

Wastewater to renewable energy at a tapioca factory in Vietnam

In-situ evaluation of anaerobic covered pond treating
high strength industrial wastewater



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Water and Environmental Engineering
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by

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Picture on front page: covered anaerobic digestion pond at Wusons tapioca factory, taken by author.

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Preface and acknowledgements

The project presented in this report has been performed as a minor field study, MFS, to conduct a master thesis in environmental engineering at the faculty of engineering, Lund University. Preparation began during the spring of 2014 when initial contacts were made. Håkan Rosqvist, currently working at Thyréns but formerly having a private consulting company where I have done an internship and worked, introduced me to Thomas Hertzman who is working at the Swedish-Vietnamese collaboration organisation Centec in Hanoi. Mr Hertzman kindly redirected me to Duong Nguyen Khang who is the coordinator of the research cooperation program for livestock-based sustainable agriculture in the lower Mekong-basin (MEKARN) and senior lecturer at Nong Lam University, situated in the suburbs of Ho Chi Minh City. Together with Mr Khang and Thomas Reg Preston, who is also involved in the MEKARN project, professor at Nong Lam University and with long experience in the biogas field, planning of the project started. During this time contact was also made with the biogas-consulting company BioMil AB through the formerly CEO Björn Goffeng after recommendation from Eva Leire, the head of the Technology and Society department at the Faculty of Engineering, Lund University. After a meeting at the company it was decided that Anders Hjort, working at the company and with experience from biogas projects in developing countries in Asia and South-America, would serve as a supporting supervisor during the project. It was also decided that prior to going to Vietnam I would have an office space at the company in Lund where I could prepare for the project ahead. Contact was also made with the department of Chemical Engineering to find a suitable supervisor and examiner of the thesis. It was decided that Åsa Davidsson, research associate at the department and with long experience of biogas would be the supervisor and Jes la Cour Jansen, professor at the department, would be the examiner. I would like to thank all of the above, without you the project would never have been formed in the first place. I would also like to thank all of the co-workers at BioMil AB for their support and for sharing their experience within the field during my stay there. Furthermore, I would like to thank Gerhard Barmen and the rest of the MFS group in Lund for granting me the scholarship, and all the co-workers and other MFS students at the educational institute in Härnösand for their interesting thoughts and useful information.

During the stay in Vietnam help has come from both expected and unexpected directions, but I would like to begin by thanking everyone I have met through this project for their effort to help, and their effort to make my stay in Vietnam as pleasant as it was. Furthermore I would like to thank Nguyen Manh in the environmental lab at Nong Lam University for his help with both preparing and conducting the lab analysis. I would also like to thank Nguyen Minh Triet who introduced me to Mr Manh, and helped me contact the Quatest 3 lab, who performed the analysis of cyanide. Thanks also to all of the students who have helped me in the project and made me feel welcome at the university, especially Tu Pham who has helped and supported me even though he is not involved in the project at all. I am also very grateful to Vu Hoang Son, manager at the factory, for letting me stay in his home at the factory and for giving his time to support me with all that I needed for the project, both practically and theoretically. Thanks also to Le Chi Cuong for his company and help at the factory and for providing me with data and information.

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Gerhard Barmen

Local MFS Programme Officer

Summary

Anaerobic digestion is a cost-effective way of treating high organic content wastewater, as it efficiently removes large amounts of organics at the same time as biogas is produced. The production of starch from cassava roots, named tapioca, creates large amounts of high organic content wastewater and uses large amounts of thermal energy for drying the starch. At Wusons tapioca factory in southern Vietnam the wastewater is treated in an anaerobic covered pond, a low technology system for anaerobic digestion which has become popular at tapioca factories in Vietnam. The performance of the digester is however not optimal and process failures occur regularly which can partly be ascribed to the fact that the understanding of the system is poor and other than pH no measurements has previously been done on the wastewater. In this project the influent and effluent wastewater from the digester has therefore been characterised and the conditions at the factory investigated with the aim of coming up with in-situ adapted suggestions of how the performance of the digester could be improved.

The results from the characterization showed that the influent wastewater was close to optimal for anaerobic digestion, with a ratio between organics and nutrients (nitrogen and phosphorus) close to the theoretically optimal value commonly found in literature. Furthermore the results showed that the concentration of nitrogen and phosphorus were kept constant through the digestion process, but the ammonia concentrations doubled, according to the expected. Solids removal showed to be high, as did the removal of organics, but the discharge standards were still not met for any of these parameters. Cyanide, present in the wastewater because of the cassava roots special composition, was found to be removed very well and the levels met the discharge standards.

The results indicate that the digester had problem with low pH, which is normal for this kind of wastewater. This problem could be addressed by for example adding calcium carbonate in the influent to increase the alkalinity (instead of sodium hydroxide which is used at the factory today), using fungi as primary treatment for increasing alkalinity or separating the acidifying phase of the digestion from the biogas-forming phase. Furthermore it was found that sodium hydroxide, which is used both for cleaning the equipment in the factory and regulating pH, might have an inhibitory effect on the digester and alternatives should be sought for. It was also found that improvements to the digestion process could be done by regulating the flow to the digester. During the project an additional anaerobic covered pond was built at the factory but as the results of the wastewater characterization performed showed that there was not much biodegradable matter left in the effluent from the first digester and that ammonia levels were high it is suggested that the flow is regulated for better use of both anaerobic ponds. For example the ponds could be used to separate the phases of the digestion process as suggested above. Further suggestions consider the removal of big solids in the influent wastewater, better usage of primary pond, and keeping the outlet from the digester clean.

In addition to the above it was found that the factory should keep better track of what is happening in the digester by starting to monitor some parameters and in this way introduce some forward planning and thus avoid process failures. First of all alkalinity should be measured instead of pH to be able to regulate the alkalinity before pH drops and causes process failure as was observed. The flow should also be monitored as the big variations, that are normal in the factory, can cause problems for the digester.

Keywords: anaerobic digestion, wastewater treatment, cassava, tapioca, biogas, Vietnam, minor field study

Abbreviations

COD	Chemical Oxygen Demand
BOD	Biochemical Oxygen Demand
FAN	Free Ammonia Nitrogen
HRT	Hydraulic Retention Time
MDL	Minimum Detection Limit
OLR	Organic Loading Rate
TAN	Total Ammonia Nitrogen
TS	Total Solids
TVS	Total Volatile Solids
TSS	Total Suspended Solids
UASB	Upflow Anaerobic Sludge Blanket
VFA	Volatile Fatty Acids
VS	Volatile Solids
VSS	Volatile Suspended Solids
WW1	Wastewater 1, influent from root washing
WW2	Wastewater 2, influent from centrifugation
WW3	Wastewater 3, effluent from Anaerobic digestion 1

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1 Introduction

The production of starch from cassava roots, commonly named tapioca, generates big amounts of high organic content wastewater which if not treated has a big negative impact on the environment. In Vietnam cassava is the third most produced crop after rice and sugar cane (FAOSTAT, 2014). Most of the cassava is used for production of tapioca and there are nearly 100 tapioca factories in Vietnam (MOIT, 2013). The wastewater treatment at these factories are varying, most of them use open pond systems (Mai, 2006) but there are also a number of factories that have installed anaerobic digestion as a treatment step (CDM, 2011; CDM, 2006; Deutsche Welle, 2013). Anaerobic digestion offers an efficient way of removing organics at the same time as biogas is produced which provides the factories with a cost-effective way of drying the tapioca starch, a process which normally requires large amounts of energy. However, even if tapioca wastewater in theory and at lab-scale is highly suitable for anaerobic digestion the performance of the digesters is varying and usually not optimal as the understanding of these systems is generally low (Mai, 2006). The composition of the wastewater can be very different depending on the production process used to extract the starch and the quality of the raw product. This, in addition to the fact that each factory has different prerequisites in terms of for example the building-techniques used and the space available makes it necessary to find in-situ solutions to solve each factories problems for improving both the wastewater treatment and biogas production. In this project the performance of a covered anaerobic pond, treating wastewater from Wusons tapioca factory situated in southern Vietnam, has been evaluated. Field work to access the specific conditions at the factory and sample collection for wastewater characterisation was performed and the performance of the digester evaluated. Attention was put on identifying problems with this specific type of digester under the prevailing circumstances and finding easy and feasible solutions to improve it, as opposed to replacing the system with a more efficient one. In literature more advanced techniques like the upflow anaerobic sludge blanket (UASB) are generally evaluated and recommended for treatment of tapioca wastewater (Mai, 2006) but in reality most systems at tapioca factories in Vietnam and other developing countries where tapioca production is common are more simple, like the one investigated in the project, and the problems they face concern operational and practical problems.

1.1 Aim and research questions

The aim of this project was to propose and evaluate in-situ adapted solutions of how to improve the anaerobic digestion process at Wusons tapioca factory in Vietnam. This was assessed by the following research questions (RQ):

RQ1 What factors are usually a problem with this type of wastewater and treatment process?

RQ2 How does the wastewater treatment and biogas production work at the factory today?

RQ3 What could be done to improve the wastewater treatment and biogas production at the factory and how would this be implemented?

1.2 Method

To meet the aim of the project a literature study in combination with field work and lab analysis was performed. The literature study was focused on finding out what kind of

problems others had found with this specific wastewater and treatment process as well as finding solutions to these problems (RQ1 & RQ3). Research performed in Vietnam or other developing countries with similar conditions were sought for, as well as research specifically about tapioca processing and anaerobic digestion in covered ponds. However, due to the lack of research in this area, research from other countries as well as on other substrates and treatment methods were also studied. In these cases the relevance of the research was considered in respect to the subject at hand. To evaluate how the wastewater treatment and biogas production worked at the factory today (RQ2) field work and subsequent lab analysis of a chosen set of parameters was performed: pH, temperature, total suspended solids (TSS), volatile solids (VS), total nitrogen, total phosphorus, ammonia nitrogen, cyanide, chemical oxygen demand (COD) and biochemical oxygen demand (BOD₅) of the wastewater, and gas content (methane, carbon dioxide and hydrogen sulphide) of the gas. The parameters were chosen because of their ability to give information about the performance of the digester, and limited according to the below stated delimitations. The results from the field work were combined with the literature study to fully answer RQ3. The methodology and material used for field work and lab analysis is further described in Chapter 4.

1.3 Delimitation

The anaerobic digestion is only part of the wastewater treatment at the factory and in this project it is only the anaerobic digestion step that has been evaluated, while the other parts of the treatment process are only considered in respect to the results of this evaluation. The evaluation itself has primarily been limited by time and money when it comes to how many and which parameters should be measured and how many samples should be collected, but also the available analysis technique. The sampling procedure was also limited by practical issues like when the factory could be visited and how the samples could be stored and transported, as well as the working hours of the factory and stability of the process. The number of samples taken has affected the credibility of the results, as more sampling sessions would have given the results more credibility and a broader understanding of the system.

2 Tapioca starch processing industry

2.1 Generally about cassava

Cassava (*Manihot esculenta* Crantz), is a woody, perennial shrub which grows from 1-5 m in height and has large tuberous roots from which tapioca starch is produced, as seen in Figure 2.1. It is one of agriculture's oldest crops originating from South America but today spread all over the world's tropical and subtropical regions (FAO, 2013). Because of its tolerance against drought and for marginal soils it is commonly grown by poor farmers in developing countries, and today millions of small-scale farmers in more than 100 countries grow cassava (FAO, 2013) and it is the third most important source of calories in the tropics after rice and maize (FAO, 2008). Production of cassava has increased significantly during the last decade and the view of cassava as the "food of the poor" is now changing, according to the Food and Agriculture Organization of the United Nations, FAO (2013). The many advantages of the multipurpose cassava is being realized as it responds well to the priorities of developing countries, to trends in the global economy and to the challenge of climate change. In Asia, where 30 % of the world's cassava production is carried out, most cassava is grown to meet the demand for dried cassava chips and tapioca starch for use in commercial livestock feed and for industrial processing. An important developing field is also as feedstock for the production of biofuel (FAO, 2013). In Vietnam, cassava is the third most produced crop (measured in tonnes) after rice and sugar cane (FAOSTAT, 2014) and the production has more than quadrupled since 2000, as can be seen in Figure 2.2.



Figure 2.1. Photos of cassava. To the left a cassava plantation as frequently seen in southern Vietnam on the side of the road, bordering the rubber tree plantations. In the middle one cassava plant, and to the right cassava roots.

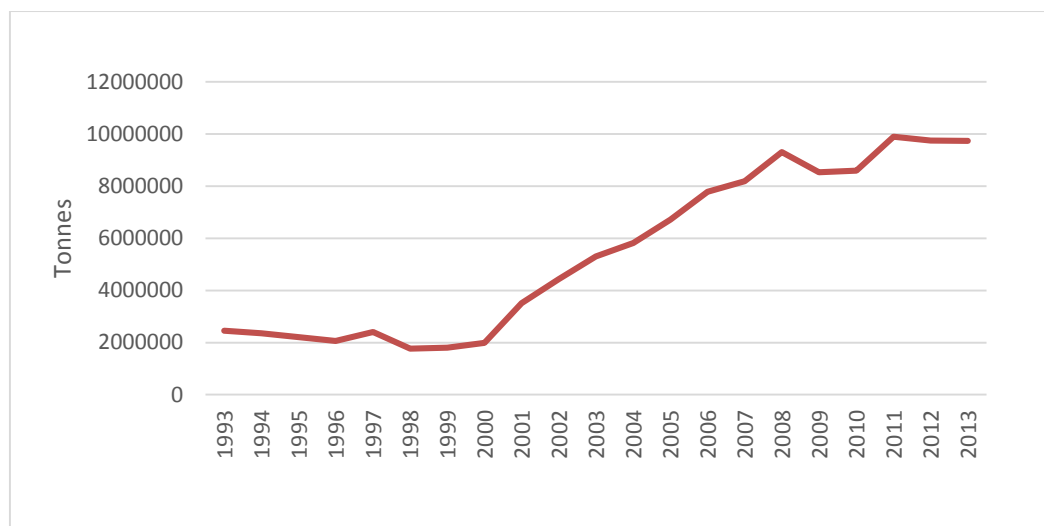


Figure 2.2. Cassava production in Vietnam during the last 20 years, 1993-2013 (FAOSTAT, 2014). No permission needed according to FAOSTAT terms and conditions.

Cassava is a truly versatile crop and in fact the whole plant can be used. The roots, which are the main product, can be processed in to a variety of food products and animal fodder, but they can also be used for industrial purposes. For making noodles and cakes, for frying meat and fish, in textiles, pharmaceuticals, cardboard, monosodium glutamate (MSG), glucose, maltose and plywood; these are all just a few examples of how the roots can be used. The leaves, which contain up to 25 % protein, can be used as animal fodder and the stem as firewood (FAO, 2013). However, since the whole plant contains high levels of cyanogenic glycosides it is always processed in some way before consumption to avoid intoxication (FAO, 2013).

The composition of cassava roots is 60-65 % moisture, 20-31 % carbohydrate (of which 60-65 % is starch), 0.2-0.6 % ether extracts, 1-2 % crude protein and comparatively low concentrations of vitamins and minerals (Tewe, 2004). The peel of the cassava generally has higher concentrations of protein, fat, fibre and minerals (Montagnac, et al., 2009), but also cyanogenic glycosides (Tewe, 2004).

2.2 Production process of tapioca starch

The starch content of a fresh cassava root varies from 25-30 percent, and normally four tons of fresh cassava roots yield one ton of dry tapioca starch (Mai, 2006). In Vietnam, starch processing is carried out in large- to middle scale factories or in rural households by traditional methods (Mai, 2006). In general terms the fresh roots are peeled and rinsed from dirt and sand, chopped and grinded into smaller pieces and then the starch is extracted through a series of steps where the starch is separated from the fibres and bleaching is performed through addition of chemicals (Mai, 2006). The extraction process looks different depending on the scale of the process but generally it can be said that large scale factories have more extraction steps than household-scale manufactures and can therefore produce a higher quality starch. However, all processes can generate starch of different quality at different extraction steps which are used for different purposes. Household-scale manufactures in Vietnam generally only produce wet starch due to the lack of space for drying while large-scale factories centrifuge and dry the wet starch into higher quality dry starch (Mai, 2006). Figure 2.3 describes the production process at a large-scale tapioca factory in Vietnam.

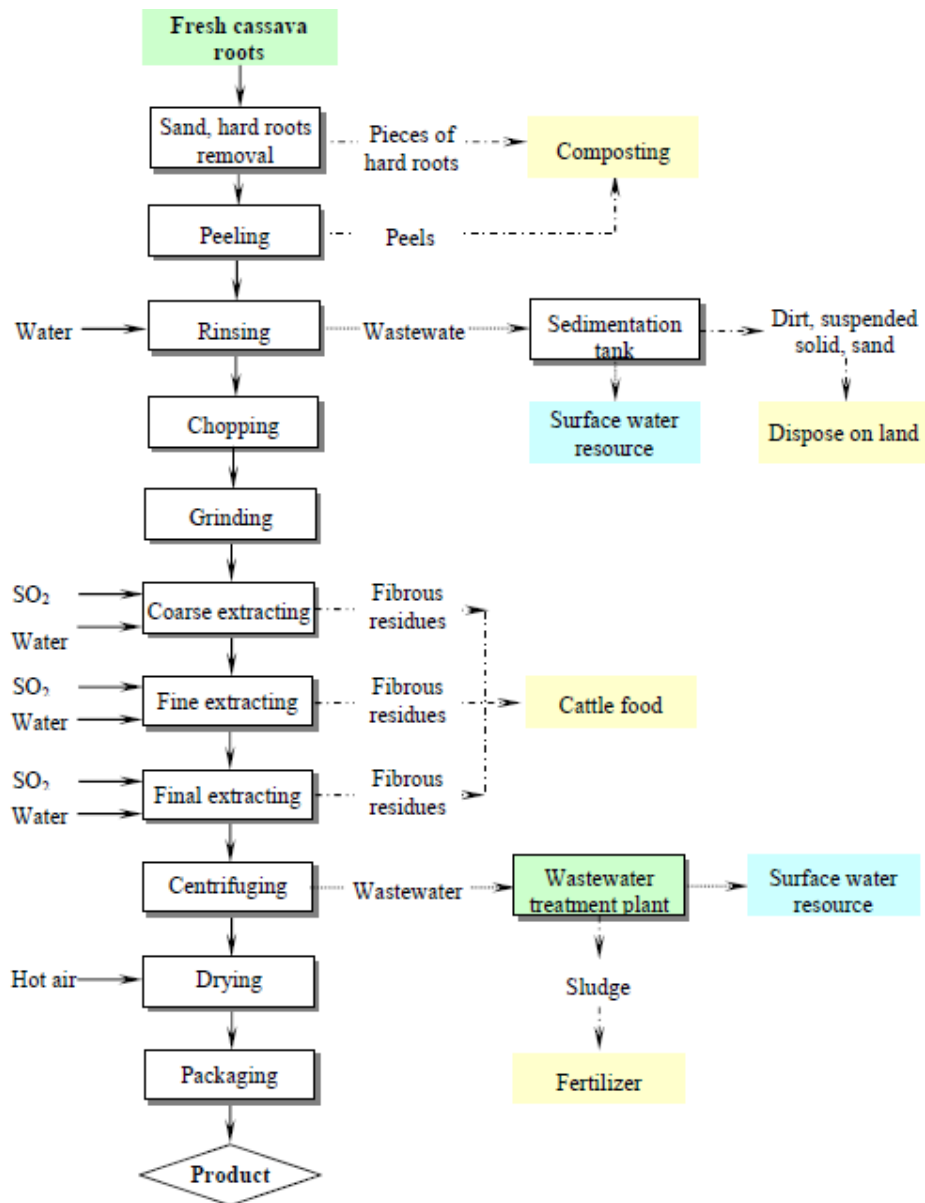


Figure 2.3. Illustration of the large-scale tapioca production process at the factory Phuoc Long Tapioca Co., Ltd in Binh Phuoc province, Vietnam. (Mai, 2006) Published with kind permission from Mai.

