

Lappeenranta University of Technology

School of Engineering Science

Chemical and Process Engineering

Master's Thesis

Lauri Welling

Use of Secondary Condensates as Bleaching's Wash Water

Examiners: Tuomas Koiranen, Professor

Advisor: Eeva Jenström, Doctor of Science (Technology)

ABSTRACT

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2019

49 pages, 18 figures, 18 tables

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Keywords: secondary condensate, pulsed, corona, discharge, sulfur, black liquor, bleaching

Black liquor evaporation at pulp mill creates secondary condensates that are a potential source for mill process water. For its part it can help in closing of mills' water circulations and decrease of fresh water usage. Secondary condensates contain many volatile organic compounds of which odorous sulfur compounds are most troublesome for further usage.

Secondary condensate samples from pulp mill were treated with pulsed corona discharge method and aim was to oxidize troublesome compounds. Sampling was based on received energy dosage that was between 0-5000Wh/m³.

Conductivity, TOC and COD analyses didn't show a consistent development in a used energy range. Color analyses showed a slight brightening but the difference was not apparent. Sulfates analyses showed a slight increase of sulfates with all the treatments that is caused by oxidation of sulfides. Unexpectedly pH dropped with all the treatments from over nine to under four. Drop can be explained with formation for acetic acid and formic acid. Acid analyses showed notable increase of concentration of formic acid. Acetic acid on other hand barely showed in results.

TIIVISTELMÄ

Lappeenranta Teknillinen yliopisto

School of Engineering Science

Kemiantekniikan koulutusohjelma

Lauri Welling

Sekundäärilauhteiden käyttö valkaisun pesuissa

Diplomityö 2019

49 sivua, 18 kuviota, 18 taulukkoa

Työn tarkastajat: Tuomas Koironen, Professori

Ohjaaja: Eeva Jenström, Tekniikan tohtori

Hakusanat: sekundäärilauhde, pulssi, korona, purkaus, rikki, mustalipeä, valkaisu

Sellutehtaan mustalipeän haihdutuksesta syntyvät sekundäärilauhteet ovat potentiaalinen lähde sellutehtaan prosessivesiksi. Osaltaan tämä auttaa myös sellutehtaan vesikiertojen sulkemista sekä raakaveden tarpeen vähentämistä. Sekundääri lauhteet sisältävät monia herkästi haihtuvia yhdisteitä, joista haisevat rikkiyhdisteet ovat ongelmallisimpia jatkokäytön kannalta.

Sekundäärilauhdenäytteitä tehtaalta käsiteltiin pulssikoronapurkaus-menetelmällä ja tarkoituksena pyrkiä hapettamaan haitallisia yhdisteitä. Näytteiden otto perustui sekundäärilauhteen saamaan energia-annokseen, joka oli välillä 0-5000 Wh/m³.

Johtokyky, TOC ja COD analyysit käsitellyistä näytteistä eivät osoittaneet johdonmukaista kehitystä käytetyllä energiavälillä. Väri analyysit osoittivat pientä kirkastumista mutta ero ei ollut silmällä nähtävissä. Lievä sulfaattien määrän kasvaminen mitattiin tasaisesti kaikissa näytteissä, jonka taustalla on sulfidien hapettuminen. Odottamattomasti pH laski kaikilla käsittelyillä merkittävästi yli yhdeksästä alle neljään, joka selittyy todennäköisesti muurahais- ja etikkahapon muodostumisella. Analyysit osoittivat muurahais- ja etikkahapon määrän kasvavan käsittelyjen edetessä. Etikkahapon muodostuminen jäi analyysien perusteella lähes olemattomaksi.

LIST OF ABBREVIATIONS

AOP	Advanced oxidation processes
BL	Black liquor
COD	Chemical oxygen demand
DMS	Dimethyl sulfide
DMDS	Dimethyl disulfide
DRE	Destruction and removal efficiency
ECF	Elemental chlorine free
FF	Falling film
NGS	Non condensable gases
OH	Hydroxyl radical
PCD	Pulsed corona discharge
RF	Rising film
SEI	Specific energy input
TCF	Totally chlorine free
TRS	Totally reduced sulfur
VOC	Volatile organic compounds

