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ANAEROBIC WASTEWATER TREATMENT FROM FINNISH FOREST INDUSTRY: VFA ANALYSIS

The acidic wastewater effect on volatile fatty acids concentration

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Abstract

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Abstract

METVI, the efficient waste water pre-treatment project for forest industry wastewater is to strengthen the wastewater treatment process of paper mills. It is to reduce organic load in wastewater by more cost-effectively and significantly and improve the energy efficiency of the process.

Influent is the wastewater from Finnish forest industry. Recycled plant wastewater and part of debarking plant wastewater (very acidic one) is operated and added in the influent. These two types of wastewater are rich in COD. The measurement of volatile fatty acids is the key to the experiment.

In this study, the samples from influent, reactor 1, reactor 2, and effluent was done monitoring analyses by the anaerobic wastewater treatment: VFA analysis method. The ultimate aim of it is to reduce sludge management and recover energy in the form of biogas. The direct purpose is not only to investigate how different ratios of recycled plant wastewater and debarking plant wastewater influences the activity of biogas process, but also to evaluate the methanogenic bacteria from point the view of how the acidic wastewater effect of water volatile fatty acids concentration.

As a result of this, experiments show that with the increasing of debarking plant wastewater, acetic acid propionic acid, ethanol, butanediol and other organic matter also increased. The energy and carbon sources of methanogenic bacteria increased, the production of methane increased. This is an advantage of increasing the proportion of debarking plant wastewater. At the same time, if the ratios of debarking plant wastewater is increased too much, the pH of the influent would reduced too much. The balance of the original bacteria would be destroyed. If an imbalance occurs, the amount of volatile fatty acids produced by acid bacteria would increased. Increasing VFA would cause pH decreases to a harmfully low level. This may weaken the activity of methanogens and may completely stop the production process. Because the optimum pH range for methanogens is between 6.8 and 7.2 (Cioabla, Ionel, Dumitrel and Popescu, 2012).

Keywords
biogas production, anaerobic digestion, methanogenic bacteria, volatile fatty acids

CONTENTS

1 INTRODUCTION

Generally, an anaerobic digester with suspended bacterial growth is used to degrade (digest) the sludge in a municipal waste water treatment plant (Gerardi, H. M, 2003). The purpose of the anaerobic digester is to destroy most of the volatile solids in the sludge and to minimize the corrosiveness of the sludge. The main products of the anaerobic digestion tank are biogas and harmless digestion sludge solids. Biogas is mainly composed of methane (CH_4) and carbon dioxide (CO_2). Anaerobic sludge digestion consists of a series of bacterial events that convert organic compounds into methane, carbon dioxide and new bacterial bacteria.

Influent is the wastewater from Finnish forest industry which uses recycled plant wastewater and part of debarking plant wastewater (very acidic one). These two kinds of wastewater are rich in COD, and the methane yield is quite promising. The measurement of volatile fatty acids is the key to the experiment. Effluent is the wastewater which has gone through the biogas process, thrown by the bio-reactors. Influent consists of lots of organic materials. In bio-reactors, microbes consumes the organic materials and produce biogas.

This experiment was conducted during 10 February to 24 March, including week 6, week 7, week 8, week 9, week 11 and week 12. In this study, monitoring analyses were done on samples taken from influent, reactor 1, reactor 2 and effluent by anaerobic wastewater treatment: VFA analysis method on each Monday, Wednesday, Friday. This thesis will study how the debarking plant wastewater effect of volatile fatty acids concentration. By studying the anaerobic wastewater treatment: VFA analysis technology in the wastewater treatment process to research how to achieve maximum biogas production. And how the debarking plant wastewater influences the activity of biogas process and the methanogenic bacteria frm the point of view of how the acidic wastewater effect of water volatile fatty acids concentration will be evaluated.

2 BACKGROUND

The METVI project is to strengthen the pulp and paper mill wastewater treatment process. This allows the wastewater contained in the organic load to be reduced more economically and meanwhile significantly improve the energy efficiency of the process.

METVI, an efficient wastewater pre-treatment project for forest industry wastewater is to strengthen the wastewater treatment process of paper mills. It is to reduce the organic load in wastewater by more cost-effectively and significantly and improve the energy efficiency of the process. Wastewater activity enhanced by the development of the process from the process water by applying the pre-treatment process of anaerobic effluent (UASB technology: Upflow Anaerobic Sludge Blanket Reactor) the reduction of the organic load (Janhunen 2016). At the same time the apparatus can be produced in addition to the degradation under anaerobic conditions, bio-methane organic compounds contained in wastewater microbiologically (Janhunen 2016).

2.1 The biochemical process of AD

AD (anaerobic digestion) is a microbial process that decomposes organic matter in the absence of oxygen (Al Seadi, Rutz, Prassl, Köttner, Finsterwalder, Volk, Janssen 2008). The main products of this process are biogas and digestion. Biogas is a combustible gas consisting mainly of methane and carbon dioxide. Digestion is a decomposition substrate for biogas production. During AD, contrary to aerobic decomposition (the presence of oxygen), little heat is produced, just like composting. The energy defined by the chemical composition in the matrix is mainly retained in the methane produced in the form of methane. The formation process of the biogas is the result of the connected process steps in which the starting material is continuously broken down into smaller units (Al Seadi et al. 2008). Each individual step involves a specific microbial population. These organisms in turn decompose the product of the preceding steps (Al Seadi et al. 2008).

A simplified diagram of the AD process is shown in Figure 2.1, highlighting four major process steps: hydrolysis, acidification, fermentation and methane production (Al Seadi et al. 2008).

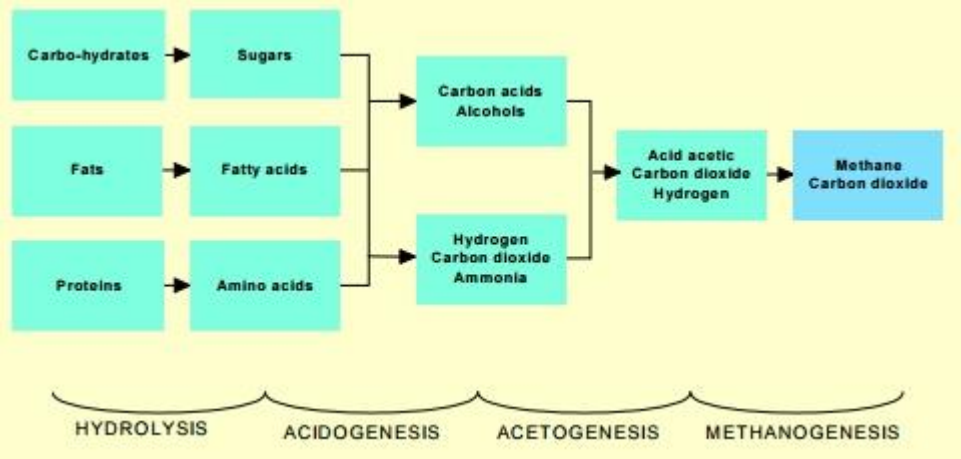

FIGURE 2.1The main process steps of AD (Al SEADI 2001)

The process steps referenced in Figure 2.1 run in parallel in a cooking tank in time and space. The rate of the total decomposition process is determined by the slowest response of the chain. During the hydrolysis, a relatively small amount of biogas is produced. Biogas production reaches its peak in methane production (Al Seadi et al. 2008).

