM}</math> [kg/ ton<sub>manure</sub>]</b>	0	689	64	639	108	399	1000
<b>P <math>x_P</math> [kg/ ton<sub>manure</sub>]</b>	104	2	95	7	89	20	0
<b>P yield <math>\eta_{P,tot}</math> [%]</b>	79	1	78	2	76	4	0

Incineration produces most of the heat, because all of the organic matter is converted into gas, which is shown in Table 19. Pyrolysis oil can be valuable, however, the biochar contains still organic matter due to the partial combustion. Incineration energy can cover the required amount of energy in drying. In this way the energy costs can be decreased and on the other hand surplus is decreased.

Table 19 Energy input and production in incineration, gasification and pyrolysis of dried solid pig manure.

	Incineration	Gasification	Pyrolysis
<b>Energy input <math>E_{in}</math> [MJ/ton<sub>manure</sub>]</b>	229 (dried solid)	229 (dried solid)	229 (dried solid)
<b>Energy use by utilities <math>E_U</math></b>			
Thermal [MJ/ ton <sub>manure</sub> ]	0	47	47
Electric [MJ/ ton <sub>manure</sub> ]	0	0	0
<b>Energy production <math>E_{out}</math></b>			
Thermal [MJ/ ton <sub>manure</sub> ]	229 (gas)	183 (gas)	175 (gas)
Electric [MJ/ ton <sub>manure</sub> ]	0	0	0
<b>Energy efficiency <math>\eta_e</math> [%]</b>	100,0	79,9	76,4

Based on the comparison of the methods for the solid fraction of pig manure the best way is to dry and then incinerate the solid fraction. The product stream ash is most concentrated in phosphorus and the energy from incineration can be recycled for drying. Also, the highest yield of phosphorus is in the ash stream, 79,2 %. Although, the ash itself as indicated in the previous chapter is still not applicable as fertilizer. The ash will be treated by wet chemical extraction combined with precipitation as discussed in the process for LEACHPHOS treatment of sewage sludge ashes. By applying this process route the phosphorus can be recovered as a concentrated phosphate fertilizer.

### 3.4. Liquid fraction

The process schemes for the different manure liquid fraction treatments evaporation, reverse osmosis and ultrafiltration are shown in Figure 19, Figure 20 and Figure 21. Calculations were also done for precipitation, which is shown in Appendix I. Precipitation only removes specific inorganics and the liquid fraction must still be treated after precipitation. This led to the comparison of only the presented 3 methods. Microfiltration and nanofiltration were also introduced in the previous chapter, but because more literature was found for already applied ultrafiltration and reverse osmosis treatments of manure, only they were considered.

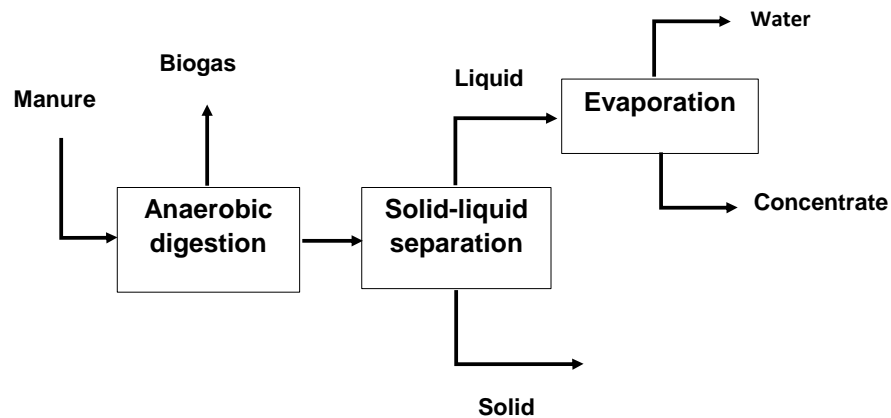


Figure 19 Process scheme for pig manure liquid fraction treatment with evaporation

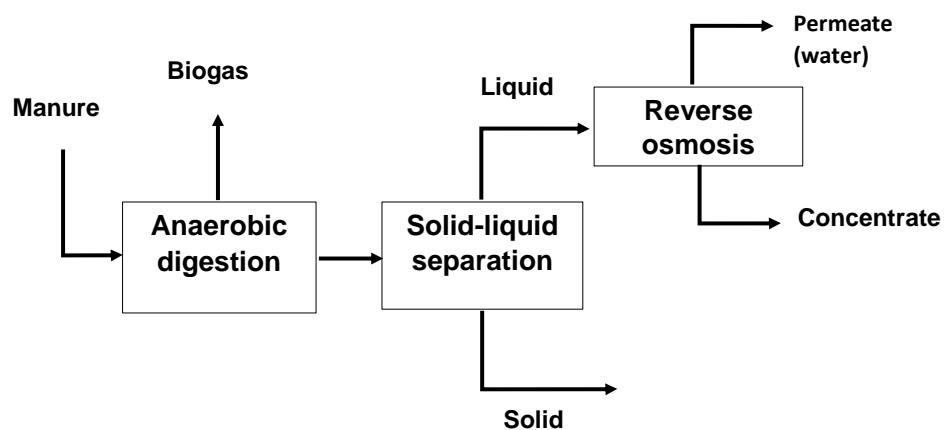


Figure 20 Process scheme for pig manure liquid fraction treatment with reverse osmosis.

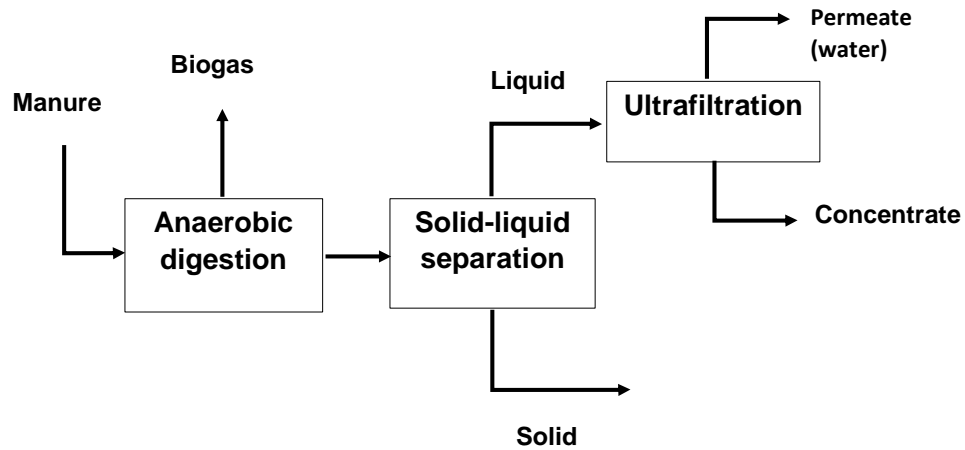


Figure 21 Process scheme for pig manure liquid fraction treatment with ultrafiltration.

Table 20 presents the dry matter, organic matter and phosphorus contents and phosphorus yield for the different liquid fraction processing methods. As mentioned in earlier chapters most of the inorganics end up in the water stream from ultrafiltration, whereas the organic matter is found in the concentrate. Based on this ultrafiltration is not yet efficient enough to treat the liquid fraction and it should be combined with other methods. Evaporation and reverse osmosis are efficient in purifying the water stream. As indicated before the feed to reverse osmosis should be treated before to avoid fouling.

Table 20 Dry matter, organic and phosphorus contents and phosphorus yield for streams in evaporation, reverse osmosis and ultrafiltration of liquid fraction from pig manure.

	Evaporation		Reverse osmosis		Ultrafiltration	
	Concentrate	Water	Concentrate	Water	Concentr.	Water
Flow $\dot{m}$ [kton/year]	106	1058	140	1022	68	1094
Dry matter $x_{IM}$ [kg/ton <sub>manure</sub> ]	250	2	189	2	170	16
Organic matter $x_{OM}$ [kg/ton <sub>manure</sub> ]	69	0	51	0	107	0
P $x_P$ [kg/ton <sub>manure</sub> ]	12	0	9	0	5	1
P yield $\eta_{P,tot}$ [%]	0	0	0	0	0	0

The energy use in each liquid treatment method has been based on literature. To evaporate all the water a great amount of energy is needed. For this reason, mechanical vapor compression (MVC) is considered. MVC is relatively new technology with reduced energy consumption. It can be seen from the Table 21 that still large amount of energy is required for evaporation even, when energy consumption for a MVC is considered as the evaporation method. Required amount of energy for reverse osmosis is depending on the pressure

applied in the process. Based on energy consumption and phosphorus yields most suitable option for treating the liquid fraction is reverse osmosis.

*Table 21 Energy input and production for evaporation, reverse osmosis and ultrafiltration of the liquid fraction from pig manure.*

	Evaporation	Reverse osmosis	Ultrafiltration
<b>Energy input <math>E_{in}</math> [MJ/ton<sub>manure</sub>]</b>	98 (liquid)	98 (liquid)	98 (liquid)
<b>Energy use by utilities <math>E_U</math></b>			
Thermal [MJ/ton]	73,6	0,0	0,0
Electric [MJ/ton]	73,6	19,1	0,5
<b>Energy production <math>E_{out}</math></b>			
Thermal [MJ/ton]	0,0	0,0	0,0
Electric [MJ/ton]	0,0	0,0	0,0
<b>Energy efficiency <math>\eta_e</math> [%]</b>	0,0	0,0	0,0

### 3.5. Overall process route

The results from the comparison of different manure treatment methods led to the application of following process route, which is presented in Figure 22. After the conventional process the solid fraction will be dried and then combusted. Drying is necessary prior to the combustion. The highest energy efficiency and phosphorus yield were obtained from incineration and therefore chosen. Liquid fraction will be filtrated first with ultrafiltration and then with reverse osmosis. This was based on the lower energy consumption compared to the evaporation. Retentate from ultrafiltration can be recycled to drying of the solid fraction in order to decompose as much from the initial organic matter as possible. Recycling also increases the overall phosphorus yield in the ash stream after incineration. Water coming from the reverse osmosis has relatively high purity and can be led to surface waters. The mineral concentrate from reverse osmosis, which is high in inorganic nitrogen and potassium, can be applied as a N,K fertilizer (Velthof 2015).



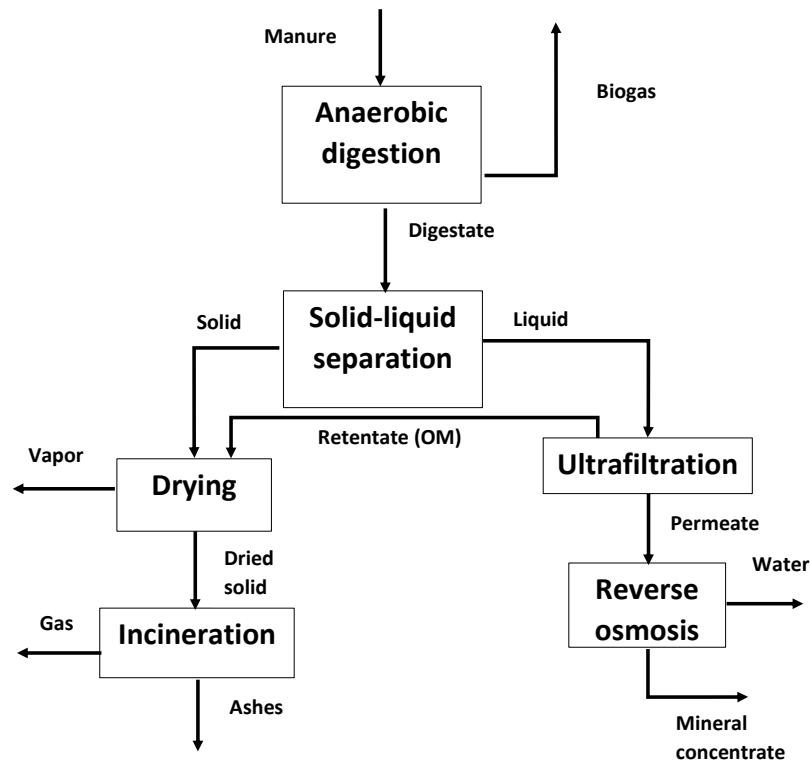


Figure 22 Process scheme for the treatment of pig manure based on the results from process comparison.

Final mass and energy balance are shown in Table 22 and Table 23. The overall energy balance shows that energy is produced in the chosen process. Also, the ash stream should contain approximately 10 wt-% of phosphorus with total phosphorus yield of 84.4 %. In total 118 MJ/ton<sub>manure</sub> of energy is produced in the proposed process. The total energy efficiency in the process is 80.5 %, which is based on the initial energy content in manure and all the energy, which is produced in the system. Yield of phosphorus in Table 22Table 22 is not 100 %, when summed up together, because phosphorus is lost in other product streams.

Table 22 Dry matter, organic and phosphorus contents and phosphorus yield in the final process for treating pig manure.

	Drying		Incineration		Ultrafiltration		Reverse osmosis	
	Dried solid	Vapor	Ash	Gas	Retent.	Permeate	Concent.	Water
<b>Flow <math>\dot{m}</math></b> <b>[ton/year]</b>	88945	200661	53960	34985	68257	1093758	123008	970750
<b>Dry matter</b> <b><math>x_{IM}</math> [kg/</b> <b>ton<sub>manure</sub>]</b>	881,3	0,0	1000	698	169,8	15,6	124,7	1,8
<b>Organic</b> <b>matter <math>x_{OM}</math></b> <b>[kg/ ton<sub>manure</sub>]</b>	274,6	0,0	0	698	107,3	0,0	0,0	0,0
<b>P <math>x_P</math> [kg/</b> <b>ton<sub>manure</sub>]</b>	62,6	0,0	102,2	1,6	5,1	0,9	7,7	0,0
<b>P yield</b> <b><math>\eta_{P,tot}</math> [%]</b>	85,3	0,0	84,4	0,9	0,1	0,1	0,1	0,0

Table 23 Overall energy balance for final process route of pig manure.

	Energy use by utilities $E_u$		Energy production $E_{out}$		Balance	
	Thermal [MJ/ton]	Electric [MJ/ton]	Thermal [MJ/ton]	Electric [MJ/ton]	Thermal [MJ/ton]	Electric [MJ/ton]
<b>Anaerobic digestion</b>	37,5	11,8	171,2	137,0	133,7	125,2
<b>Solid-liquid separation</b>	0,0	5,3	0,0	0,0	0,0	-5,3
<b>Drying</b>	446,2	19,6	0,0	0,0	-446,2	-19,6
<b>Incineration</b>	0,0	0,0	349,7	0,0	349,7	0,0
<b>Ultrafiltration</b>	0,0	0,5	0,0	0,0	0,0	-0,5
<b>Reverse osmosis</b>	0,0	19,1	0,0	0,0	0,0	-19,1
				<b>Total</b>	<b>37,2</b>	<b>80,7</b>

As mentioned before the ash stream itself cannot be applied yet as a phosphate fertilizer. Process route with leaching the ashes with acid will be applied and studied for the solid fraction of pig manure. This is presented in Figure 23. As it was indicated in the previous chapter there was no research done for the recovery of phosphates from acid leached solutions originated from the pig manure ashes. Sulfuric acid has been also applied in studies, where the pig manure ashes have been leached with sulfuric acid (Azuara, Kersten et al. 2013). Calcium hydroxide will be then used in precipitation to produce calcium phosphates, preferably DCPD, which can be then used as phosphate fertilizers or as phosphate components for fertilizers (Kongshaug, Brentnall et al. 2000, Ferreira, Oliveira et al. 2003).

