FEASIBILITY STUDY OF DIFFERENT CLEANING TECHNIQUES IN THE ABATEMENT OF VOC EMISSIONS FROM AEROBIC AND ANAEROBIC WASTE WATER TREATMENT IN MECHANICAL PULPING

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ABSTRACT
In the paper a pilot plant for the abatement of VOC from Mechanical Pulping waste waters is described. In the Life project (LIFE09 ENV/FI/568) 3 different abatement technologies were tested at the aerobic and anaerobic waste water treatment plants in mechanical pulping: catalytic oxidation, UV filtration and biofiltering. The aim was to find the most feasible VOC emission abatement technology for such application.

In the paper results of infield experimentation are shown.

Keywords: VOCless, VOC emissions, mechanical pulping, Biofiltering

1. INTRODUCTION
VOC emissions have received a growing interest in the last decades. This because of some pollution effect, such as summer smog and also because of odour abatement issues

Mechanical pulping is an industrial method for pulp making and it is very interesting for its high yields and low costs in pulp production.

Mechanical pulping and also Thermomechanical pulping do not use any chemicals.

So in this case VOC emissions are natural and do not belong the European VOC directive. Nevertheless there is an interest to consider these emissions both for workplace safeness and odour reduction.

In particular the goal of the LIFE+ European Union project "Life09 ENV/FI/000568, abatement of VOC load from waste water treatment in mechanical pulping" is about minimizing the VOCs emissions from the mechanical pulping waste waters treatments plants. It is estimated that VOC emissions from waste waters could account for 50% of the total Mechanical Pulping VOC emissions.

In order to minimize such emissions, some combination of VOC abatement techniques is considered.

In the paper such techniques are discussed and compared in a waste waters treatment plant.

In the following a related research, the VOCless Pulping Waste Waters project, and VOC measurements are shown and discussed.

2. RELATED RESEARCH
Environment is an important issue in Modeling and Simulation (Bruzzone et al., 2009a) (Bruzzone et al., 2009b).

Concerning, in general, the issue of waste waters from pulping processes, useful information can be found in (Pokhrel and Viraraghavan, 2004). All pulping processes are considered and the available abatement techniques shown. Possible techniques are: Sedimentation, Flotation, Adsorption, Coagulation and Precipitation, Chemical Oxidation, Membrane filtration, Ozonation, Aerobic treatment, Aerated lagoons, Aerobic biological reactors, Anaerobic treatment and fungal treatment. Also integrated solutions that combines 2 or more of the above techniques are considered. Nevertheless there are no mentions to the fact that in the case of Mechanical Pulping VOC emissions are natural.

Considering this point in (Kivimäenpää, 2012) VOC emissions from Scot pine are considered. Main VOCs are monoterpene and they depend also on tree provenance.

In (Qu et al., 2012) a combination of thermophilic submerged aerobic membrane bioreactor and electrochemical oxidation is studied with the aim to "close" the system. The quality of the water at the output of process is so high, that it could be reused as new water in the system, even if energy used of the system should be still improved.

In (Stephenson and Duff, 1996) waste waters emissions in Mechanical Pulping are considered. First of all one of the main advantage of pulping is the lower use of water in the cycle, unlike the Kraft process. After the problem of toxic extractives, such as fatty acid, are considered. They are removed by metal salt enhanced precipitation and coagulation.

In (Harinath et al, 2011) a model of the TMP, thermo mechanical pulping. The model is analytical and it is used for investigating production strategies. First results seems to be good, but the model itself still needs more development.

In (Zhang et al., 2009) a model for technology forecast is shown for the pulping industry. This model is used to forecast the emissions in the future of COD, SO_2 in China. In this manner it is possible to support the 11^{th} Five Year Plan period Chinese aim of reducing such emissions by 10%. In the paper mechanical pulping or TMP pulping are not considered within pulping technologies considered, probably because of their small impact in Chinese pulping industry.

A model of VOC abatement techniques can be found in (Dunn and EI-Halwagi, 1994) where the VOC separation techniques of condensation is modeled. Model is used to optimize the process. Decision variable concern refrigerant, the load to remove, waste stream/refrigerants matches and system configuration.

Another model of abatement techniques that is considered (Kolade et. Al, 2009) is VOC adsorption. In the paper a mathematical model of this techniques is shown and then discussed.