2.3 Environmental problems with tapioca production

The tapioca processing industry give rise to a number of environmental problems more or less easily solved.

2.3.1 Resource consumption

Tapioca processing requires large amounts of fresh water for washing the roots from contaminants and for the extraction process. According to Mai (2006) this water mainly constitute surface and groundwater and amounts to about 10-30 m³ water per ton starch produced. The amount varies depending on the process but in general more washing, meaning more water, improves the starch quality. According to the UN, Vietnam has made good progress towards the Millennium Development Goal target for drinking water supply. However, an increasing agricultural and industrial sector combined with a rapid economic

development, high population growth, worsening environmental conditions and frequent natural disasters is creating competition between water users, especially in areas where water shortage during dry season and water pollution are major issues. Furthermore, as a downstream riparian state Vietnam faces issues related to management outside the state boundaries, as almost 60 % of the total water resources are generated in another country. (UN-water, 2013)

Tapioca processing also requires electric energy for machine drive and thermal energy in the case of large scale factories for drying. For production of 1 kg tapioca starch about 0.3-0.9 MJ electrical and 1.1- 2.7 MJ thermal energy is needed (Mai, 2006).

2.3.2 Wastewater

Tapioca processing generates large amounts of wastewater with extremely high concentrations of organic pollutants. Large scale factories produce around 3-5 m³ wastewater per ton of fresh cassava roots (Mai, 2006). Household-scale manufacturers in Vietnam rarely treat the wastewater but discharge it directly into the sewer drainage of the city or a receiving water source. In Dong Nai and Tay Ninh province this has resulted in a pollution of wells and springs which can be directly attributed to the household-scale tapioca processing, and according to Mai (2006) this should be viewed as a warning for all areas with this type of processing. Large-scale factories typically treat the wastewater in pond systems, but the effluent does usually not meet the Vietnamese discharge standards (as seen in appendix B) (Mai, 2006). This can partially be attributed to the poor design, maintenance and likely also very poor understanding of these systems (Mai, 2006).

In Thailand the environmental problems with water pollution from tapioca processing has been reported to be serious, according to a literature study by Rajbhandari and Annachatre (2004). The acidic nature of tapioca wastewater can harm aquatic organisms and reduce the self-purification capacity of the receiving stream. Suspended solids can settle on the streambed and spoil fish-breeding areas as well as deoxygenate the water because of the solids often organic nature. In a similar way the high BOD of the wastewater can cause oxygen depletion and promote growth of nuisance organisms.

2.3.3 Cyanide

Cyanide, which is highly toxic to most living organisms, is synthesized in the leaves of the cassava plant and present in all parts of the plant, with exception from the seeds (FAO, 2008). Cyanide works as a metabolic inhibitor by binding to metal functional groups or ligands of many enzymes and in this way it inhibits for example the electron transfer chain and photosynthesis (McMahon, et al., 1995). During tapioca processing cyanide is released to the wastewater and ends up in the environment if not treated. Balagopalan and Rajalakshmy (1996) showed significantly higher concentrations of cyanide in groundwater sources near cassava processing plants in India. Released to the environment cyanide can have serious effects on fish and other aquatic life, and historically cyanide has caused many disastrous fish mortalities (Doudoroff, 1976).

2.3.4 Solid waste

Tapioca processing generates solid waste, or by products, in the form of root peels mixed with sand and soil and fibrous residues, also called cassava pulp. 1 ton of fresh cassava roots generates 0.24, 0.33 and 0.09 ton of starch, fibrous residue, root peel and sand (on a wet basis) respectively (Chavalparit & Ongwande, 2009). The subsequent wastewater treatment also give rise to solid waste, referred to as digestate, and the composition of it will vary depending on the wastewater treatment used. The peel can be composted as in the

example shown in Figure 2.3, but it can also be dried and used as a carbohydrate source for animal feeding (Men, et al., 2003). In fact, Men et al. (2003) has shown that cassava root peel can completely replace cassava root meal as part of a balanced diet for fattening of pigs, provided that it also includes 5 % catfish oil, readily available in southern Vietnam. This diet is cost-effective and contributes to a sustainable cycle of materials.

The cassava pulp still contains high amounts of starch and can be sold as animal fodder after drying. The drying process can generate noxious odours, especially during the wet season when the pulp is exposed to rain. Some of the pulp is dumped or composted which may also become a source of malignant odours and environmental pollution (Mai, 2006).

2.3.5 Air pollution

Tapioca processing contributes to air pollution in a variety of ways. The main contribution is from the combustion of fuel used to run the process. According to Mai (2006) a factory producing 100 ton starch per day will consume about 3500 litres of fossil oil which in turn generates about 71 kg SO_x, 35 kg NO_x and 9.9 kg dust. In addition to this dust is generated during drying, sieving and packing, and the storage of cassava pulp can generate noxious odours. The wastewater treatment and degradation of solid waste can also contribute to the release of greenhouse gases, depending on the conditions (Mai, 2006). Open pond systems for wastewater treatment, intended as aerobic, can become anaerobic when badly managed releasing greenhouse gases to the atmosphere. Anaerobic ponds where biogas is not utilised also release greenhouse gases, as do leaking covered anaerobic ponds.

3 Anaerobic digestion

Anaerobic digestion has historically primarily been used for the treatment of waste sludge and high strength wastes (Tchobanoglous, et al., 2004). Applications for dilute waste streams are however becoming more common (Tchobanoglous, et al., 2004) and a large number of studies on the treatment of agro-industry wastewater exist (Mai, 2006). The studies clearly show that anaerobic technology is the most suitable option for treating high-strength organic wastewaters, such as tapioca processing wastewater, which is also confirmed by Tchobanoglous et al. (2004). Anaerobic treatment has shown to be a highly cost-effective alternative to aerobic processes due to the advantages of lower energy need (no aeration needed and possible recovery of biogas), less sludge production due to lower biomass production, fewer nutrients required again due to the lower biomass production and the possible application of higher volumetric loadings leading to possible area requirement reductions (Tchobanoglous, et al., 2004). Disadvantages with anaerobic treatment are the longer start-up period and possible operational difficulties (sensitivity to toxics, stability problems, odour problems etc), the possible need for alkalinity addition and that the effluent quality is not as good and thus further treatment may be needed (Tchobanoglous, et al., 2004).

3.1 The anaerobic digestion process

Anaerobic digestion is the process where biodegradable matter is converted into methane and carbon dioxide (biogas) by several different groups of microorganisms in an oxygen free environment. The process can be divided into four steps, as summarized in Figure 3.1, but in reality there are many different reactions continuing simultaneously in a reactor. For the process to work properly the microorganisms need to cooperate at the same time as their respective needs regarding temperature, pH, nutrition and so on needs to be met (Schnürner & Jarvis, 2009).

Hydrolysis

The first step in anaerobic digestion is hydrolysis, where particulate matter is broken down into soluble compounds which can be hydrolysed further into simple monomers (Tchobanoglous, et al., 2004). Basically large organic molecules such as sugar, fat and proteins are converted into smaller organic molecules such as amino acids, simple sugars, fatty acids and alcohol which can be taken up by the microorganisms and used as a source of nutrition and energy. The process can be enzymatic, in which case different sets of microorganisms produce enzymes that enhance the rate of the process. Some microorganisms are specialized on certain substrates, others are specialized on for example sugars and yet others can produce a variety of enzymes (Schnürner & Jarvis, 2009). The rate of the process depends a lot on the characteristics of the substrate (Schnürner & Jarvis, 2009), and is normally limiting for the overall process if the substrate is in particulate form (Vavilin, et al., 1996).

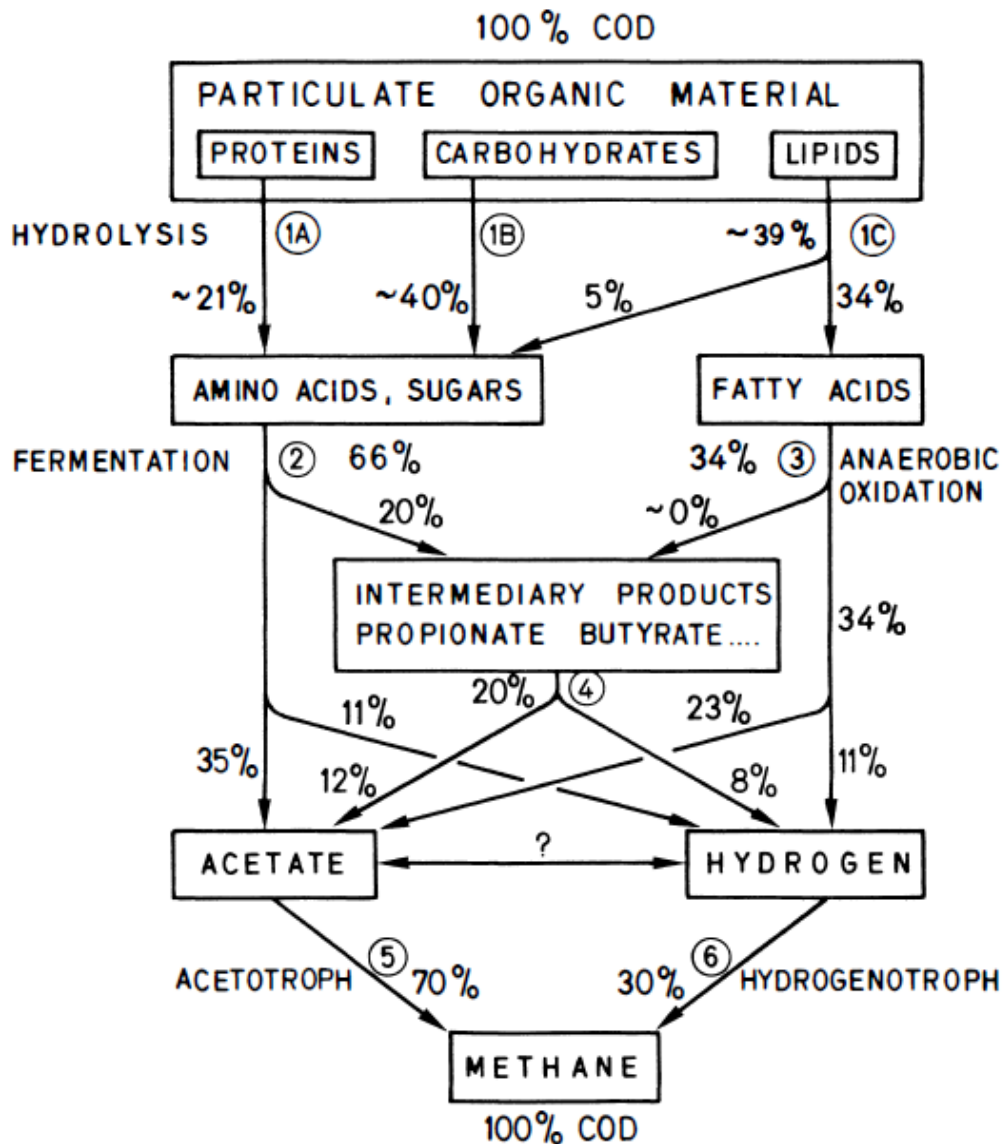


Figure 3.1. The four steps of anaerobic digestion: hydrolysis, fermentation (acidogenesis), anaerobic oxidation (acetogenesis) and methanogenesis. Percentages indicate substrate flow in the form of COD or CH₄ equivalents for anaerobic digestion of domestic sludge. Numbers in circles identify different processes. (Gujer & Zehnder, 1983) Published with kind permission from IWA publishing and Gujer.

Fermentation

The second step of anaerobic digestion is fermentation, also called acidification or acidogenesis when it leads to the formation of organic acids. In this step the microorganisms further degrade the soluble organic matter from the hydrolysis through a series of steps into primarily organic acids (acetic acid, butyric acid, lactic acid etc), alcohols, ammonia, carbon dioxide and hydrogen oxide. Fatty acids are however not used by the fermentative organisms, these are instead degraded in the next step of anaerobic oxidation (Schnürner & Jarvis, 2009). The products from the fermentation depends on the organism at work, and residual matter from one organism is further degraded by other microorganisms (Schnürner & Jarvis, 2009) creating a truly dynamic and complex

environment. At the same time fermentation is often the fastest step in the anaerobic digestion process and thus the rate constant does not adversely affect the overall methane production rate (Vavilin, et al., 1996).

Anaerobic oxidation

The third step is anaerobic oxidation, or acetogenesis, where the products from the fermentation and fatty acids are further degraded into substrates appropriate for the last step of the process, methanogenesis. The formed substrates include acetate, hydrogen and carbon dioxide. The two steps of anaerobic oxidation and methanogenesis are closely interrelated and dependent on each other because the organisms involved have a close, and very complex, relationship (Schnürner & Jarvis, 2009). Simplified it has to do with the concentration of hydrogen gas which from thermodynamic reasons must be kept at a low level if the anaerobic oxidation is to proceed, and thus the hydrogen needs to be continuously consumed, which is done by the methanogens. This kind of symbiotic relationship between organisms is called syntrophy, and it can be more or less obligate. Some organisms can change their metabolism in the absence of a hydrogen consuming partner and produce a different end product than hydrogen, often fatty acids and alcohols. Others continue their hydrogen production but at a much lower level (Schnürner & Jarvis, 2009).

Methanogenesis

The last step of anaerobic digestion is methanogenesis, where methane and carbon dioxide is formed. The formation is performed by so called methanogens, the largest group of archaea microorganisms. The dominating methanogens, responsible for about 70% of the methane production during anaerobic digestion, are called aceticlastic methanogens and use acetate as substrate to produce methane and carbon dioxide (Tchobanoglous, et al., 2004). The other group is called hydrogen-utilizing methanogens and produce methane from hydrogen and carbon dioxide. Generally the methanogens grow very slowly and therefore this step is highly rate limiting, and in the case of digesters it sets the limit for the retention time needed in the reactor. These are also the organisms most sensitive to disruptions such as change of pH or contaminants (Schnürner & Jarvis, 2009) and they are strict obligate anaerobes as compared to the organisms involved in the previous steps who consist of both facultative and obligate anaerobes (Tchobanoglous, et al., 2004).

3.2 Parameters affecting the anaerobic process

As can be understood from the above, a vast number of parameters affect the anaerobic process, and many of them are interrelated, making it even more complicated. A massive amount of different measurements can be done to evaluate this, which ones are of interest depends on the answers you seek, the time and money you have and practical limitations at the sight in question. In the following subchapters the parameters of interest in this specific project are presented in respect to how they affect and get affected by the anaerobic process in general and for tapioca wastewater in particular. For the parameters being measured in the project a presentation of what information the different measurements give is also done.

3.2.1 Substrate

The substrate in the anaerobic digestion process, in this case tapioca processing wastewater, sets the conditions for many subsequent parameters as it constitutes the foundation of the microorganism's metabolism. The composition of the substrate thus affects the overall stability and efficiency of the process, how much gas that can be produced and the quality of the gas and digestate.

In general terms it can be said that for the microorganism to grow the substrate must provide them with a source of energy, an electron acceptor, building blocks for new cells and different types of vitamins and trace metals (Schnürner & Jarvis, 2009). The source of energy in an anaerobic process are different inorganic and organic chemical compounds such as hydrogen gas, sugars, fat and proteins, which are oxidised and energy is formed by electron donation. For this to happen there is a need for an electron acceptor which can be different organic compounds or inorganic compounds like for example sulphate, iron or carbon dioxide. How much energy that can be produced depends on the electron acceptors electronegativity, and this is the reason to why sulphate reducing bacteria (discussed below in Chapter 3.2.3) can outcompete methanogens. Methanogens normally use carbon dioxide as acceptor, which gives them less energy in exchange than sulphate (sulphate has a higher electronegativity than carbon dioxide). The energy produced is used to build new cells and for this the most important building blocks are carbon, oxygen, nitrogen and hydrogen. When the source of energy is organic this compound is normally used as building block but when the source of energy is inorganic carbon dioxide and ammoniac are usually used as building blocks. Vitamins and trace metals are also essential for the microorganisms even if they are only needed in small amounts. Vitamins can sometimes be synthesised by the organism itself but trace metals are always taken from the surrounding environment (Schnürner & Jarvis, 2009). Trace metals, such as nickel, cobalt, iron and zinc, play an important role primarily as a structural element in various enzymes (Madigan, et al., 1997). The nutrients needed in most abundant amounts is nitrogen and phosphorus and for anaerobic digestion it is normally recommended to have a COD:N:P ratio of 250:5:1 (Metcalf and Eddy, 1991).

Methanogenic potential

The methanogenic potential of a substrate is the potential of the substrate to produce biogas. It is commonly measured with the biochemical methane potential, BMP, test as first described by Owen et al., (1979). The test measures the degradability and methane production potential of a substrate by degrading it under controlled conditions. The substrate is mixed with microorganisms and incubated under anaerobic conditions at a specific temperature. Over time the methane production is then measured and when the production, as well as the degradation, stops the accumulated production is calculated and this corresponds to the BMP of the substrate. The result is commonly given in ml methane produced per g organics reduced in VS (volatile solids) or chemical oxygen demand (COD). BMP can also be calculated theoretically if the composition of the substrate is known, but as consideration to degradability is not taken in this case the risk of overrating the substrate is high (Schnürner & Jarvis, 2009). For tapioca wastewater Jijaia et al (2014) found that the BMP was around 161 ml CH₄/g COD removed. This can be compared to the theoretical value of 400 ml CH₄/g COD at 35 °C, using the universal gas law and molar relations where the substrate is assumed to be glucose (Tchobanoglous, et al., 2004).