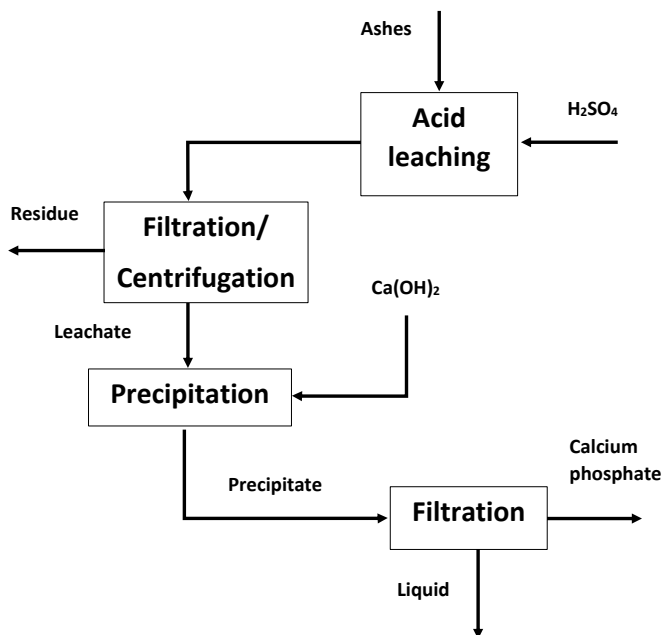


Figure 23 Treatment of ashes from the incineration of dried solid pig manure.

### 3.6. Conclusions

The process comparison was based on the phosphorus concentration in process streams, phosphorus yields and also energy balances of the different methods. The process route, which achieved the most to the goals, was the route with digesting the manure and further drying and combusting the solid manure. In this way 84.4 % of the initial phosphorus can be found in the ash stream from the combustion. Liquid fraction could be treated first by ultrafiltration followed by reverse osmosis. In total 118 MJ/ton<sub>manure</sub> of energy can be produced in the process. Based on these results experimentals will be done for the acid leaching of pig manure ashes and precipitation of phosphates from the solution as the precipitation from these solutions has not been studied yet.

## 4. EXPERIMENTS AND METHODS

Based on the proposed process route in the previous chapter an experimental plan was created. As indicated in the process comparison the final route to be followed and studied was the wet chemical extraction of manure ashes. Char from gasification would be also included to the same route. Followed by this the experimental part finally consists of treating and combusting manure, acid leaching of the manure ash and char and finally precipitation from the acid leached solution.

### 4.1. Manure

Experiments were performed with pig manure, which was separated into solid and liquid fractions by a Dutch company called Houbraken. The manure is collected from the local farms in the South of Netherlands. The collected manure is led to a flotation unit followed by a belt press, from where the liquid fraction is treated in RO and the solid manure will be applied on the fields. The permeate from RO is then taken to a local wastewater treatment plant. The process scheme is presented in Figure 24 and the mass balance for the process streams and the compositions of the streams are presented in Table 24. (Velthof 2011, Velthof 2013)

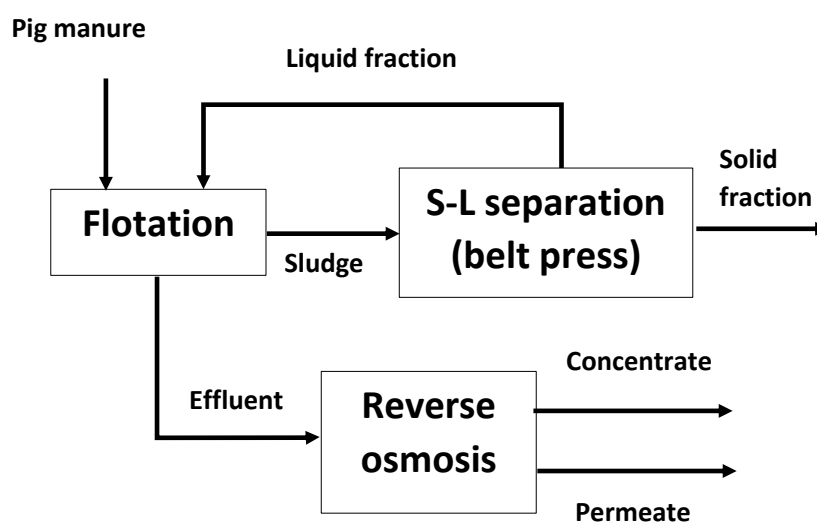


Figure 24 Manure treatment process at Houbraken.

Char was obtained also from Houbraken. Houbraken has a gasification plant for pig manure in the South of the Netherlands. Char was included into the experiments as well, starting from acid leaching of char and further treat it in the same way as the ash. In this way the

comparison could be also done including the gasification route and comparing it to the conventional and the combustion process.

*Table 24 Mass balance for the manure treatment process by Houbraken and the compositions of the streams. (Velthof 2011, Velthof 2013)*

	<b>Solid fraction</b>	<b>Effluent</b>	<b>RO concentrate</b>	<b>RO permeate</b>
<b>Fraction from original manure</b>				
<b>Total</b>	18	82	40	42
<b>Dry matter</b>	89	21	21	0
<b>Organic matter</b>	99	12	12	0
<b>Inorganic matter</b> %	-	-	-	-
<b>Total nitrogen</b>	42	55	53	2
<b>Ammonium</b>	26	73	70	3
<b>Total phosphorus</b>	93	7	7	0
<b>Total potassium</b>	17	81	80	1
<b>Dry matter</b>	316	16,7	33,9	0,36
<b>Organic matter</b>	243	7,01	13,7	0,08
<b>Inorganic matter</b>	73	9,69	20,2	0,28
<b>Total nitrogen</b> g/kg	13,7	4,15	8,12	0,31
<b>Ammonium</b>	5,77	3,47	7,13	0,29
<b>Total phosphorus</b>	7,95	0,14	0,26	0,01
<b>Total potassium</b>	3,76	3,86	8,08	0,08

## 4.2. Chemicals

Sulfuric acid solutions were diluted from 98% purity sulfuric acid with demineralized water to make 1.0M sulfuric acid for acid leaching. Ash and char solutions were prepared by weighting 10 g of ash and char and making 100 mL solutions with demineralized water. Precipitation was done by addition of 0.05M  $\text{Ca}(\text{OH})_2$ , which was diluted from 96 % purity  $\text{Ca}(\text{OH})_2$ . Both chemicals were obtained from Sigma Aldrich.

## 4.3. Experiments

The solid manure from Houbraken was first dried at 105C until no changes in weight were observed. Dried manure was then combusted in a furnace, which had a ramping program. Temperatures used in the ramping program were 250C and 575C according to the NREL LAP method for ash composition determination (Sluiter, Hames et al. 2004).

The program was set to reach pH of 2 and the pH should remain constant for 2 min before the addition of acid would be stopped. This pH was applied, because by using sulfuric acid,

then most of the phosphates will be leached as it is indicated in previous studies (Azuara, Kersten et al. 2013). After reaching constant pH, solutions were left for mixing with magnetic stirrer and with the speed of 500 rpm for 1 and 4 hours. Some of the solutions were separated directly after reaching the constant pH. After acid leaching the ash solutions were separated in a centrifuge with 9000 rpm for 5 min. The char solutions were separated by vacuum filtration. These solutions were used for further precipitation.

Precipitation was done batchwise in a 250 mL beaker including a magnetic stirrer with a speed of 800 rpm. Solutions of 0.05M  $\text{Ca(OH)}_2$  and separated solutions from acid leaching were fed into the beaker together. The concentration of the  $\text{Ca(OH)}_2$  solution was based on the water solubility of 1.73 g/L of  $\text{Ca(OH)}_2$ . Precipitation of HAP and DCPD is affected by the dissolution of  $\text{Ca(OH)}_2$  into water, which then led to the application of lower concentrations of  $\text{Ca(OH)}_2$ . (Ferreira, Oliveira et al. 2003) At the time of addition of the solutions, timer was started and mixing times of 10, 20 and 30 min were used. Leached solution volume was always 50 mL whereas  $\text{Ca(OH)}_2$  was added in volumes of 50, 70, 100 and 200 mL depending on the precipitation experiment. Finally, precipitates were separated from the aqueous solutions by vacuum filtration and dried in the oven till constant weight was achieved.

#### **4.4. Analyses**

Ashes and char were analyzed with X-ray fluorescence to determine the elemental compositions. Fusion bead samples were prepared by dissolving produced ashes in lithium tetraborate  $\text{Li}_2\text{B}_4\text{O}_7$ . The ash was already in powdery form, but the char was grinded for the preparation of samples. Solid residuals from the acid leaching were also analyzed with XRF to determine the how much of components have been leached. After separation from the aqueous solutions, solids were dried in the oven at 105°C and then grinded to make fine powder for analysis.

Separated aqueous samples were analyzed with UV-VIS DR5000 spectrophotometer using Hach Lange kit LCK-349 for phosphate measurements. Separated aqueous solutions from precipitation were also analyzed with the same method to determine the phosphate content in the solutions. In this way the phosphorus yield in precipitation could be determined.

Ash, char and precipitation products were analyzed with XRD Bruker D2 Powder to determine the crystalline compounds. After separation and drying of the precipitation

products, they were grinded and then analyzed by XRD. First the range of 10° to 60° was used for the 2 $\theta$ , but after first analyses of the precipitation products, where no peaks occurred higher than at 40°, the maximum limit was set to 40°. For analysis of ash and char the range of 10 – 60° was applied. Rotation speed was set to 0 rpm, step size was 0.05 and time for each step was 0.5 s.

#### 4.5. Theoretical considerations

Conversion factors for different forms of phosphorus were used and values used are presented in Table 25. (Kongshaug, Brentnall et al. 2000)

*Table 25 Conversion factors for different forms of phosphorus and calcium.*

Form	Conversion factor
<b>P<sub>2</sub>O<sub>5</sub></b>	2,291 x P
<b>P<sub>2</sub>O<sub>5</sub></b>	0,724 x H <sub>3</sub> PO <sub>4</sub>
<b>P</b>	0,436 x P <sub>2</sub> O <sub>5</sub>
<b>P</b>	0,316 x H <sub>3</sub> PO <sub>4</sub>
<b>H<sub>3</sub>PO<sub>4</sub></b>	1,38 x P <sub>2</sub> O <sub>5</sub>
<b>CaO</b>	1,40 x Ca

The yields of different components after acid leaching in aqueous solution was calculated as follows

$$\eta_a = \frac{c_{s,i} - c_{s,e}}{c_{s,i}} \cdot 100\% \quad (26)$$

where  $\eta_a$  (%) is the yield of the component in the aqueous solution after leaching,  $c_{s,i}$  (g/L) is the initial concentration of a component in the ash and  $c_{s,e}$  (g/L) is the final concentration of a component in the ash.

The yield of phosphorus after precipitation was calculated as follows

$$\eta_p = \frac{c_{l,i} - c_{l,e}}{c_{l,i}} \cdot 100\% \quad (27)$$

where  $\eta_p$  (%) is the yield of phosphate in the precipitate,  $c_{l,i}$  (g/L) is the initial concentration of phosphate in the aqueous solution and  $c_{l,e}$  (g/L) is the final concentration of the phosphate in the aqueous solution after precipitation.

Acid consumption in acid leaching was calculated as follows

$$x_{H_2SO_4} = \frac{V_{H_2SO_4} c_{H_2SO_4}}{V_P c_P} \quad (28)$$

where  $x_{H_2SO_4}$  (kg H<sub>2</sub>SO<sub>4</sub>/kg P) is the acid consumption for recovered phosphorus,  $V_{H_2SO_4}$  (L) is the volume of added acid,  $c_{H_2SO_4}$  is the concentration of acid (g/L),  $V_P$  (L) is the volume of leached solution and  $c_P$  (g/L) is the concentration of phosphates in solution after leaching.



## 5. RESULTS AND DISCUSSION

Results from the experiments are presented for the combustion of pig manure, compositions of ash and char, acid leaching of ash and char and finally precipitation of phosphates from the acid leached solutions of ash and char.

### 5.1. Combustion

To determine the content and other minerals and metals present in the ash and char, XRF analysis was done. These compositions of pig manure ash and char are shown in Table 26 and Table 27. Due to the addition of calcium into the solid manure by Houbraken for the storage the Ca content in the ashes is relatively high 43.5 wt-%. This is comparable to the content of calcium in the phosphate rock. Amount of phosphorus does not reach the amount of phosphorus in the rock. The phosphorus content is 13.8 wt-% in the ashes. This relatively high content is beneficial for the further steps of the process. While phosphorus rock has average  $\text{CaO}:\text{P}_2\text{O}_5$  ratio of 1.5, this ratio in the ashes is 3.2. Minor components are metals and next biggest components are Si, K and Mg.

*Table 26 Ash composition of the pig manure obtained from Houbraken after gasification of dried manure and determined by XRF.*

Concentration							
$c_{i,i}$ [wt-%]							
<b>CaO</b>	<b>P<sub>2</sub>O<sub>5</sub></b>	<b>SiO<sub>2</sub></b>	<b>K<sub>2</sub>O</b>	<b>MgO</b>	<b>Cl</b>	<b>SO<sub>3</sub></b>	<b>Na<sub>2</sub>O</b>
43,50	13,80	8,96	8,44	7,77	5,12	3,18	2,40
<b>Fe<sub>2</sub>O<sub>3</sub></b>	<b>Al<sub>2</sub>O<sub>3</sub></b>	<b>ZnO</b>	<b>MnO</b>	<b>CuO</b>	<b>TiO<sub>2</sub></b>	<b>SrO</b>	<b>NiO</b>
1,49	0,97	0,47	0,31	0,13	0,10	0,05	0,00

Char has high carbon content, which is 60.8 wt-%. This is due to the partial degradation of organic matter in the dried manure. As well as in the ashes, P has the second highest concentration 9.28 wt-%, respectively, also in the char, which is interesting for the further steps. Second major components are Ca, Si and Mg. Unlike the Ca content in the ashes, Ca content of the char is a relatively low 7.12 wt-%.

Table 27 Char composition of the pig manure obtained from Houbraken after gasification of dried manure and determined by XRF.