Concerning simulation there are interesting papers (Yang et al., 2001) (Huang and Haghighat, 2002) (Yan et al., 2009), where VOCs emitted by dry building material wood products, insulation material) are estimated. The aim is that VOCs emissions can affect indoor air quality.

The exterior dimensions of the cylinder shaped pilot biofilter is: the diameter 1,6 m, the height 2,1 m. The air flow direction is vertical from bottom to top. The face area of biofilter bed is 1,3 m^2 and the bed thickness can vary from 1 000 to 1 500 mm. The biofilter contains a prefilter stage as well. This acts as humidifying and normalizing scrubber, avoiding the unpleasant pH peaks origin from waste waters of the refinery and grinding plants. The waste water itself is neutralized already in the pump station, and the filter material pH was controlled regularly and modified when needed. The inlet exhaust gas was preheated when needed by the channel heater (25-30 °C).

3. WASTE WATER ABATEMENT SYSTEM CONSIDERED

The abatement system considered in this paper is part of the VOCless Pulping Waste Waters project.

All waste waters from the paper mill, board mill and mechanical pulping including TMP and PGW production as well debarking are collected to the equalization station for pH control and mixing. Total waste water amount is about 30.000 m^3/d and COD load from 50 to 60 t/d. Solid suspense are settled in primary clarifier and the waste waters are cooled in cooling tower to 37 °C. The process flow-chart is illustrated in Figure1.