Another approach is to measure the specific methane activity, SMA, which evaluates the anaerobic sludge capability to convert an organic substrate into methane, which escapes easily to the gas phase, reducing the COD in the liquid phase. The test is performed by placing a known amount of biomass in a serum bottle to which a known amount of substrate is added which is enough for maximum biogas production, and then the resulting methane is measured. It is commonly expressed as the biogas produced in ml CH₄ or g COD removed per day per g VSS added. For tapioca wastewater Jijaia et al. (2014) found that the SMA was 0.28 g COD/g VSS/day, which was the highest SMA in the experiments

performed. The other substrates, wastewater from a seafood factory and a palm oil mill had a SMA of 0.26 and 0.16 g COD/g VSS/day respectively.

3.2.2 Physical wastewater characteristics

Appearance and odour

The physical appearance of a wastewater describes the colour and turbidity of the water, the presence of suspended solids, organisms, sediment, floating material and to some degree particulate matter (APHA, 2012). Odour simply describes how the wastewater smells. Some odours have a very specific smell, like for example hydrogen sulphide which smells like rotten eggs, and are thus easily detected. The parameters can be quantified according to APHA regulations however, in this project an unaided, arbitrary approach was taken to these parameters, and the results were only used as a simple and tangible way of describing the wastewater for reference.

Temperature

The temperature of a wastewater is a highly important characteristic as it affects chemical and biological reactions and their reaction rates. The optimal temperature for anaerobic digestion, meaning the temperature at which the microorganisms grow and work the fastest, depends on the microorganisms at hand as different microorganisms have different optimal temperatures, often dependent on their origin (Schnürner & Jarvis, 2009). In general microorganisms can be divided into four groups according to their working temperature range: psychrophile (4-25 °C), mesophile (25-40 °C), thermophile (50-60 °C) and hyperthermophile (>65 °C) and therefore most anaerobic digestion processes are run at either one of these intervals, most commonly mesophile or thermophile (Schnürner & Jarvis, 2009). Heating of the process may thus be needed which is commonly discussed as a drawback with the anaerobic digestion process (Tchobanoglous, et al., 2004). However, in the tropical regions of southern Vietnam outside temperatures lie at around 25-29 °C all year around (FAO & IFAD, 2001) giving different conditions than generally considered in literature.

For tapioca wastewater Mai (2006) tested the effect of temperature on the hydrolysis and fermentation step. The results showed that the hydrolysis rate was 8 times higher at a temperature of 30 °C than at 20 °C and the acidification rate was 5 times higher at the higher temperature. Boncz et al. (2008) found that the methanogenic activity in tapioca wastewater seemed more sensitive to lower temperatures than acidification.

Solids

Wastewater can contain a variety of solid materials, depending on the source, which can be characterized in a number of ways. In general the characterization of solids is used to assess the reuse potential and to determine the most suitable type of treatment measures (Tchobanoglous, et al., 2004). The most important characteristic is the total solids, TS, content which is the residue remaining after a wastewater sample has been evaporated and dried at a specified temperature (103 to 105 °C). The total suspended solids, TSS, is the portion of TS retained on a filter with a specified pore size after being dried at a specific temperature. The volatile solids, VS, is the portion of solids that can be volatilized and burned off when the TS or TSS are ignited (500 ± 50°C) giving TVS and VSS from TS and TSS respectively. In general VS are presumed to be organic matter and the parameter is thus used to characterize the wastewater with respect to organic matter present (Tchobanoglous, et al., 2004).

Tapioca wastewater generally has a very high solids content however, reported values vary a lot. Mai (2006) summarized values from different reports and found that TSS varied between 330-4400 mg/l for large scale tapioca factories in Vietnam, while Rajbhandari and Annachhate (2004) report TSS values of 9130 ± 3067 mg/l from just one tapioca factory in Thailand. The wide variations can be subscribed to the different industrial processes and the raw material used. The solids mainly consist of highly biodegradable starch granules (Rajbhandari & Annachhate, 2004) and according to a settling experiment performed by Rajbhandari and Annachhate tapioca wastewater has a very good settling capacity as 90-95 % of TSS removal occurs within 120 min due to sedimentation at and above TSS concentrations of 1600 mg/l. However, at lower TSS values the settling capacity decreases, and the actual removal in anaerobic ponds was observed to be less than the experimental values. The reason was that starch granules accumulated in the pond which reduced the actual volume of it, and that the bubbling up of biogas, due to methanogenesis, close to the outlet of the pond caused re-suspension of settled solids that were then flushed with the effluent.

3.2.3 Chemical wastewater characteristics

pH and alkalinity

The pH of a wastewater and its capacity to handle addition of acids (alkalinity) is crucial for the anaerobic digestion process. Anaerobic bacteria, and especially methanogens, are generally sensitive to extremes of pH and the best pH range appears to be around neutrality, while the range between pH 6.5-7.8 is generally believed to be optimal according to Anderson, et al., (2003). There are four major types of chemical reactions that influence the pH in an anaerobic digester, as described by Anderson, et al., (2003):

1. Ammonia consumption and release
2. Volatile fatty acid production and consumption
3. Sulphide release by dissimilatory reduction of sulphate or sulphite
4. Conversion of neutral carbonaceous organic carbon to methane and carbon dioxide

Tapioca wastewater contains high amounts of easily biodegradable sugars and the fermentation step is therefore usually very fast which leads to a high production of acids, which in turn may lead to a low pH. In fact, Mai (2006) showed that even small and temporary changes in pH can have a severe effect on both removal efficiency and biogas production for tapioca wastewater. There is however an abundant amount of reports addressing this issue, also for other high-strength industrial wastewaters, and the most basic solution is to add alkalinity in the form of for example bicarbonate (Tchobanoglous, et al., 2004) but this option is generally seen as too expensive (Boncz, et al., 2008). Another solution is to increase the retention time in the digester to give the methanogens more time to convert the acids (Anderson, et al., 2003). A different solution is to apply a two-step process where fermentation and methanogenesis are separated, creating a process where either organic removal or biogas production can be favoured (Barana & Cereda, 2000). In fact, Rajbhandari and Annachhate (2004) observed that this division happens spontaneously in subsequent pond systems where the first pond's primary function is as settling basins and methanogenesis is first observed in the succeeding ponds. Paing, et al., (2000) observed the same pattern in a primary pond where sludge accumulated near the inlet of the pond and acidogenesis was the major active process. Methanogenesis primarily

took place near the outlet of the pond and all in all it was concluded that this staged distribution seemed to increase the efficiency of the process compared to septic tanks. Yet another solution, recently tested in lab, is to increase the buffering capacity by pre-treating the wastewater with fungi (Paulo, et al., 2013).

Nitrogen

Nitrogen is an essential building block in the synthesis of protein and thus nitrogen data is necessary to assess the treatability of wastewater by a biological process since insufficient nitrogen levels can prevent the biological process (Anderson, et al., 2003).

Nitrogen has several oxidation states which can be induced by living organisms or chemical conditions like pH. Both positive and negative changes to the oxidation state is possible, which makes the chemistry of nitrogen complex. The most common and important forms of nitrogen in wastewater are ammonia (NH₃), ammonium (NH₄⁺), nitrogen gas (N₂), nitrite ion (NO₂⁻) and nitrate ion (NO₃⁻) (Tchobanoglous, et al., 2004). These forms, together with the organic nitrogen, compose the total nitrogen of a wastewater. Organic nitrogen is a mixed fraction of compounds including amino acids, amino sugars and proteins (polymers of amino acids) which can be soluble or particulate (Tchobanoglous, et al., 2004).

In the anaerobic digestion process organic nitrogen is converted to ammonia nitrogen when proteins, nucleic acids and other nitrogen containing compounds degrade (Babson, et al., 2013). Ammonia nitrogen exists in two forms, the often for microorganisms toxic free ammonia (NH₃) and generally innocuous ammonium ion (NH₄⁺). The equilibrium between the two forms depend on pH and temperature. At 20 °C ammonia ion is predominant at pH below 7, and it is not until much higher pH that the concentration of free ammonia takes over (Tchobanoglous, et al., 2004). For higher temperatures the equilibrium is shifted to free ammonia, but in low pH water like tapioca wastewater the ammonium ion should be dominant. Inhibition levels of ammonia in the biogas process vary in literature, in a review by Yenigün and Demirel (2013) it is found that reported values differ between 1100-6000 mg/l total ammonia nitrogen, with higher levels for reactors that have been acclimatized to ammonia. For free ammonia nitrogen however, much lower inhibitory levels of 150-1450 mg/l are reported (Yenigün & Demirel, 2013).

Phosphorus

Phosphorus is, like nitrogen, essential to the growth microorganisms and like nitrogen it too has many forms. In water the most common forms of phosphorus are orthophosphates (e.g. PO₄³⁻, HPO₄²⁻, H₂PO₄⁻ and H₃PO₄), polyphosphates (molecules with two or more phosphorus atoms, oxygen atoms and, in some cases, hydrogen atoms in a complex molecule), and organic phosphate (organically bound phosphate). The orthophosphates are available for biological metabolism without further breakdown while the polyphosphates undergo hydrolysis to the orthophosphate form. This process can however be quite slow (Tchobanoglous, et al., 2004).

Organic content and oxygen demand

The organic matter in wastewater can typically consist of proteins, carbohydrates, oils and fat (Tchobanoglous, et al., 2004) while tapioca wastewater typically consists of carbohydrates (Mai, 2006). There are many ways to indicate organic matter but the most widely used parameter is the 5-day biochemical oxygen demand, BOD₅ (Tchobanoglous, et al., 2004). The parameter gives an estimate of how much dissolved oxygen is needed by aerobic organisms to break down organic material during a 5 day period at most commonly 20 °C. BOD is commonly used to determine how much oxygen is needed to biologically

stabilize the organic matter present, to determine the size of wastewater treatment facilities, to measure the efficiency of some treatment processes and to determine compliance with wastewater discharge permits. An easier test to perform is to measure the Chemical Oxygen Demand, COD. The test measures the oxygen equivalent of the organic material in wastewater that can be oxidized chemically using dichromate in an acid solution. Tapioca wastewater generally has a very high organic content, and Mai (2006) has found reported values of COD to vary between 7000-20 700 mg/l.

Cyanide

Cyanide works as a metabolic inhibitor by binding to metal functional groups or ligands of many enzymes, and in this way it inhibits for example the electron transfer chain and photosynthesis (McMahon, et al., 1995) and it can thus have a negative effect on the anaerobic digestion process. However, reports show that microorganisms are able to adapt, making shock loads more inhibiting than a continuous flow (Gijzen, et al., 2000). In water, cyanide can exist as undissociated hydrogen cyanide (HCN) or free cyanide ion (CN⁻). Since hydrogen cyanide is a very weak acid, HCN is the dominant form in neutral and acid waters, but this is also the most toxic form of cyanide (APHA, 2012). Simple cyanide salts, like NaCN, are completely dissolved in water but stable complexes can be formed with metal cations, however the stability of these vary with pH. The most stable complexes are formed with iron, which are generally seen as non-toxic. These complexes can however be decomposed by ultraviolet light, which should be born in mind if a removal technique with iron precipitation is used (APHA, 2012).

Cyanide in tapioca wastewater stems from the cyanogenic glycosides synthesised by the plant, linamarin and lotaustralin, which when processed are hydrolysed to hydrogen cyanide (FAO, 2008). The concentration of cyanide in tapioca wastewater differs a lot when studying different reports. For example, Rajbhandari and Annachhatre (2004) report values in factories in India that range between 10-15 mg/l while Mai (2006) report values from Vietnamese factories ranging between 3-61 mg/l. These wide variations can be due to the fact that the raw material holds different concentrations of cyanide depending on cultivar (type of cassava), environmental conditions, cultural practices and plant age (McMahon, et al., 1995). Anaerobic digestion can be used to degrade cyanide (for example some microorganisms can use cyanide as nitrogen or carbon substitute), but it does seem to have a negative effect on methane production (Annachhatre & Amornkaew, 2000). Mai (2006) showed that cyanide has a distinct negative effect on hydrolysis and methanogenesis for tapioca wastewater, while the acidification process proceeds as normal. Mai (2006) also proposed that the observed lag phase during start-up of the reactors was due to bacteria adaptation to cyanide as well as cyanide degradation. Rajbhandari and Annachhatre (2004) report that the removal rate of cyanide from tapioca wastewater in anaerobic ponds is about 0.84 mg CN/g VSS/day.

Trace metals

Trace metals are essential for many of the microbial processes involved in anaerobic digestion. The need for addition of trace metals depends on the substrate and operational conditions at hand. For tapioca wastewater an indication that trace metals and nutrients is not a major concern can be drawn from the experiments performed by Mai (2006). In these experiments, conducted in UASB reactors, no significant effect on treatment efficiency could be seen as a result from trace metals and nutrient addition, except for a small improvement during the start-up period. Trace metals and nutrients were however found to have a slight positive impact on the biogas production. The results showed an increased

average production for the reactors with additives, however a small addition seems sufficient as there was no significant difference between the reactors with more or less additives.

Sulphur

The presence of sulphur compounds such as sulphate, sulphite and thiosulfate can become an inhibitor of the anaerobic process (Tchobanoglous, et al., 2004). Sulphate reducing bacteria use sulphur to form hydrogen sulphide which in higher concentrations is toxic to methanogens. In addition to that the sulphate-reducing bacteria compete with the methanogens for food and can thus reduce the biogas production (Schnürner & Jarvis, 2009). Furthermore hydrogen sulphide is a malodorous compound, corrosive to metals and in fact all combustion products from sulphur oxidation are considered air pollutants (Tchobanoglous, et al., 2004).

3.2.4 Hydraulic performance

The hydraulic performance of a reactor describes the flow in and out of the reactor. The hydraulic detention time is a measure of the average length of time that a soluble compound spends in a reactor. The theoretical hydraulic detention time, assuming ideal flow, is defined as the volume of the reactor divided by the volumetric flowrate. The parameter is used to regulate the flow in the reactor to a level where the microorganisms are given enough time to degrade the substrate. This simple calculation does not consider the fact that the flow inside the reactor is not constant or evenly distributed, with the most apparent difference in flow between the sludge layer and the liquid phase. This means that the compounds can spend more or less time in the reactor than the theoretical value depending on which route in the reactor it has followed. For this reason non-ideal flows can be modelled, and tracer tests performed (Tchobanoglous, et al., 2004).

Another important parameter is the organic loading rate which gives a measure of how much organics is applied to the process, commonly measured in kg BOD per day or kg BOD per volume of the reactor. This can be directly related to the retention time needed, if the organic loading rate is high the retention time probably needs to be longer if the effluent values are to meet the same standard. Wide variations in influent flow and organic loads can upset the balance between the different steps of the anaerobic process. For soluble, easily degradable substrates such as tapioca, the fermentation and anaerobic oxidation processes may be significantly faster at high loading rates which in turn may increase the concentration of volatile fatty acids, VFA, hydrogen and lower pH which in turn can affect the methanogenesis negatively (Tchobanoglous, et al., 2004).

3.3 Covered anaerobic ponds

Anaerobic ponds are used for high-strength industrial wastewaters because of their ability to handle a wide range of waste characteristics, their simple and relatively economic construction, and their ability to handle large volumes (Tchobanoglous, et al., 2004). Disadvantages are their requirement for large land areas, potential feed flow distribution inefficiencies, maintenance of the geomembrane cover, production of bad smell, biogas slippage, that they fill up with solids and that effluents usually need further treatment (Tchobanoglous, et al., 2004). The efficiency of anaerobic ponds is usually found to be lower than other higher technology anaerobic treatments. Rajbhandari and Annachatre (2004) found that the potential methane production was lower for anaerobic ponds than for reported values from UASB reactors, an observation that was confirmed by other reports

on the subject. This could explain the usually longer retention time needed for anaerobic ponds.

There are two main mechanisms that are responsible for the removal of organic matter in the anaerobic pond, sedimentation in the liquid layers and anaerobic digestion in the sediment layers (Rajbhandari & Annachhatre, 2004). Spatial variations in the pond are however frequently discussed. Paing, et al., (2000) found that near the inlet to the pond, fresh organic matter settled continuously and the sludge was therefore not stabilized. It was also observed that acidogenesis was the dominant reaction and pH was not favourable for methanogenesis, as also reported by Rajbhandari and Annachhatre (2004) and discussed in Chapter 3.2.3. Near the outlet however, sludge had a longer detention time and a more favourable pH for methanogenesis. However, Paing, et al., (2000) found that even if the conditions were more favourable near the outlet and the methanogenic potential greater, methane production per unit of the pond surface area was not greater because sludge depth was lesser. Regarding the solids removal Rajbhandari and Annachhatre (2004) found that it was lower than the potential because of accumulation of starch granules and subsequent reduction of actual pond volume. The solids that were left in the methanogenic part of the ponds were also observed to be re-suspended due to bubbling up of biogas as well as scouring of settled materials near the outlet. To promote longer solids retention time McAdam, et al., (2012) suggest that primary sedimentation tanks are not used but instead both soluble and particulate solids should sediment to promote methane production and minimise sludge production.

4 Methodology for field study and lab analysis

4.1 General output and parties involved

The planning of the field study and lab analysis started several months before arrival in Vietnam and naturally many changes has been made during the course of the project. Some of these changes are explained in the following chapters, as they motivate the final method used, while others are not.

The tapioca factory was visited three times during the 10 week stay in Vietnam. The first visit was made a few days after arrival, 13 October, together with Mr Khang (Duong Nguyen Khang, associate professor at Nong Lam University, director of the MEKARN project and hired as a consultant by the factory for improving the anaerobic digestion process) and Mr Preston (Thomas Reg Preston, professor involved in the MEKARN project with long experience of digesters). The visit lasted only a couple of hours and was made as an introduction to the project ahead. No sample collection or measurements were done, the premises were simply inspected and first contact with Mr Son (Vu Hoang Son, the son of the owner of the factory working as director of the company), and Mr Cuong (Co Chi Cuong, environmental science graduate working at the factory as part of Mr Khangs consultant company) was made. The second visit to the factory was made 29-30 October primarily to prepare for the coming visit and gather further information through discussion with Mr Cuong and inspection of the premises. During this visit the information-technology student Tu Pham, in fact not involved in the project, accompanied for assistance and translation. Samples were collected, primarily to test the analysis technique. The third visit to the factory was made 12-17 November and during this visit the primary study and sample collection was made. The reason to that the primary study was done at this time and not before was that before this the performance of the digester was assumed to be unstable. This was based on low pH measurements in the outflow and the fact that the production in the factory was unstable. After the realization that the process would probably not be stable until after departure the study was made knowing that the process was probably still unstable. During the third visit the biotechnology students Hồ Hoàng Dữ and Phan Trọng Trí accompanied and assisted for some days, and Mr Cuong assisted the other days. Discussion with Mr Son was also made continuously during the visit.