Concentration							
$c_{i,i}$ [wt-%]							
C	P <sub>2</sub> O <sub>5</sub>	CaO	SiO <sub>2</sub>	MgO	SO <sub>3</sub>	K <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>
60,80	9,28	7,12	6,96	4,87	3,39	2,98	2,51
Cl	Al <sub>2</sub> O <sub>3</sub>	ZnO	MnO	CuO	TiO <sub>2</sub>	SrO	NiO
0,80	0,67	0,29	0,14	0,11	0,08	0,03	0,00

The ash and char were analyzed with XRD to study how the minerals and metals are present. XRD patterns of ash and char are shown in Figure 25. It seems that ashes contain apatites, probably hydroxylapatites ( $2\theta = 26.9^\circ, 32.0^\circ - 33.2^\circ, 40.2^\circ$ ) (Bircan, Naruse et al. 2013). This means that phosphates are as well found as apatites in ashes similar to the phosphate rock. Also whitlockite  $\text{Ca}_9\text{Fe}(\text{PO}_4)_7$  ( $28.4^\circ, 29.1^\circ, 32.6^\circ$ ) (Lazoryak, Morozov et al. 1996), silica oxide  $\text{SiO}_2$  ( $2\theta = 21.3^\circ, 26.9^\circ$ ), magnesium oxide  $\text{MgO}$  ( $2\theta = 43.5^\circ$ ) (Rownaghi and Huhnke 2012) and hematite  $\text{Fe}_2\text{O}_3$  ( $2\theta = 33.6^\circ$ ) (Lian, Wang et al. 2004) seem to be present. Char seems to contain  $\text{CaCO}_3$  ( $2\theta = 29.8^\circ$ ), silica oxide  $\text{SiO}_2$  ( $2\theta = 21.3^\circ, 26.9^\circ$ ) and  $\text{Ca}_9\text{Fe}(\text{PO}_4)_7$  ( $28.4^\circ, 29.1^\circ, 32.6^\circ$ ).

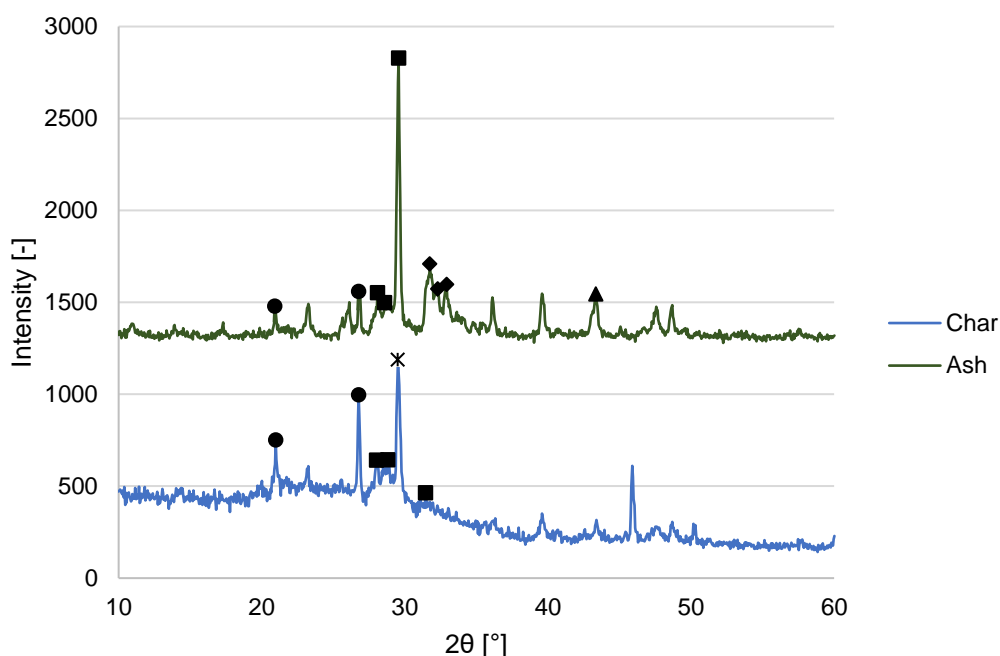


Figure 25 XRD patterns of ash and char. ● is silica oxide, ■ is whitlockite, x is calcium carbonate, ◆ is hydroxylapatite and ▲ is magnesium oxide.

## 5.2. Acid leaching of ashes and char

Yields of phosphates via acid leaching of ash and char are shown in Figure 26. Higher yields of phosphates were obtained for leaching of ash, where all of the phosphates were leached. Yields of P from char were lower, achieving 94 % yield of P with longer leaching time.

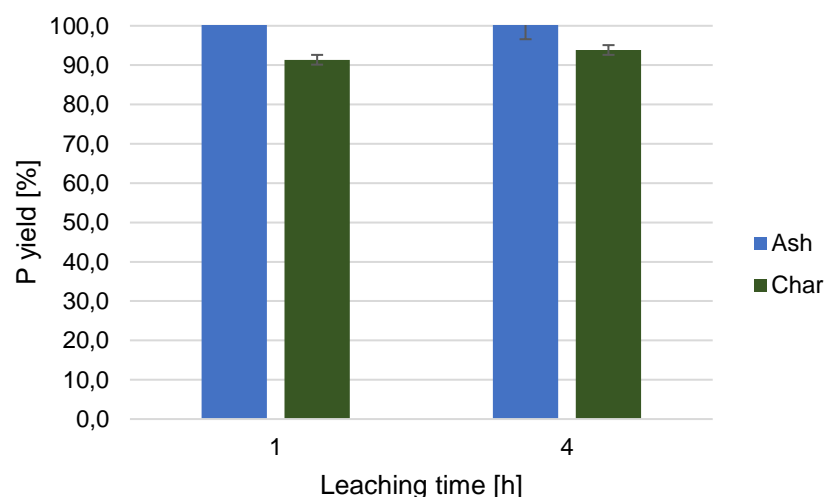


Figure 26 Acid leaching of pig manure ash and char with sulfuric acid addition till pH of 2 with two different leaching durations.

The leaching of the different components during acid leaching of both ash and char are shown in Table 28. Besides leaching of P, acid leaching of ash ended up to leaching of Ca, Mg, K, S and Cl into the aqueous solution. These are the major components in the solution after acid leaching. Some other components, such as, Al and Fe were also leached, but with smaller amounts. Due to the high initial amount of Ca in the ash also the leached amount of Ca is relatively high in the final solution. This might influence the further steps of treating the leached solution.

Table 28 Leached components during acid leaching of ash and char with different leaching times analyzed with XRF.

Component	Yield $\eta$ [%]			
	1h char	4h char	1h ash	4h ash
<b>CaO</b>	0	0	13	12
<b>SiO<sub>2</sub></b>	0	0	28	22
<b>MgO</b>	100	80	100	100
<b>SO<sub>3</sub></b>	0	0	0	0
<b>K<sub>2</sub>O</b>	40	45	91	92
<b>Fe<sub>2</sub>O<sub>3</sub></b>	0	10	22	38
<b>Cl</b>	53	59	100	100
<b>Al<sub>2</sub>O<sub>3</sub></b>	0	0	100	100
<b>ZnO</b>	0	8	66	68
<b>MnO</b>	59	56	43	70
<b>CuO</b>	0	0	100	64
<b>TiO<sub>2</sub></b>	0	0	100	0
<b>SrO</b>	57	61	6	27

Initial pH of char solution was slightly acidic (pH of 6.5) whereas initial pH of ash solution was highly basic (pH of 11.8), acid consumption in acid leaching of ash was 14.0 H<sub>2</sub>SO<sub>4</sub>/kg P. Also, due to high Ca content in the ash acid consumption is higher. For char the acid consumption was only 3.4 kg H<sub>2</sub>SO<sub>4</sub>/kg P.

### 5.3. Precipitation from ash originated solutions

The precipitation experiments were first done for fixed calcium hydroxide addition with different precipitation times of 10, 20 and 30 min. These experiments were done as a trial experiment to examine what is the final product and how much of the product is formed with different precipitation duration times. Table 29 shows the change in pH, P yield in precipitates and the Ca/P ratios for different precipitation duration times from the acid leached ash solutions. With precipitation time of 10 min, higher P yield is obtained than with precipitation time of 20 and 30 min. Different precipitation experiments were done from different acid leached solutions due to volume limitations and this can also lead to some differences and fluctuation in the results. Leaching solutions might contain slightly different amounts different components, which can lead to varying phosphate yields in precipitation.

The second set of experiments was done by adding 3 different amounts of calcium hydroxide, 50, 70 and 100 mL. This set was done to see what the final product is and how much of the product is formed with different amounts of calcium hydroxide. The precipitation time was set to 20 min. The results for this set are also shown in Table 29. A higher P yield is obtained with less  $\text{Ca(OH)}_2$  addition. Higher P yields would be expected with higher amounts of  $\text{Ca(OH)}_2$  added.

*Table 29 Change in pH, P yields in precipitates and Ca/P ratios in precipitation experiments with 10, 20 and 30 min precipitation times from ash solutions with fixed  $\text{Ca(OH)}_2$  addition of 100 mL and with  $\text{Ca(OH)}_2$  additions of 50, 70 and 100 mL with fixed precipitation time of 20 min.*

Precipitation time $t_p$ [min]	Lime addition $V_L$ [L]	$\Delta\text{pH}$ [-]	P yield in precipitate $\eta_p$ [%]	Ca/P [-]
10	0,10	4,0	87,9	0,32
20	0,10	-	79,0	0,59
30	0,10	4,0	86,6	0,59
20	0,05	4,1	94,4	0,16
20	0,07	3,7	85,0	0,22
20	0,10	-	79,0	0,59

XRD results of the precipitation products from ash with short leaching times are shown in Figure 27. It can be concluded that with precipitation times of 10, 20 and 30 min, the final product is DCPD ( $11.7^\circ$ ,  $20.8^\circ$ ,  $29.3^\circ$ ) (Karampas and Kontoyannis 2013). Scattering occurred before the  $2\theta$  value of  $10^\circ$  and HAP has some peaks below  $10^\circ$ . Although, it seems the final product is mainly DCPD, because most of the peaks are very clearly same peaks as the ones of DCPD. Fluctuation of the graph could be explained by the presence of mother liquid still in the precipitate after drying.

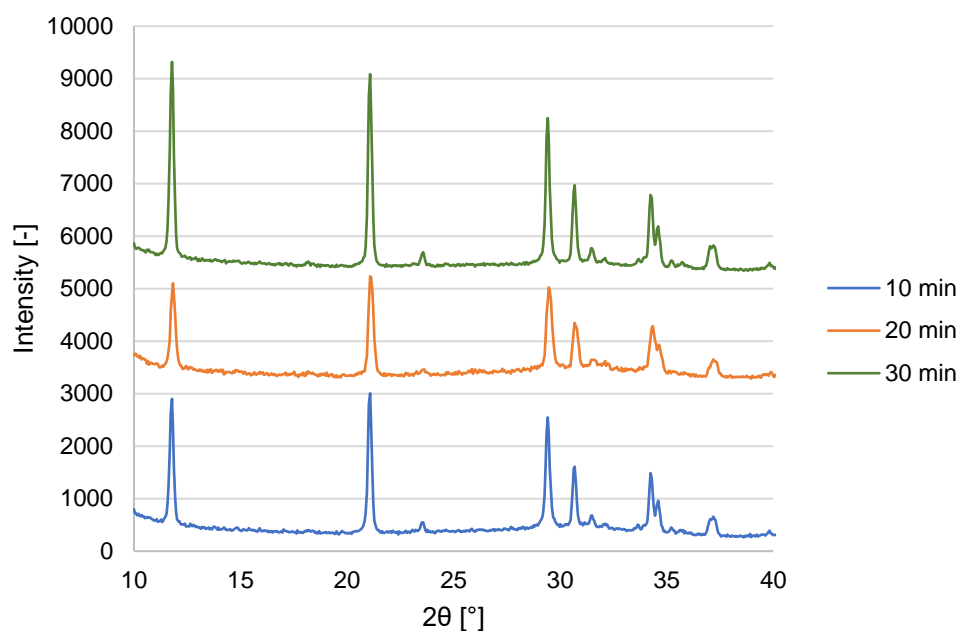


Figure 27 Precipitation of phosphates from ash originated solutions with mixing times of 10, 20 and 30 min and addition of 100 mL of  $\text{Ca(OH)}_2$ .

Figure 28 shows the XRD patterns for precipitates with different amounts of lime added. As with experiments with different duration times also with these experiments the final crystalline product is DCPD. Highest peaks are obtained for solution with 50 mL  $\text{Ca(OH)}_2$  addition. For this experiment the yield was also the highest.

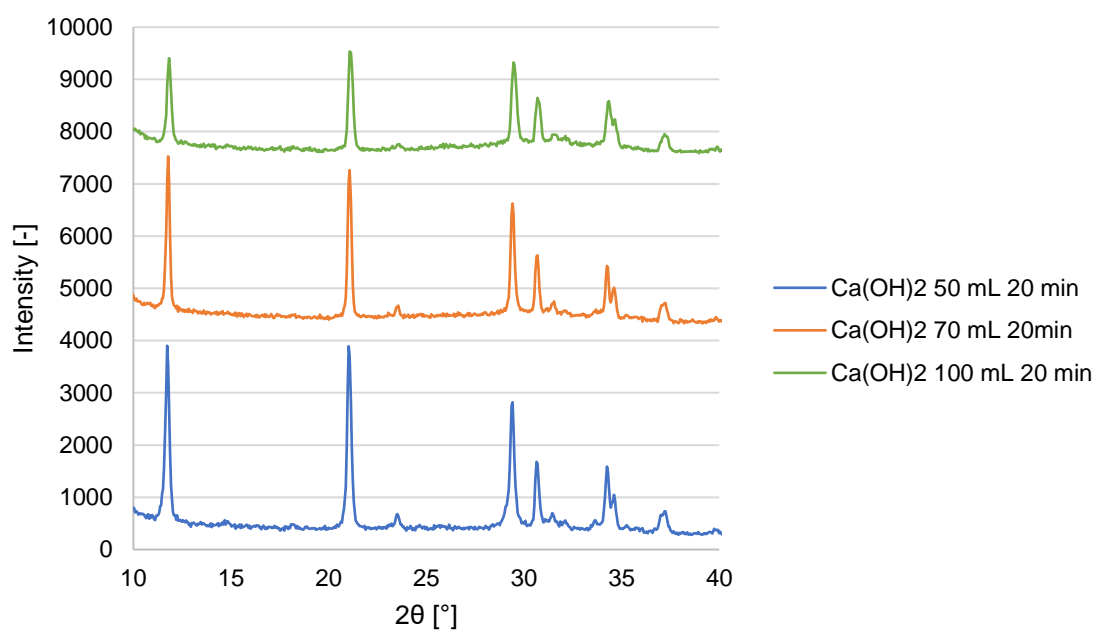


Figure 28 Precipitation of phosphates from ash originated solutions with  $\text{Ca(OH)}_2$  additions of 50, 70 and 100 mL having mixing time of 20 min.

The next set of experiments was done for the solutions originated from longer acid leaching of ashes. The calcium hydroxide addition was fixed to 100 mL for this set. The purpose was to see whether the same product is still formed after longer acid leaching, when other leached components can affect the precipitation. Table 30 shows the results for precipitation from solutions, which were leached for 1 and 4 hours. P yields from solutions with 4 h leaching are higher than for solutions with 1 h leaching, respectively. Changes in pH are similar between different experiments and the final pH was in the range of 5.8 – 6.2. One experiment with short leaching time and shorter precipitation time gives very low P yield of 24.7 %, respectively. The highest yield of P 72.3 % was obtained from the 4h leaching and precipitation time of 30 min.