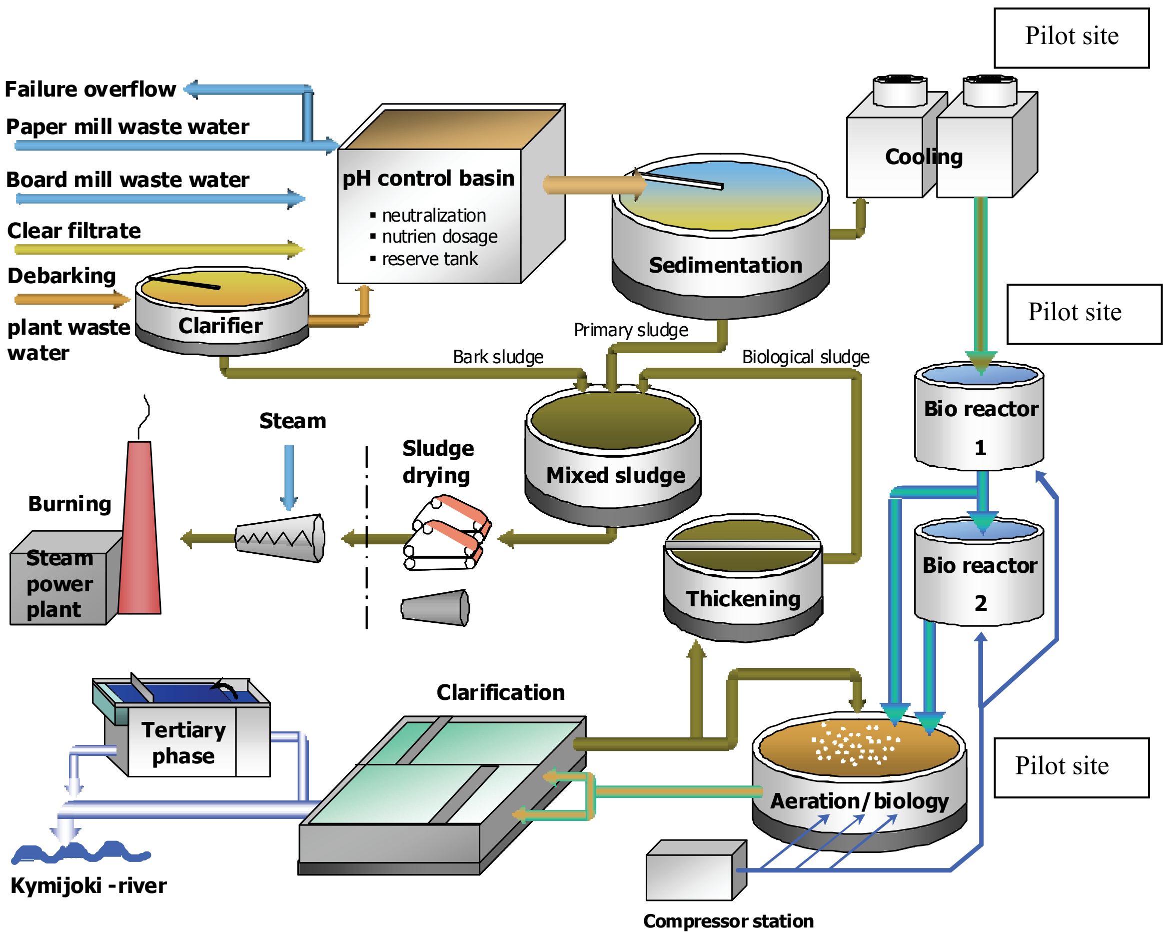

Figure 1 the waste treatment plant considered

Nutrients, phosphor and urea will be added, and waters are pumped to the biological waste water treatment. The aim of this process is to remove soluble and insoluble organics from waste water stream and to convert the material into flocculant microbial suspension that is readily settleable and will permit the use of gravitational solids liquid separation techniques.

The process used in this case is so called nutrient restricted MBBR/activated sludge process (moving bed biofilm reactor). The easily degradable organic materials will be degraded in MBB-reactors. The amount of organic material in waste waters is descripted with the biological oxygen demand BOD7.

In aerated reactors the microbes are cleaning the waste water using the soluble materials as nutrition and consuming oxygen. Additional nutrients (like phosphor and urea) are needed. The yield will be carbondioxide, water, heat and new microbes. Microbes, activated sludge will be returned after the final sedimentation to the aeration basin, and the excess sludge to the sludge handling.

Process conditions are restricted, pH about 7, temperature under 40°C. After the final sedimentation clarification, the cleaned water is led to the river Kymijoki. The tertiary treatment can be used in extreme situations. The excess sludge from the biological waste water handling and other sludges are mixed, dewatered, dryed and incinerated in the boiler house.

The process phases to be piloted with the abatement systems were chosen based on the results of the VOC emission measurements from the previous VOCless Pulping LIFE project and the analysed water samples gathered in advance.

3.1 Pilot tests

Three different abatement systems namely UV-filtration, biofiltration and catalytic incineration were tested at the aerobic waste water treatment plant.

Each plant was tested at the cooling towers and the moving bed biofilm reactor (MBBR) pilot sites (see the process flow-chart, Figure 1). The idea was to test the operation of the abatement systems and to measure the cleaning efficiency from each of the small-scale pilot plants at least for the two-week period of time. VOC emissions measurements were carried out before the start of each test period and after two weeks, at the end of the test period. During the test periods certain biofilter parameters were measured by the online data recording system in case of malfunctions and possible breakdowns.

3.2 UV. filtration (supported by Desinfinator)

UV Filtration is based on Desinfinator technology. This is a combination of reactions and the process combines various different phases to reach the maximum cleaning efficiency. By adding special diffusion filters coated by using the latest nanotechnology and adding other air cleaning processes this product is of high technology level. One main element is the control of the airflows and the antiseptical surfaces within processes. By using a special honeycomb, a laminar airflow is created and this increases the efficiency of the UV-light significantly. Another important function of the UV-radiation is to activate the diffusion filters and start creating radicals. Additionally a huge amount of Ions are created into the air. This air cleaning technology is capable of removing bacteria, mould, particles, yeast and odors with a rate of close to 100%.

The unit being designed for the Life+ -project uses the proven Desinfinator-technology customized for the water treatment plant to clean the air from VOCs. For testing purposes the unit was based on a portable platform and it is weather proof. The whole system was built on a trailer to make it mobile.

The main technologies for VOC filtering include:

- Pre-filtering
- UV-C –light
- photocatalysis filters
- OH –radicals
- Ozone
- VOC filters; active carbon filters re-generated by ozone

Pre-filters are used for collecting extra particles from the inlet air to keep up the performance of the system. Any extra particles will be harmful for the internal components of the system.

Photocatalysis or photocatalytic oxidation is achieved when UV light rays are combined with a TiO_2 coated filter. This process creates hydroxyl radicals and super-oxide ions. These highly reactive radicals and ions aggressively combine with other elements in the air, such as bacteria and VOCs. Once bound together, the chemical reaction takes place between the super-charged ion and the pollutant, effectively "oxidizing" (or burning) the pollutant.

The hydroxyl radical is often referred to as the "detergent" of the troposphere because it reacts with many pollutants, often acting as the first step to their removal. It also has an important role in eliminating some greenhouse gases like methane and ozone.

Free radicals are highly reactive, imbalanced molecules that are the byproducts of normal metabolism and are associated with the degenerative aging process. Free radicals steal electrons from healthy cells to neutralize their own charge, causing cellular damage.