From the first visit to the factory to the third, many changes were made to the wastewater treatment which forced changes to the sampling procedure, which is described in the following chapter. The third visit was however the primary visit for sampling and is therefore described in more detail. The map in appendix A shows the layout of the factory premises which can be helpful when reading the following chapter. Furthermore, the layout, the production process and the wastewater treatment is described in more detail in Chapter 5.

4.2 Sampling procedure

During the field study samples of the influent and effluent water was collected with the aim of characterizing the water in subsequent lab analysis. In addition to this the gas going out from the digester was also sampled. The influent water to the digester is a mixture of the water from the root washing (WW1) and from the starch production (WW2), see Figure 4.1. Since the approach of mixing WW1 and WW2 was new for this season (see further description in Chapter 5) characterization of these streams was made separately. The

effluent water comes out through three identical underground pipes. The composition of the water was assumed to be the same in all pipes and therefore a composite sample was made for WW3a, WW3b and WW3c, namely WW3. For further understanding of the layout of the factory see the map in Appendix A.

Recommendations for sampling procedure from APHA (2012) was used to the fullest extent possible during the field study. In the case when recommendations have not been followed this is noted and motivated.

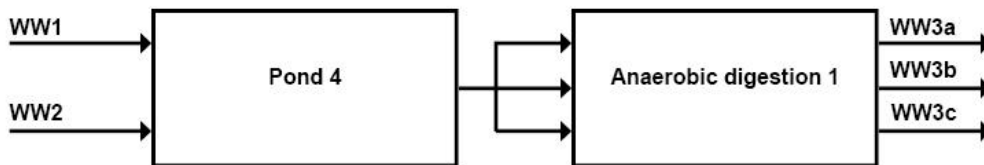


Figure 4.1. Block diagram of the wastewater streams to be characterized in the project. WW1 is the influent wastewater from the root washing, WW2 is the influent wastewater from the starch production and WW3a, WW3b and WW3c is the effluent wastewater from the digester. These three streams are assumed equal and referred to as WW3. For further understanding of the location of the ponds, and naming, see the map in Appendix A.

Sampling locations

WW1 was sampled in the open stream leading out from the root-washing. During the second visit this was done close to the root washing process, but during the third visit an extension of the open stream leading to Pond 4 had been built and the samples were instead taken from this, close to the pond, as seen in Figure 4.2.

WW2 was also sampled in two different ways. During the second visit samples were taken from a hose which was connected to the outlet pipe inside the factory. During the third visit samples were instead taken from the outlet of WW2 into Pond 4, as seen in Figure 4.2, for easier access.



Figure 4.2. Sampling points for WW1 and WW2. See map in Appendix A for further understanding of the layout.

WW3 was accessed through the submerged concrete boxes, see Figure 4.3, into which the water from the digester was led before further directed to the next digester (Anaerobic digestion 2 as seen in the map in Appendix A). The outlet from the digester into the box was in the bottom of the box. Effort was made to take samples as close to the outlet as possible for which reason the person taking the sample went down into the box. After doing this myself at the first sampling of the third visit it was however realized that this stirred up the soil, which filled the boxes to a certain extent, and that this might influence the results. For the rest of the sampling, samples were therefore instead collected by reaching as far down into the box as possible without getting into the box. During the third visit the flow into the boxes was so high that the water was bubbling up from the outlet, and this was assumed to increase the probability of taking representative samples.

Gas was sampled from a valve located on the pressure tank preceding the oven where the biogas was burnt.



Figure 4.3. Sampling point for WW3. The photo is of WW3b, taken during the second visit to the factory. The concrete boxes look the same for WW3a and WW3c, with more or less soil filling the box. It should be noted that the colour of the water was darker than this during the third visit.

Number of samples and handling/preservation

During the second visit to the factory one sample from each stream, WW1, WW2 and WW3b was taken on the morning of departure. A composite sample of WW3 was not taken as it was not until this visit that it was realised that there was three outlets and not one and therefore no equipment was available for doing a composite sample. The samples were put in a fridge box and transported by bus back to the lab where analysis of ammonia, total nitrogen and total phosphorus was planned with the SMART 3 equipment. When no results of ammonia for WW1 was obtained due to the small range of the SMART 3 equipment, analysis was instead performed by the environmental science lab at Nong Lam University by standard methods. This was done two days after the samples were collected and during this time the samples were stored in a freezer.

During the third visit to the factory samples from each stream, WW1, WW2 and WW3 (composite) was taken at three different occasions. The samples were collected in a 10 l plastic bucket and then transferred to the respective containers (see Chapter 4.3 below, and especially Table 4.1). For WW3 three litres from each stream WW3a, WW3b and WW3c was mixed together in the bucket.

Four different groups of handling/preservation was used. The first group were the samples for direct analysis at the factory, denoted FA. The second group was the samples to be analysed in lab which did not need preservation, denoted LNP. The third group was the samples which needed preservation with acid (H_2SO_4), denoted LP. The fourth group was the samples which needed preservation with base (NaOH) and were sent to a separate lab for analysis of cyanide, denoted C. See also Table 4.1 in next chapter.

The gas was collected in plastic bags that were put over the valve, filled, and closed with rubber bands. Two samples were collected at three different occasions (same dates as the water samples) during the third visit to the factory. Gas leakage was observed during storing as the volume of the bags decreased, and this was the reason for duplicate samples.

4.3 Material

Containers for sample collection

Wastewater samples were collected in different containers according to APHA (2012) recommendations and volume needed for analysis, as summarized in Table 4.1. The plastic water bottles were cleaned with deionized water and dried before usage. The glass containers and plastic containers were cleaned more carefully, first with warm water and detergent, then with weak acid (HCl) followed by deionized water. The glass containers were also heated to 150 °C in an oven for 2 hours for drying and killing bacteria. No ovens of 500 °C, as recommended by APHA (2012), were available.

Gas samples were collected in thick plastic bags provided by the environmental lab and commonly used for this purpose. The bags were closed with rubber bands.

Table 4.1. The containers used for wastewater sample collection during the third visit to the factory. The abbreviations stand for the different groups of handling: FA (analysis at factory, no preservatives); LNP (analysis at lab, no preservatives); LP (analysis at lab, preserved with H₂SO₄); C (analysis by other lab, preserved with NaOH).

Sampling 1		Ammonia	TSS	VS	BOD5	Tot-P	Tot-N	COD	Cyanide
	WW1	FA	LNP	LNP		LP	LP	LP	C
	WW2	FA	LNP	LNP		LP	LP	LP	C
	WW3	FA	LNP	LNP		LP	LP	LP	C
Sampling 2		Ammonia	TSS	VS	BOD5	Tot-P	Tot-N	COD	Cyanide
	WW1	FA	LNP	LNP		LP	LP	LP	C
	WW2	FA	LNP	LNP		LP	LP	LP	C
	WW3	FA	LNP	LNP		LP	LP	LP	C
Sampling 3		Ammonia	TSS	VS	BOD5	Tot-P	Tot-N	COD	Cyanide
	WW1	LP	LNP	LNP	LNP	LP	LP	LP	C
	WW2	LP	LNP	LNP	LNP	LP	LP	LP	C
	WW3	LP	LNP	LNP	LNP	LP	LP	LP	C

Legend:

Plastic water bottle (500 ml)
Glass container (1 litre)
Glass container (2-2.5 litre)
Plastic container (2 litre)

pH meter

At the factory pH was measured using a pHTestr 30 from Eutech instruments, see Figure 4.4. The meter was calibrated before usage with 2 standard buffer solutions (pH 4.01 and pH 7.0) and conditioned and used according to the instruction manual. The range of the meter is pH -1.00-15.00 and the resolution and relative accuracy pH 0.01. During calibration, and in accordance with previous experience provided by Mr Son, the meter did however not show this kind of accuracy. This might be due to the meter being old or the sensor being disrupted. The daily pH measurements performed at the factory since start-up is done with similar pH meters as the one borrowed.

In the lab pH was measured using a pH 211 microprocessor pH meter from Hanna instruments. The meter was not very accurate but no options were available as the better equipment could be disrupted by the extreme pH values the water samples held. The equipment was namely used for neutralization of water samples that had been preserved with acid.



Figure 4.4. Photo of the pHTestr 30 from Eutech instruments used for pH measurement at the factory.

Thermometer

Temperature was measured with an YF-160A TYPE K thermometer from YFE with the range -50°C to 1300°C , as seen in Figure 4.5.



Figure 4.5. Photo of the thermometer used in the project.

SMART3 colorimeter

For analysis of ammonia, total nitrogen and total phosphorus the SMART 3 equipment was used. SMART3 is a colorimeter from LaMotte, an American water analysis equipment company. A colorimeter determines the concentration of a chemical compound or element in a solution by the aid of a colour reagent. Basically the water sample is mixed with the colour reagent which reacts with the substance of interest, giving the sample a specific

colour which intensity depends on the concentration of the substance. The colorimeter then measures the absorbance of a particular wavelength by the sample, which in most tests is directly proportional to the concentration of the test factor producing the colour, and the path length through the sample. For some tests the amount of coloured light absorbed is inversely proportional to the concentration. (LaMotte, n.d.) Different reagent systems are used depending on the substance of interest, the reagent systems used in this project are presented in Table 4.2. Important parameters to consider are the range, minimum detection limit (MDL) and interferences as these factors limits how and for what the equipment can be used.



Figure 4.6. Photo of the SMART 3 colorimeter.

Table 4.2. Parameters measured with the SMART 3 equipment and their respective range, minimum detection level (MDL), interferences and the reagent system used. (LaMotte, n.d.)

Parameter	Range (ppm)	MDL (ppm)	Interference	Reagent system (number of reagents)
Ammonia nitrogen HR	0.00-4.00	0.05	Sample turbidity and colour may interfere and can be eliminated by filtration and blanking the instrument respectively.	Salicylate (3)
Nitrogen, total	3-25 mg/l	3	Bromide (<60 ppm) and chloride (<1000 ppm) will have a positive interference.	Chromotropic acid/digestion (6)
Phosphorus, total HR	0.0-70.0	5	Large amounts of turbidity may interfere. Silica and arsenate interfere only if the sample is heated. Arsenite, Fluoride, thorium, bismuth, molybdate, thiosulfate, and Thiocyanate cause negative interference. Ferrous iron concentrations above 100 ppm will interfere.	Molybdoranadate/ digestion (5)

4.4 Method for analysis

4.4.1 pH and temperature

pH and temperature was measured directly in the field in the plastic bucket used to collect the samples. Measurements were also done on the days that no samples were collected, in the same manner as the other days. pH has also been monitored by Mr Cuong since the start-up of the factory, primarily in the effluent. pH was not measured during the second visit to the factory since no equipment was available.

4.4.2 Ammonia nitrogen

Ammonia was meant to be analysed using the SMART 3 equipment. Samples from the second visit to the factory were analysed but gave no thrust worthy results (results were over range) and therefore analysis was instead performed by the environmental science lab at Nong Lam University using Vietnamese standard method TCVN 5988-1995 (Determination of ammonium - Distillation and titration method) which is the same as ISO 5664-1984. This gave the range of the samples and the dilution factor needed could be determined for the forthcoming analysis. Samples from the first and second sampling during the third visit were analysed at the factory soon after the samples were collected, from the FA sample. For the third sampling on the third visit to the factory there was no time to do analysis at the factory and analysis was instead made when the lab was reached from the LP samples. The samples were first warmed to room-temperature and neutralized with NaOH. Both tests measure total ammonia nitrogen, meaning both free and ionized ammonia.

Dilution was performed on all sampling occasions as the range of the SMART 3 system was very low and small. For the samples from the third visit a dilution factor 100 was used and 10 ml sample was diluted in 990 ml deionized water. In the factory this was done by measuring up 1 l deionized water four times in a 250 ml conical flask. Then 10 ml was removed by using the 10 ml cuvette for the SMART 3 and the same cuvette was used to add 10 ml sample water. In the lab a measuring glass of 1 litre was instead used for greater accuracy.

Filtration was performed on the samples from the second visit (for SMART 3 analysis) and the first samples from the third visit by recommendation according to the instruction manual. After this there were no more filters available as the first session required many trials due to the slow filtration which caused the filters to break. It was however assumed that due to the high dilution used, turbidity would not interfere with the analysis anyway and perhaps filtration was unnecessary.

4.4.3 Total nitrogen and total phosphorus

Total nitrogen and total phosphorus were meant to be analysed with the SMART 3 equipment. Samples from the second visit to the factory were however only analysed by the environmental science lab at Nong Lam University after the failure to analyse ammonia. For analysis of nitrogen they used the Vietnamese standard method TCVN 6638:2000 (determination of nitrogen – catalytic digestion after reduction with Devardas alloy), same as ISO 10048:1991 and for phosphorus the Vietnamese standard method TCVN 6202:2008 (determination of phosphorus – ammonium molybdate spectrometric method), same as ISO 6878:2004. This approach was meant to give the range of the samples for forthcoming analysis, as explained above for ammonia. Samples from the third visit to the factory was analysed using the SMART 3 equipment but gave no results (over range for phosphorus

and value 0 for nitrogen) and therefore analysis was instead again performed by the environmental science lab with the same methods as stated above.

The samples used were the LP samples and therefore neutralization with NaOH was made prior to analysis with SMART 3. The samples were also warmed to room temperature. After failure to analyse with SMART 3 samples were kept in a fridge until the lab performed their analysis, still preserved with acid as only part of the sample had been taken out of the container for analysis with SMART 3.

4.4.4 TSS and VS

TSS and VS was analysed from the LNP samples from the third visit to the factory by the environmental science lab at Nong Lam University. For TSS they used the Vietnamese standard method, TCVN 6625:2000 (determination of suspended solids by filtration through glass-fibre filters), which is accredited by ISO 17025:2005 (general requirements for the competence of testing and calibration laboratories), and the same as ISO 11923:1997. For VS they used the Vietnamese standard method, SMEWW 2540E:2012 (Fixed and volatile solids ignited at 500 °C). It should be noted that two separate methods were used and the VS is not VS of TSS, but of TS (non filtered) meaning in fact TVS.

4.4.5 COD and BOD₅

COD and BOD₅ was analysed from the LP and LNP samples respectively from the third visit to the factory by the environmental science lab at Nong Lam University. For COD they used the Vietnamese standard method, SMEWW 5220C:2012 (determination of chemical oxygen demand), which is accredited by the ISO 17025:2005 (general requirements for the competence of testing and calibration laboratories). For BOD₅ they used the Vietnamese standard method TCVN 6001:2008 (Determination of biochemical oxygen demand after n days (BOD_n)) which is the same as ISO 5815:2003. COD was analysed from all sampling occasions while BOD₅ was only analysed from the LNP sample from the last sampling session since preservation and storage is not recommended for accurate results. Analysis of BOD₅ started at the same day the samples were provided to the lab and COD the day after (before any other analysis was made from the LP samples to avoid oxygen interference in the samples).

4.4.6 Cyanide

Cyanide was analysed from the C samples from the third visit to the factory by the Quatest 3 lab using the HACH method 8027 (Pyridine-pyrazalone method). Cyanide was meant to be analysed with the SMART 3 equipment but the chemical kits were not ordered. The environmental science lab at Nong Lam University had no method for analysis of cyanide and therefore the samples were delivered to the Quatest 3 lab. Quatest 3 lab is an organization under the ministry of science and technology and follows international standards (Quatest 3, 2014).

4.4.7 Gas

The gas samples were attempted to be characterized for methane, carbon dioxide and hydrogen sulphide by the environmental science lab at Nong Lam University using a Testo 350 XL portable emission analyser.

5 Wusons tapioca factory

5.1 General conditions

5.1.1 Wusons CO. LTD

Wusons CO. LTD. is the name of the company running the tapioca factory investigated in the project. It is part of the DAWU Corporation which consist of 12 Vietnamese and foreign enterprises, including four tapioca factories in Vietnam (DAWU cooperation, 2011). The company was established in 2003 and has a charter capital of 55 billion VND (DAWU cooperation, 2011), approximately 4.2 million SEK or 0.55 million USD (Forex bank, 2014). The factory has two main products: tapioca starch with food grade (for human consumption) and tapioca residue powder with feed grade (for animal feed and nutrient supply) (DAWU cooperation, 2011). The tapioca starch is mainly exported to Asian countries such as Singapore, China, Taiwan, Malaysia, Indonesia and the Philippines (DAWU cooperation, 2011). The residue powder is however harder to market and is only sold domestically, mainly in the surrounding area as the cost for transport cannot be too high (Son, 2014).

The company is currently planning an expansion of the tapioca factory, and an additional factory for higher quality starch production is being built which will receive starch material from the current factory for further processing (Son, 2014). There is also a rubber factory close to the tapioca factory which is not part of Wusons CO. LTD but has the same owner (Son, 2014). In addition to the factory the company also has 10 ha of cassava plantations and 40 ha of rubber three plantations (Son, 2014). The cassava plantation is primarily used to show customers how the plant looks and not for commercial use, as the amount is not even enough for one day of starch production (Cuong, 2014). The company has also recently purchased around 40 cows and had from before around 30 pigs which are all fed with the cassava residue powder for supplying fibre and nutrients. The animals are however not held for commercial purpose (Son, 2014). Appendix A shows a map of the factory premises and surrounding area.

5.1.2 Surrounding area

The factory is situated in Minh Tam, Hon Quan district, Binh Phuoc province in the western regions of southwest Vietnam, north of Ho Chi Minh City and close to the Cambodian border. The climate in the region is tropical with two distinct seasons: the rainy season between May and November and the dry season between December and April. The temperature lies at 26 °C and is stable through the year, although it can fluctuate 7-9 °C between night and day, especially in the dry season (Binh Phuoc Portal, 2014). There is a large system of rivers in the province including Saigon River, Song Be, Dong Nai River, Mang River, and a number of springs, lakes and dams. There is also a rich source of ground water (Binh Phuoc Portal, 2014)

The area surrounding the factory mainly consist of rubber tree plantations, and the closest town is about 18 km away (Son, 2014). The electricity connection is good but power cuts are regular, often due to rubber trees falling on the electricity net (Son, 2014).