*Table 30 Change of pH, P yield in precipitate and Ca/P ratio with different precipitation times from different leached solutions with ash. 100 mL of  $\text{Ca}(\text{OH})_2$  was added in each experiment.*

Precipitation time $t_p$ [min]	$\Delta\text{pH}$ [-]	P yield in precipitate $\eta_p$ [%]		Ca/P [-]	
		1h leaching	4h leaching	1h leaching	4h leaching
10	4	24,7 ( $\pm 49,9$ )	61,1 ( $\pm 2,2$ )	0,70	0,92
20	3,9	66,9 ( $\pm 5,0$ )	66,7 ( $\pm 5,4$ )	0,75	0,96
30	4,2	63,8 ( $\pm 14,8$ )	72,3 ( $\pm 0,5$ )	0,70	0,96

DCPD was also precipitation product from ash solutions with longer leaching times, which can be seen from Figure 29 and Figure 30. However, one precipitation experiment, where phosphates were precipitated from solution leached for 1 hour and with mixing time of 10 min, the final product was amorphous with slight peaks of DCPD. The precipitation might have been too short for DCPD crystallization. With longer mixing times the final product was DCPD. This would indicate effect of shorter mixing time leading to a formation of an amorphous product and not complete formation into DCPD. This exception was only for the particular experiment and other experiments with also 10 min mixing time did not give the same amorphous product. The lowest P yield was also obtained for these conditions as seen in Table 30.

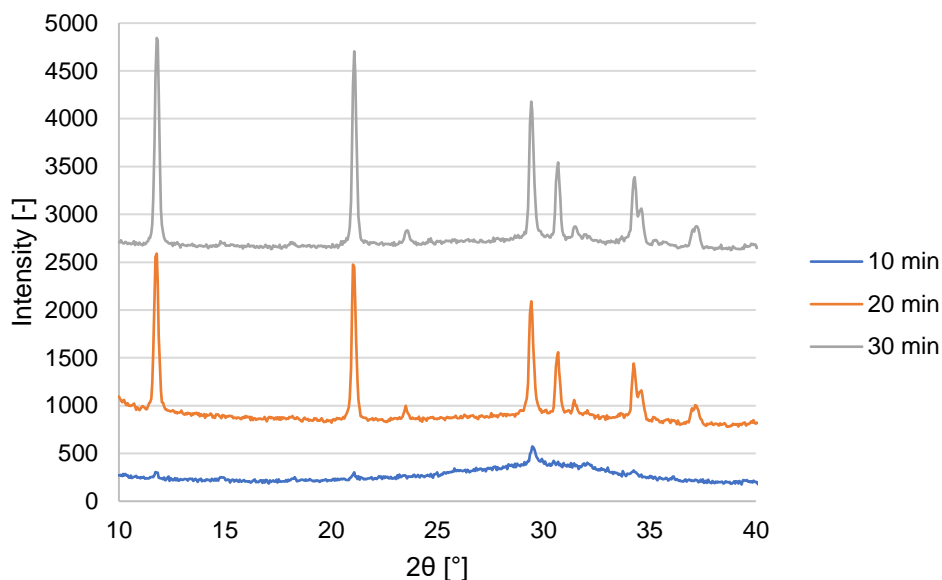


Figure 29 Precipitation of phosphates from 1 hour acid leached ash solution with mixing times of 10, 20 and 30 min and addition of 100 mL of  $\text{Ca}(\text{OH})_2$ .

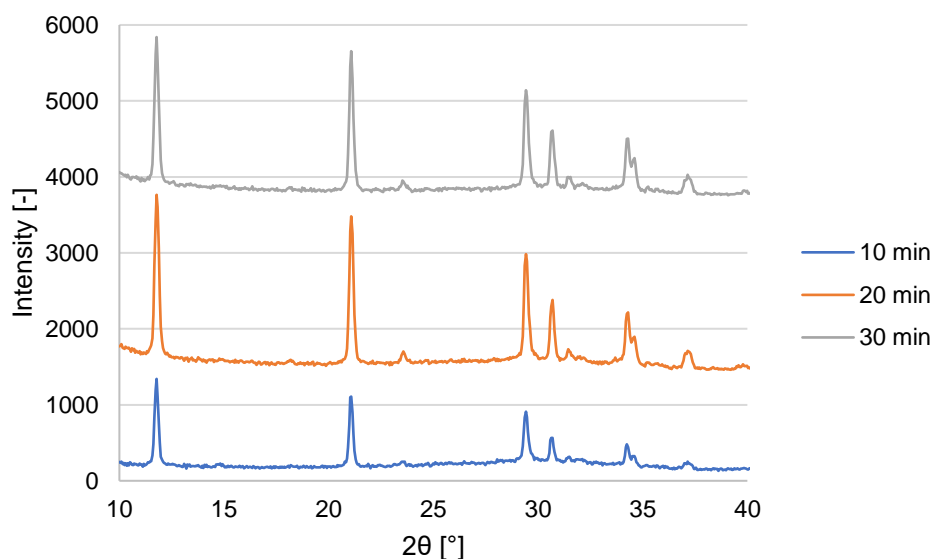


Figure 30 Precipitation of phosphates from 4h acid leached ash solution with mixing times of 10, 20 and 30 min and addition of 100 mL of  $\text{Ca}(\text{OH})_2$ .

#### 5.4. Precipitation from char originated solutions

XRD patterns for precipitates originated from char solutions are presented in Figure 31 and Figure 32. This set of experiments was done with different precipitation times, but with fixed calcium hydroxide addition of 100 mL. Similar to the set of experiments with ash solutions, the aim of this set was also to see, which product is formed. Unlike the clear crystalline product formed from the ash originated solutions, precipitates from char solutions are amorphous and have only one slightly clear peak. This is the same peak, which is the peak



of  $\text{CaCO}_3$ . Some carbon was leached together with the phosphates, which means carbon is probably present as carbonate in the solution. This could lead into the formation of  $\text{CaCO}_3$ , when  $\text{Ca(OH)}_2$  is added into the solution.  $\text{CaCO}_3$  has a crystalline structure, which could explain the peak at  $29.4^\circ$  whereas, the presence of amorphous calcium phosphates would explain the absence of clear peaks, but still precipitation of phosphates. (Camargo, Soares et al. 2007) Even with varying mixing times and different amounts of added  $\text{Ca(OH)}_2$  XRD patterns fluctuate. Similar to XRD diffractograms from ash solution precipitates, again presence of HAP cannot be detected.

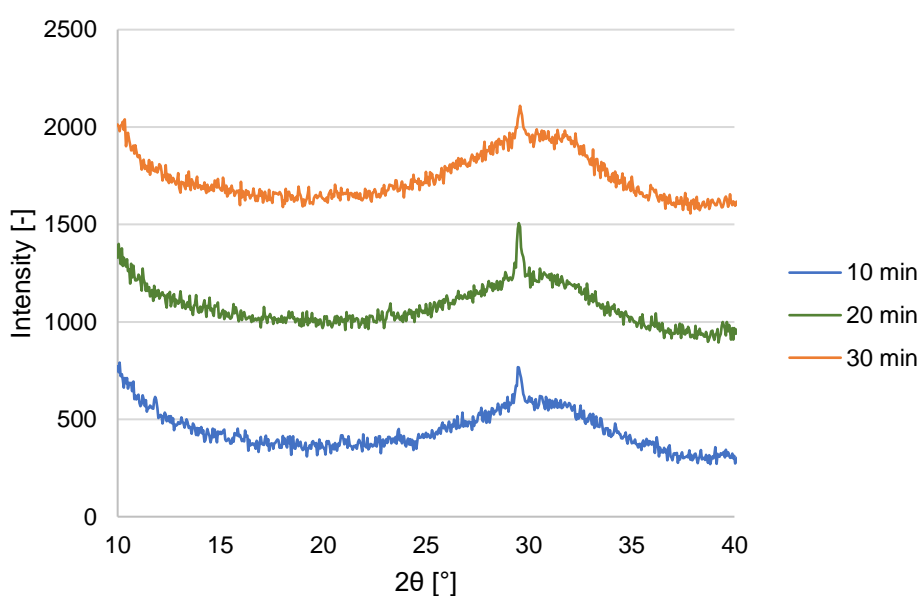


Figure 31 Precipitation of phosphates from char originated solutions with mixing times of 10, 20 and 30 min and addition of 100 mL of  $\text{Ca(OH)}_2$ .

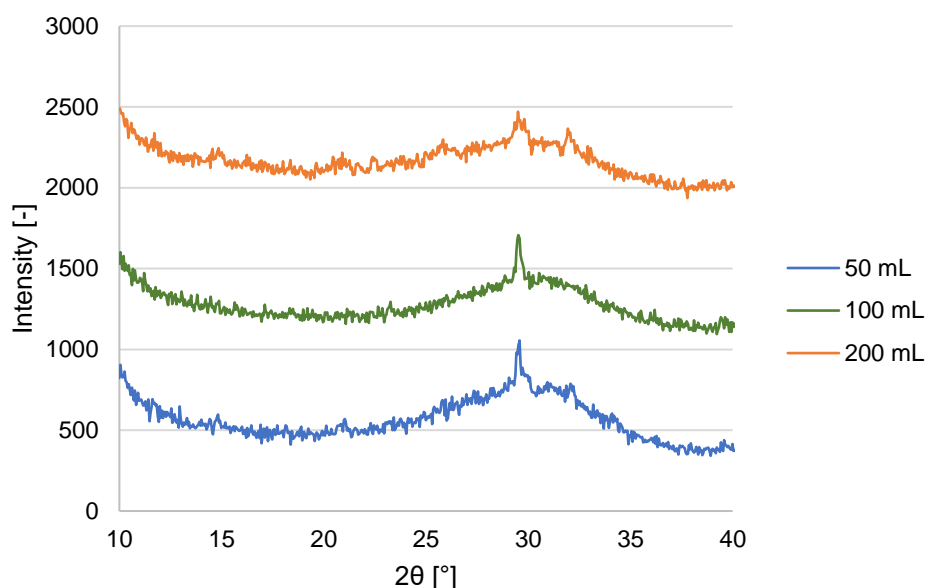


Figure 32 Precipitation of phosphates from char originated solutions with addition of 50, 100 and 200 mL of  $\text{Ca}(\text{OH})_2$  having mixing time of 20 min.

The next set of experiments were done similar to the ones, which were done for the ash solutions from longer leaching, when precipitation was done with 10, 20 and 30 min of mixing time with fixed calcium hydroxide addition. The aim again is to see whether the product and yields change, when other components might be leached and have an effect on the precipitation. Table 31 shows the results for precipitation from char originated solutions, which were leached for 1 and 4 hours. P yields from solutions with 4 h leaching are again higher than for solutions with 1 h leaching, respectively. Changes in pH are similar between different experiments and the final pH was in the range of 5.9 – 6.4. Phosphates yields are significantly lower than for experiments from ash originated solutions. Highest yield achieved is 50.9 %, respectively.

Table 31 Change of pH, P yield in precipitate and Ca/P ratio with different precipitation times from different leached solutions with char.

Precipitation time $t_p$ [min]	$\Delta\text{pH}$ [-]	P yield in precipitate $\eta_p$ [%]		Ca/P [-]	
		1h leaching	4h leaching	1h leaching	4h leaching
10 min	3,9	32,7 ( $\pm 4,9$ )	49,9 ( $\pm 11,3$ )	0,92	0,92
20 min	4,0	43,2 ( $\pm 3,8$ )	50,9 ( $\pm 13,1$ )	0,96	0,96
30 min	4,1	40,9 ( $\pm 3,1$ )	39,2 ( $\pm 11,5$ )	0,96	0,96

Figure 33 and Figure 34 show again the same XRD patterns, which were also obtained from the precipitation from char originated solutions, but now with longer leaching times. It is probable that with applied conditions and solutions, the products are  $\text{CaCO}_3$  and

amorphous calcium phosphates. Experiment done from the 1 h leached char solution with mixing time of 30 min shows slight peaks of DCPD. Similar to one of the experiments from ash solutions the DCPD might have been forming, but the product is still amorphous. Also the same  $\text{CaCO}_3$  peak, which was obtained from the previous experiments, can be detected. Compared to the previous char precipitation experiments XRD pattern from longer leached solutions has less scattering in the beginning.

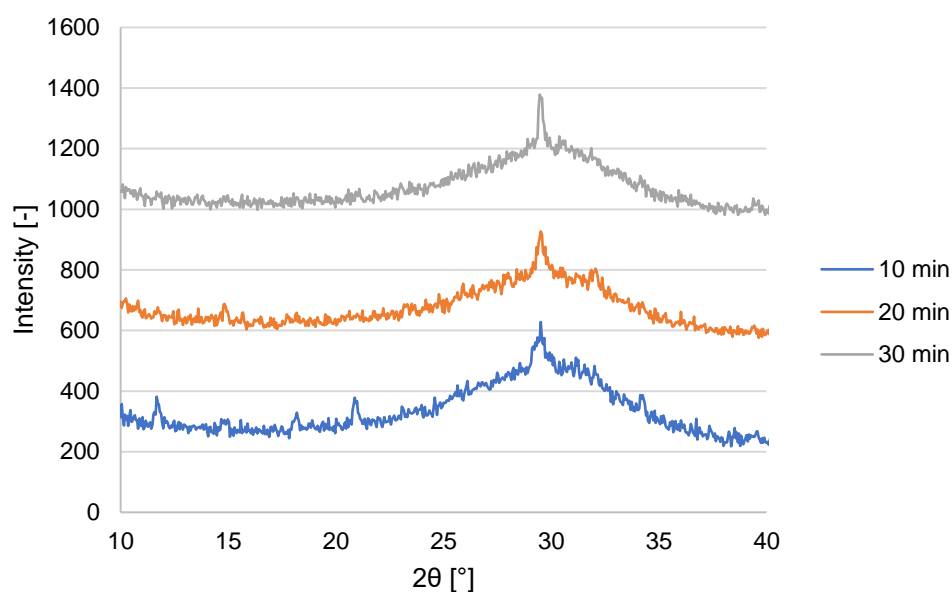


Figure 33 Precipitation of phosphates from 1h acid leached solution with mixing times of 10, 20 and 30 min and addition of 100 mL of  $\text{Ca}(\text{OH})_2$ .

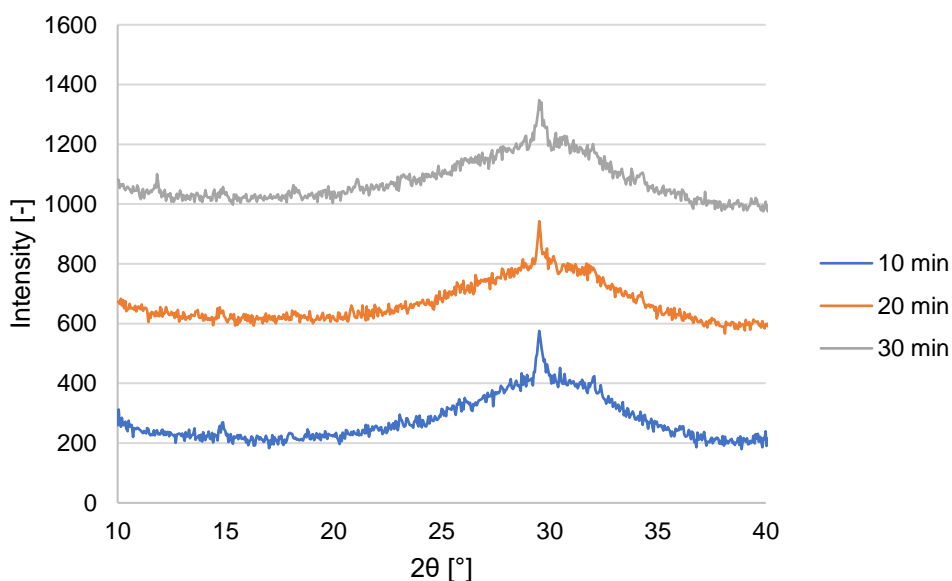


Figure 34 Precipitation of phosphates from 4h acid leached solution with mixing times of 10, 20 and 30 min and addition of 100 mL of  $\text{Ca}(\text{OH})_2$ .