LIST OF SYMBOLS

C_n	Chlorine bleaching stage
D_n	Chlorine dioxide bleaching stage
ϵ	Energy [Wh/m ³]
E_n	Extractive bleaching stage
GE	Generator power [W]
L_n	Liquid flow with pulp [t/t _{fiber}]
M	Non-reacting molecule
O_n	Oxygen delignification stage
O_{3n}	Ozone bleaching stage
Q_n	Chelation stage
R	Radical
V_n	Wash liquid of filtrate flow [t/t _{fiber}]
W	Wash ratio
W_R	Weight ratio
W_{DF}	Dilution factor
W_{DP}	Displacement ratio
W_Y	Washing yield
W_E	Washing efficiency
x_n	Concentration of dissolved substance [kg/ton]
y_n	Concentration of dissolved substance [kg/ton]

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1 BACKGROUND

Decreasing of fresh water usage of pulp mills has been on going trend and is becoming even more important in the future. In many locations around the world even the availability of fresh water is becoming more uncertain as population grows and shared available water resources shrink. This is going to put pressure on companies to further decrease use of fresh water and reusing existing process water streams. This is going to also enable use of different treatment methods for liquid streams that might to currently otherwise considered too expensive.

2 OBJECTIVE

Objective of this work is to study, is it possible to use treated secondary condensates as wash waters in the ending stages of bleaching? Secondary condensates from evaporation of black liquor contain many chemicals such as methanol, ethanol, acetone and sulfur bearing compounds. It is vital that use of condensates in washings does not leave unwanted remains that affect to the pulp. Beside the chemical remains, sulfur has distinct odor which cannot be allowed to end up in the end product. Before use of condensates they are treated with pulsed corona discharge method in an attempt to oxidize part of contaminants. Analyses are done to determine the effect of pulsed corona discharge to the contaminants of the condensate.

3 EVAPORATOR PLANT AND BLEACHING

3.1 Evaporator Plant

3.1.1 Principle

Black liquor (BL) from chemical pulping process consists of dissolved parts of wood and cooking chemicals. Black liquor before evaporation has a low dry solids content of under 20% and in order to use it as a fuel in recovery boiler solids content must be increased.

The two main types of evaporators are rising film (RF) and falling film (FF) evaporators although nowadays RF has been preceded by FF design. In RF evaporators BL is fed into vertical tubes that are placed inside outer evaporator shell. BL rises upwards inside the tubes and it is simultaneously heated by the steam that is fed inside the outer shell. BL starts to boil gradually and at the top of the tubes vapor and liquor are separated by deflector plate. Following Figure 1. shows a structure of typical RF evaporator and major flows. (Holmlund & Parviainen, 2000 p. 46)

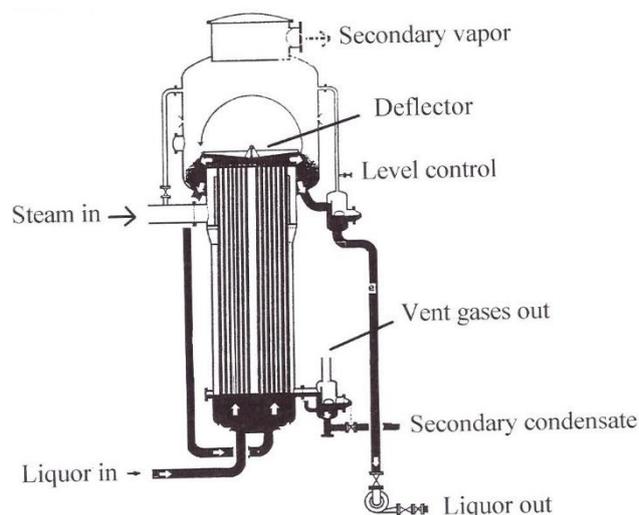


Figure .1 Principle of rising film evaporator (Holmlund & Parviainen, 2000, p. 46).

In FF evaporators BL is pumped to the top of evaporation surfaces and evenly distributed on them after which BL is allowed to flow to the bottom of the tank by gravity. The two main types of FF evaporators are lamella and tubular evaporators. In tubular types BL either flows inside or outside of vertical tubes and steam correspondingly is on other side. In lamella evaporators BL flows on the outside surfaces of vertically placed lamellas. A constant level of BL is kept at the bottom of the evaporator while circulation pump keeps cycle going on raising BL to the top of evaporation surfaces and concentrated BL flowing back down. Figure 2 shows an arrangement of lamella type FF evaporator. (Holmlund & Parviainen, 2000, p. 47).