Ozone created with UV-C radiation is partly neutralizing VOC emission. This is commonly known reaction and used inside the Desinfinator system designed for the LIFE+ project.

Active carbon is known to work as a VOC filter. The challenge with active carbon as a VOC filter is the short life cycle of the material. In this Desinfinator system active carbon was used in small amounts only. The exception to commonly known usage was the chemical re-generation of the filter material using reactive gas mix including ozone. This expands the life cycle radically. Also, the active carbon collects humidity and in other occasions the reactive gas produced by

Desinfinator technology reduces the humidity level. Too high humidity levels reduce the filtration rate of the active carbon and reactive gas works as a humidity reducer.
In the gas flow inside the system and on the active carbon surface the following chemical reactions are the target. These chemical reactions are commonly known to occur when ozone is created with UV-C radiation and the gas from this process reaches H_2O.

$$O_2 + e^- \rightarrow O_{2*}^-$$
$$2O_{2*}^- + H_2O \rightarrow O_2 + HO_{2*}^- + HO*$$
$$2O_{2*}^- + O_3 + H_2O \rightarrow 3O_2 + HO^- + HO*$$

According to these reactions the process creates highly reactive hydroxyl radicals and these are partly helping the cleaning process.

3.3 Catalytic incinerators (supported by Formia Emissions Control)

Thermal and catalytic incinerators are the most common methods in fulfilling the VOC emissions regulations with incineration. Those incinerators are used in industries where VOC emissions are restricted by legislation. During incineration process VOC-compounds are oxidized to carbon dioxide and water by heat. The main difference between thermal and catalytic incineration is amount of needed heat. Thermal process normally requires over 800°C temperature for good VOC destruction while catalytic process requires only 300°C temperature.
Catalytic oxidation offers several advantages in comparison to thermal oxidation, especially with low VOC contents. The most important are cost savings by reduced energy consumption, cleanness of the process, and small size. In addition, the quality of catalysts has been significantly improved and new generation noble metal catalysts offer a service life of more than 15 years.
The biggest problem for VOC abatement is the low VOC content, which is typically in the range of 0.1 to 10 g/Nm3. In order to oxidize such a small concentration of VOC, an enormous amount of air must be heated to a temperature where the reactions can happen. In many cases the energy contained in the VOCs is not high enough to maintain continuous oxidation (autothermal operation). A lot of supporting energy is needed. With a good heat exchanger, 90% of the energy can be transferred to the incoming gas stream but still a lot of supporting energy would be needed. If this supporting energy is made by burning liquefied petroleum gas, more CO_2 is created. One kilo of propane creates 3 kilos CO_2.
Catalysts lower the activation energy for oxidizing VOCs and thereby the required reaction temperatures. By using a catalyst and efficient heat exchanger, only one third of the energy is needed compared to thermal oxidation.

3.4 Pilot sites

Adaptation

The adaptation period of biofilter pilot plants last for 2 months. During that time exhaust air from one of the cooling towers was conducted to the biofilters and the conditions of the filter media were controlled via the data logger.

Table 1 VOC abatements with the 3 pilot plants at the cooling tower

Site	Unit	Airflow	Voc concentration		Variation	Tolerance	VOC Concentration				
			before	after			before	after	before	after	Cleaning rate
		Nm^3/h	ppm CH4-eq.	ppm CH4-eq.			factor	mg/Nm^3	factor	mg/Nm^3	%
Cooling Tower	Biofilt 1		6,9	19,3	-180%	±240%	0,543	3,7	0,250	4,8	
			4,6	2,5	46%	±47%	0,543	2,5	0,250	0,63	75
	Biofilt 2	0,6	6,1	2,8	54%	±40%	0,543	3,3	0,250	70	79
		1,9	6,2	2,6	58%	±36%	0,543	3,4	0,250	0,66	81
	Desinfinator	0,8	7	2,9	59%	±36%	0,587	4,1	0,298	0,87	79
		1,3	5	3,1	38%	±53%	0,587	2,9	0,298	0,93	68
	Formia	4	6,4	2,3	64%	±31%	0,564	3,9	0,372	0,86	76
		4	5,6	1,9	66%	±29%	0,564	3,2	0,372	0,72	77

Cooling tower

All waste waters from the paper mill, board mill and mechanical pulping including production from TMP and PGW plants as well debarking are collected to the equalization station for pH control and mixing. After this waste waters are cooled in cooling towers to around 37 °C.