Amorphous structure of the calcium phosphates can be due to the formation of  $\text{CaCO}_3$ . DCPD was the final product from the precipitation of ash originated solutions and the difference between these solutions is that ash solutions do not contain carbon compounds, because of full combustion. Because the solubility of  $\text{CaCO}_3$  is lower than the solubility of calcium phosphates,  $\text{CaCO}_3$  might be first forming followed by formation of the calcium phosphates (Haynes 2014).  $\text{CO}_3^{2-}$  might be competitive ion to  $\text{PO}_4^{3-}$ , which then decreases the calcium phosphate precipitation (Cao and Harris 2007). This needs further research whether this is the case.

## **5.5. Conclusions**

Phosphate was found in apatites and whitlockite in the ashes. Phosphate in the char was mainly whitlockite. High yields of phosphates were obtained in acid leaching of ash and char, ash having higher yields than char. Precipitation product from ash originated solutions was DCPD, which was also the aim product. High yields of phosphates from 60 to 94 % were obtained in the precipitation from the ash originated solutions with one exception. Precipitation products from char originated solutions were  $\text{CaCO}_3$  and amorphous calcium phosphates. Yields of phosphates in precipitation were varying between 30 – 60 %, which means that only some of the phosphates were still recovered from the char originated solutions. The data from experiments will be used for technical and economical evaluations of the processes.

## 6. ASPEN MODEL

A model was created in AspenPlus to predict the precipitation of calcium phosphates and compare it with the experimental results. The salt equilibria in the precipitation of calcium phosphates was modelled. Aspen electrolyte model was applied, which is meant for systems, where ions are present or salts are being precipitated. Due to the nonideal thermodynamical behaviour of ions present in the liquid electrolyte model can be used for this purpose. (Technology 2013)

### 6.1. Description of the model

To study the salt equilibria several components were included into the model. First water,  $\text{H}_3\text{PO}_4$ ,  $\text{Ca}(\text{OH})_2$ , DCP, DCPD and HAP were added from the Aspen databanks: ASPENPCD, AQUEOUS, SOLIDS, INORGANIC and PURE32. Aspen tool Elec wizard was applied to determine all the ionic species present and their reactions for the chosen components. ELECNRTL property method was applied, because this method can be applied for both diluted and highly saturated solutions. (Technology 2013) Some dissociation and precipitation reactions of  $\text{H}_3\text{PO}_4$  were excluded. Precipitation reactions of HAP and DCPD are not included in Aspen library and were thus added manually. It is possible to add equilibrium constants also manually, which was done due to some differences between the constants obtained from Aspen and compared to the ones found in literature. Applied ions, reactions and the equilibrium constant are presented in Table 32 and in Table 33. (Ferguson and McCarty 1971, Iqbal, Bhuiyan et al. 2008)

Table 32 Equilibrium reactions and their equilibrium constants of the molecular species in the Aspen model of calcium phosphate precipitation.

	Ions	Equilibrium	$\text{pK}_{\text{sp}}$
<b><math>\text{H}_2\text{O}</math></b>	$\text{OH}^-$ , $\text{H}_3\text{O}^+$	$2\text{H}_2\text{O} \leftrightarrow \text{OH}^- + \text{H}_3\text{O}^+$	14.0
<b><math>\text{Ca}(\text{OH})_2</math></b>	$\text{Ca}^{2+}$ , $\text{OH}^-$	$\text{CaOH}^+ \leftrightarrow \text{Ca}^{2+} + \text{OH}^-$	1.37
<b><math>\text{H}_3\text{PO}_4</math></b>	$\text{H}_3\text{O}^+$ , $\text{PO}_4^{3-}$ , $\text{HPO}_4^{2-}$ , $\text{H}_2\text{PO}_4^-$	$\text{H}_2\text{O} + \text{H}_3\text{PO}_4 \leftrightarrow \text{H}_3\text{O}^+ + \text{H}_2\text{PO}_4^-$	2.13
		$\text{H}_2\text{O} + \text{H}_2\text{PO}_4^- \leftrightarrow \text{H}_3\text{O}^+ + \text{HPO}_4^{2-}$	7.2
		$\text{H}_2\text{O} + \text{HPO}_4^{2-} \leftrightarrow \text{H}_3\text{O}^+ + \text{PO}_4^{3-}$	12.32
<b><math>\text{CaHPO}_4</math></b>	$\text{Ca}^{2+}$ , $\text{HPO}_4^{2-}$		
<b><math>\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2</math></b>	$\text{Ca}^{2+}$ , $\text{PO}_4^{3-}$ , $\text{OH}^-$		

Table 33 Dissociation and precipitation reactions and their precipitation constants of the molecular species in the Aspen model of calcium phosphate precipitation.

	Dissociation	Precipitation	pK <sub>sp</sub>
H <sub>2</sub> O			
Ca(OH) <sub>2</sub>	Ca(OH) <sub>2</sub> → CaOH <sup>+</sup> + OH <sup>-</sup>		
H <sub>3</sub> PO <sub>4</sub>			
CaHPO <sub>4</sub>	CaHPO <sub>4</sub> → Ca <sup>2+</sup> + HPO <sub>4</sub> <sup>2-</sup>	CaHPO <sub>4</sub> ·2H <sub>2</sub> O (s) ↔ Ca <sup>2+</sup> + HPO <sub>4</sub> <sup>2-</sup> + 2H <sub>2</sub> O	57.8
Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub>		Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub> (s) ↔ 10Ca <sup>2+</sup> + 6PO <sub>4</sub> <sup>3-</sup> + 2OH <sup>-</sup>	6.55

Aspen analysis tool for mixtures was used to study solubilities of the calcium phosphates. In this particular tool, it is possible to add components and study the molar fractions of species at different values of pH.

## 6.2. Results and discussion

The model gives the molar fractions of the species at every pH with the chosen increment. The input parameters, which were chosen for the model, are presented in Table 34.

Table 34 Input parameters for the Aspenplus model for calcium phosphate precipitation.

Temperature [°C]	Pressure [atm]	Molar fractions in the mixture [-]		
		Ca(OH) <sub>2</sub>	H <sub>2</sub> O	H <sub>3</sub> PO <sub>4</sub>
25	1	0,15	0,84	0,01

The chosen molar fractions were used, because otherwise the results for components were not reasonable. For instance, solid concentration of DCPD had polynomial behavior with negative values of pH, which should not be the case (TAFU, KAGAYA et al. 2002). Molar fractions were adjusted till these values in order to obtain reasonable results.

Model results for the HAP and DCPD equilibria are shown in Figure 35. According to the Aspen model and the graph DCPD is dominant below pH of 4.7, because the concentration of the solid DCPD is highest in this range. Precipitation of HAP, on the other hand, will be dominant at pH values above 4.7, because for HAP the solid concentration is highest at higher pH values.

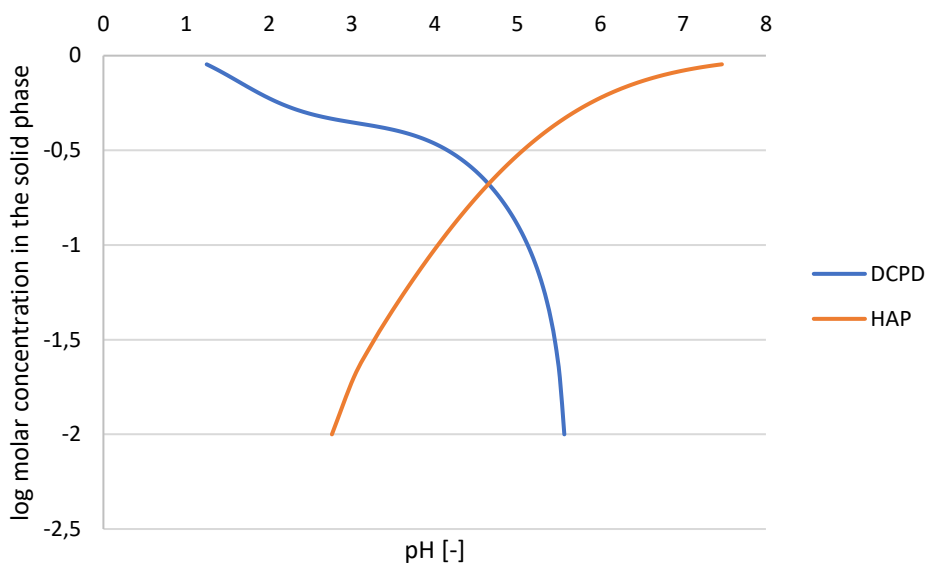


Figure 35 Solubility curves for calcium phosphate precipitation. Curves represent the logarithmic molar concentrations of HAP and DCPD in the solid phase.

Results from the experiments showed that even, when the pH was around 6, still DCPD was formed. Based on the observed XRD diffractograms no HAP would be present at the pH of 6, which indicates the experimental results do not match with the model made in Aspen. This can be also due to limitations in Aspen and possibility of unreliable model results for solubility even that equilibrium constants were obtained from literature and not determined by Aspen itself. In addition, it has been indicated in the literature that DCPD formation occurs in the pH range of 5 – 6, whereas HAP formation occurs at pH values higher than 7 (Ferreira, Oliveira et al. 2003). Other leached components were not included into the model, which can influence the difference between the model and results. Although this needs further study and modelling in Aspen whether the model could predict better the results by including other components.

### 6.3. Conclusions

Salt equilibria was studied in Aspen by creating a model including DCPD and HAP precipitation. It was studied whether the model could predict the experimental results. Based on results obtained by the model, DCPD should be precipitated below pH of 4.7. Although, what was obtained from the experimental results, DCPD was precipitating at pH values of 6. Experimental results also match the results found in literature. According to the Aspen model, with used conditions HAP should be precipitating. This leads to the conclusion that this model does not predict the precipitation of DCPD and HAP for this case.

## 7. EVALUATION

Evaluation of the examined process routes is done on the technical and economical point of view. Both process routes with acid leaching and precipitation from incineration ash and gasification char are included. They will be compared between each other and finally, they are compared to the conventional treatment method of pig manure, which is the direct application on to the fields.

### 7.1. Technical evaluation

As indicated in the previous chapter with results from experiments with manure ash, high phosphorus yields are possible to reach with the chosen process route. Nearly full combustion was achieved for the dried manure. Acid leaching with  $\text{H}_2\text{SO}_4$  till pH of 2 and leaching time of 1 hour is efficient enough to reach nearly 100 % recovery of phosphorus. Acid consumption in acid leaching of ashes is similar to what is indicated in earlier studies 14 kg  $\text{H}_2\text{SO}_4$ / kg P.

Regarding to the acid consumption in acid leaching of char it is more feasible than the acid leaching of ash. Less acid is needed in acid leaching of char. Nearly all the phosphates are found in the leachate with leaching times of 1 and 4 hours. However, some other components are leached together with phosphates, such as, carbon as carbonate, silica, calcium, iron and magnesium. These components can have the effect on the further process steps and the purity of the final product. As in LEACHPHOS process, where the metals are removed by additional process steps, it might be also required for the process of treating manure ashes.

Precipitation of crystalline DCPD was achieved almost in every experiment with one exception, where amorphous DCPD was formed. Some adjustments can be done for the precipitation conditions to reach higher yield of phosphorus, but with current conditions 60.0 – 90.0 % of phosphorus in the acid leached solutions can be precipitated. Purity of the final product is not studied in this research. The final product can be sold as a phosphate fertilizer.

Final precipitate product from char solutions is partly amorphous DCPD and partly calcium carbonate. Calcium carbonate is not used in agriculture and it has other applications. Presence of carbonate ion is influencing the precipitation by decreasing the phosphate



yield.  $\text{CaCO}_3$  is less soluble in water than DCPD, which makes it preferable product in precipitation. To avoid this char should be further thermally treated to decrease organic matter and on the other hand recover the remaining energy from the organic matter.

## **7.2. Economical evaluation**

The plant, where the pig manure would be treated and DCPD would be produced, should be a centralized plant, where pig manure could be brought for treatment. For evaluation, it is considered that the pig manure is brought raw and the plant contains all the units from anaerobic digestion to the treatments of the liquid and solid fractions. Because the plant would be centralized for pig manure treatment, it should be placed in the southern part of the Netherlands, where the amount of pigs is the greatest.

Following assumptions have been used for the economical evaluation. DCPD from treatment of ashes and char can be sold for same price as TSP 0.25 €/kg. (WorldBank 2017) Yield of P from ash to DCPD is used as 80 % and yield of P from char to DCPD is used as 40 %. Concentrate from reverse osmosis can be sold as mineral concentrate for fertilizer use for 5 €/ton (Menamo, van den Berg et al. 2012). Based on the energy balance energy is produced in the process, which is in total 650 MJ/ton manure via incineration route and 550 MJ/ton manure via gasification route excluding the energy consumption. The energy consumption is considered to be included in the operational costs, which can be estimated to be 5 % of the total capital investment costs as it is assumed in several economical evaluations of manure treatment plants. (Schoumans, Rulkens et al. 2010, Menamo, van den Berg et al. 2012) Annual costs of the acid leaching and precipitation unit has been estimated to be equal to the annual costs of LEACHPHOS process, which are 5 €/kg P recovered (Egle, Rechberger et al. 2016). Finally, the manure treatment plant, where DCPD is produced, will be compared to the costs of conventional manure application with 25 €/ton manure costs (Balcazar, Fougret et al. 2013).

Table 35 Capital investment and operational costs and annual benefits of the proposed processes for pig manure treatment.

	Ash route	Char route
<b>CAPEX million €</b>	182	182
Pretreatment facility, storage facility, RO, installations, buildigs initial working capital (Menamo, van den Berg et al. 2012)	2,3	2,3
Anaerobic digestion (Menamo, van den Berg et al. 2012)	3,5	3,5
Drying + incineration/gasification plant (Schoumans, Rulkens et al. 2010)	150,0	150,0
Acid leaching + precipitation (Egle, Rechberger et al. 2016)	26,5	26,5
<b>OPEX (5 % of CAPEX) million €/year</b>	9,1	9,1
<b>Annual benefit €/year</b>	31,9	26,6

The comparison between the proposed processes and the conventional method has been done using the cumulative cash flow, which is calculated with Net Present Value (NPV). The NPV was calculated as follows

$$NPV = \sum_{t=1}^T \frac{C_{tNPV}}{(1+r)^{tNPV}} - C_0 \quad (29)$$

where  $C_t$  is the net cash flow during time period  $t$ ,  $r$  is the discount rate,  $t_{NPV}$  is number of time periods and  $C_0$  is the total initial investment costs.

The cumulative cash flow of the examined process from pig manure to DCPD via incineration route with discount rate is presented in Figure 36. It is compared to the price, which farmers must pay for the conventional method of applying manure on the fields. It shows after 9 years it would be more feasible than the conventional method. After 13 years, the manure treatment plant would be paid back and it would start making profit.