5.1.3 Prerequisites for production

The factory is open during the harvesting season of cassava, which is dependent on the rainy season, and normally occurs between September and April, with the peak season being in January and February (Cuong, 2014). The production at the factory runs according

to the availability and price of cassava roots which means that when the availability is high and the price is low the factory runs 24 h a day with full capacity, and when the availability is low and the price is high the factory may run in shifts, at lower capacity or stop production for a couple of days (Son, 2014). Normal working shifts are between 7 AM – 7 PM, and 7 PM to 7 AM and the decision to run a shift or not is done about one day in advance, and sometimes only a couple of hours in advance (Son, 2014). When deciding to run a shift or not consideration must, in addition to the price and availability, be taken to that cassava roots should not be stored for more than 48 hours (Son, 2014). After this the starch content of the roots and quality of the product is impaired. This can be solved by addition of chemicals in the production process, as mentioned in Chapter 2.2, but this method is not applied at Wusons factory who instead are trying to constantly keep their supply of roots fresh (Son, 2014). There are also other circumstances which may force the production to stop, for example power cuts or problems with the machinery.

Fresh cassava roots are continuously delivered to the factory by the cassava root suppliers who are paid according to the estimated weight of clean roots, estimated percentage of starch in the roots and current market price. This, together with the amount of product produced, is the only statistics held by the factory and Figure 5.1 shows the statistics of delivery from the current season (from start-up to one and a half week after the third visit to the factory when data was provided). As can be seen the delivery of cassava roots and estimated starch production has increased since the start-up of the season, and the market price has decreased. The weight of starch does not follow the weight of clean roots perfectly as the percentage of starch varies between 19-30 %, with 26 % being the average during this period (calculated from the same data as shown in Figure 5.1).

Figure 5.2 shows the production of tapioca since the start-up of the factory to the middle of December when data was provided. As can be seen production has increased since the start-up, from being low and run in shifts, to full capacity in December with production of more than 150 tonnes of tapioca each day. Figure 5.3 shows both the estimated and actual production of tapioca which shows how the actual production is shifted from the deliveries and estimated values because of the different storage times. For example, around 14 October deliveries of roots were done, but no production was done for a couple of days. When the production started again on 17 October the actual production is high since the root storage is big. The following days the estimated and actual production follow each other very well as the roots are not stored for a longer period of time. The total amounts agree quite well, for the total period shown in the figure the sum differs with 78 514 kg, with the actual production being more than the estimated.

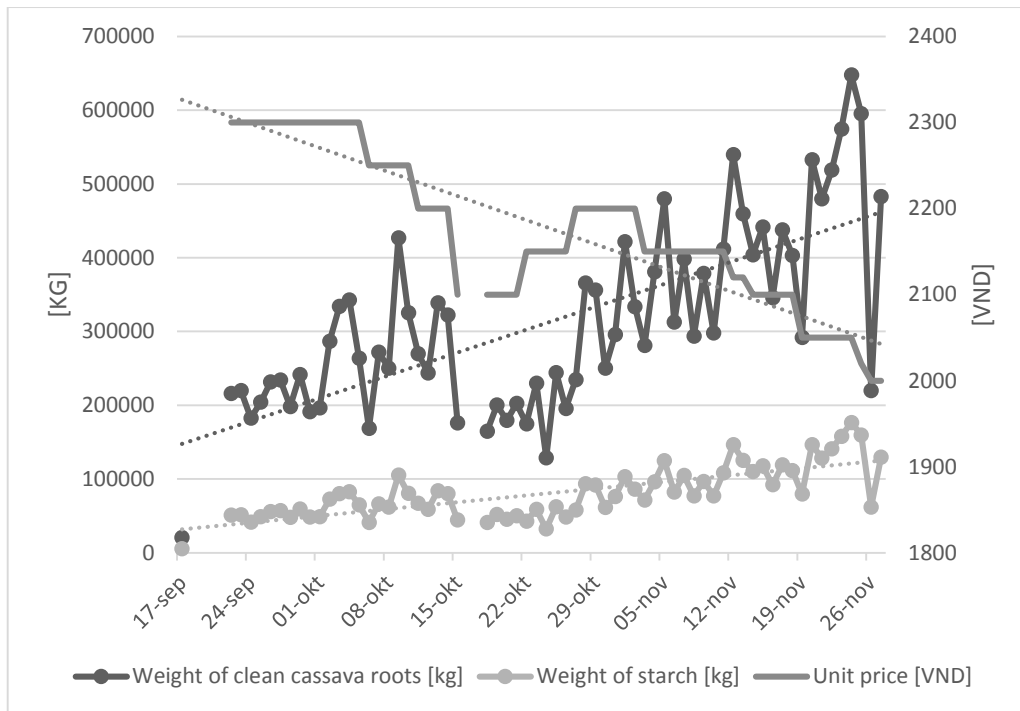


Figure 5.1. The delivery of cassava roots to the factory from 17 September to 27 November. The weight of clean cassava roots is the total amount of roots delivered to the factory during one day where the ash content of the respective deliveries has been estimated and subtracted. The weight of starch is calculated from the weight of clean cassava roots where the respective starch content has been estimated. The unit price is the price paid to the suppliers for each kg of estimated starch, during each specific day, and is given in Vietnamese dong (VND). The trend lines are linear regressions. The absence of data (from 18-21 September and 16-17 October) means that no deliveries were made during those days. (Linh, 2014)

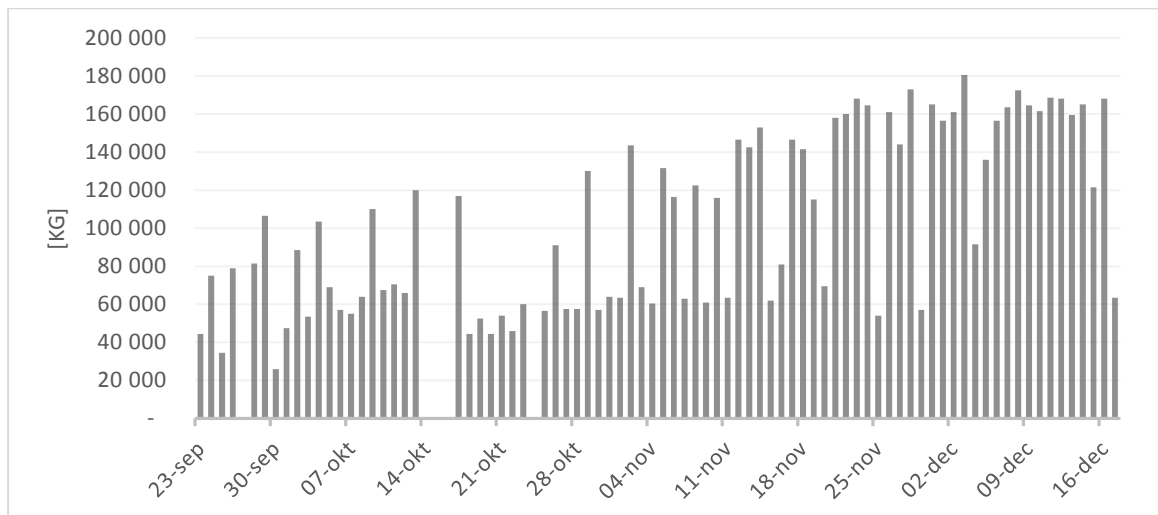


Figure 5.2. The total amount of tapioca produced during each day from 23 September to 17 December. Missing data indicates that no production was done during that day while the days that have around half the amount produced indicate that only one shift was run during that day. (Linh, 2014)

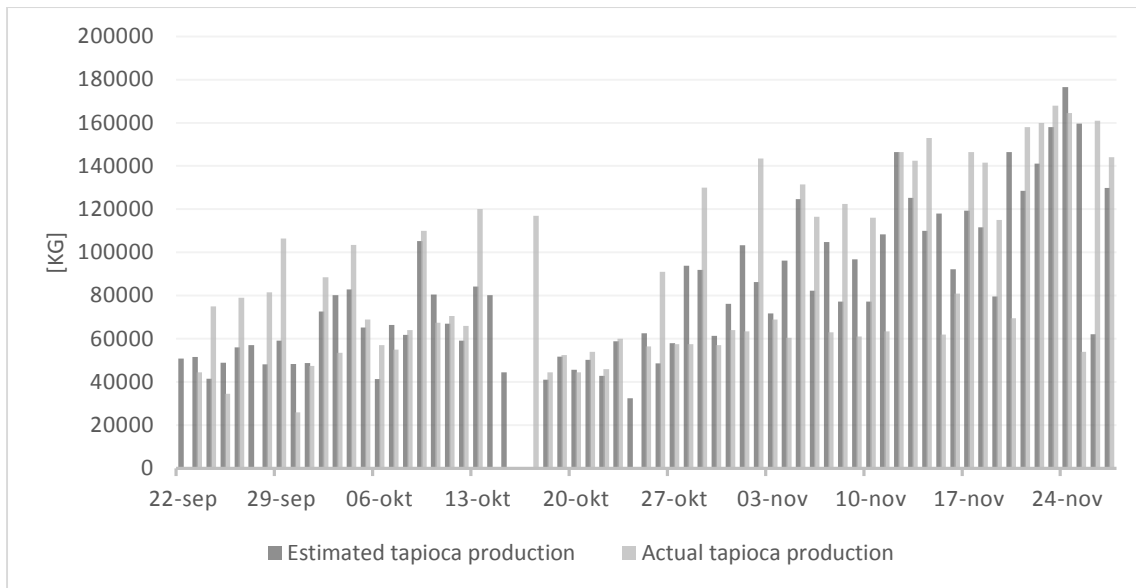


Figure 5.3. The estimated tapioca production calculated from the root delivery as seen in Figure 5.1 and the actual tapioca production as seen in Figure 5.2, from 22 September to 27 November. The estimated and actual production are not the same each day since the roots are stored different amounts of time and the production at the factory varies.

5.2 Outline of factory

5.2.1 Production process

Wusons tapioca factory is a middle-scale tapioca factory (according to definition by Mai, 2006) with the capacity of producing around 150 tons of starch and 60 tons of residue powder per day (Cuong, 2014), but as seen in Figure 5.2 above the production varies each day. The production process at the factory, as seen in Figure 5.4 below, is similar to other factories with small exceptions. One difference is that no chemicals are added for bleaching. It is estimated that 3.4 kg of fresh cassava roots on average yields 1 kg of tapioca starch (Son, 2014), however according to the statistics from the period spent in Vietnam, as seen in Figure 5.1, one kg of starch requires 3.9 kg clean cassava roots. The real value depends on the starch content of the root, and subsequently on the quality of the delivery.

The biogas produced from the anaerobic digestion is fed to an oven situated in the factory which heats air for drying of the tapioca powder, and the amount of biogas fed to the oven is automatically regulated by the temperature in the oven which is held at 230 °C (Son, 2014). No measurement of the amount of biogas used is done and the efficiency of the oven is unknown (Son, 2014). When the availability of gas is insufficient rice husk is instead used as energy supply in the oven.

The machines for extraction and pipes are cleaned twice a day with sodium hydroxide, NaOH, which is first dissolved in a water tank outside and then pumped through the pipe system and the equipment. After that, clean water is pumped through the system to clean out the remaining NaOH. For this 25 kg of NaOH is used each time, meaning 50 kg of NaOH per day (Linh, 2014). NaOH is also added for pH regulation. This is done to the slurry which is created before the extraction step on the occasion that pH is below 5.5, to regulate pH to 5.5-6.5. NaOH is again dissolved in a separate tank and poured in to the slurry. The amount added differs depending on the pH and volume of the slurry, and is estimated based on the experience of the workers and not recorded (Linh, 2014).

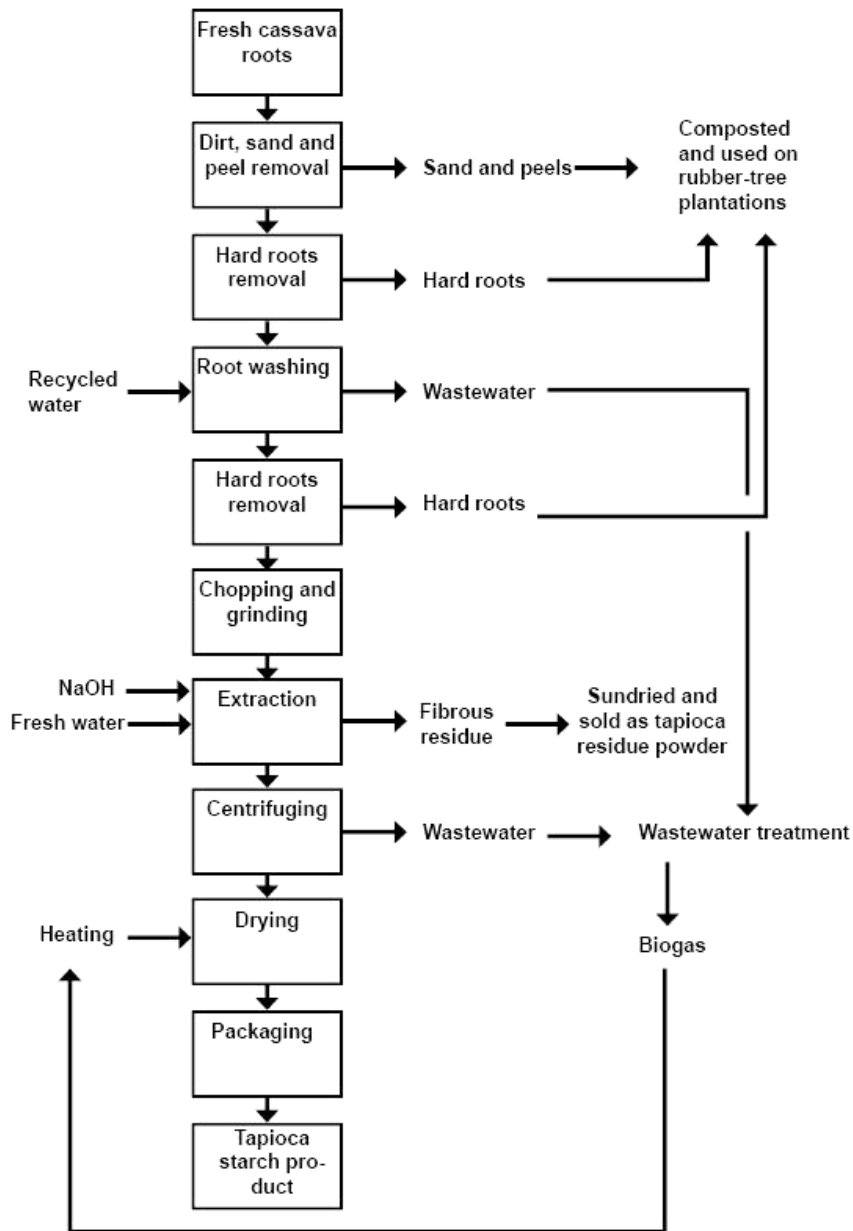


Figure 5.4. Block diagram over the general production process at Wusons tapioca factory. The extraction and centrifuging processes are in fact performed in several steps but here they are summarized as one box.

5.2.2 Wastewater treatment

The circulation of water in the factory is described by the block diagram in Figure 5.5, which can be compared to the map in Appendix A for further understanding. The figure describes how the water was circulated during the third visit to the factory when the primary measurements were done, however this is not how the circulation looked like during the first and second visit to the factory and more alterations can be expected in the future. During previous seasons wastewater from the root washing (WW1) has been emitted directly to Pond 3 (see appendix A for map) followed by Pond 1 and 2 (Son, 2014). This season WW1 has stepwise been redirected to the anaerobic digestion process. During the first and second visit to the factory only part of the water was directed to the anaerobic digestion but during the third visit all of WW1 was going to Pond 4, which had been built

between the second and third visit, and subsequently to the anaerobic digestion. Pond 3, as seen in the map, is therefore no longer in use as wastewater treatment and thus not included in the block diagram in Figure 5.5. WW1 is transported to Pond 4 in an open stream as shown in Figure 4.2 while WW2 is transported in a closed pipe.

The Anaerobic digestion 1 has been in use for 4 seasons (Cuong, 2014) while the construction of Anaerobic digestion 2 was just finished by the third visit to the factory. During the first visit to the factory Anaerobic digestion 1 had been in use for approximately 3 weeks, since the start-up of the factory around 20 September, and the performance was not yet stable. This was indicated by the low pH values for the effluent water and the fact that the production of biogas was not enough to support the heating process why rice husk was used. During the second visit the process was still not believed to be stable but the gas production was now enough to support the heating process and no more rice husk was needed as supplementary fuel. During the third visit to the factory the process was seen as more stable as the pH had increased to almost neutral levels, the biogas production was high (a significant difference could be seen in the volume of the gas storage, as seen in figure 5.7) and the colour of the effluent water from the digester had changed.

The water from Pond 2 is mainly directed to the nearby Trau river which is connected to Saigon river, which runs through the metropolis Ho Chi Minh City, and eventually empties into the East Sea north-east of the Mekong Delta. Some of the water is used for irrigation of the rubber-tree plantations, however this is mostly discussed as a future alternative which will first be investigated (Triet, 2014). Reuse of water from Pond 2 for root washing is done around 2 hours per day, the rest of the water comes from the reuse of WW2 (Son, 2014)

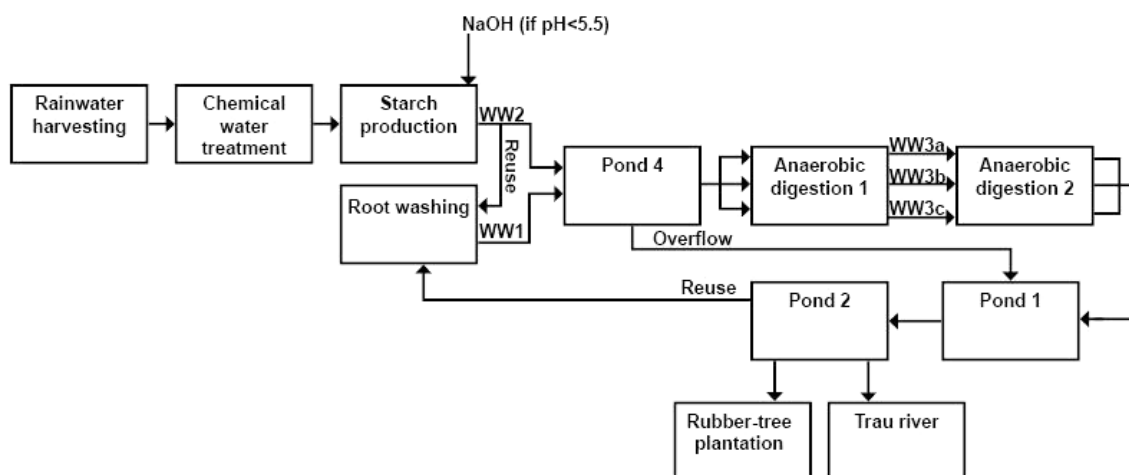


Figure 5.5. Block diagram over the water usage and treatment at Wusons tapioca factory.