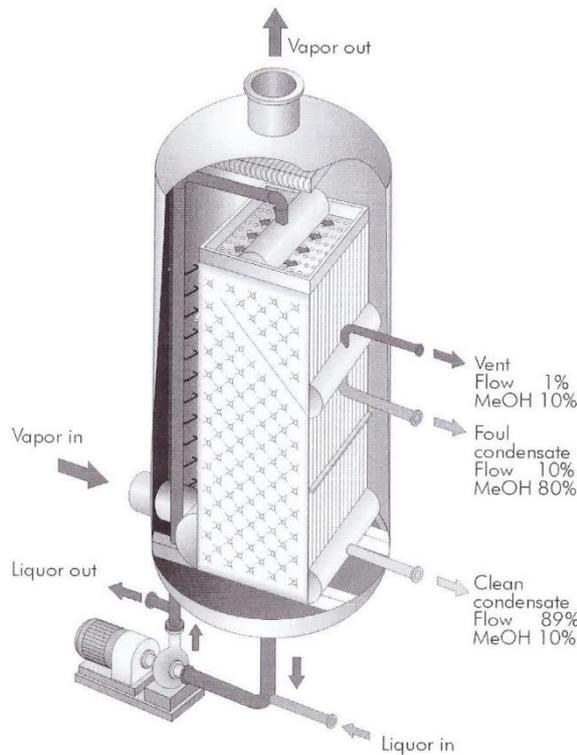


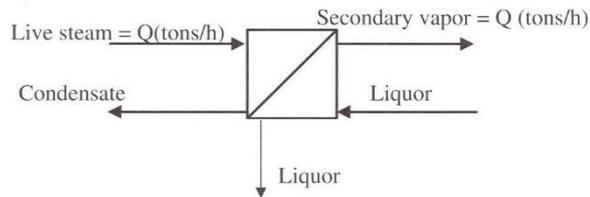
Figure 2. Falling film lamella evaporator (Holmlund & Parviainen, 2000, p. 47).

As can be seen in the previous Figure 2. if a separation of condensates is wanted steam or vapor must be fed to the bottom of the lamellas. As steam condenses it can be separated into clean and foul fractions by having pre-and after-condensing sections build into heating surfaces (Holmlund & Parviainen, 2000, p. 47-48).

When vapor used is coming from other evaporation stage it most likely contains non condensable gases (NGS). If NGS are allowed to accumulate they decrease efficiency of heat transfer and so they must be vented as can be seen also in the Figure 2. NGS include for example methanol and reduced sulphur compounds. (Krotscheck & Sixta, 2006a, p.975).

Using several evaporators linked in series enables to re-use of vapor and more economical process. Fresh steam is used only in the first unit and vapor released from BL is fed to heating element of second unit where it condenses as it heats BL. Second unit's vapor is then fed into third effect and so on. (Krotscheck & Sixta, 2006a, p.977). Way to estimate economy of evaporation is to look amount of evaporated water per ton fresh steam (ton H₂O/t steam). If one stage evaporation uses fresh steam amount of Q (tons H₂O/h) then theoretically three-stage system would need Q/3 of fresh steam. Steam and BL circulate in countercurrent fashion meaning that steam is fed into first unit and BL into last unit. This way fresh steam is used to heat most concentrated BL that has risen boiling point and vapors with lowered temperature are enough to evaporate unconcentrated BL in the higher unit. Following Figure 3. shows principle of multi-stage evaporation and how it compares with one-stage system (Holmlund & Parviainen, 2000, p. 41).

One-stage evaporation, capacity = Q (tons H_2O/h)



Three - stage evaporation, capacity = Q (tons H_2O/h)

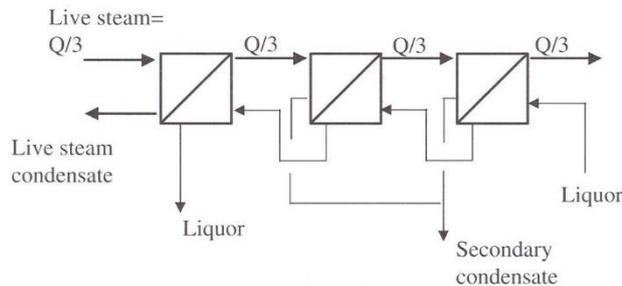


Figure 3. Principle of multi-stage evaporation with comparison to one-stage design (Holmlund & Parviainen, 2000, p. 41).

In the previous Figure 3. BL is fed into third unit but in practice the actual feed positions depends on various factors such as temperature of the thin BL and temperatures of the units. One major thing to remember is the stage into which fresh low concentration BL is fed because it is going to have vapors contaminated with most of the BL's volatile compounds. Contaminated vapors form after condensing of foul condensate that must be treated. Secondary condensates from other stages are less contaminated and have use in other processes in the mill. (Krotscheck & Sixta, 2006, p.978). Following Figure 4. shows a development of water content in BL in a five stage plant stage by stage (Krotscheck & Sixta, 2006, p.979).