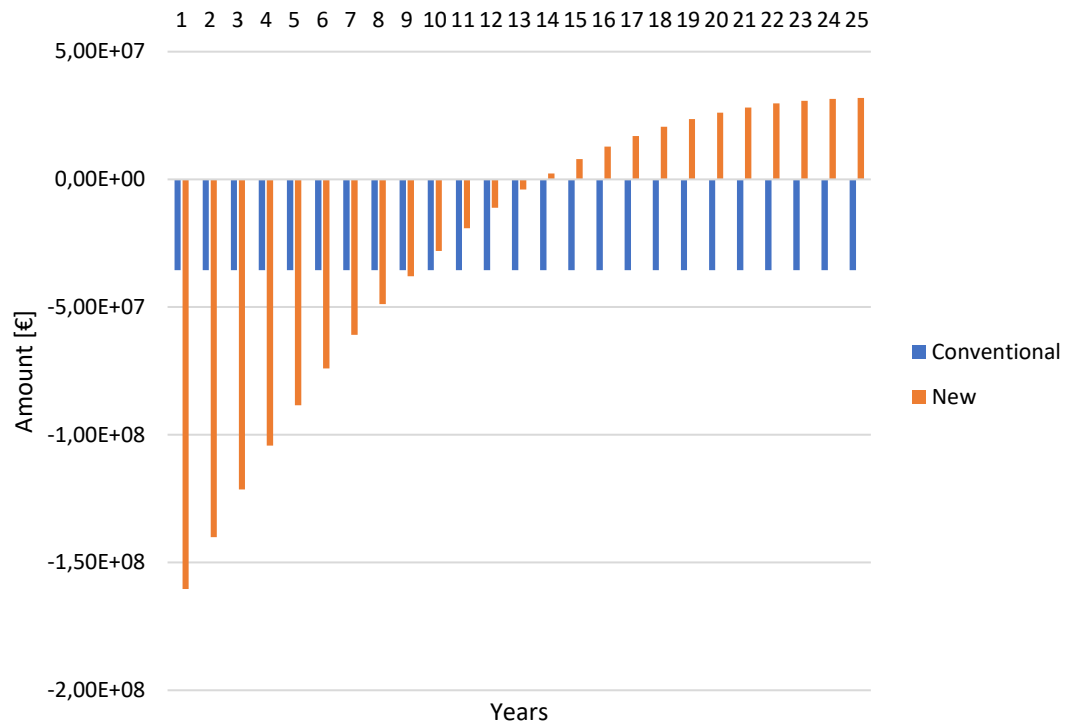


Figure 36 Cumulative discounted (discount rate 4.0 %) cash flow for the examined production of DCPD from pig manure via incineration compared to the conventional method of application of pig manure on the fields.

The cumulative cash flow of the examined process from pig manure to DCPD via gasification route with discount rate is presented in Figure 37. It shows that after 15 years it would be more feasible than the conventional method. However, this process itself would not begin making profit. Due to the less amount of energy, which is produced in gasification and also the low yield of P into DCPD in precipitation, the process is not economically feasible unlike the incineration route.

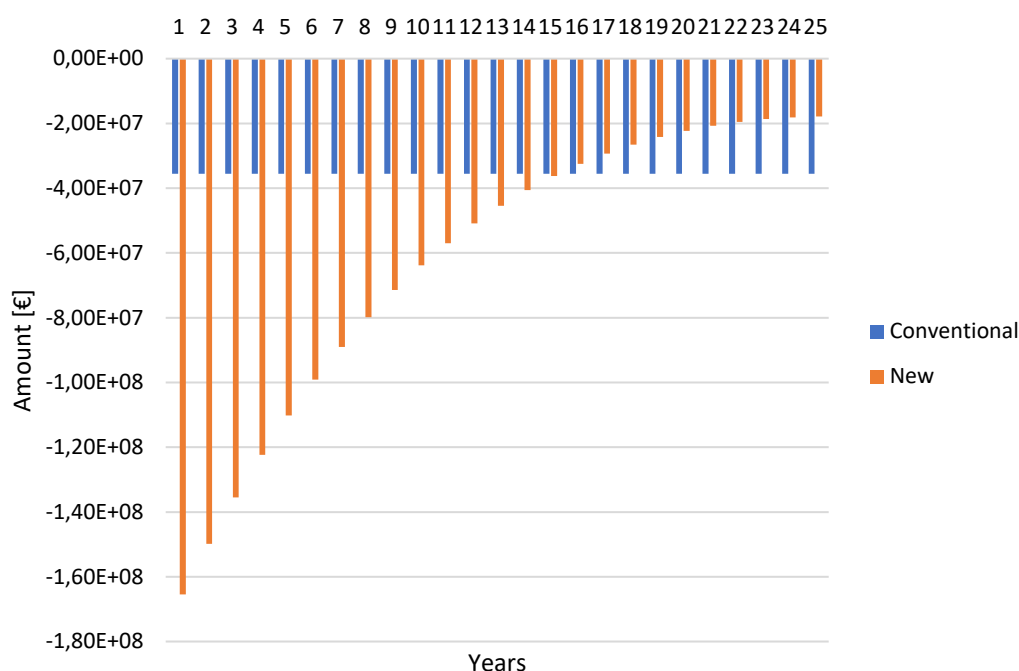


Figure 37 Cumulative discounted (discount rate 4.0 %) cash flow for the examined production of DCPD from pig manure via gasification compared to the conventional method of application of pig manure on the fields.

Economically due to the new process route of producing DCPD from pig manure, it is still quite expensive to produce. Although, when it is compared to the conventional method, after 9 years producing DCPD and treating manure would become cheaper. In addition, if the surplus keeps increasing and more interest is put into the new processes, payback period would become shorter.

### 7.3. Conclusions

Based on technical and economical evaluations, processing pig manure via incineration and producing DCPD is more feasible than processing pig manure with gasification. If dried solid pig manure is gasified, it should be further combusted to completely degrade the organic matter in the char and produce ashes. Further treatment with acid leaching and precipitation gives higher yields from ashes. When both process routes are compared to the conventional method, again the incineration route would become more feasible in less years than the gasification route. Also, the proposed process is achieving the goal of avoiding surplus of manure in the Netherlands and avoiding the loss of valuable phosphorus as a nutrient source. This fact would make the incineration route and production of DCPD even more interesting for the society. If the surplus keeps on increasing, more actions might be taken, which could decrease investment costs.

## 8. CONCLUSIONS AND RECOMMENDATIONS

The purpose of this study was to examine what would be a feasible process to treat manure further than what has been done so far. Aim was to find a way to recover phosphorus from manure to avoid loss of valuable nutrients, utilize the organic matter content in manure to produce energy and finally decrease the manure surplus in the Netherlands. This was done by first studying all possible treatment methods of manure and possibilities to recover phosphorus. Then a process comparison was made between the methods based on phosphorus concentrations, yields and energy balance over the process. The result was to treat the solid fraction of pig manure with drying and incineration followed by acid leaching of produced ashes. Final step was precipitation of phosphates from the leachate. Same was done for char obtained by a gasification plant.

Results from experiments showed that DCPD could be formed in the precipitation from acid leached ash solution with high yields of phosphate. DCPD could be sold as a phosphate fertilizer. Technically this route is feasible and comparable with the LEACHPHOS process of sewage sludge ashes, where also calcium phosphates are produced for fertilizer use. Based on economical evaluation this process route would become economically more feasible than the conventional method of treating pig manure after 9 years. This is a long time, but if the manure surplus keeps on increasing, more interest could be put into this treatment. For instance, by the help from government the process would become economically more feasible already before the 9 years.

DCPD was also formed from the acid leached solutions of char, but with lower yields and the final product was amorphous. Calcium carbonate was also formed, which originates from the acid leaching of char, where carbonate is found in the leachate. This lead to the unfeasibility of treating the manure further by gasification combined with acid leaching and precipitation of phosphates. Even, when the gasification route was compared with the conventional process, it would take 15 years before the process would be more feasible than the conventional one. Unlike the incineration route, where it might be possible to speed up the payback period, gasification is not economically feasible and probably would not receive much interest. There is a possibility that this route would become more feasible, if the char would be combusted and then the ashes would be treated in the same way as from direct incineration. However, this needs further research and experiments.

For further recommendations, treatment of side products was not studied. Residual from acid leaching and water treatment after precipitation should be taken into consideration. Also, purity of final product DCPD should be studied, whether it would affect the selling price and this way the feasibility of the process. On the other hand, optimization of the precipitation process should be done further, whether phosphates can be recovered with higher yields and more selectively.

It is possible to also use the pig manure ashes for phosphoric acid production by excluding precipitation step and adding a concentration step instead. In this way, also other phosphate fertilizers could be produced. Possibility to combine the phosphate product with the N,K separated in the treatment of the liquid fraction could be studied. By combining the two products, it would be possible to produce N,P,K compound fertilizers.

Feasibility analysis included the price of TSP, which has been increasing till May 2017 (WorldBank 2017). In this study it was not considered, whether the market price changes of fertilizers would affect the feasibility of the proposed process.

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## APPENDICES

### I Mass balances

### II Experimental results

**APPENDIX I Mass balances*****Anaerobic digestion and solid-liquid separation of pig manure***

Distribution coefficients for the components in streams for the anaerobic digestion and solid-liquid separation are shown in Table 36. Results for both of these methods using the presented coefficients are shown in Table 37, Table 38, Table 39 and Table 40.

*Table 36 Distribution factors for components in the manure in anaerobic digestion and solid-liquid separation.  
(Hoeksma, Buissonjé et al. 2014)*

<b>Component</b>	<b>Anaerobic digestion</b>	<b>Solid-liquid separation</b>
	<b>Digestate</b>	<b>Solid</b>
<b>Water</b>	1,00	0,12
<b>Dry matter (DM)</b>	OM + IM	OM + IM
<b>Inorganic matter (IM)</b>	1	0,70
<b>Organic matter (OM)</b>	0,40	0,70
<b>Total P</b>	Inorganic P + Organic P	Inorganic P + Organic P
<b>Inorganic P</b>	1,00	0,80
<b>Organic P</b>	1,00	0,80
<b>Total K</b>	1,00	0,14
<b>Total N</b>	Inorganic N + Organic N	Inorganic N + Organic N
<b>Organic N</b>	1,00	0,70
<b>Inorganic N</b>	1,00	0,01
<b>Mg</b>	1,00	0,70
<b>Ca</b>	1,00	0,70
<b>Fe</b>	1,00	0,70
<b>Zn</b>	1,00	0,70
<b>Cu</b>	1,00	0,70

*Table 37 Compositions of the initial manure and streams from anaerobic digestion.*

	Anaerobic digestion		
	Manure	Biogas	Digestate
Flow ton/year	1420000	36636	1383364
H <sub>2</sub> O kg/ton	907	0,0	931,0
Dry matter kg/ton	93	1000,0	69,0
Inorg. Matter kg/ton	50	0,0	51,3
Org. Matter kg/ton	43	1000,0	17,7
Total P kg/ton	4,6	0,0	4,7
Min P kg/ton	3,22	0,0	3,7
Org. P kg/ton	1,38	0,0	1,1
Total K kg/ton	5,8	0,0	6,0
Total N kg/ton	7,1	0,0	7,3
Org. N kg/ton	4,6	0,0	3,8
Min. N kg/ton	2,5	0,0	3,5
Mg kg/ton	1,8	0,0	1,8
Ca kg/ton	4	0,0	4,1
Fe kg/ton	0,04	0,0	0,0
Zn kg/ton	0,07	0,0	0,1
Cu kg/ton	0,03	0,0	0,0

*Table 38 Components flows for initial manure and streams from anaerobic digestion.*

	Anaerobic digestion		
	Manure	Biogas	Digestate
H <sub>2</sub> O ton/year	1287940	0	1287940
Dry matter ton/year	132060	36636	95424
Inorg. Matter ton/year	71000	0	71000
Org. Matter ton/year	61060	36636	24424
Total P ton/year	6532	0	6532
Min P ton/year	4572,4	0	5059
Org. P ton/year	1959,6	0	1473
Total K ton/year	8236	0	8236
Total N ton/year	10082	0	10082
Org. N ton/year	6532	0	5226
Min. N ton/year	3550	0	4856
Mg ton/year	2556	0	2556
Ca ton/year	5680	0	5680
Fe ton/year	61,1	0	61
Zn ton/year	99,4	0	99
Cu ton/year	42,6	0	43

Table 39 Compositions of streams from solid-liquid separation of manure.

	Solid-liquid separation	
	S4 (solid)	S5 (liquid)
Flow ton/year	221350	1162014
H <sub>2</sub> O kg/ton	698,2	975,4
Dry matter kg/ton	301,8	24,6
Inorg. Matter kg/ton	224,5	18,3
Org. Matter kg/ton	77,2	6,3
Total P kg/ton	23,6	1,1
Min P kg/ton	18,3	0,9
Org. P kg/ton	5,3	0,3
Total K kg/ton	5,2	6,1
Total N kg/ton	16,7	5,5
Org. N kg/ton	16,5	1,3
Min. N kg/ton	0,2	4,1
Mg kg/ton	8,1	0,7
Ca kg/ton	18,0	1,5
Fe kg/ton	0,2	0,0
Zn kg/ton	0,3	0,0
Cu kg/ton	0,1	0,0

Table 40 Component flows for streams from solid-liquid separation of manure.

	Solid-liquid separation	
	S4 (solid)	S5 (liquid)
H <sub>2</sub> O ton/year	154553	1133387
Dry matter ton/year	66797	28627
Inorg. Matter ton/year	49700	21300
Org. Matter ton/year	17097	7327
Total P ton/year	5226	1306
Min P ton/year	4047	1012
Org. P ton/year	1179	295
Total K ton/year	1153	7083
Total N ton/year	3706	6376
Org. N ton/year	3658	1568
Min. N ton/year	48,6	4808
Mg ton/year	1789	767
Ca ton/year	3976	1704
Fe ton/year	43	18
Zn ton/year	70	30
Cu ton/year	30	13

### ***Drying and combustion processes of solid pig manure***

Distribution coefficients for the components in streams for drying, incineration, gasification and pyrolysis of pig manure are shown in Table 41. Results for drying using the presented

coefficients are shown in Table 41 and results for the combustion processes are shown in Table 42, Table 43, Table 44 and Table 45.