All three abatement systems were tested and measured. The two biofilter pilot plants were constructed with slightly different content. During the test period measurements of all pilot plants were recorded via online data logger. At the beginning of the test period, first VOC emission measurements were carried out. Each pilot plant was measured for at least three hours.

3.5 Activated sludge process (MBBR)

After the presedimentation basin, waste water is conducted via cooling towers to the pumping station and further to the MBB reactor number 1 and then to the second basin. The two reactors are sequential. The aim of the activated sludge process is to remove soluble and insoluble organics from the waste water stream and to convert the material into flocculant microbial suspension that is readily settled and will permit the use of gravitational solids liquid separation technique.

. This process is so called nutrient restricted MBBR/activated sludge process. In this process the easily degradable organic materials will already be degraded in MBB reactors. These organic materials are best nutrients also for organisms building filaments,
poor settling and bulking particles. This prevents the bulking problems in the settling.

The amount of organic material in waste waters is described with biological oxygen demand BOD7. In aerated reactors the microbes are cleaning the waste water by using soluble materials as nutrition and consuming oxygen. Additional nutrients (phosphor and urea) are needed. The yield is carbon dioxide, water, heat and new microbes. Microbes and activated sludge will be returned after the final sedimentation to the aeration reactors and excess sludge is going to the sludge handling. Process conditions are also restricted; pH about 7, temperature under 40 degree. In these two reactors micro-organisms are growing on the surface of carriers and also in the water. Those two reactors are connected in series. Two turbo compressors are blowing air into reactors. Air volume can be regulated. There is also oxygen measuring. Water jets or antifoaming agents can be also used against foaming.

The pilot tests at the MBB reactor started after the first tests. The cleaning efficiencies of biofilters were measured every 2nd week and some modifications concerning nutriens and humidification were made. The intention was to continue the tests at the same MBB reactor due to the higher VOC concentration compared to the cooling towers and the aeration basin, and to gather more data of the changes made under the same conditions.

Results of the tests are shown in table 1 and table 2.
Desinfinator is responsible for the UV filtering abatement system, while Formia Emissions Control is responsible for the catalytic oxidation system.

Table 2 VOC abatements with the 3 pilot plants at the Moving Bed Bio Reactor

Site	Unit	Airflow	Voc concentration		Variation	Tolerance	VOC Concentration				
			before	after			before	after	before	after	Cleaning rate
		Nm^3/h	ppm CH4-eq.	ppm CH4-eq.			factor	mg/ Nm^3	factor	mg/N m^3	%
Moving Bed Bioreactore	Biofilt 1	1,1	70,8	62,5	12%	±76%	0,156	11,1	0,056	3,5	68
		0,0	110	83,4	24%	±65%	0,165	18,1	0,056	4,7	74
		0,0	363	243	33%	±57%	0,082	29,9	0,056	13,6	55
		42,5	297	248	17%	±0%	0,084	25,0	0,056	13,9	*
		35,5	228	214	6%	±0%	0,057	12,9	0,014	2,9	78
	Biofilt 2	1,0	77,0	78,1			0,156	12,1	0,056	4,4	64
		1,3	60,6	49,8	18	±71	0,165	10,0	0,056	2,8	72
		1,5	267	233	13	±75	0,082	22,0	0,056	13,0	*
		43,6	138,9	117	15	±0	0,084	11,7	0,056	6,6	*
	Desinfinator	4	62,3	45,4	27	±62	0,156	9,7	0,068	3,1	68
		4	122	84,8	30	±60	0,148	18,0	0,068	5,7	68
		2	267	161	40	±52	0,082	22,0	0,068	10,9	50
		3	208	131	37	±0	0,084	17,4	0,021	2,7	85
	Formia	3	93,6	61,9	34	±57	0,156	14,7	0,040	2,4	83
		3	81,9	60,2	26	±63	0,165	13,5	0,040	2,4	82
		2	261	158	39	±52	0,082	21,6	0,040	6,3	71
		3	235	139	41	±51	0,084	19,8	0,067	9,4	53

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CONCLUSIONS

Three different abatement systems were tested in the aerobic and anaerobic waste water treatment plants in mechanical pulping processes. Results were satisfactory for biofiltering, even if their set up is very space demanding. The best performance were obtained with Formia Emissions Control catalytic oxidator. New invention, Desinfinator UV-filtration, reached the cleaning efficiency of 70 % as well.

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