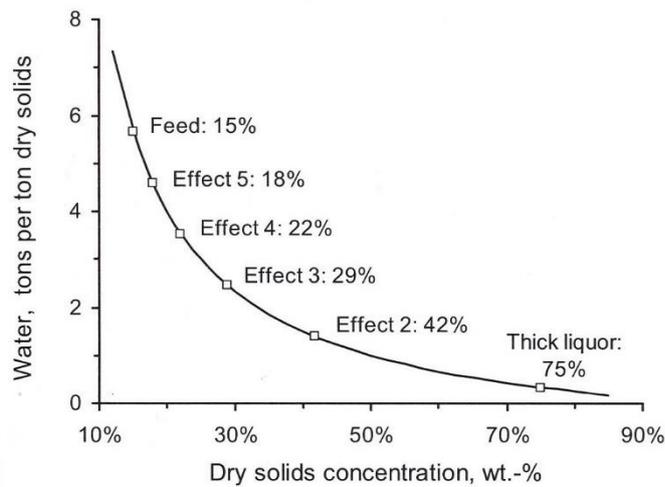


Figure 4. Development of water content in BL as a function of dry solids concentration in five stage (effect) evaporation plant (Krotscheck & Sixta, 2006a, p.979).

3.1.2 Composition of Condensates

As all ready touched multi-stage evaporation produces secondary condensates with varying amounts on contaminants. They are known as volatile organic compounds (VOC) such as methanol, ethanol and odorous total reduced sulfur compounds (TRS) like hydrogen sulfide. Odorous compounds include hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide (Sebbas, 1987, p. 54,56). Niemelä et al. (1998) studied use of secondary condensates from black liquor evaporation in bleaching stages and they presented typical composition of secondary condensates which are seen in the following Table 1.

Table 1. Typical compositions of industrial secondary and foul condensates (Niemelä et al. 1998, p. 150)

Constituent	Secondary condensate [mg/l]	Foul condensate [mg/l]
Methanol	300	7500
Ethanol	10	300
Acetone	1	130
Acetaldehyde	4	140
Dimethyl sulphide	traces	200
Dimethyl disulphide	2	200
TOC	200	12500

As can be clearly seen in the previous Table 1. values of foul condensate are many times higher than regular secondary condensate. Ala-Kaila et al. (2004) also studied usage of condensates in bleaching and in their study they reported conductivity and COD values for different secondary condensate fractions which can be seen in the following Table 2.

Table 2. Conductivities and CODs for different secondary condensate fractions (Ala-Kaila et al. 2004, p. 37)

Property	Secondary Condensate A	Secondary Condensate B	Secondary Condensate C
Conductivity [mS/m]	7,6	5,7	54,33
COD [mg/l]	1400	2200	51100

Secondary condensate A seen in the previous Table 2. was the stripped fraction. Secondary condensate B was collective fraction. Foul condensate C has much higher values compared to other two as it was not stripped.

3.2 Bleaching

3.2.1 Stages of Bleaching

Pulp coming from cooking has dark brown appearance due to residual lignin and other impurities in it. A bleaching process aims to remove residual lignin selectively and in a way bleaching can be said to be continuation of a cooking process with different set of chemicals. Unbleached pulps have ISO brightness of under 30% whereas after the bleaching it is around 90%. (Klemetti et al. 2005, pp. 122). In unbleached oven dry pulps residual lignin amounts up to 3-6 % with softwoods and 1,5-4% with hardwoods (Krotscheck et al. 2006b, pp. 609). Following Table 3. shows a list of different bleaching chemicals and stages that they define as principal bleaching agents. Generally speaking a pulp bleaching system has multiple stages that incrementally remove colored components from the pulp. Stages may use same chemicals or different ones that complement bleaching capabilities of each other.

Table 3 Different bleaching chemicals and their corresponding stage designations in a pulp bleaching applications. (Klemetti et al. 2005, pp. 122-123).

Oxidizing bleaching chemicals	Formula	Corresponding bleaching stage
Chlorine	Cl ₂	C-stage
Sodium hypochlorite	NaOCl	H-stage
Chlorine dioxide	ClO ₂	D-stage
Oxygen	O ₂	O-stage
Ozone	O ₃	Z-stage
Hydrogen peroxide	H ₂ O ₂	P-stage
Sodium peroxide	Na ₂ O ₂	P-stage
Extractive bleaching chemicals		
Sodium hydroxide	NaOH	E-stage

Besides primary bleaching chemicals shown in the Table 3. there are also other necessary chemicals such as sulfur dioxide or acid that are used to remove remnants of bleaching chemicals. Stage designation for sulfur dioxide or acid is A-stage. Sodium hydroxide is used also as pH adjustment (Klemetti et al. 2005, pp. 123).