*Table 41 Distribution factors for components in the manure in drying (Hoeksma, Buissonjé et al. 2014), incineration, pyrolysis and gasification (Schoumans, Rulkens et al. 2010).*

Component	Drying	Incineration	Pyrolysis		Gasification
	Dried solid	Ashes	Biochar	Oil	Biochar
<b>Water</b>	0,05	0,00	0,00	1	0
<b>Dry matter (DM)</b>	OM + IM	OM + IM	OM + IM	OM + IM	OM + IM
<b>Inorganic matter (IM)</b>	1,00	1,00	1,00	0	1,00
<b>Organic matter (OM)</b>	1,00	0,00	0,35	0,3	0,20
<b>Total P</b>	Inorganic P + Organic P	Inorganic P + Organic P	Inorganic P + Organic P	Inorganic P + Organic P	Inorganic P + Organic P
<b>Inorganic P</b>	1,00	0,99	0,95	0,05	0,97
<b>Organic P</b>	1,00	0,99	0,95	0,05	0,97
<b>Total K</b>	1,00	0,99	0,99	0,01	0,99
<b>Total N</b>	Inorganic N + Organic N	Inorganic N + Organic N	Inorganic N + Organic N	Inorganic N + Organic N	Inorganic N + Organic N
<b>Organic N</b>	1,00	0,01	0,4	0,36	0,01
<b>Inorganic N</b>	0,05	0,01	0,01	0,2	0,01
<b>Mg</b>	1,00	0,95	0,95	0,05	0,95
<b>Ca</b>	1,00	0,95	0,95	0,05	0,95
<b>Fe</b>	1,00	0,95	0,95	0,05	0,95
<b>Zn</b>	1,00	0,95	0,95	0,05	0,95
<b>Cu</b>	1,00	0,95	0,95	0,05	0,95

*Table 42 Compositions of streams from drying of solid manure.*

	<b>Drying</b>	
	<b>Water vapor</b>	<b>Dried solid</b>
<b>Flow ton/year</b>	146825	74524
<b>H<sub>2</sub>O kg/ton</b>	1000,0	103,7
<b>Dry matter kg/ton</b>	0,0	896,3
<b>Inorg. Matter kg/ton</b>	0,0	666,9
<b>Org. Matter kg/ton</b>	0,0	229,4
<b>Total P kg/ton</b>	0,0	70,1
<b>Min P kg/ton</b>	0,0	54,3
<b>Org. P kg/ton</b>	0,0	15,8
<b>Total K kg/ton</b>	0,0	15,5
<b>Total N kg/ton</b>	0,3	49,1
<b>Org. N kg/ton</b>	0,0	49,1
<b>Min. N kg/ton</b>	0,3	0,0
<b>Mg kg/ton</b>	0,0	24,0
<b>Ca kg/ton</b>	0,0	53,4
<b>Fe kg/ton</b>	0,0	0,6
<b>Zn kg/ton</b>	0,0	0,9
<b>Cu kg/ton</b>	0,0	0,4

*Table 43 Component flows for streams from drying of manure.*

	<b>Drying</b>	
	<b>Water vapor</b>	<b>Dried solid</b>
<b>H<sub>2</sub>O ton/year</b>	146825	7728
<b>Dry matter ton/year</b>	0	66797
<b>Inorg. Matter ton/year</b>	0	49700
<b>Org. Matter ton/year</b>	0	17097
<b>Total P ton/year</b>	0	5226
<b>Min P ton/year</b>	0	4047
<b>Org. P ton/year</b>	0	1179
<b>Total K ton/year</b>	0	1153
<b>Total N ton/year</b>	46	3660
<b>Org. N ton/year</b>	0	3658
<b>Min. N ton/year</b>	46	2
<b>Mg ton/year</b>	0	1789
<b>Ca ton/year</b>	0	3976
<b>Fe ton/year</b>	0	43
<b>Zn ton/year</b>	0	70
<b>Cu ton/year</b>	0	30

Table 44 Compositions of streams from incineration, gasification and pyrolysis of solid manure.

	Incineration		Gasification		Pyrolysis		
	Gases	Ashes	Gases	Biochar	Gases	Biochar	Oil
Flow ton/year	24824	49700	21405	53119	5984	55684	12857
H <sub>2</sub> O kg/ton	311,3	0,0	361,0	0,0	0,0	0,0	601,1
Dry matter kg/ton	688,7	1000,0	639,0	1000,0	1000,0	1000,0	398,9
Inorg. Matter kg/ton	0,0	1000,0	0,0	935,6	0,0	892,5	0,0
Org. Matter kg/ton	688,7	0,0	639,0	64,4	1000,0	107,5	398,9
Total P kg/ton	2,1	104,1	7,3	95,4	0,0	89,2	20,3
Min P kg/ton	1,6	80,6	5,7	73,9	0,0	69,0	15,7
Org. P kg/ton	0,5	23,5	1,7	21,5	0,0	20,1	4,6
Total K kg/ton	0,5	23,0	0,5	21,5	0,0	20,5	0,9
Total N kg/ton	146,0	0,7	169,3	0,7	147,0	26,3	102,5
Org. N kg/ton	145,9	0,7	169,2	0,7	146,7	26,3	102,4
Min. N kg/ton	0,1	0,0	0,1	0,0	0,3	0,0	0,0
Mg kg/ton	3,6	34,2	4,2	32,0	0,0	30,5	7,0
Ca kg/ton	8,0	76,0	9,3	71,1	0,0	67,8	15,5
Fe kg/ton	0,1	0,8	0,1	0,8	0,0	0,7	0,2
Zn kg/ton	0,1	1,3	0,2	1,2	0,0	1,2	0,3
Cu kg/ton	0,1	0,6	0,1	0,5	0,0	0,5	0,1

Table 45 Component flows for streams from incineration, gasification and pyrolysis of solid manure.

	Incineration		Gasification		Pyrolysis		
	Gases	Ashes	Gases	Biochar	Gases	Biochar	Oil
H <sub>2</sub> O ton/year	7728	0	7728	0	0,0	0	7727,6
Dry matter ton/year	17097	49700	13677	53119	5983,9	55684	5129,0
Inorg. Matter ton/year	0	49700	0	49700	0,0	49700	0,0
Org. Matter ton/year	17097	0	13677	3419	5983,9	5984	5129,0
Total P ton/year	52	5173	157	5069	0,0	4964	261,3
Min P ton/year	40	4006	121	3925	0,0	3845	202,3
Org. P ton/year	12	1167	35	1143	0,0	1120	58,9
Total K ton/year	12	1142	12	1142	0,0	1142	11,5
Total N ton/year	3624	37	3624	37	879,8	1463	1317,3
Org. N ton/year	3621	37	3621	37	877,9	1463	1316,9
Min. N ton/year	2	0	2	0	1,9	0	0,5
Mg ton/year	89	1700	89	1700	0,0	1700	89,5
Ca ton/year	199	3777	199	3777	0,0	3777	198,8
Fe ton/year	2	41	2	41	0,0	41	2,1
Zn ton/year	3	66	3	66	0,0	66	3,5
Cu ton/year	1	28	1	28	0,0	28	1,5

### ***Precipitation, evaporation, ultrafiltration and reverse osmosis of the liquid fraction of pig manure***

Distribution coefficients for the components in streams for precipitation, evaporation, ultrafiltration and reverse osmosis of liquid pig manure are shown in Table 46. Results for precipitation and evaporation using the presented coefficients are shown in Table 47 and



Table 48. Results for ultrafiltration and reverse osmosis using the presented coefficients are shown in Table 49 and Table 50.

*Table 46 Distribution coefficients for components in the manure in precipitation (Doyle and Parsons 2002), ultrafiltration (Fugère, Mameri et al. 2005), evaporation (Hoeksma, Buissonjé et al. 2014) and reverse osmosis (Johnson, Culkin et al. 2004).*

Component	Precipitation Precipitate	Ultrafiltration Retentate	Evaporation Concentrate	Reverse osmosis Retentate
Water	Equimolar amount	0,05	0,07	0,10
Dry matter (DM)	Total P + Total N + Mg	OM + IM	OM + IM	OM + IM
Inorganic matter (IM)	Inorganic P + Inorganic N + Mg	0,20	0,90	0,90
Organic matter (OM)	0,00	1,00	1,00	0,98
Total P	Inorganic P + Organic P	Inorganic P + Organic P	Inorganic P + Organic P	Inorganic P + Organic P
Inorganic P	0,99	0,05	1,00	0,98
Organic P	0,05	1,00	1,00	0,98
Total K	0,00	0,50	1,00	0,98
Total N	Inorganic N + Organic N	Inorganic N + Organic N	Inorganic N + Organic N	Inorganic N + Organic N
Organic N	0,00	1,00	1,00	0,98
Inorganic N	Equimolar amount	0,05	0,10	0,98
Mg	Equimolar amount	0,95	0,90	0,98
Ca	0,00	0,95	0,90	0,98
Fe	0,00	0,95	0,90	0,98
Zn	0,00	0,95	0,90	0,98
Cu	0,00	0,95	0,90	0,98

*Table 47 Compositions of streams from precipitation and evaporation of the liquid fraction of manure.*

	Precipitation (struvite)		Evaporation	
	Precipitate	Liquid	Concentrate	Water
Flow ton/year	2614	1159400	105834	1058377
H <sub>2</sub> O kg/ton	442,1	976,6	749,6	995,9
Dry matter kg/ton	557,9	23,4	250,4	2,0
Inorg. Matter kg/ton	552,3	17,1	181,1	2,0
Org. Matter kg/ton	0,0	6,3	69,2	0,0
Total P kg/ton	388,7	0,3	12,3	0,0
Min P kg/ton	383,1	0,0	9,6	0,0
Org. P kg/ton	5,6	0,2	2,8	0,0
Total K kg/ton	0,0	6,1	66,9	0,0
Total N kg/ton	69,7	5,3	19,4	4,1
Org. N kg/ton	0,0	1,4	14,8	0,0
Min. N kg/ton	69,7	4,0	4,5	4,1
Mg kg/ton	99,5	0,4	6,5	0,1
Ca kg/ton	0,0	1,5	14,5	0,2
Fe kg/ton	0,0	0,0	0,2	0,0
Zn kg/ton	0,0	0,0	0,3	0,0
Cu kg/ton	0,0	0,0	0,1	0,0

Table 48 Components flows for streams from precipitation and evaporation of the liquid fraction of manure.

	Precipitation (struvite)		Evaporation	
	Precipitate	Liquid	Concentrate	Water
H2O ton/year	1155,8	1132231,4	79337,1	1054050,1
Dry matter ton/year	1458,7	27168,5	26497,2	2130,0
Inorg. Matter ton/year	1444,0	19856,0	19170,0	2130,0
Org. Matter ton/year	0,0	7327,2	7327,2	0,0
Total P ton/year	1016,3	290,1	1306,4	0,0
Min P ton/year	1001,6	10,1	1011,7	0,0
Org. P ton/year	14,7	279,9	294,7	0,0
Total K ton/year	0,0	7083,0	7083,0	0,0
Total N ton/year	182,3	6193,3	2048,5	4327,1
Org. N ton/year	0,0	1567,7	1567,7	0,0
Min. N ton/year	182,3	4625,6	480,8	4327,1
Mg ton/year	260,1	506,7	690,1	76,7
Ca ton/year	0,0	1704,0	1533,6	170,4
Fe ton/year	0,0	18,3	16,5	1,8
Zn ton/year	0,0	29,8	26,8	3,0
Cu ton/year	0,0	12,8	11,5	1,3

Table 49 Compositions of streams from ultrafiltration and reverse osmosis of the liquid fraction of manure

	Ultrafiltration		Reverse osmosis	
	Retentate	Permeate	Retentate	Permeate
Flow ton/year	68257	1093758	139689	1022325
H2O kg/ton	830,2	984,4	811,4	997,8
Dry matter kg/ton	169,8	15,6	188,6	2,2
Inorg. Matter kg/ton	62,4	15,6	137,2	2,1
Org. Matter kg/ton	107,3	0,0	51,4	0,1
Total P kg/ton	5,1	0,9	9,2	0,0
Min P kg/ton	0,7	0,9	7,1	0,0
Org. P kg/ton	4,3	0,0	2,1	0,0
Total K kg/ton	51,9	3,2	49,7	0,1
Total N kg/ton	26,5	4,2	44,7	0,1
Org. N kg/ton	23,0	0,0	11,0	0,0
Min. N kg/ton	3,5	4,2	33,7	0,1
Mg kg/ton	10,7	0,0	5,4	0,0
Ca kg/ton	23,7	0,1	12,0	0,0
Fe kg/ton	0,3	0,0	0,1	0,0
Zn kg/ton	0,4	0,0	0,2	0,0
Cu kg/ton	0,2	0,0	0,1	0,0

*Table 50 Component flows for streams from ultrafiltration and evaporation of the liquid fraction of manure.*

	Ultrafiltration		Reverse osmosis	
	Retentate	Permeate	Retentate	Permeate
<b>H2O ton/year</b>	56669,4	1076717,8	113338,7	1020048,5
<b>Dry matter ton/year</b>	11587,2	17040,0	26350,7	2276,5
<b>Inorg. Matter ton/year</b>	4260,0	17040,0	19170,0	2130,0
<b>Org. Matter ton/year</b>	7327,2	0,0	7180,7	146,5
<b>Total P ton/year</b>	345,3	961,1	1280,3	26,1
<b>Min P ton/year</b>	50,6	961,1	991,5	20,2
<b>Org. P ton/year</b>	294,7	0,0	288,8	5,9
<b>Total K ton/year</b>	3541,5	3541,5	6941,3	141,7
<b>Total N ton/year</b>	1808,1	4567,4	6248,0	127,5
<b>Org. N ton/year</b>	1567,7	0,0	1536,3	31,4
<b>Min. N ton/year</b>	240,4	4567,4	4711,7	96,2
<b>Mg ton/year</b>	728,5	38,3	751,5	15,3
<b>Ca ton/year</b>	1618,8	85,2	1669,9	34,1
<b>Fe ton/year</b>	17,4	0,9	18,0	0,4
<b>Zn ton/year</b>	28,3	1,5	29,2	0,6
<b>Cu ton/year</b>	12,1	0,6	12,5	0,3

## APPENDIX II Experimental results

### *Acid leaching of ash*

Acid consumption, P concentrations before and after acid leaching of ashes with sulfuric acid are shown in Table 51.

*Table 51 Acid addition, acid concentration and initial P concentration in acid leaching of ashes.*

Experiment [-]	Material [-]	Leaching time [h]	Initial P concentration [g/L]	Acid addition [L]	Acid concentration [mol/L]	Corrected P initial [g/L]	Final P concentration [g/L]
1	Ash	-	0,60	0,011	1,0	0,5	0,63
2	Ash	-	0,60	0,010	1,0	0,5	0,56
3	Ash	-	6,02	0,088	1,0	3,3	3,36
4	Ash	-	6,02	0,085	1,0	3,3	4,80
5	Ash	1	6,02	0,087	1,0	3,3	3,55
6	Ash	1	6,02	0,085	1,0	3,3	3,66
7	Ash	4	6,02	0,087	1,0	3,3	3,23
8	Ash	4	6,02	0,085	1,0	3,4	3,65
9	Ash	4	6,02	0,085	1,0	3,3	3,18

### *Acid leaching of char*

Acid consumption, P concentrations before and after acid leaching of char with sulfuric acid are shown in Table 52.

*Table 52 Acid addition, acid concentration and initial P concentration in acid leaching of char.*

Experiment [-]	Material [-]	Leaching time [h]	Initial P concentration [g/L]	Acid addition [L]	Acid concentration [mol/L]	Corrected P initial [g/L]	Final P concentration [g/L]
1	Char	-	0,40	0,007	1,0	0,4	0,37
2	Char	-	0,40	0,003	1,0	0,4	0,34
3	Char	-	4,05	0,022	1,0	3,3	4,89
4	Char	-	4,05	0,023	1,0	3,3	5,99
5	Char	1	4,05	0,025	1,0	3,2	2,95
6	Char	1	4,05	0,026	1,0	3,2	2,98
7	Char	1	4,05	0,027	1,0	3,2	2,87
8	Char	4	4,05	0,025	1,0	3,2	3,11
9	Char	4	4,05	0,027	1,0	3,2	2,92

***Precipitation from ash originated solutions***

Experimental conditions and results for pH and P concentrations before and after precipitation from ash originated solutions are shown in Table 53. Initial P concentrations are corrected to the addition of lime into the solution.