2.1.1 Hydrolysis

Hydrolysis is the first step in AD, where complex organic matter (polymer) into smaller units (mono- and oligomers). In the hydrolysis process, polymers such as carbohydrates, lipids, nucleic acids and proteins are converted to glucose, glycerol, purines and pyridines. Hydrolyzed microorganisms to excrete hydrolases, convert biopolymers into simpler and more soluble compounds, as shown in Figure 2.2 (Al Seadi, et al. 2008) :

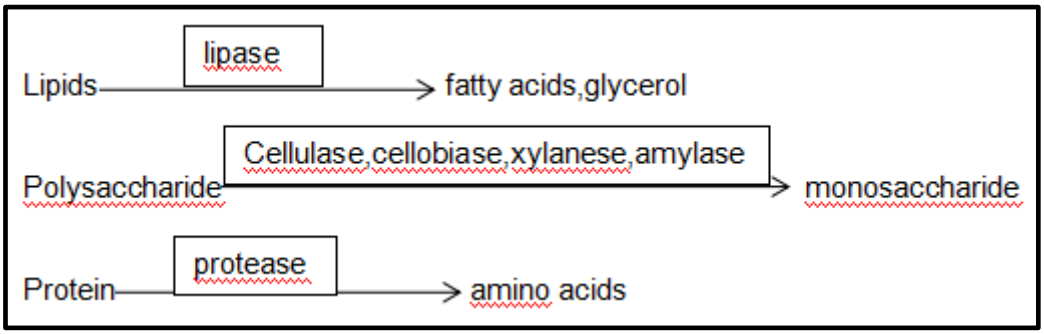

FIGURE 2.2 Hydrolysis (Al Seadi 2008)

Various microorganisms are involved in hydrolysis, which is carried out by exonuclease produced by those microorganisms that break down the undissolved particulate material. The products produced by the hydrolysis are further decomposed by the microorganisms involved and used for their own metabolic processes (Al Seadi, et al. 2008).

2.1.2 Acidogenesis

In the acidogenesis, the hydrolyzate is converted from the acid-producing (fermented) bacteria to the methyl-producing substrate (Al Seadi, et al. 2008, 5). Simple sugars, amino acids and fatty acids are broken down into acetate, carbon dioxide and hydrogen (70%) and volatile fatty acids (VFA) and alcohols (30%) (Al Seadi, et al. 2008).

2.1.3 Acetogenesis

Products from acidogenesis, which cannot be directly converted to methane by methanogenic bacteria, are converted into methanogenic substrates during acetogenesis (Al Seadi, et al. 2008). VFA and alcohols are oxidized to produce methyl substrates such as acetate, hydrogen and carbon dioxide. Hydrogen generation increases the hydrogen partial pressure. This can be thought of as a "waste" of acetylation, which inhibits the metabolism of acetyl yeast. During the methane generation process, hydrogen is converted to methane. Development and methane production are usually parallel to the two groups of biological symbiosis.

2.1.4 Methanogenesis

The production of methane and carbon dioxide from the intermediate product is carried out by methanogens. 70% of the formed methane is derived from acetate and the remaining 30% is produced by the conversion of hydrogen (H) and carbon dioxide (CO_2) as shown in Figure 2.3:

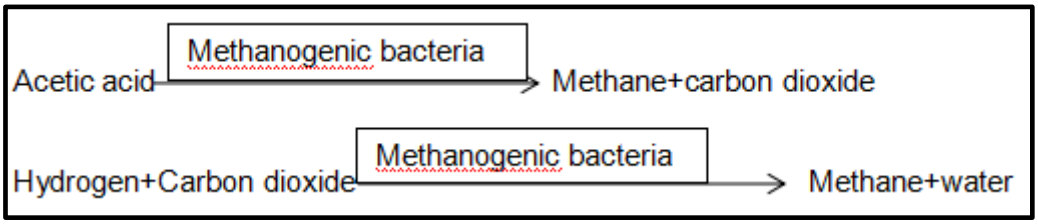

FIGURE 2.3 Methanogenesis equations (Al Seadi, et al. 2008)

Methane production is a key step in the entire anaerobic digestion process because it is the slowest biochemical reaction in the process. Methane production is severely affected by operating conditions. The composition of the feed-stock, feed rate, temperature and pH are examples of factors that affect the methane generation process. Digestion overload, temperature changes or oxygen ingress will lead to the termination of methane production (Al Seadi, et al. 2008).

2.2 AD parameters

The efficiency of AD is influenced by some critical parameters. Such as exclusion of oxygen, constant temperature, pH-value, nutrient supply, stirring intensity as well as the presence and amount of inhibitors (e.g. ammonia). The methane bacteria are very sensitive the

presence of oxygen, which should be strictly avoided in the digestion process strictly avoided (Al Seadi, et al. 2008).

2.2.1 pH-values and optimum intervals

The pH is a measure of the acidity / alkalinity of the solution (the substrate, respectively) Mixture, in the case of AD), expressed in parts per million (ppm). The pH of the AD substrate affects the growth of the methane-producing microorganisms and affects the dissociation of some of the compounds that are important for the AD process (ammonia, sulfide, organic acid). Experience has shown that methane formation occurs within a relatively narrow range of pH intervals from about 5.5 to 8.5, with an optimum interval of 7.0-8.0 for most methanogens (Al Seadi, et al. 2008).

In UASB technology, the optimum pH is 7.2. Acidic microorganisms usually have a lower optimum pH. The pH can be increased by the presence of ammonia in the process of protein degradation or the presence of ammonia in the feed stream, while the accumulation of VFA reduces the pH.

The pH value in the anaerobic reactor is primarily controlled by the bicarbonate buffer system. Therefore, the pH in the digestion tank depends on the partial pressure of carbon dioxide and the concentration of basic and acidic components in the liquid phase. If accumulation of base or acid occurs, the buffer capacity counteracts these changes in pH, up to a certain level (Al Seadi, et al. 2008). When the buffer capacity exceeds the system, a sharp change in pH occurs and the AD process is completely inhibited. Therefore, pH is not recommended as an independent process monitoring parameter. It is important to note, however, that the pH may be a fast, relatively reliable and inexpensive method of recording system imbalances in a weaker buffer system, such as AD for various types of waste water (Al Seadi, et al. 2008).

2.2.2 Volatile fatty acids (VFA)

VFA includes formic acid, acetic acid, propionic acid, butyric acid, valeric acid, hexanoic acid and their isomers (Baidu, 2012).

The stability of the AD process is reflected in the concentration of intermediate products such as VFA. VFA is an intermediate compound (organic short chain acid) having a carbon

chain of up to six atoms produced during acid generation. In most cases, from the instability of the AD process will result in the accumulation of VFA in the digester, which may result in a decrease in pH (Al Seadi, et al. 2008). However, due to the buffering capacity of the digester, the accumulation of VFA does not always show a decrease in pH through the type of biomass contained therein. Animal feces have excess alkalinity, which means that VFA accumulation should exceed a certain level, before a significant reduction in pH can be detected. At this point, the VFA concentration in the digester will be high, so the AD process will be strictly suppressed.

3 EXPERIMENTAL SET-UP

3.1 The set-up of biogas reactors in the tests

There are mainly four parts in the reactor device, which are influent, reactor 1, reactor 2, and effluent.

The reactor schematic in the laboratory is shown in Figure 3.1. During the project process, first, the recycled plant waste water is mixed fully with the debarking plant waste water in the influent tank, which is controlled by an automatic stirrer and pH is adjusted to level 7.2 with NaOH (The mass fraction is 20%). Second, influent is pumped into the reactor 1. The effluent from the reactor 1 flows into reactor 2. Both reactor 1 and reactor 2 produce gas, 80 % of the biogas is collected in reactor 1, consisting essentially of biogas and carbon dioxide. The gas collection bag is mounted on the corresponding reactor. Finally, the remaining waste water flows out of the effluent tank.