Pond sizes and construction

The construction of Anaerobic digestion 1 and 2 are the same, but the size is different. Anaerobic digestion 1 is about $115 \times 105 \text{ m}^2$ while Anaerobic digestion 2 is about $65 \times 125 \text{ m}^2$, and the depth of the ponds are approximately 7 m (Cuong, 2014). There are three inlets and three outlets to the ponds constructed with underground pipes which are evenly distributed along the short ends of the ponds and with the openings just by the edge of the pond. The outlets are accessed by a submerged concrete box, as seen in Figure 5.6, where the inlet to the box is approximately 0.5 m above the bottom of the box and the outlet is

about 0.9 m above the bottom of the box. The bottom of the ponds are covered with plastic and the gas is collected in a HDPE canopy which is dug 1 m underground all the way around the respective pond, see Figure 5.7. The canopy is totally sealed and there is no way of accessing the anaerobic ponds without removing the canopy.

Pond 1 is about 30 000 m² and Pond 2 is about 12 000 m², the depth of both ponds is about 3 m (Cuong, 2014). Pond 4 was built between the second and third visit to the factory to achieve mixing of WW1 and WW2 and has an area of 14×32=448 m². The construction was however not yet finished during the third visit as there was a problem with the pump getting clogged. During the last day at the factory this was addressed by putting up a grid around the pump, but the performance after leaving the factory is unknown. The depth of the pond is 6 m however the overflow outlet to Pond 1 is at around 3 m from the bottom of the pond, which hinders the water from filling the pond. The reason is that the wall on this side of the pond is weak and not believed to be able to hold the pressure from a full pond (Son, 2014). All ponds are constructed with a plastic cover in the bottom (Cuong, 2014). Pond 5, as seen in the map in appendix A, has been used for primary storage during previous seasons but is now out of use. The pond is smaller than Pond 4 (7×18=126 m² and 5 m deep), it is totally made out of concrete, and it has two propellers for mixing. When used the propellers had problems with getting clogged (Son, 2014).



Figure 5.6. Concrete box for accessing the outlet from the anaerobic ponds. This photo was taken on the outlet from Anaerobic digestion 2 before construction was finished. The pipe to the left in the figure was later connected to the pipe directing the water to Pond 1, and covered with soil. The inlet to the box, meaning the outlet from Anaerobic digestion 2, is to the right in the figure but can not be seen as it is underground.



Figure 5.7. Photo of Anaerobic digestion 1 during the third visit to the factory. The grey HDPE canopy covers the whole pond to create a gas storage.

Hydraulic performance

The wastewater flow to Anaerobic digestion 1 is about 1000-1500 m³/day but varies according to how the production varies (Cuong, 2014), and as can be seen in figure 5.2 above the production varies quite a lot which implies the same kind of variations for the wastewater flow. The volume of the reactor is assumed to be around 70 000 m³ since the whole pond is not filled (Cuong, 2014). This means that the theoretical hydraulic detention time in the reactor lies between 47-70 days depending on the flow. In reality this value may be smaller due to a further decreased reactor volume caused by sludge accumulation. The detention time may also vary in different parts of the pond, again due to sludge accumulation causing non ideal flow.

No regulation or measurement of the flow is done at the factory. The mixed wastewater from Pond 4 is supposed to be pumped to Anaerobic digestion 1 but since the system was new, and not fully functioning yet, there was no clear apprehension of how it would work during the third visit to the factory. Before the construction of Pond 4 part of WW1 and all of WW2 was pumped directly in to the digester in separate pipes without mixing.

The concrete boxes which access the outlets from the digester are partially filled with soil from the surrounding environment and sludge from the wastewater. Other than the obstacle this causes there is no regulation of the outflow and the outlets are always open. During the second visit to the factory it was observed that the flow in the boxes seemed different, as the water level was different, but it is hard to tell if this was due to a lower water level which revealed the pile of soil (which was in different size and shape) or if the soil in fact was blocking the outlet somehow.

5.3 Wastewater characteristics

The results of the analysis of wastewater characteristics are presented in the following chapter. The average results are calculated from the results from the third visit to the factory as the process was more stable at this time and samples were handled more appropriately.

5.3.1 Appearance and odour

The appearance and odour of the wastewater streams was observed during all three visits to the factory. WW1 had a brown colour with apparent bits of roots and peel (about 0.5-5 cm). The water had a distinct but not very strong odour. WW2 had a white, milky colour, a smoother appearance and a stronger odour than WW1. WW3 was observed to change appearance and odour during the three visits. During the first and second visit to the factory

the colour of WW3 was dark brown and had a very strong, bad odour. At the third visit to the factory the colour had changed to black/grey and the odour was perceived to be less strong than during the previous visits.

It can also be noted that the samples changed colour when preserved with acid and base, and changed again when neutralized. Furthermore it can be noted that during the third visit to the factory the water going out from Anaerobic digestion 2 was observed to be almost clear in colour and with no odour.

5.3.2 pH

The pH has been monitored in the effluent of the digester since the start-up of the factory. The results of these measurements are shown in Figure 5.8 and show that during start-up pH decreased for the first weeks, probably due to a high acidogenesis. In the beginning of October pH values started to increase, to almost neutral values in the end of November (around the time of the third visit), probably due to the methanogenesis catching up. In the beginning of December something happened with the digester, pH dropped to around 5 and the biogas production at this time was not sufficient for heating of the process and rice husk was again used as complementary energy.

The results of the self-performed measurements of pH are shown in Table 5.1. These results indicate a slightly higher pH for WW2 compared to WW1, which does not match with previous measurements performed on these streams. These measurements showed a higher pH of WW1, around 4.5-4.8, compared to the very low pH of WW2, around 3.3-3.7 (Cuong, 2014). This was one of the underlying reasons to mix WW1 and WW2. The reason for this difference in results is unclear. When comparing the values of WW3 in Table 5.1 with the values from Figure 5.8 from the same date the values in Figure 5.8 are constantly lower, so perhaps there was a difference in the measuring technique or the pH meter used. The difference is however not as big as for the influent values. There is also a possibility that the values have changed since the start-up of the factory when these measurements of influent were performed. This could be explained by a lower production which might influence the strength of the wastewater, how the reuse of WW2 has been performed or differences in the cassava root supply and handling. The values could also have been influenced by the addition of NaOH to WW2, perhaps the previous measurement where performed when no addition of NaOH had been done even if pH was low, or not enough NaOH was added to keep the pH higher throughout the process.

The results for WW3 show almost neutral values and is within the range of the discharge standard of pH 6-9 (as seen in appendix B). However, after the third visit to the factory pH dropped, as described above, to levels out of the range of the discharge standards. pH was not measured during the second visit to the factory (31 October) as the equipment was not available. Measurement performed later that same day (as seen in Figure 5.8) gave a pH of 6 for WW3.

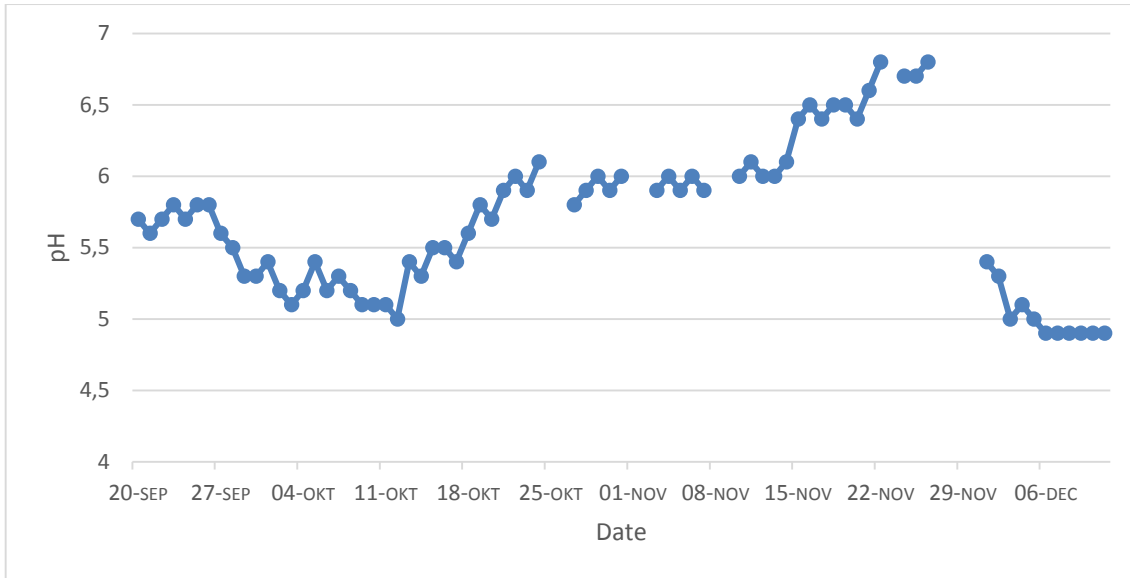


Figure 5.8. pH of WW3 from 20 September to 11 December. The missing values indicate either that the factory was not working or that no one performed measurements that day (Cuong, 2014)

Table 5.1. The results of the measurements of pH

DATE	WW1	WW2	WW3
13-NOV	4.61	4.67	6.66
14-NOV	4.63	5.08	6.57
15-NOV	4.73	5.00	6.60
16-NOV	NW*	NW*	NW*
17-NOV	4.55	5.05	6.68
AVERAGE	4.63	4.95	6.63

*NW: factory not working and therefore no data could be retrieved

5.3.3 Temperature

The temperature of all wastewater streams varied between 30-34°C, with an average of 32°C, as can be seen in Table 5.2. It can be noted that the temperature was only measured during daytime and a slight decrease in temperature can be expected during night time in the influent streams as they are subject to intensive sunlight during the transport from the factory process to the digester. This is also indicated by the fact that temperature measurements from the second visit to the factory (31 October) are the lowest values and these measurements were performed closer to the factory process (in reality without transport). In any event, the temperature inside the digester seems to be within the mesophilic temperature range which is suitable for anaerobic digestion. The temperature is also below the discharge standard of 40°C (as seen in Appendix B).

Table 5.2. The results of the measurement of temperature in °C

DATE	WW1	WW2	WW3
31-OCT	31*	30.7*	31.3*
13-NOV	32.9	32.6	33.1
14-NOV	32.8	33.3	32.3
15-NOV	31.4	32.5	31.6
16-NOV	NW**	NW**	NW**
17-NOV	31.8	31.7	31.7
AVERAGE	32	32	32

* Value not included in average

** NW: factory not working and therefore no data could be retrieved

5.3.4 Solids (TSS, VS)

The results of analysis of TSS show a higher TSS for WW1 than WW2, about double the amount, as can be seen in Table 5.3. This result can be expected since WW1 constitutes recycled WW2 in addition to the solids from the root washing. It should also be noted that the bigger matter (bits of root and peel) are included in the values which will naturally increase the results a lot. TSS for WW3 show that a big part of the TSS is removed in the digester (around 60-90 %) but the values are still far from the discharge standard of 50 mg/l (as seen in appendix B). The values for influent water is varying a lot while the effluent values are more stable which corresponds to the expected.

The results of analysis of VS show similar levels of VS for WW1 and WW2 but with a higher average for WW1, as can be seen in Table 5.4. VS for WW3 show that a big part of VS is removed by the digester (around 83-89 %), but the concentration is still high (however there are no discharge standards for VS). Also here the influent values are varying a lot while the effluent values are more stable.

VS is larger than TSS since it is the VS from the TS and not TSS, meaning in fact TVS. Some conclusions can still be made between the two parameters. Since VS is more similar for WW1 and WW2 than TSS it can be suspected that the solids added by the root washing are to the most part not biologically degradable. This might be due to that a large part of the added TSS in WW1 is made up of bigger bits of root and peel, and also soil particles.

Table 5.3. The results of analysis of TSS in mg/l

DATE	WW1	WW2	WW3
13-NOV	5410	1430	570
15-NOV	3490	2350	570
17-NOV	3240	2340	535
AVERAGE	4047	2040	558

Table 5.4. The results of analysis of VS in mg/l

DATE	WW1	WW2	WW3
13-NOV	8144	5204	850
15-NOV	6916	7040	764
17-NOV	6121	6623	761
AVERAGE	7060	6289	792

5.3.5 Ammonia-nitrogen

The results of analysis of ammonia-nitrogen indicate a similar concentration of ammonia in WW1 and WW2, with a slightly higher average for WW2, as can be seen in Table 5.5. The results clearly show an increase of ammonia nitrogen caused by the anaerobic digestion process as effluent values are double the influent values. The method used gives the total ammonia nitrogen but at pH values this low it can be assumed that it mostly constitutes free ammonia ions. The discharge standard of 0.1 mg/l (as seen in Appendix B) is for free ammonia nitrogen and thus it is not possible to say for sure if the standard is met or not.

The values from the second visit to the factory, where analysis was performed by the environmental lab at Nong Lam University, differ a lot from the values attained from the analysis performed with SMART 3 from the third visit to the factory. According to the SMART 3 manual (LaMotte, n.d.) and APHA (2012) recommendations ammonia nitrogen should be analysed immediately due to its changeable character and since the handling of the samples during the third visit to the factory was better than during the second visit, and due to the conformity of the results, these are seen as more representative. It is also important to notice that if the samples from the second visit had these low concentrations of ammonia the dilution factor used during the attempted analysis with SMART 3 should have given results and it did not. In addition the values are disregarded on the same basis as the other values from the second visit: the process was not yet stable.

Table 5.5. The results of analysis of total ammonia-nitrogen in mg/l

DATE	WW1	WW2	WW3
31-OCT	27.8*	19.3*	227*
13-NOV	80	73	174
15-NOV	66	67	176
17-NOV	83	127	215
AVERAGE	76	89	188

*Measurement performed by lab, instead of SMART 3, and value is not included in the average.

5.3.6 Total nitrogen

The results of analysis of total nitrogen indicate a similar concentration of nitrogen for all wastewater streams, as seen in Table 5.6, with a slightly higher average for WW1 compared to WW2 and the highest average for WW3. Influent values seem to vary a lot which can explain why the effluent value is slightly higher than the influent (previous days the influent might have had higher concentrations of nitrogen). As the effluent values seem more stable this might also indicate that influent values are normally higher than measured during these days. The higher effluent value might also indicate that some of the larger solids from WW1 have been hydrolysed and released nitrogen to the water which are, as opposed to in WW1, detectable. It can be noted that ammonia nitrogen constitutes 25-63 % of the influent total nitrogen and 76-97 % of the effluent total nitrogen. Furthermore, the effluent values are far from the discharge standard of 30 mg/l (as seen in Appendix B).

Table 5.6. The results of analysis of total nitrogen in mg/l

DATE	WW1	WW2	WW3
31-OCT	170.2*	272.1*	300*
13-NOV	261.8	161.9	228
15-NOV	217	275	227
17-NOV	174	202	221
AVERAGE	218	213	225

*Value is not included in the average

5.3.7 Total phosphorus

The results of analysis of total phosphorus indicate a similar concentration of phosphorus in all wastewater streams, with a slight decrease for WW3, as seen in Table 5.7. The influent values vary more than the effluent values which might explain why the effluent value is smaller. Perhaps influent values are normally lower than during the days of the field work. The decrease of phosphorus might also be due to settling of phosphorus in the digester. The effluent values are far from the discharge standard of 4 mg/l (as seen in Appendix B).

Table 5.7. The results of analysis of total phosphorus in mg/l

DATE	WW1	WW2	WW3
31-OCT	35.3*	36.4*	22.4*
13-NOV	50.9	44	38.1
15-NOV	45.1	52.1	37.1
17-NOV	31.7	36.9	34.9
AVERAGE	43	44	37

*Value not included in the average

5.3.8 Organics (COD and BOD₅)

The results of analysis of COD show a similar COD for WW1 and WW2, with a slightly higher average for WW1, as seen in Table 5.8. COD for WW3 show that COD has decreased a lot during the digestion process (around 80-90 %) but levels are still high, and do not meet the discharge standard of 50 mg/l (as seen in Appendix B). The COD:N:P ratio for WW1 is 274:5:1 and for WW2 243:4.8:1 (calculated from the average values). The recommended ratio is 250:5:1 which would imply that both wastewaters are close to the optimal ratio.

The results of analysis of BOD₅ show that the BOD₅ is around 50 % of the COD for the influent water but much smaller for the effluent water (50% for WW1, 47% for WW2 and 5 % for WW3). The estimated values of BOD₅ together with the real values show a large reduction of BOD₅ caused by the digestion process (around 98%) but the values do still not meet the discharge standard of 20 mg/l (as seen in appendix B).

Table 5.8. The results of analysis of COD in mg O₂/l

DATE	WW1	WW2	WW3
13-NOV	13513	9416	918
15-NOV	11385	11651	1357
17-NOV	10427	11012	2075
AVERAGE	11775	10693	1450

Table 5.9. The results of analysis of BOD₅ (17 November) and estimated values (13 and 15 November) in mg O₂/l

DATE	WW1	WW2	WW3
13-NOV	6792*	4441*	46*
15-NOV	5067*	5659*	96*
17-NOV	5241	5194	103
AVERAGE	5700	5098	82

*Value calculated from the relationship between BOD₅ and COD from 17 November and the COD values from the same date.

5.3.9 Cyanide

The results of analysis of cyanide indicate that the concentration of cyanide might be higher in WW1 than in WW2, see Table 5.10. The values do however seem to vary a lot, which corresponds to what could be expected, but an average higher value for WW1 is also corresponding to the expected as the peel often holds higher concentrations of cyanide than the rest of the root. The effluent water seems to have very low concentrations of cyanide indicating that the process removes cyanide very well, and the levels meet the discharge standard of 0.05 mg/l (as seen in appendix B).

Table 5.10. The results of analysis of cyanide (CN⁻) in mg/l

DATE	WW1	WW2	WW3
13-NOV	8.8	0.07	ND*
15-NOV	6.3	3.8	0.05
17-NOV	6.3	8	ND*
AVERAGE	7	4	<0.05

*ND: no data. Value is less than 0.05, which is the MDL of the method

5.4 Biogas production

The biogas production at the factory could not be characterized as planned. When the samples were put in the equipment it did not show any results, only zero value for all samples. The reason for this is unclear. It was observed that gas escaped from the plastic bags, as the volume decreased during storage, and this might be an indication that gas might also have slipped in to the bags which would dilute the concentration. It is also possible that there was something wrong with the measuring technique. What can be said is that the odour of the gas did not indicate any high concentrations of hydrogen sulphide, and the methane concentration during the third visit was high enough to support the heating process. However, after the third visit when pH dropped, gas production was no longer enough to support the process.