*Table 53 Precipitation results from ash originated solutions.*

Experiment [-]	Precipitation time [min]	Leaching time [h]	pH <sub>i</sub> [-]	pH <sub>e</sub> [-]	Lime addition [L]	Initial volume of solution [L]	Corrected initial P concentration [g/]	Final P concentration in aqueous solution [g/L]
1	10	-	2,0	6,0	0,10	0,05	3,22	0,26
2	20	-	2,0	-	0,10	0,05	1,75	0,37
3	30	-	2,0	6,2	0,10	0,05	3,22	0,19
4	10	-	2,0	6,2	0,10	0,04	1,75	0,24
5	30	-	2,0	6,0	0,10	0,05	1,75	0,37
6	20	-	2,0	6,1	0,05	0,05	3,22	0,27
7	20	-	2,0	5,7	0,07	0,05	3,22	0,60
8	10	1	2,0	6,0	0,10	0,05	1,46	1,61
9	20	1	2,0	5,8	0,10	0,05	1,29	0,38
10	30	1	2,0	6,3	0,10	0,05	1,46	0,68
11	10	1	2,0	6,0	0,10	0,05	1,50	0,60
12	20	1	2,0	6,0	0,10	0,05	1,50	0,55
13	30	1	2,0	6,0	0,09	0,05	1,50	0,39
14	10	4	2,0	5,9	0,10	0,05	1,33	0,52
15	20	4	2,0	5,9	0,10	0,05	1,33	0,37
16	30	4	2,0	6,1	0,10	0,05	1,49	0,38
17	10	4	2,0	5,8	0,10	0,05	1,49	0,58
18	20	4	2,0	5,9	0,10	0,05	1,30	0,51
19	30	4	2,0	6,1	0,10	0,05	1,30	0,39

***Precipitation results from char originated solutions***

Experimental conditions and results for pH and P concentrations before and after precipitation from char originated solutions are shown in Table 54. Initial P concentrations are corrected to the addition of lime into the solution.

Table 54 Precipitation results from char originated solutions.

Experiment [-]	Precipitation time [min]	Leaching time [h]	pHi [i]	pHe [-]	Lime addition [L]	Initial volume of solution [L]	Corrected initial P concentratio n [g/l]	Final P concentratio n in aqueous solution [g/L]
1	30	-	2	5,9	0,05	0,05	2,92	0,66
2	30	-	2	5,9	0,05	0,05	2,92	0,57
3	10	-	2	5,9	0,10	0,05	1,95	-
4	20	-	2	-	0,10	0,05	1,95	0,60
5	30	1	2	6,0	0,10	0,05	1,08	0,66
6	20	1	2	5,9	0,10	0,05	1,10	0,65
7	10	1	2	5,9	0,09	0,05	1,10	0,70
8	10	1	2	5,9	0,09	0,05	1,12	0,79
9	30	1	2	6,1	0,10	0,05	1,06	0,60
10	20	1	2	6,1	0,10	0,05	1,06	0,57
11	10	4	2	6,3	0,10	0,05	1,14	0,48
12	20	4	2	6,4	0,10	0,04	0,98	0,39
13	30	4	2	6,2	0,10	0,05	1,08	0,57
14	10	4	2	6,0	0,08	0,04	1,08	0,63
15	20	4	2	6,0	0,10	0,05	1,06	0,62
16	30	4	2	5,9	0,08	0,04	1,06	0,73

**Analysis method verification**

Analysis methods were tested with known concentrations. Results for the UV-VIS using the Hach Lange kit method for phosphate measurements are shown in Figure 38. Phosphoric acid was diluted to different concentrations for the measurements. Results from UV-VIS can be considered reliable concerning the graph in Figure 38.

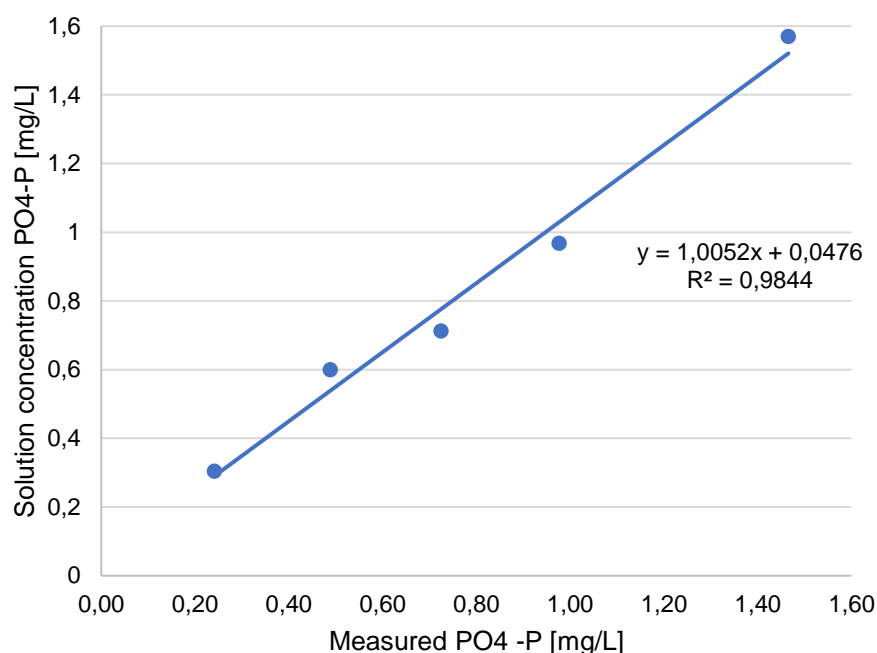


Figure 38 Measured phosphorus concentrations with UV-VIS compared to the initial known concentrations of phosphorus.

### **Acid leaching experiments using $\text{Na}_2\text{CO}_3$**

Acid leaching experiments for ashes have been done before by using different acids, sulfuric acid, maleic acid, citric acid and oxalic acid. Most promising is the oxalic acid, because high P recovery has been achieved with less acid addition and with higher pH values. With sulfuric acid pH of 2 has to be applied in order to reach close to 100 % P recovery. With oxalic acid pH of 4 is sufficient to recover nearly all P. Experiments were done also by adding sodium oxalate to the solution before sulfuric acid addition. This also gave good results and less acid was needed. (Kootstra A.M.J 2015) However, sodium oxalate is relatively expensive for which sodium carbonate has been considered instead. Experiments, which were similar to the acid leaching experiments described earlier in this report, were also done by adding 0.85 g of sodium carbonate into 1g/100mL ash solution. Experiments were done by reaching pH values from 2 to 9 using sulfuric acid. Results are shown in Figure 39 with P concentrations in aqueous solutions after acid leaching at different pH values, Figure 40 with P yields after acid leaching at different pH values and Figure 41 with sulfuric acid consumption at different pH values.

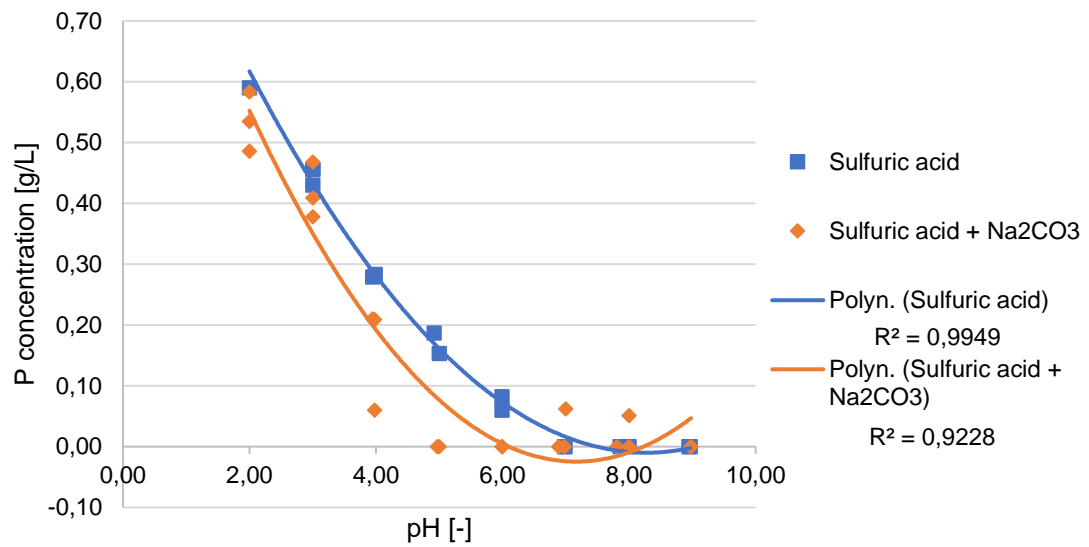


Figure 39 Phosphate concentration in the aqueous solution after acid leaching with sulfuric acid and with sulfuric acid + Na<sub>2</sub>CO<sub>3</sub>.

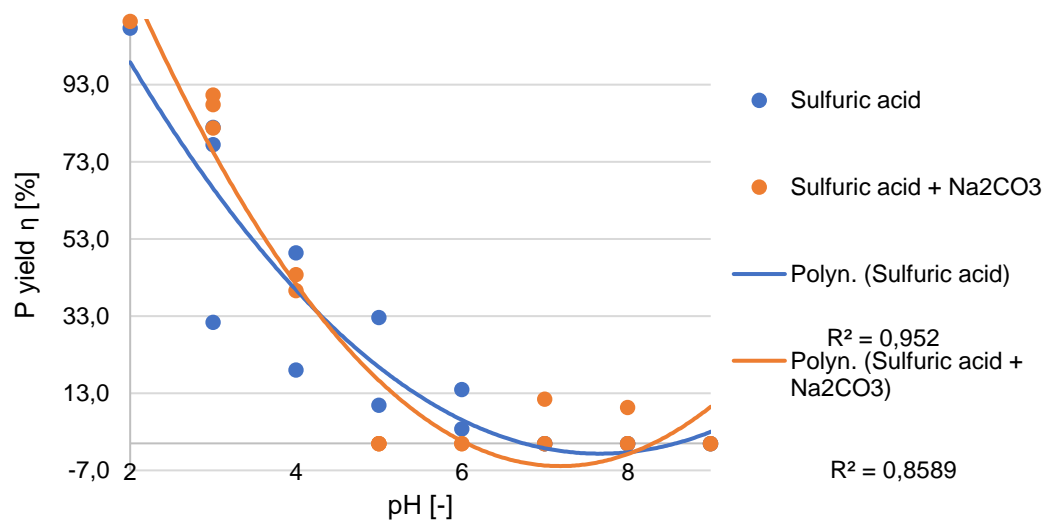


Figure 40 Phosphate yield in the aqueous solution after acid leaching with sulfuric acid and sulfuric acid + Na<sub>2</sub>CO<sub>3</sub>.



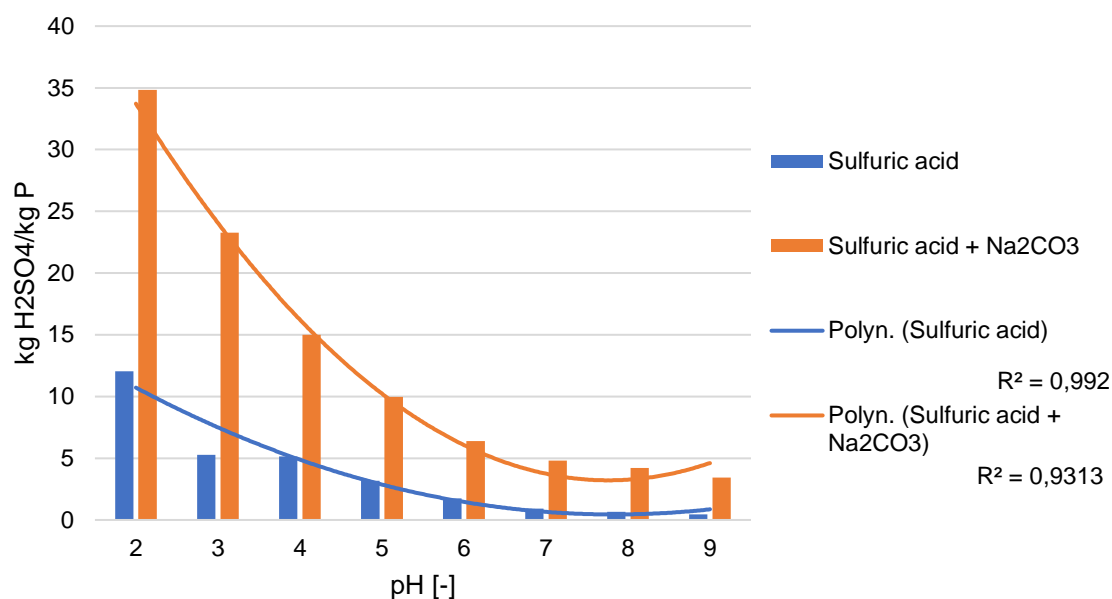


Figure 41 Acid consumption in acid leaching with sulfuric acid and with sulfuric acid + Na<sub>2</sub>CO<sub>3</sub>.

Based on results the presence of Na<sub>2</sub>CO<sub>3</sub> does not enhance the acid leaching of phosphates. Concentration of P is lower and yield of P is also lower than with use of only sulfuric acid. Acid consumption increases remarkably, when Na<sub>2</sub>CO<sub>3</sub> is also present. This can be explained by the carbonic acid equilibrium shown in Figure 42. Carbonate ion, which should precipitate with calcium, is only present at higher pH values. In this case the Na<sub>2</sub>CO<sub>3</sub> performs as a buffer.

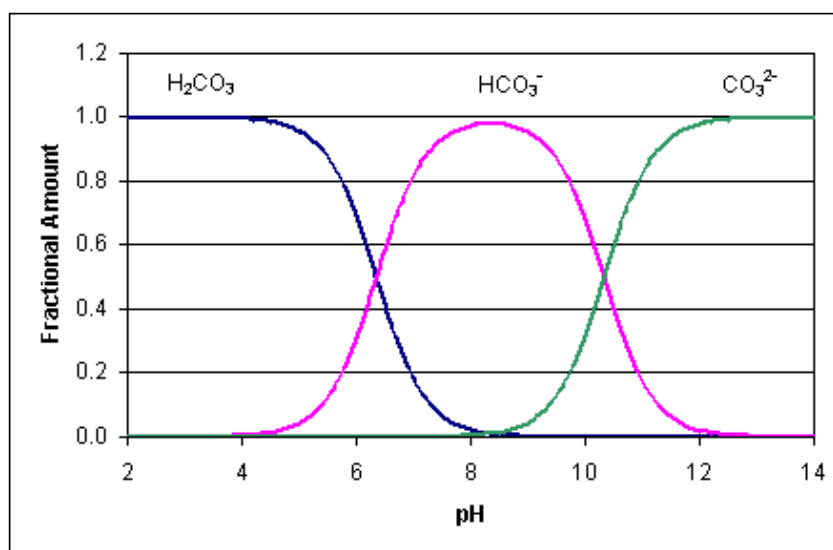


Figure 42 Carbonic acid equilibrium.