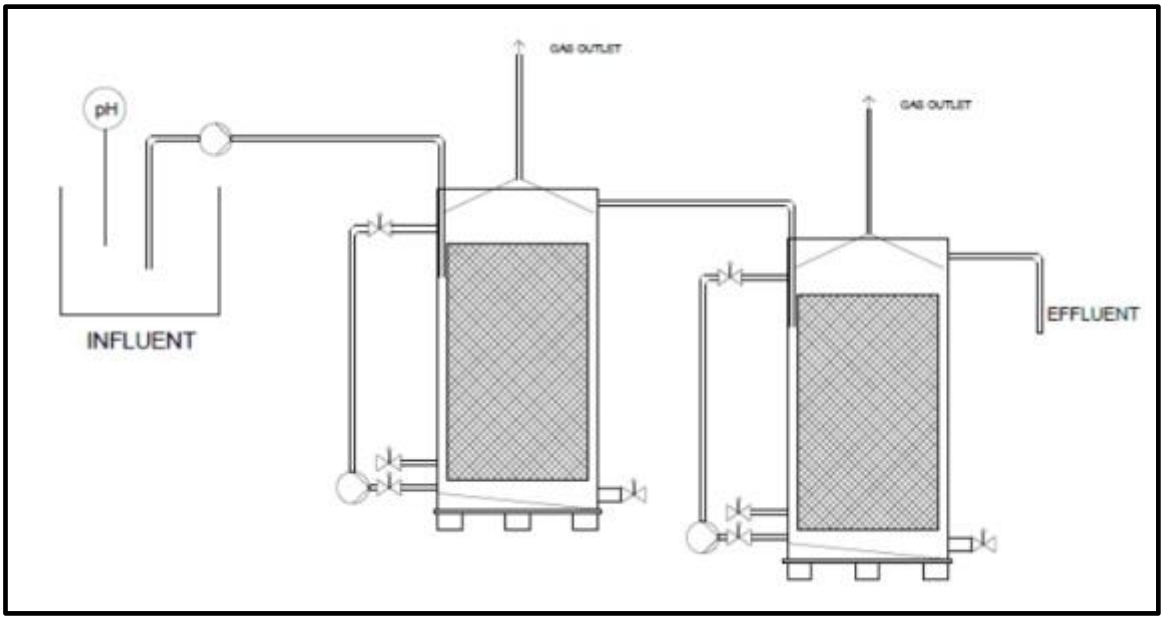

FIGURE 3.1 Laboratory equipment process diagram. Figure Tero Kuhmonen, 2017.

In this project, a two-stage anaerobic process has been used. The process can be seen in Figure 3.1. Most organic carbon removal can take place in the reactor 1. The gray area of rectangle is a fixed bed reactor which containing plastic fillers. The bacteria accumulate on the surface of the plastic filled plate and the bacteria begin to multiply.

The process parameters including the entire storage time of 24 hours, the temperature is +38℃, the organic loading is 5 000 mg COD / Rm3 / d, and the pH value is 7 (Kuhmonen 2017, 9). The filling plate can be filled with calcium and iron. During these two stages, there is a cycle inside the reactors for the mixing process. In this process, with the methanogenic activity to increase the content of CO_2, HCO_3 and NH_3, the degradation capacity of water will increase. During the mixing process, the size of the reactor material is mixed during the day.

In the mixture of processes, the size of the reactor material is mixed during the day. Buffer capacity will rise. The lethal bacterial activity increased the contents of CO_2, HCO_3 and NH_3. All the organic matter will not be removed in this process. A portion of the organic material sinks to the bottom of the reactor and the remainder is converted to methane or carbon dioxide through the process (Kuhmonen 2017). About 80% of the organic carbon will be removed on the reactor 1, and the reactor 2 verifies the effectiveness of the reactor 1. The gas was collected in two reactors in a separate gas collection bag and analyzed with volume and content including CH_4, CO_2, O_2 and H_2S (Kuhmonen 2017).

The sketch of the reactor is shown in Figure 3.2. There are four parts in both reactor 1 and reactor 2, including influent, sludge bed, filling plates, gas.

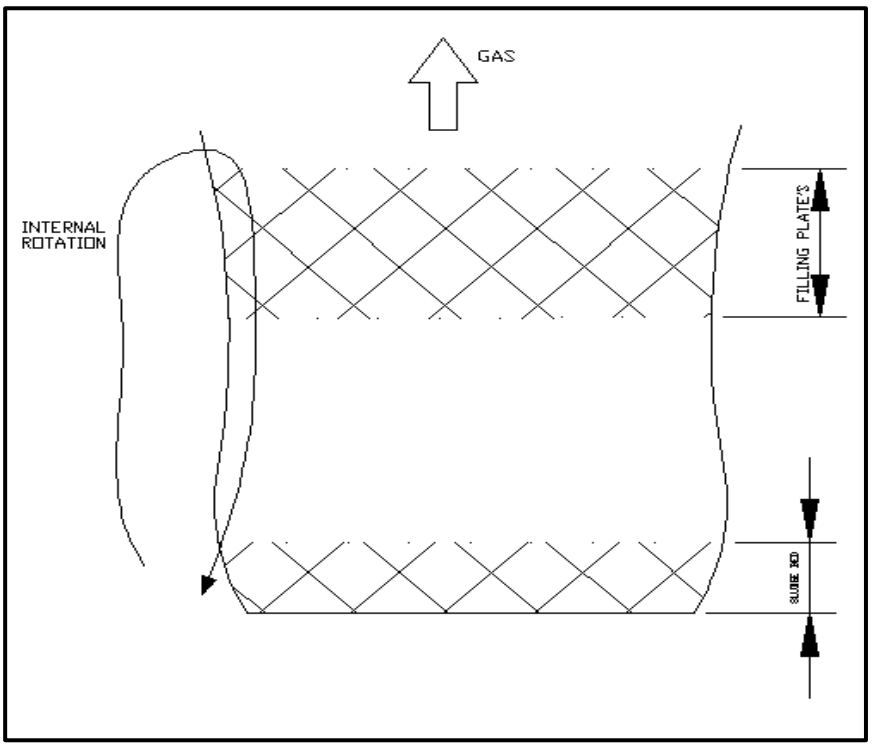

FIGURE 3.2 The sketch of the reactor. (Janhunen, 2017)

When sampled, the syringe passes through the filling plate and is sampled above the sludge bed. The methane and other bacteria in the reaction tank consume various organic acids, and the generated methane and carbon dioxide escape from the above of filling plate.

In the current research, organic acids/alcohols found in the debarking plant wastewater are the following (Janhunen, M. 2017. Final Thesis_VFA analysis [Email]. Recipient Xingrong Li& Merja Tolvanen. Sent 2017. [accessed 2017]) :

- Acetic acid (around 250 mg/l)
- Propionic acid (200 mg/l)
- Methanol (around 9 mg/l)
- Ethanol (100 mg/l)
- Butanediol (30 mg/l)

And for the recycled plant wastewater:

- Formic acid (10 mg/)
- Acetic acid (500 mg/l)
- Butyric acid (130 mg/l
- Propionic acid (200 mg/l)
- Lactic acid (1 200 mg/l)
- Methanol (2 mg/l)

- Ethanol (50 mg/l)
- Butane diol (40 mg/l)

Therefore, as can be seen above, influent contains lots of organic short chain acids.

TABLE 3.1The pH and average COD of recycling plant wastewater and debarking plant wastewater.

	Recycling plant wastewater	Debarking plant wastewater
pH	7	4.2
Average COD	4 000 mg/l	10 000 mg/l

In general, the substrate such as butyrate, propionate or ethanol is oxidized to acetate, hydrogen and / or formate; or acetate, hydrogen / formate and carbon dioxide; is a negative reaction. However, when the hydrogen partial pressure is lowered, the reaction becomes too high, for example, due to the presence of methanogenic bacteria used in the presence of hydrogen or formate. The final stage is defined by methanogens that produce strictly anaerobic bacteria and have a very different cell morphology from regular and irregular coconut cell shapes to short rods and long fragments. They may be hydrogen or hydrogen nutrients that form methane by reducing the H_2 / CO_2 or acetyl-debris or acetyl nutrients that produce methane by decarboxylation of the acetate. In both cases, the chlorophylline bacterium is more important because 70% of the total methane produced during the anaerobic digestion is mediated by its mediation (P.H. Smith & R.E. Hungate 1958). Saccharomyces cerevisiae can convert VFAs to CH_4 (P.H. Smith & R.E. Hungate 1958).