The amount of gas produced is not monitored but it has never been so much that the storage got filled (Son, 2014). Furthermore, in the future even more biogas will be needed to support the new tapioca factory. In addition, if the production increased the gas could be used in the rubber factory (Son, 2014).

6 Identification of problems and suggestion of improvements

6.1 Regulating pH

The pH of the influent wastewater (WW1 and WW2) is very low, and it can be suspected that it will lower even more inside the digester due to a fast acidogenesis, and this is probably affecting the methanogenesis in a negative way. As explained above one of the main reasons for introducing WW1 to the digester was that this water was suspected to have a higher pH than WW2. However, the measurements do not show any significant difference between the two, and in fact WW2 has a higher average pH than WW1 as presented above. After the third visit to the factory pH in the effluent dropped to around 5 and the gas production decreased to below necessary levels indicating that the process does indeed have a problem with stabilizing pH. This problem can be addressed by the following suggestions.

Calcium carbonate instead of sodium hydroxide as pH regulator

Sodium hydroxide (NaOH), which is used as pH regulator at the factory today, is not a very good choice as it merely affects the pH and not the alkalinity or buffering capacity of the water which is what is really needed to be able to handle the high production of acids. Furthermore sodium (Na) is a known inhibitor of anaerobic digestion as it impacts on methanogens through an increase of osmotic pressure or complete dehydration of microorganisms (Hierholtzer & Akunna, 2012). Inhibition normally occurs at higher levels of sodium (and depends on the sludge adaption) but Hierholtzer and Akunna (2012) found that sodium inhibition occurs at much lower levels when the concentration of free ammonia is high, and thus a high level of both ammonia and sodium can cause process failure. The tapioca wastewater investigated in this project does show high levels of total ammonia nitrogen, but it is suspected that the concentration of free ammonia is low due to the low pH. If however pH is raised this might change, and it should be noted that high temperatures also shift the equilibrium towards free ammonia.

Calcium carbonate (CaCO_3) is a better choice as it does increase alkalinity and buffering capacity of the water. CaCO_3 is cheaper than NaOH per kilo, and readily available in Vietnam. On Alibaba global trade webpage the price for CaCO_3 ranges between 50-200 USD/tonne while the price for NaOH ranges between 350-450 USD/tonne (Alibaba, 2014). However, since the reactions that take place and the molar masses of the substances are different a simple calculation of how much needs to be added to higher the pH of one litre of water from 4 to 6 has been done, as seen in Appendix D. This shows that 4.95 mg CaCO_3 versus 3.96 mg NaOH needs to be added per litre of water for the same increase in pH. This must be taken into consideration if the prices are evaluated.

It is also recommendable that Pond 4, or any point closer to the digester, is used for pH regulation instead of adding the dissolved chemicals to the slurry as this approach would give a better control of what is actually going in to the digester. The pH of WW2, when measured right before discharge to Pond 4, has a lower pH than supposedly regulated inside the factory implying that the water changes character through the production process, after addition of NaOH.

Fungi as pH regulator

A more cost effective alternative for pH regulation (as opposed to addition of chemicals) that could be applicable at the factory has been suggested by Paulo, et al. (2013). In their study they pretreat tapioca wastewater with fungi which provides the wastewater with a buffering capacity large enough to handle the high acid production in tapioca wastewater. The experiment has only been applied at lab scale but seems promising as both alkalinity and COD-removal was improved. The fungi used was growing naturally at the inlet of an anaerobic digester treating tapioca wastewater in Brazil. The genera was identified to be *Aspergillus*, *Scedosporium*, *Penicillium*, *Paecilomyces*, *Neurospora*, *Eupenicillium*, *Acremonium*, *Fusarium*, *Eumericella*, *Curvularia* and *Cladosporium*. At Wusons factory the fungi could be used as pre-treatment step in Pond 4. More research is however necessary to find the suitable fungi and to test it in full scale. If Wusons factory are interested a possible approach could be to make contact with other tapioca factories in Vietnam to see if they have observed any fungi growing in their ponds which could then be evaluated and used. A suggestion is that they first go through the DAWU cooperation, to also see if there is any interest from the other factories to co-finance the necessary research. If the other tapioca factories also use anaerobic digestion it is likely that they also have a problem with low pH and therefore it would be in everyone's interest to find a cost effective way of solving the problem. Since Wusons factory already have good contact with the agricultural university in Ho Chi Minh City, Nong Lam University, it would probably also be possible to find students who are interested in the project. This would help keeping the cost down and above all they could leave the responsibility of planning and conducting the project with the students and not have to put in much extra work at the same time as the students will get valuable experience.

Mixing influent with other wastewater streams

Another way of increasing pH of the influent wastewater is to mix it with water that has a higher pH, the same method intended with introducing WW1 to the digester. For this there are some different possibilities. The effluent wastewater could be used as it does indeed have a higher pH. However, this wastewater is low in biodegradable matter (low COD but especially low BOD) and high in nitrogen and phosphorus with especially high ammonia concentrations which could instead inhibit the anaerobic digestion process. Furthermore the alkalinity of the wastewater is probably low. Another option is to use the treated water from Pond 2. This alternative is simplified by the fact that a pump and pipe already exist to direct this water to the root washing, and to extend this system would probably not be too complicated. The water composition is however unknown as no measurements has been done on it and the efficiency of the total pond system unexplored. The water should be low in all parameters if the treatment system is working properly but it can be suspected that nutrient levels are still significant, however the solids content should be low and the BOD and VS are probably also low providing a water not suitable for anaerobic digestion.

Another alternative is to use the wastewater from the rubber factory which normally has a high pH around 8-9 (Nguyen & Luong, 2012). However, the report by Nguyen and Luong (2012), evaluating the situation of rubber three wastewater in southeast Vietnam, show that the wastewater is also high in suspended solids, organic matter and nitrogen-containing pollutants. Normal problems in relation to anaerobic treatment of rubber wastewater are therefore fast acidogenesis and ammonia inhibition and since sulphur is normally used in the production process sulphur inhibition is also a normally occurring problem. This means that the method could induce some problems, not only related to pH, and that the method would add water which also has a high acidifying rate. On the other hand wastewater from

rubber factories seems to be suitable for anaerobic digestion, a method which is not used at the rubber factory today. The present wastewater treatment is a pond system which is currently being expanded with an aerobic treatment step. If the two wastewater streams were combined perhaps this aerobic step could also be used to treat all of the wastewater for removal of nitrogen and phosphorus which could improve the overall treatment for both factories at the same time as more biogas can be produced. Both wastewaters are subject to A-level discharge standards.

If the influent is mixed with other streams consideration must be taken to that the retention time in the digester is still sufficient. This is discussed further in Chapter 6.3 below.

Separate acidogenesis and methanogenesis

One way to promote methanogenesis is to separate it from the acidogenetic phase. As presented this might happen spontaneously in an anaerobic pond but it can also be promoted by introducing a two-step digestion. At the factory this could be done by using Anaerobic digestion 1 for acidogenesis and Anaerobic digestion 2 for methanogenesis. To achieve this the flows must be controlled and further measurements must be done to distinguish between the two phases. A suitable parameter to measure is volatile fatty acids, VFA, since a high VFA indicates a high acidogenesis and a subsequent low VFA thus indicates a high methanogenesis. How to change the flow is discussed further in Chapter 6.3 below. This suggestion does however require a higher understanding of the anaerobic process, and outside help or a new employment at the factory would probably be needed to supervise this change.

Alkalinity as indicator instead of pH

Measuring pH is easy and requires minimum knowledge and simple equipment. However, to use pH as the only indicator of the performance of the anaerobic digester, as done at the factory today, is not ideal. When pH in the effluent is changed the damage in the process is already done and it may take a long time for it to recover. A better choice would be to measure the alkalinity of the wastewater instead. In this way measurements to increase the alkalinity and pH can be done before the process is damaged and biogas production drops. Alkalinity can be measured with a titration method according to APHA (2012) but there is also a reagent system in SMART 3 for measuring alkalinity. The range of this is 0-200 mg/l and since properly working anaerobic digesters should have an alkalinity of 2000-4000 mg/l this is not seen as a suitable method even if the tapioca wastewater probably has a much lower alkalinity for the moment. The experience learned from this project with SMART 3 is that it is best suited for measuring values in a rather well known range and as the performance of the digester is not that stable it does not seem like a suitable system. Dilution can be applied, as done in this project, but it will affect the credibility of the results and cause extra work when the range of the samples is continuously changing.

6.2 Cleaning of equipment

As discussed above, addition of sodium might have a negative effect on the digestion process, especially methanogenesis and subsequently the production of biogas. For cleaning the equipment at the factory large amounts of NaOH is added two times a day, which might have a much more severe effect on the digester than the pH regulation because of the way it is conducted. The NaOH for cleaning is not mixed with the slurry when it comes to the digester, as the NaOH for pH regulation is, giving a shock load of NaOH to the digester. There is no mechanical mixing inside the digester, and therefore the flow probably resembles a plug flow reactor. However, there is always some dissociation and

axial mixing and thus the extremely basic environment introduced by the shock load might lead to free ammonia formation which in turn, together with the sodium, might harm the microorganisms at work in the digester. High pH in itself is also harmful for the microorganisms who are adapted to a low pH and as presented above sodium is also inhibiting in itself in high concentrations.

It is not clear what the main objective of the cleaning is and therefore it is hard to come up with suggestions of an alternative measure. It can be suspected that NaOH is used for its ability to dissolve clogging, but it is primarily good for dissolving fat which is not present in this wastewater. NaOH also has a disinfecting quality, which is more likely the reason for usage but it is also the reason why it is so harmful for the digestion process. If a less harmful substance for cleaning can not be found an alternative is to stop this water from reaching the digester by redirecting the pipes during cleaning. The question is to where this water should be directed with the least negative impact. It should not be directed to a pond where ammonia levels are high as this can cause free ammonia formation which is also harmful for the aerobic microorganisms at work in the open ponds, as is high pH. Perhaps the water could be saved, for example in Pond 5, for later use as pH regulator by portioning out small amounts of the highly basic water. It could also be redirected to this pond to be able to mix it with another water for neutralization to avoid discharge of highly concentrated water. These problems with this suggestion show that it seems better to find an alternative way of cleaning the equipment but since the factory is a food processing industry there might be regulations to follow.

6.3 Optimizing and controlling flow

Optimizing use of Anaerobic digestion 1 and 2

WW3 has a COD:N:P ratio of 39:6:1 which is far from the recommended ratio for anaerobic digestion (250:5:1), which may cause problems for Anaerobic digestion 2. Furthermore the COD left seems to constitute low concentrations of biodegradable matter as indicated by the very low BOD (only 5 % of COD). This means that for the moment it cannot be suspected that there will be much biogas-production in Anaerobic digestion 2. If both ponds are to be used for production of biogas the flow must be regulated and the hydraulic retention time in first of all digester 1 decreased to ensure that there is sufficient amounts of biodegradable matter left for digester 2. This approach could also promote a separation between acidogenesis and methanogenesis as discussed above which can improve the overall removal of organics. For the moment a lot of the wastewater is not going to the digestion step at all (because of the overflow in Pond 4) so first of all it should be ensured that the pump-system works properly from Pond 4 to increase the flow to the digestion and ensure that all of WW1 and WW2 are directed to the digestion ponds. It is also recommendable that the flow is monitored, for example by installing a flow meter, for easier control and to enable calculations for optimisation. When increasing the flow to the digesters it is important to consider wash out of the microorganisms. The flow should not be increased so much that the microorganisms do not have time to duplicate, as this will gradually decrease the concentration of microorganisms and subsequently the performance of the digesters.

It would also be possible to run the two digesters in parallel, meaning using the same influent for both digesters. This method provides the advantage of backup, if one digester is not working properly hopefully the other one will. This suggestion also provides the option of only running one digester when production in the factory and thus the flow is

smaller, as in the start and end of the season. Applicability must however be evaluated further, as for the above, to ensure suitable flow levels.

Removal of big solids prior to anaerobic digestion

The big pieces of root and peel added by the root washing to WW1 are suspected to not be degradable in the anaerobic process as implied by the much higher TSS but not so much higher COD, BOD₅ or VS. Furthermore, these solids are suspected to settle fast (because of their large size and as observed during lab analysis) and will therefore cause a large build-up of sludge in the digester which over time will impair the performance of it. Removal of these solids could be done by filtration or sedimentation and the waste created could be composted together with the roots and peels collected from the production process which are already composted. A sedimentation method would require that a new pond was built which had a mechanism for sludge removal. It is possible that Pond 4 or 5 could be rebuilt and used for this purpose. The problem with this method is that it is likely that a lot of the biodegradable matter would sediment as well, which means a loss of substrate for the anaerobic digestion. In this case a filtration method therefore seems more suitable as the size of the grid can be adjusted to only collect the really big solids which will not degrade. This method does however require that the filter is cleaned regularly to ensure the performance and avoid clogging. This could be done either with an automatic system which is probably more expensive, or manually which would require extra labour. Other than that it should not be hard to install a filtration step in the open stream now leading WW1 to Pond 4.

Usage of primary pond

Pond 4 is currently primarily being used to collect and mix the influent wastewater and thus avoid direct discharge into the digester as done before. To ensure an even and controlled flow to the digesters, as preferred by the microorganisms at work, Pond 4 could also be used for storage. This could especially be applied during the events that the factory is shut down to ensure that the digesters are continuously fed.

The full volume of Pond 4 is 2688 m³ which gives a hydraulic retention time, and time it takes to fully fill or empty the pond, of 43-65 h with a flow varying between 1000-1500 m³/day. If the full volume is not used, but the pond is filled to 3 m which is where the overflow outlet to Pond 1 is, the volume of the pond will be about 1344 m³ which gives a hydraulic retention time of 21-32 h with the same variation of flow. This means that for most occasions, when the factory is closed for just one shift or two (12 h per shift), Pond 4 could indeed be used for storage and provide the digestion process with an even flow. The flow could also be regulated to a continuous flow during the event that the factory is closed for a longer time by decreasing the flow to suitable levels. For the moment it is however likely that Pond 4 will fill up very fast with solids if used for storage, as there is no mixing in the pond and tapioca wastewater is observed to settle very fast. Pond 5 thus seems as a more suitable option for storage, however the volume of this pond is smaller and only provides a HRT of 10-15 h with the flow used. Furthermore, experience from previous seasons when the pond was used show that there is a problem of clogging of the propellers. This could be helped by a primary treatment step as discussed above for removal of big solids. This option is however intended to only address the big solids in WW1, which was not even used during the usage of Pond 5 implying that the solids in WW2 is enough to cause clogging problems. Perhaps a different technique for mixing could be used, but this must be explored further. The other problem with this method concerns what will happen in the pond during storage. As the wastewater and outside temperature are high it can be

suspected that chemical and biological reactions will happen in a fast rate which might lead to the formation of odorous and for the digestion process unwanted compounds. In addition this means a loss of substrate to the digestion process, even if relatively small. To avoid this problem the retention time in the pond must be kept short even during storage, how short must be tested and regulated at the factory. Storage during one or two shifts (12 hours per shift) is probably not a problem while several days of storage will very likely cause problems.

Keeping the outlet clean

During the field study it was observed that the concrete boxes, through which access to the effluent was made, were filled with soil and matter from the surrounding environment. This might be a problem if the outlet gets clogged, and it is also adding contaminants to the wastewater. Therefore it is recommended that the outlets are cleaned and kept clean. The task should be included in a job assignment to ensure that it is done regularly. Another possibility is to build some kind of screen around the concrete boxes, and a roof to cover it.

7 Discussion

7.1 Stable process/representable results

Prior to conducting the field work performed during the third visit to the factory consideration was taken to the stability of the process and subsequently how representative the results would be for the performance of the digester. pH of effluent, production process performance and gas availability was the only information available to decide when the process was stable enough to analyse. pH had reached almost neutral levels in time for the third visit which was seen as a positive indication that the process was stabilizing as it had been steadily increasing since the start-up of the factory. There was not time enough to wait for the pH to increase even more, and no assurance of that it actually would (in reality pH decreased again shortly after the third visit). The production process performance changes from day to day at the factory and thus the wastewater characteristics and flow changes. This presumption was confirmed by the analysis of wastewater characteristics that indeed show varying values for both influent streams for most characteristics. All of this is however the normal scenario for the digester, as the feed is totally reliant on the production process, and even if it might make the process unstable it is representative in the way that it is the normal case. The effluent values are more similar which indicates that the process is stable and can handle the variations in the influent quite well. To verify this measurements from a wider time scale would however be necessary, as was planned prior to going to Vietnam but not practically feasible. The gas production is also an indication of stability but since it is not measured it can only be indicated. The visual expansion and reduction of the pond cover tells something about the storage volume but since the cover is so big and changes shape according to the wind it is hard to value it. The other indication is simply based on the performance of the oven, when it is up and running and there is enough gas to support the heating process it indicates that the gas production is working. The connection between this and pH was verified when pH dropped after the third visit to the factory and the biogas production subsequently was no longer enough to support the process. All in all, the results presented in this report are not representing the performance of the digester at all times, and it is not possible to say how big the variations actually can be. The conclusions from the results do however coincide with what has been found in literature about this kind of wastewater and thus seem reasonable and not totally out of range.

7.2 Controlling the digester

As implied by many of the suggestions it is recommendable that the factory starts monitoring the digester more than just measuring pH if they want better control of the system. To achieve a stable and functioning process it is necessary to keep track of what is happening every day, especially since the influent wastewater is highly changeable both in character and quantity. The parameters must however be easy to analyse at the factory, which limits the available choices. VFA and alkalinity can both be measured with a titration method which requires little equipment and could probably be performed at the factory by installation of a simple lab, and the parameters are highly relevant for the biogas process. It would be recommendable to also monitor COD, or even better BOD, but as this might require some expertise it is perhaps not a realistic suggestion. SMART 3 is in theory a suitable equipment that would simplify the analysis but the experience from this project show that it is not suitable for this type of wastewater and requires some experience. Perhaps another more suitable automatic system exist, however this needs further

exploring. Whatever parameters are chosen it is important that the results can be understood and used by the workers at the factory to apply regulations. For example, if alkalinity is measured and found low it is important that there is a control system that ensures that something is done to increase the alkalinity, and in that case that there is something that actually can be done about it. In contrast it seems unnecessary for the moment to measure cyanide as there is no measurement available to address the problem even if noticed.