IMAGE 3.3 UASB apparatus in Savonia . From left to right are reactor 1, reactor 2, Effluent. Photograph Antti Koskenlahti, 2017

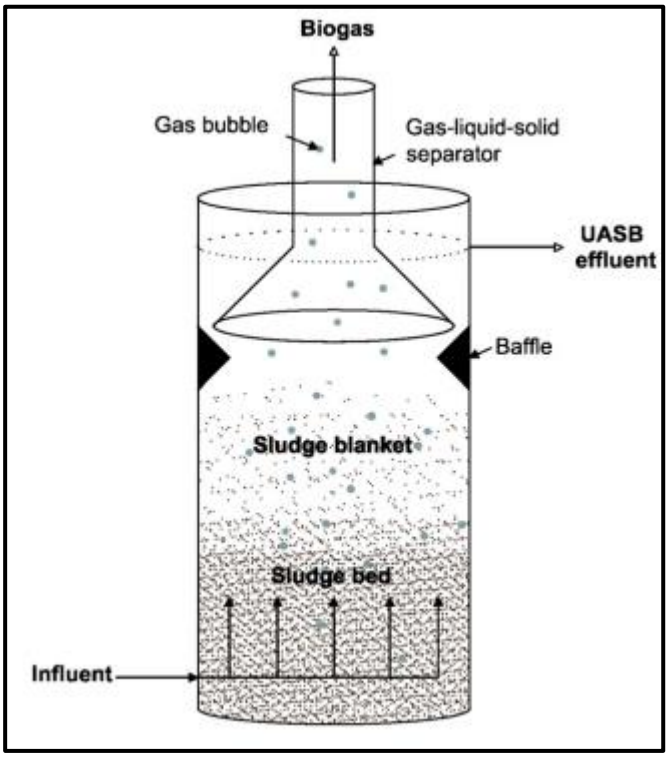

FIGURE 3.4 Schematic of a UASB reactor (Lettinga and Hulshoff Pol, 1991)

The reactor was inoculated with about 30% of the reactor volume inoculum in the beginning, such as digested sludge or activated sludge. The rest of the reactor was filled with inflows. The internal circulation confirmed the flow inside the reactor and the influent was put into the fill plate. The sludge entered from the bottom of the reactor.

Appropriate conditions, light and scattered particles will be washed off. Heavier components will be retained, thereby minimizing the growth of finely divided sludge. The formation of aggregates or flocs of inert organic, inorganic and small bacterial aggregates in seed sludge (Hulshoff Pol, L.W., de Castro Lopes, S.I., Lettinga, G., Lens, P.N.L., 2004). After a period of time (usually 2-8 months), depending on the operating conditions and waste water and seed sludge, very dense, granular or flocculent sludge beds may have essentially high sedimentation properties.

Above the dense sludge bed, there is a sludge-covered zone with great diffusion growth and lower particle set speed (Aiyuk, Forrez, Lieven, van Haandel & Verstraete. 2006). Biological reactions occur throughout the highly active sludge bed and area. Upwards, the soluble organic compounds in the influent are converted to biogas consisting mainly of methane and carbon dioxide. The resulting biogas and the trapped bubbles are separated from the effluent. By returning the settling solids to the reaction zone, the baffles are as effective as possible to prevent viable wash out bacterial substances or floating granular sludge (Lettinga and Hulshoff Pol, 1991; Hickey, Wu, W.-M., Veiga, Jones, 1991).

3.2 The control unit of biogas plant

The biogas plant is a complex installation, and all parts are closely interrelated. Only through the regular monitoring and recording of important data in order to achieve AD process technology standardization and further development. Process stability also requires monitoring and recording (Al Seadi et al. 2008).

3.2.1 pH-value

The measurement of pH is done on a representative sample from the digester content. The pH is measured manually, using ordinary pH-meters, available on the market.

3.2.2 Determination of volatile fatty acids (VFA)

VFA monitoring helps evaluate and optimize the AD process. The measured values refer to the concentration of short chain fatty acids.

3.3 Volatile fatty acids (VFA) analysis in activated, excess and bio- gasified sludge

An effective biogas process depends on the balance between existing bacteria. If there is an imbalance, the amount of volatile fatty acids produced by acid bacteria increases and the pH decreases to a potentially low level. The efficiency of the process can be checked by VFA content determination. The excess sludge and activated sludge in the wastewater have a natural content of volatile fatty acids due to aeration. The assay is based on the addition of an acid cooking sludge fraction to dissolve the (Bi) carbonate and remove the carbon dioxide(Volatile fatty acids (VFA) analysis in activated, excess and bio- gasified sludge). The following is carbon dioxide elimination way:

$H_2CO_3 \rightarrow H_2O + CO_2\uparrow$

The titrant (in the titrification) is sodium hydroxide (neutralization). By the use of this potentiometric procedure all volatile matter will be fatty acid. The amount of acid can be calculated on the basis of the base consumed during the reaction. This method of determination is appropriate when the determination range is 100–1000 mg CH_3COOH/l with a 6.5% tolerance in parallel determinations (Janhunen, 2017).

3.3.1 The Content of Volatile Fatty Acids (VFA) Analysis in Activated, Excess and Bio- gasified Sludge

1) Reagents & Apparatus

During the experimental time, reagents needed to be used are respectively sulfuric acid (0.2 mol/l), deionised water and sodium hydroxide (0.1 mol/l). The needed apparatus are an automatic titrator (Image 3.5), magnet stirrer, magnets, pH meter (Image 3.5), hob (Image 3.6), 150 ml Erlenmeyer flasks, 50 ml full pipettes and beakers.

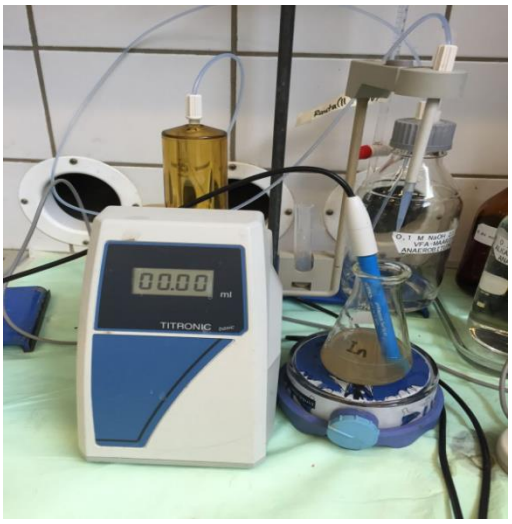

IMAGE 3.5 Automatic titrator and pH meter (manufacture: wtw, model 3210)

IMAGE 3.6 Hob: with a magnetic stirrer and a magnet to cook a homogeneous solution.

3.3.2 Experimental Procedure

1) Experimental story

When sampling, firstly, samples was taken from reactor 1, reactor 2, influent and effluent. Each beakers was filled with at least 120 ml sample. A magnet was added to the beaker and kept the stirring speed at a level where the whirl is barely detectable. Secondly, 0.2 mol/l H_2SO_4 was used to adjust pH value to 3.5. Thirdly, samples was cooked on hob with a magnetic stirrer and a magnet. The step wasn't stop in the fume hood until thin foam develops on the surface. Continue cooking as long as foam develops, but avoid boiling (Image 3.7-4.1). Fourthly, when foaming stops, the beaker was removed from the hob immediately and cooled to room temperature (19 - 23 °C) by cold water. Fifthly, sodium hydroxide solution was put into automatic titrator and air bubbles was emptied from pipe. Cooled sample (50 ml) was placed to Erlenmeyer flask with a magnet and pH electrode was inserted to sample. Finally, read the initial pH value and record it in the measurement log. NaOH (mass fraction is 20%) was titrated to sample to adjust pH to 7.00. Record NaOH consumption in the measurement log. Make two parallel determinations.

2) Results calculating equation:

VFA concentration in units of mg CH_3COOH/l can be calculated by using the following formula:

$$a = (V \cdot T \cdot Ma)/0.05$$

In which,

V = NaOH consumption, ml

T = NaOH molarity, mol/l

Ma = molar mass of acetic acid, g/mol

The sample volume is checked by dividing by 0.05 l

a = result/concentration of volatile fatty acids mg/l of acetic acid.

IMAGE 3.7 Sample was from reactor 1. During cooking time, there was some foam on the surface.

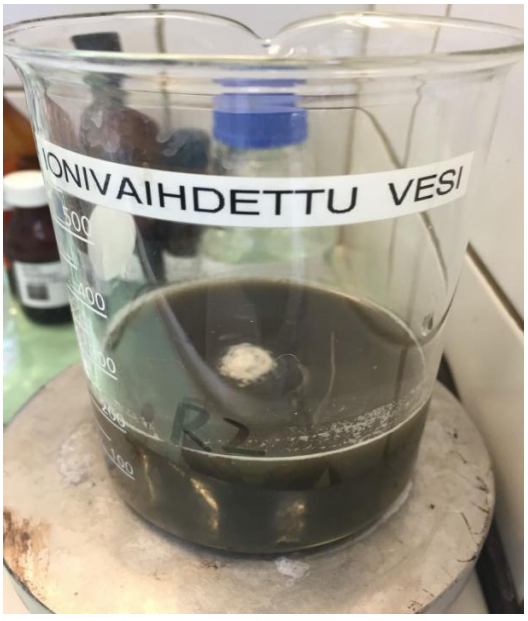

IMAGE 3.8 Sample was from reactor 2. During cooking time, there was some white foam on the surface.

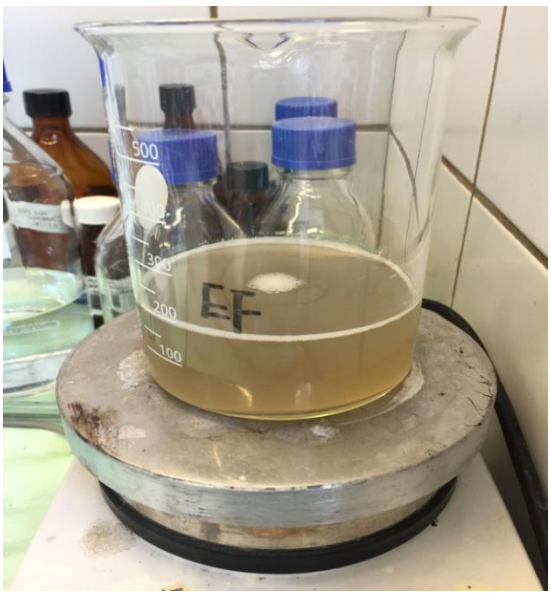

IMAGE 3.9 Sample was from Effluent tank. During cooking time, there was some white foam on the surface. The color of the sample was brown.

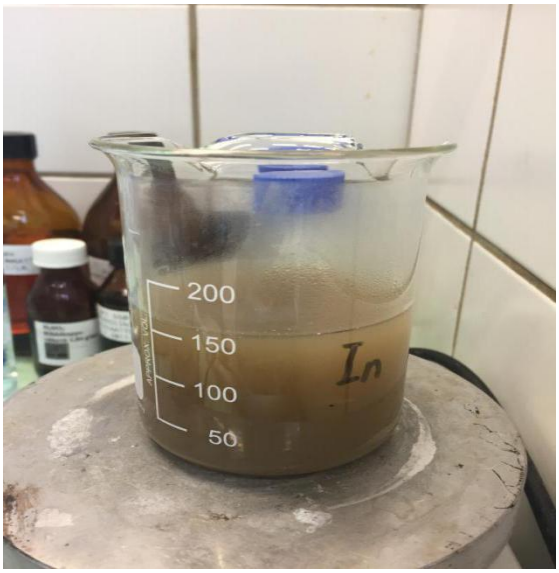

IMAGE 4.1 Sample was from influent tank. During cooking time, there was some foam on the surface.

4 RESULTS AND DISCUSSION

This experiment was conducted during the week 6, week 7, week 8, week 9, week 11 and week 12. In this study, monitoring analyses were done on samples taken from the influent, reactor 1, reactor 2 and the effluent by anaerobic wastewater treatment: VFA analysis method on each Monday, Wednesday, Friday. Experiment procedure is given in Table 4.1.

Influent used for the tests is used the waste water from the Finnish forest industry. Recycled plant wastewater and debarking plant wastewater (very acidic one) was operated and added in influent. These two kinds of waste water are rich in COD. The results of tests are shown in Appendix 1.

TABLE 4.1. Experimental procedure

Bio-reactor process	
Week	**Amount of influent**
2017	%
6	10
7	10
8	20
9	30
11	30
12	30
Influent is wastewater coming from debarking plant (acidic). Rest (100 % - amount of influent) is wastewater coming from recycled plant	

Influent is wastewater from the Finnish forest industry, which consisted of recycled wastewater and debarking wastewater with different ratios. VFA has fluctuated in the process between 600-1200 mg CH_3COOH/l in reactor 1 and 200-700 mg CH_3COOH/l in reactor 2 (Janhunen 2017).

Week 6	Influent	R1	R2	Effluent	Week 9	Influent	R1	R2	Effluent
Monday	0	0	0	0	Monday	1710	642	205	116
Wednesday	0	0	0	0	Wednesday	1781	1131	635	548
Friday	1550	593	366	351	Friday	1517	297	479	121
Average	1550	593	366	351	Average	1670	690	440	262
Week 7	Influent	R1	R2	Effluent	Week 11	Influent	R1	R2	Effluent
Monday	1445	901	240		Monday	1517	297	479	121
Wednesday	1454	846	265	301	Wednesday	1495	719	417	159
Friday	1490	623	327	391	Friday	1452	547	281	169
Average	1463	790	277	346	Average	1488	521	392	149
week 8	Influent	R1	R2	Effluent	Week 12	Influent	R1	R2	Effluent
Monday	1493	638	342	393	Monday	1467	447	317	172
Wednesday	1614	616	342	125	Wednesday	1489	312	212	160
Friday	1648	384	256	181	Friday	1452	547	281	169
Average	1585	546	313	233	Average	1469	435	270	167

FIGURE 4.2 The results of whole weeks (The unit is mg CH_3COOH/l)

Whole of the results has been shown in Figure 4.2. There is only a set of data in week 6. Because Friday in week 6 was the beginning day of experiment. On the whole, from rector 1, reactor 2 to effluent, the results showed a downward trend in the same day, besides Wednesday and Friday in week 7, Monday in week 8 and Monday in week 11. These data of the four days have not been showing a downward trend. But these data are within a reasonable range. Clearer data can be seen in Figure 4.3.

Average					
Week	%	Influent	R1	R2	Effluwnt
6 & 7	10%	1507	692	322	349
8 & 9	20%	1628	627	377	248
11 & 12	30%	1479	478	331	158

%: The percentage is from debarking plant wastewater in influent.

FIGURE 4.3 The average results of six weeks (The unit is mg CH_3COOH/l)

From Figure 4.3 can be clearly seen that all the results from reactor 1, reactor 2 to effluent has shown a downward trend in the same proportion apart from reactor 2 in week 6 & 7. But these data in week 6 & 7 is in the reasonable range. From the vertical point of view, with the increasing of debarking plant wastewater, the results of reactor 1, reactor 2 and effluent has been declining, besides reactor 2 between week 6 & 7 and week 8 & 9. In addition, it is worth noting that the result of reactor 1 in week 11 & 12 is 478 mg CH_3COOH/l, which less than 600 mg CH_3COOH/l. It is abnormal, because VFA has fluctuated in the process between 600-1200 mg CH_3COOH/l in reactor 1 in this system. VFA is too low to increase the production of methane, there is less organic matter can be consumed by anaerobic digester. The reason why it is lower than 600 mg CH_3COOH/l can be explained. Both the average results of week 11 and week 12 is lower 600 mg CH_3COOH/l. If the anaerobic bioreactor is operating normally, the VFA content will remain within a relatively stable range (Cheng, L. 2015). So the reactor 1 in both week 11 and week 12 has been operated abnormally.

Compared Figure 4.3 with Figure 4.4, the results of reactor 1 during week 11 and week 12 is lower 600 mg CH_3COOH/l. It proves that 30% debarking plant wastewater in influent will cause VFA to be too low. 30% of the acidic wastewater and 70% of the recycled plant wastewater are not the best flow ratios. In Figure 4.3, compared week 6 & 7 with week 11 & 12, the average result of reactor 1 is close. So 10% debarking plant wastewater and 90% recycled plant wastewater are the best flow ratios. Because it is more cost-effective and more economical.

In the following, the charts will be displayed about different ratios debarking plant wastewater and recycled plant wastewater in different and typical weeks.