7.3 Mixing of WW1 and WW2

The approach of introducing WW1 to the digester was new for this season and it was suspected that this would improve the performance of the digester by providing it with water with a higher pH and higher nutrient concentration. This hypothesis has not been verified by the results of the wastewater characterization, the concentration of nitrogen, phosphorus and ammonia are similar for WW1 and WW2 and the average pH is in fact higher for WW2. WW1 might still have higher concentrations of trace metals, as implied by the fact that the peel normally has higher mineral concentrations than the rest of the root, but this has not been investigated in the project. Furthermore, the fact that WW1 is based on recycled WW2 to which even more substrate is added makes the results rather surprising. Perhaps the reason for this is that the added substrate is to the most part made up of larger particulate matter and the nutrients are therefore not suspended in the water and thus not detected by the analysis, as implied by the much higher TSS but not so much higher COD/BOD₅ and similar nutrient concentration. The parts that are suspended are perhaps mostly consistent of soil particles and since cassava is mostly grown on nutrient poor soils this will not affect the mineral or nutrient concentration of the wastewater.

The approach of mixing WW1 and WW2 is still highly recommendable for a number of reasons. First of all it is unlikely that the open pond system can treat WW1 enough to meet the outlet demands, and the wastewater will have a high negative impact on the surrounding environment. Secondly, the composition of WW1 is highly suitable for digestion as indicated by the COD:N:P ratio. Mixing will also increase the flow to the digesters, which is probably needed to support both digester 1 and 2 with substrate. The start-up of the digester seemed to be going faster than previous years which would imply that the mixing is indeed affecting the process in a positive way (Son, 2014). This might however be due to other circumstances, for example the fact that the process has been running for a couple of seasons which has probably improved the microorganisms adaptation to the substrate. It could also be that the digester is favoured by the higher flow.

7.4 Further treatment

The effluent wastewater from the digestion process (Anaerobic digestion 1 and 2) will have remaining high concentrations of nitrogen and phosphorus, with especially high concentrations of ammonia nitrogen. For removal of these compounds further treatment is needed and the open pond system existing at the factory today is probably not suited for this. For biological removal of nitrogen a nitrification and denitrification process is necessary, which requires aerobic and anaerobic treatment steps. Planning of an aerobic treatment step is currently being investigated at the factory, but as discussed above the possibility of using the aerobic treatment currently being built at the rubber factory could also be applied. Another possibility would be to transform one of the ponds into a wetland. The other suggestion discussed, which will be investigated during spring 2015, is to use the wastewater for irrigation of the rubber-three plantations. The results of this study imply that the water would probably be suited for this, as TSS and COD will probably be low in the

final effluent while nutrient levels will be high. Measurements must however be done to further understand what happens in the open pond system (Pond 1 and 2).

7.5 Follow-up, applicability of suggestions and future research

Four months after the project was finished contact was made to see how the rest of the season went and if any changes had been made to the process. The biggest, and only reported change at this time is that NaOH is no longer used at the factory. For pH regulation carbonate is instead used but it is unclear what they use to clean the equipment as carbonate is not likely to be a suitable chemical for cleaning. After the process failure after the third visit manure was also added to the digester to get it started again and the factory reports that after this both digester 1 and 2 have been working very well for the rest of the season with enough biogas to support the drying but also some of the residue powder. It can be assumed that the pump from Pond 4 has also been fixed and it should be taken into consideration that this part of the season is the high season when the factory is always running, meaning a continuous and high flow to the digesters which has probably also been beneficial, in addition to the absence of NaOH. The higher flow is probably also the reason to why Anaerobic digestion 2 has been working well.

Throughout the project the goal has been to find easy and inexpensive solutions to improving the digestion process. To stop using NaOH is a perfect example of this kind of solution that above all does not demand any notable extra labour or money and gives an immediately positive effect for the factory, meaning more biogas. The chemical was simply replaced with another chemical and other than that no other changes were necessary. For the other suggestions a little bit more effort and thought must be put in to the change. Many of the suggestions require further research, as noted continuously in chapter 6, which might be seen as an obstacle by the factory. This includes using fungi as pH regulator and all suggestions regarding flow as no flow measurements or control is done today. Furthermore many suggestions require continuous extra maintenance meaning extra labour at the factory which might also be discouraging. Suggestions that include this are filtration of big solids, using alkalinity as indicator, using a primary pond for storage and keeping the outlet clean (depending on construction). To promote these changes a forward planning thinking must be applied. For example, if a filtration measure is not put in place there will be a problem of sludge build up in the future. This problem would occur irrespectively but now that WW1 is redirected to the digestion it is likely to happen much faster. Furthermore, if alkalinity is used for measuring pH this will give the factory the opportunity to take measures for increasing the pH before there is a break down, something that in deed seems to be a common problem for the factory, especially during start up. However, there seems to be a general lack of forward planning at the factory, as exemplified by the construction of Pond 4, and learning by doing seems to prevail planning. That the pump got clogged did not seem surprising when looking at the structure of the wastewater, nevertheless no effort was made prior to installing and testing the pump to avoid clogging and the result was that three workers had to manually shovel out the sludge surrounding the pump and try to put up a grid around the pump while there was wastewater in the pond. As it seems the implementation of the suggestions also depend on a change of mindset.

Other suggestions, like the usage of Pond 4 for storing, require a bit more risk and investment. It is highly likely that the digestion process is favoured by a continuous flow, as indicated by the fact that this is commonly suggested in literature as most microorganisms prefer a stable environment. Furthermore, the fact that the digester worked better during the high season when the flow is high and continuous confirms the theory.

However, there is no clear way of how to implement the suggestion and the factory workers will simply have to try and see what happens if decided for, which is perhaps not so appealing as a failure in this might mean a loss of biogas during for example one week of production.

An improved biogas process ultimately means less negative effect on the environment. If more biogas can be used, less rice husk is needed meaning less resource consumption. A better biogas process also means a larger reduction in organic material which if not removed would have had a great negative effect on the surrounding environment. Furthermore, a well-functioning digestion process removes the otherwise highly toxic cyanide, and together with the open pond system nutrient concentrations can hopefully also be reduced. A highly interesting alternative is to use the water for irrigation, a research topic that will probably be included in a master thesis project this year and would provide a win-win solution to irrigation and nutrient usage. In relation to this it should be noticed that even if there are strict discharge standards to be met in Vietnam the greatest driving force for the factory is to receive biogas and thus reduce the costs, which is also the reason to why anaerobic digestion is such a good option for these kind of factories. The fact that there are so many tapioca factories in Vietnam and other developing countries indicate that a great environmental gain can be made if these kind of simple biogas systems can be developed even more, and implemented at more factories. For this Wusons tapioca factory could be a pioneer, as the will and prerequisites exist.

8 Conclusions

- Anaerobic digestion of tapioca wastewater usually face problems with low pH due to a fast acidogenesis which creates an acid environment that is not suitable for methanogenesis. Furthermore, digesters may have a problem with cyanide inhibition, microorganisms are however observed to adapt.
- The digester at the investigated factory has a problem with low pH. This can be regulated by for example adding calcium carbonate in the influent, using fungi as primary treatment or separating the acidogenesis from the methanogenesis. It is also suggested that alkalinity is measured instead of pH to enable forward planning regulation.
- Cyanide does not seem to be a problem for the digester as almost all cyanide is removed and the concentration in the effluent is below discharge standards.
- Calcium carbonate (CaCO_3) should be used as pH regulator instead of sodium hydroxide (NaOH) to influence alkalinity rather than momentary pH. Furthermore NaOH might have an inhibitory effect on the anaerobic process. A different option than NaOH should also be considered for cleaning the equipment for the same reason. Shock loads of NaOH might have a severe negative effect on the digestion process, especially since ammonia levels are high.
- The wastewater from the root washing constitutes of recycled water from the extraction process and an addition of roots, peel and soil. To the most part the added material does not seem to be biodegradable, and it does not add any significant amounts of nutrients to the wastewater. The wastewater is still highly suitable for anaerobic digestion as implied by the COD:N:P ratio, but it is suggested that a filtration step is introduced to remove big parts of root and peel and avoid sludge build up.
- There is not much biodegradable matter left in the effluent wastewater from the anaerobic digestion, and ammonia levels are high. This means that it will probably be hard to achieve any digestion and biogas production in the subsequent anaerobic digester which has recently been built. This problem can be handled by regulating the flow of the digesters.

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Appendix A. Map of the factory premises and surrounding area

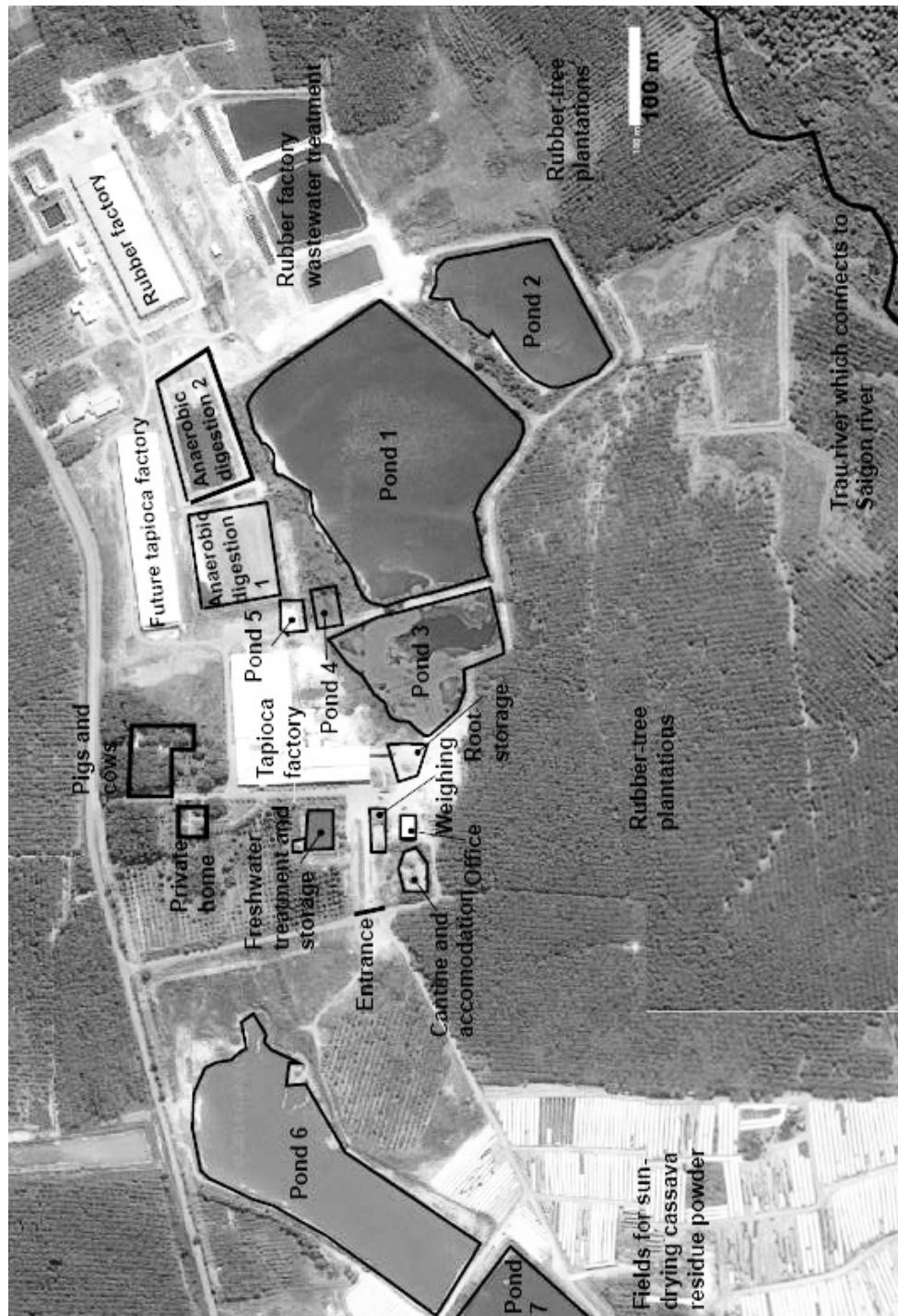


Figure A.1 Map of the factory premises and surrounding area. Pond 1, 2 and 3 have been or are used for wastewater treatment. Pond 4 is used for mixing and storing the wastewater prior to going in to the digestion process and Pond 5 used to be used for the same purpose but is now out of use. Pond 6 and 7 are used for rainwater harvesting. Modified from google maps (Google, 2014).

Appendix B. Discharge standards

Table B.1. The discharge standards relevant in this project from the Vietnamese standard TCVN 5945-1945 (Industrial waste water – discharge standard). Wusons tapioca factory are subject to A-level discharge standards.

PARAMETER	UNIT	A-LEVEL	B-LEVEL
TEMPERATURE	°C	40	40
pH	-	6-9	5.5-9
BOD₅ (20 °C)	mg/l	20	50
COD	mg/l	50	100
TSS	mg/l	50	100
FREE AMMONIA NITROGEN	mg/l	0.1	1
TOTAL NITROGEN	mg/l	30	60
TOTAL PHOSPHATE	mg/l	4	6
CYANIDE	mg/l	0.05	0.1

Appendix C. Sample log used during field study

Sample name on container:

Date and time of sample retrieval:

Sampling location:

Sampling size and container used:

Temperature of sample at retrieval:

pH of sample at retrieval:

Appearance and odour:

Sampling storage and preservation:

Parameters to be measured in sample:

Other observations in field:

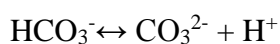
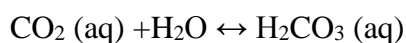
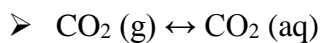
Results

Parameter	Date and time of analysis	Result	Remark

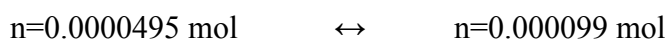
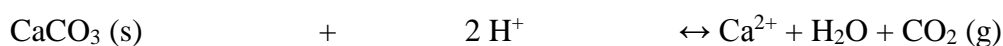
Appendix D. Calculation for pH regulation

- For increasing pH from 4 to 6 in 1 litre of water $10^{-4} - 10^{-6} = 0.000099$ mol $[H^+]$ needs to be added since $[H^+] = 10^{-pH}$

- The natural carbonic acid equilibrium reaction is:



- The equilibrium reaction for $CaCO_3$ in water can therefore be simplified to:

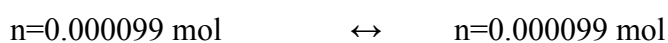


$$M=100 \text{ g/mol}$$

$$m=0.0000495 \cdot 100 = 0.00495 \text{ g}$$

→ Thus 4.95 mg $CaCO_3$ /litre water needs to be added to raise pH from 4 to 6

- The equilibrium reaction for NaOH in water is:



$$M=40 \text{ g/mol}$$

$$m=0.000099 \cdot 40 = 0.00396 \text{ g}$$

→ Thus 3.96 mg NaOH/litre water needs to be added to raise pH from 4 to 6

Appendix E. Popular scientific summary in Swedish

Från avloppsvatten till förnyelsebar energi – om att hitta enkla lösningar på stora problem

Anna Young Gustafson

2015-04-29

Under en tio veckors period i Vietnam hösten 2014 genomförde jag ett SIDA finansierat projekt med målet att hitta enkla och billiga lösningar på hur en befintlig biogasanläggning som behandlar industriellt avloppsvatten från en tapiokafabrik skulle förbättras. Jag gjorde mätningar på vattnet som gick in och ut ur lagunen för att försöka komma fram till vad som skedde där inne, och vad det var för fel på den. För så mycket visste jag; att det var någonting fel inne i lagunen som gjorde att fabriken inte fick tillräckligt med biogas. Mina mätningar visade att det framförallt var problem med att vattnet var för surt, någonting som är vanligt för den här typen av vatten och som fabriken egentligen redan var medvetna om och försökt att lösa. Efter att ha tagit mig igenom språkbarriären med hjälp av papper och penna och enkla skisser visade det sig att fabriken tillsatte stora mängder natriumhydroxid, eller soda som det kallas i folkmun, för att neutralisera surheten. Det de inte var medvetna om är att soda i för stora mängder kan döda de bakterier som lever inne i biogasanläggningen och är anledningen till att biogasen bildas. Kort efter att jag uppmärksammade detta byttes sodan ut mot det i många avseenden bättre alternativet karbonat, och anläggningen har sedan dess fungerat mycket bättre - de hade till och med ett överskott av biogas under högsäsongen den följande våren. De andra problem jag uppmärksammade på anläggningen var inte lika enkla att direkt koppla till produktionen av gas och hade inte lika enkla lösningar. Framförallt krävde de fortsatta undersökningar och stegvisa beslutstaganden för att kunna genomföras. Hur det blir med dessa förslag är därför oklart, antagligen kommer de inte att göra någonting nytt på fabriken förrän de återigen får för liten produktion av biogas. För i slutändan handlar det inte om att rädda miljön utan att skapa vinst för företaget.

Dagens teknik möjliggör fantastiska lösningar på många av de miljöproblem som industrier ger upphov till. I Sverige strävar vi efter att använda oss av bästa möjliga teknik, och vi har lagar och regler som tvingar industrin att ligga i framkant snarare än att göra minsta möjliga, någonting som kan vara kostsamt men som på längre sikt ska gynna både företagen och miljön. I Vietnam och andra utvecklingsländer ser läget annorlunda ut, i första hand för att ny bättre teknik helt enkelt är för dyr men också för att kunskapsnivån för att kunna använda sig av den är för låg. Här blir det därför extra viktigt att försöka hitta win-win lösningar, som både gynnar företagen ekonomiskt och bidrar till en hållbar utveckling och minskad miljöpåverkan. Biogas är ett utmärkt exempel på win-win lösningar där avloppsvatten renas samtidigt som värdefull biogas bildas, men som det visat sig på fabriken där jag var räcker det inte med att införa en smart lösning – det svåra är ofta att få det att fungera praktiskt i det långa loppet. Finns inte kunskapen om hur systemet fungerar kommer det förr eller senare att brista eftersom i princip alla system behöver någon slags underhåll. Enkelt och billigt har därför varit målramen när olika lösningar på hur fabriken ska förbättra sitt system

har föreslagits, och förslagen på hur det ska göras kan därför i första avseende verka triviala men det är det som gör dem så bra. Ett förslag på förbättring var att sätta in ett filtersteg som tar bort de bitar som ändå inte kan brytas ned i anläggningen och som istället förkortar livslängden på den genom att fylla den med oanvändbart material. Om detta relativt enkla förslag genomförs kanske livslängden på anläggningen förlängs och dessutom kan det bidra till att processen förbättras i helhet. Små åtgärder som gör stor skillnad. Om de genomförs på rätt sätt.