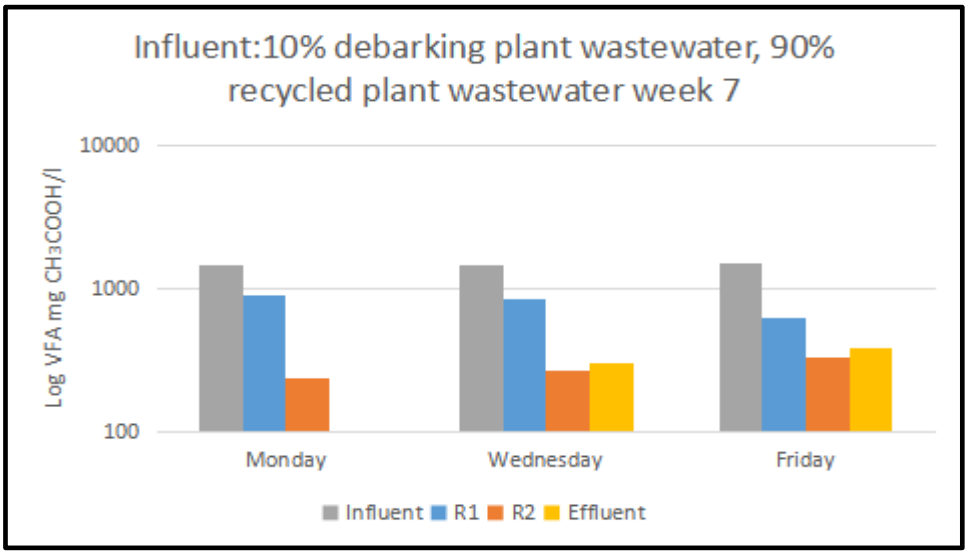

FIGURE 4.4 The VFA results of week 7 (There is no Effluent for experiment on Monday.)

Influent consists lots of organic short chain acids. The results of week 7 is shown in Figure 4.4. It can be seen that VFA has fluctuated regularly. From the influent to the effluent, the volume of VFA is gradually reduced in each sampling day during week 7. Both the reactor 1 and the reactor 2 had a VFA content in the normal range. This proves that the reactor is running smoothly, the biogas process is proceeding smoothly, and the activity of methanogens is not inhibited. This proves that methanogenic bacteria are using those acids and alcohols as nutrient and consuming them. Meanwhile, the methanogenic bacteria consume the organic acids, the VFA volume become lower from influent to effluent.

Debarking plant wastewater contains acetic acid (around 250 mg/l), propionic acid (200 mg/l), methanol (around 9 mg/l), ethanol (100 mg/l), butane diol (30 mg/l) (Janhunen, 2017), which provides an important intermediate product for the rich anaerobic digestion process. Propionic acid, ethanol, butanediol need to further change the production of acetic acid. While acetic acid and hydrogen are converted to methane by methanogenic bacteria. Methane is mainly produced by VFA, and only a small part of methane is produced from CO_2 and H_2. But the formation of CO_2 and H_2 also through the polymer organics to form VFA intermediate process (Al Seadi et al. 2008). In this way, the formation of methane is inseparable from the formation of VFA.

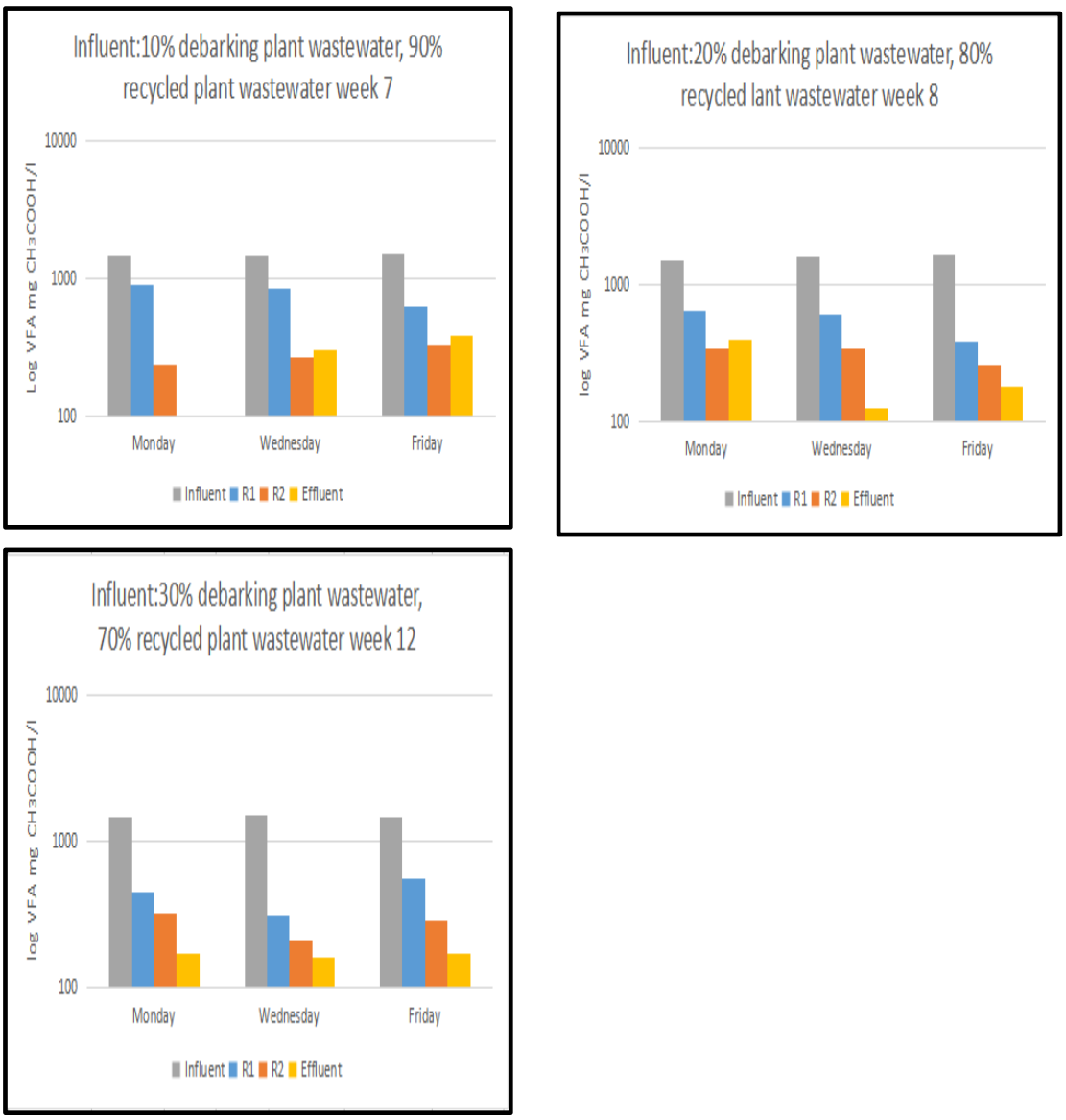

FIGURE 4.5 The results of week 7, week 8, week 12 (There is no effluent on Monday, week 7)

As can be seen from Figure 4.5 above, the VFA of influent is almost the same. However, comparing the VFA between week 7 and week 8, the VFA of reactor 1, reactor 2 and effluent in week 8 is lower than week 7. When comparing week 8 and week 12, the results in week 12 is lower than week 8. With the amount of debarking plant wastewater is increasing, the VFA of reactor 1, reactor 2 and effluent from week 7 to week 12 is decreasing. The VFA content of reactor 1 and reactor 2 in three week has reduced, but within the appropriate range, this proves that the bacteria are balanced and the activity of methanogens is not inhibited.

Anaerobic sludge digestion consists of a series of bacterial events that convert organic compounds to methane, carbon dioxide, and new bacterial cells. Methanogenesis, involves the production of methane and carbon dioxide (Gerardi, H.M 2003). Acetic acid bacteria involves the conversion of the volatile acids and alcohols to substrates such as acetic acid

or acetate (CH_3COOH) and hydrogen gas that can be used by methane-forming bacteria. Methane production occurs from the degradation of acetate (Equation 4.1) and the reduction of carbon dioxide by hydrogen gas (Equation 4.2) (Gerardi, H. M, 2003).

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad (4.1)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (4.2)$$

Debarking plant wastewater contains acetic acid (around 250 mg/l), propionic acid (200 mg/l), methanol (around 9 mg/l), ethanol (100 mg/l), butanediol (30 mg/l). With increased in desalination wastewater, the content of these organic substances also increased. There are five kinds of energy and carbon source materials for methane bacteria, namely H_2 / CO_2, formic acid, methanol, methylamine and acetic acid. Therefore, the energy and carbon source of methanogenic bacteria are also increased. Methanogenic bacteria can only be acetic acid, formic acid and methanol as substrate for the formation of methane. Propionic acid, ethanol, butane diol need to further to acetic acid, hydrogen and carbon dioxide. In the use of methanogenic bacteria, acetate can produce methane and carbon dioxide, hydrogen and carbon dioxide can produce methane. From Figure 4.5, methanogenic bacteria are using those acids and alcohols as nutrient and consuming them.

During experimental time, whole of the results was respectively reducing from influent to effluent in the same day. Comparing different weeks, with the increasing of debarking plant wastewater, the results of reactor 1 and reactor 2 in later weeks has become more and more lower than previous weeks.

5 CONCLUSION

This thesis not only successfully investigated how different ratios of recycled plant wastewater and debarking plant wastewater influences the activity of biogas process, but also successfully evaluated the methanogenic bacteria from the point the view of the acidic wastewater (debarking plant wastewater) effect of water volatile fatty acids concentration. Recycled plant wastewater and debarking plant wastewater (very acidic one) was used and added in the influent during the process. These two types of wastewater are rich in COD. The measurement of volatile fatty acids is the key to the experiment.

Volatile fatty acids are an important intermediate product of anaerobic digestion. Methane is mainly produced by VFA, and only a small part of methane is produced from CO_2 and H_2.

But the formation of CO_2 and H_2 can also through the polymer organics to form VFA intermediate process (Chen, Luo, Xu & Wu, 2008). In this way, the formation of methane is inseparable from the formation of VFA, but the accumulation of VFA in the anaerobic reactor reflects the deterioration of methane inactivity or the operating conditions of the reactors.

With the increased in acidic wastewater, the concentration of VFA in the reactors and effluent were all reduced. 10% debarking plant wastewater and 90% recycled plant wastewater are the best flow ratios.

On the one hand, the increased debarking plant wastewater provided rich methanogenic substrate for methanogenic bacteria. Because when the anaerobic digester consumed the above organic matter, the internal circulation increased the carbon dioxide content. Inside the reactors, the suitable pH is between 6 and 8, a portion of these carbon dioxide can escape and be collected by the gas collection bag. Carbon dioxide is reduced, the content of VFA is reduced. And the other is in the form of HCO^-_3. This is the most important pH buffer in anaerobic treatment. The alkalinity of the bicarbonate can consume out-of-range VFA. And acidic wastewater contains a lot of acetic acid, which can be directly consumed by methanogenic bacteria, so the increase in the impact of acidic wastewater on the VFA is positive. This is the advantage of increasing the ratios of debarking plant wastewater.

On the other hand, the pH value of the debarking plant wastewater is approximately 4, the amount of COD is almost 10000 mg/l . With debarking plant wastewater increased, the pH of influent would became lower, the COD is higher. The influent flew into the reactors would destroy balance between original bacteria and affect the activity of methanogenic bacteria. Because the optimum pH range for methanogenic bacteria is between 6.8 and 7.2 (Cioabla, Ionel, et al. 2012). The low pH and high COD of Influent would inhibit the activity of methanogens, which result in a decline in methane production.

During experimental time, whole of the results was respectively reducing from influent to effluent in the same day. Comparing different weeks, with the increasing of debarking plant wastewater, the results of reactor 1 and reactor 2 in later weeks has become more and more lower than previous weeks. It can be proved that the ratios of two kinds of wastewater is reasonable and feasible for methanogenic bacteria. It is possible to try UASB technology in pulp and paper industry wastewater pretreatment. It is also possible to verify the efficiency of the process by VFA analysis. Because the decline in VFA proved that the organic matter in the reactors was consumed more thoroughly by methanogenic bacteria. The amount of debarking plant wastewater hasn't inhibited the balance between bacteria, because it hasn’t increased the VFA production over the reasonable range or decreased the VFA lower the suitable range.

The above mentioned does not apply to 30% debarking plant wastewater. It is worthy noting that almost all of the results were less than 600 mg CH_3COOH/l within two weeks of 30% debarking plant wastewater run. The average was only 478 mg CH_3COOH/l. VFA is too low to increase the production of methane, there is less organic matter can be consumed by anaerobic digester.

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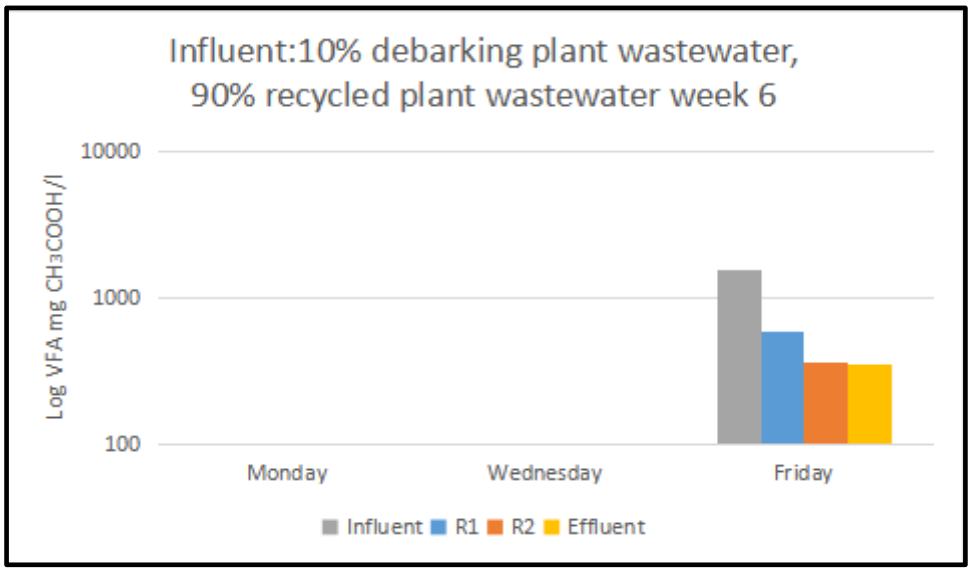
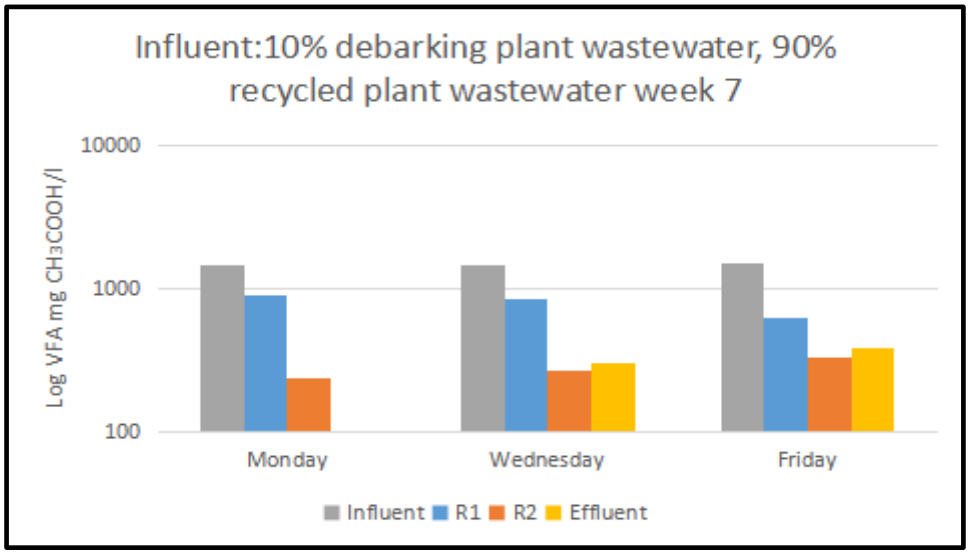
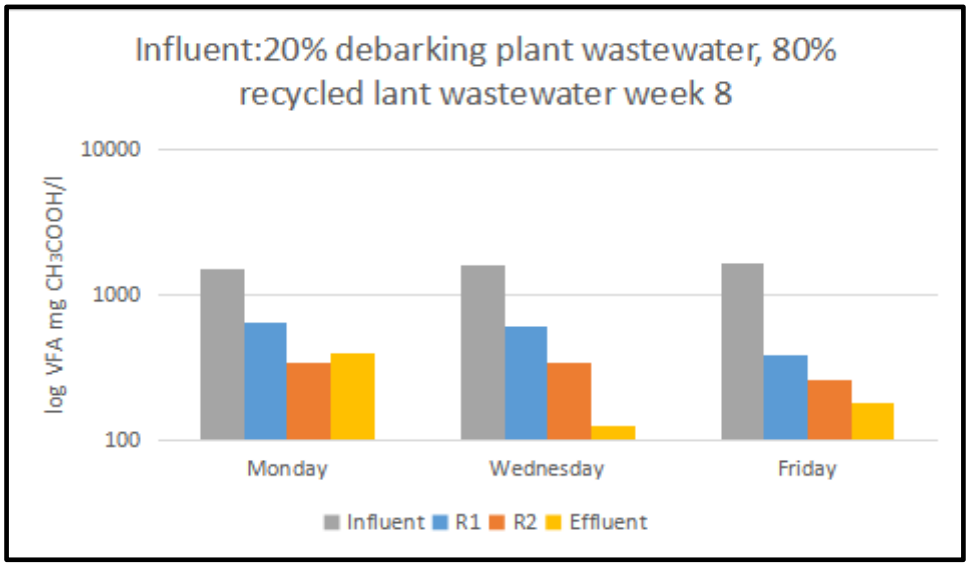
Volatile Fatty Acids (VFA) Analysis in Activated, Excess and Bio- gasified Sludge. Savonia University of Applied Sciences | PL 6, 70201 Kuopio | www.savonia.fi.

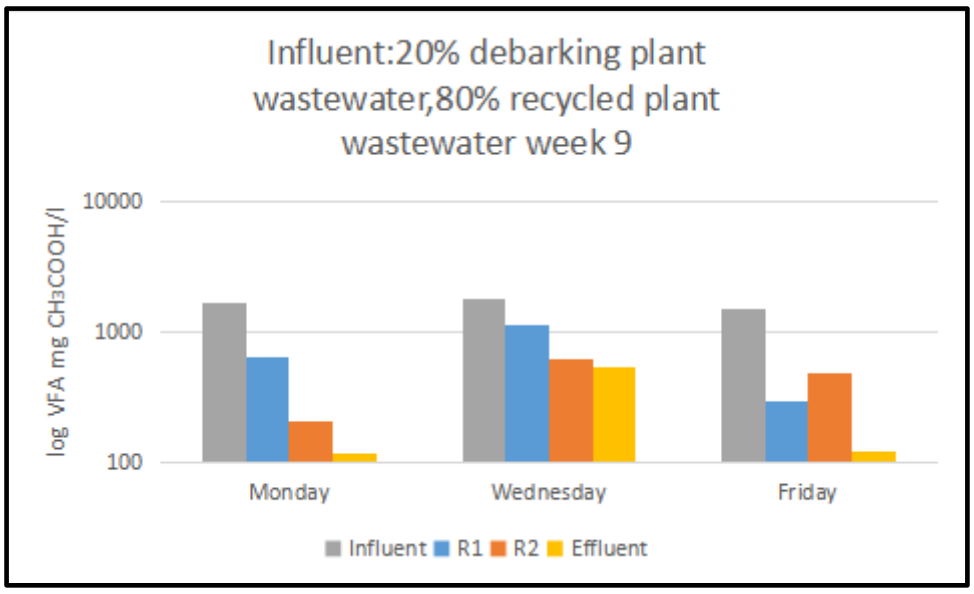
APPENDICES

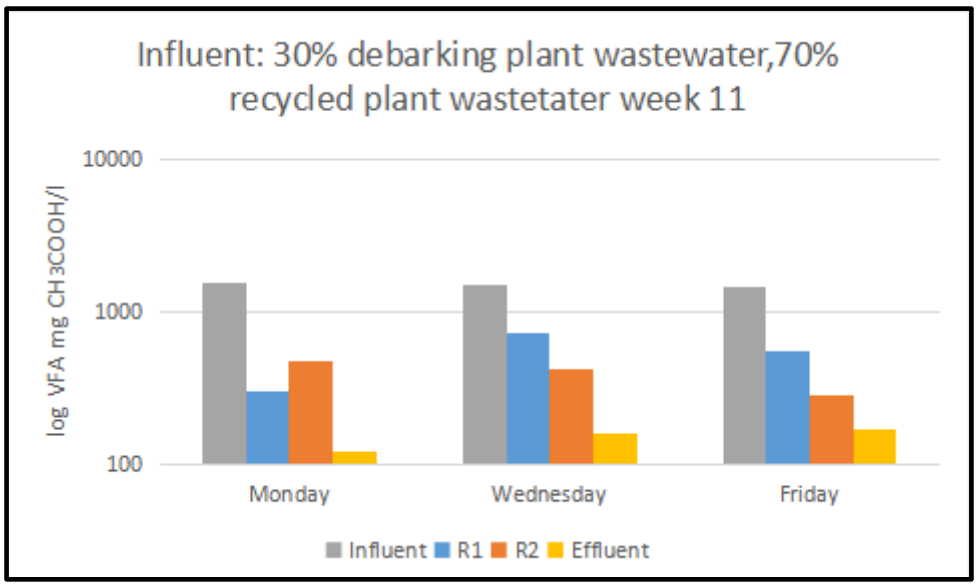
Appendix 1 Figures of different ratios recycled plant wastewater and debarking plant wastewater

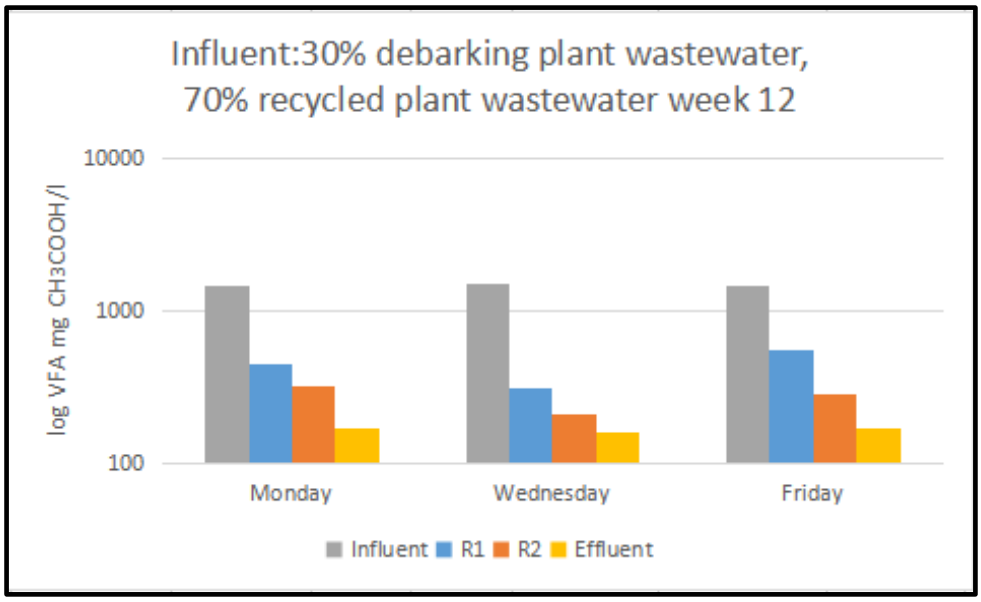







Influent:20% debarking plant wastewater,80% recycled plant wastewater week 9
log VFA mg CH3COOH/l
10000
1000
100
Monday
Wednesday
Friday
Influent
R1
R2
Effluent


Influent: 30% debarking plant wastewater,70% recycled plant wastetater week 11
log VFA mg CH3COOH/l
10000
1000
100
Monday
Wednesday
Friday
Influent
R1
R2
Effluent


Influent:30% debarking plant wastewater, 70% recycled plant wastewater week 12
log VFA mg CH3COOH/l
10000
1000
100
Monday
Wednesday
Friday
Influent
R1
R2
Effluent


SAVONIA