In chelation (Q-stage) metal ions are removed and it is especially necessary in TCF bleachings that use peroxide. Predominant metals are iron and manganese and in lesser extent copper and cobalt. Metals cause uncontrollable decomposition of peroxide and decomposition products also damage cellulose fibers. Possible chelator chemicals are EDTA (Ethylenediaminetetraacetic acid) or DTPA (diethylene triamine penta acetic acid) (Krotscheck et al. 2006b, pp. 862-864).

Oxygen delignification (O-stage) is used to continue lignin removal after cooking but before actual bleaching. Process is carried out at elevated temperature and pressure with oxygen and alkali in one (O) or two (O/O) stage set up. Process conditions and retention times for pulp in two stage delignification can be 1st : (80-85°C, 7-10bar, 20-40 min) and 2nd : (90-105°C, 3-5bar, 60-80min) (Bokström et al. 2000, pp. 634-637). Addition of oxygen delignification into pulp mills has helped to reduce bleaching chemical consumption and to achieve better yield than it is possible by just increasing chemical dosages or time in cooking. Averagely 35-50% (hardwoods) or 40-65% (softwoods) of residual lignin can be removed with one or two stage system (Krotscheck et al. 2006b, p.629, 632).

Bleaching processes can be divided into two main categories of elemental chlorine free (ECF) and totally chlorine free (TCF). ECF processes became dominant as concerns over adsorbable organic halogen (AOX) emissions of traditional chlorine gas bleaching grew in the 1980s. ECF bleaching replaced chlorine gas with chlorine dioxide. TCF bleachings have replaced chlorine chemicals totally with other chemicals such as oxygen, peroxide or ozone (Krotscheck et al. 2006b, p. 609).

An example of ECF bleaching sequence could be O/O-D0-E-D1-D2 that translates into two stage oxygen delignification followed by chlorination (D0), alkaline extraction (E) and two chlorine dioxide stages (D1 & D2) (Niemelä et al. 1998, p. 155). A TCF bleaching sequence could be Z/Q-P-Z/Q-P/P formed by ozone/chelation stage, peroxide stage, ozone/chelation stage and peroxide/peroxide stage (Klemetti et al. 2005, p. 124). Following Figure 5. shows an example of chlorine dioxide bleaching sequence.

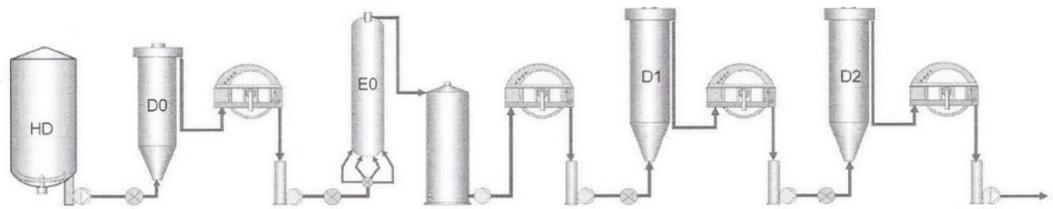


Figure 5. Example of chlorine dioxide D0-E0-D1-D2 bleaching sequence with drum washers between stages (Bokström et al. 2000, p.657).

3.2.2 Washings of Bleaching

Washings are done between bleaching stages to remove reaction products and to stop them from emanating into next stages (Krotscheck et al. 2006c, p. 511). Washing processes use combinations of dilutions, thickenings and displacements. Following Figure 6. shows a principle of washing operation. (Gullichen, 2000, p. 314).

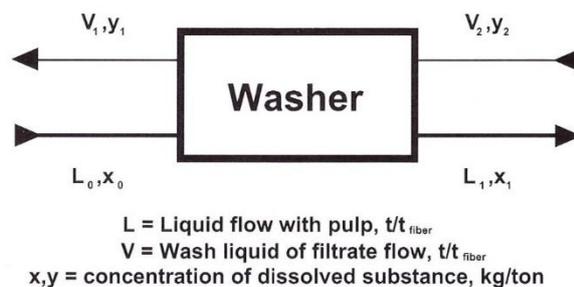


Figure 6. Schematic principle of washing stage (Gullichen, 2000, p. 314).

Based on flows and their properties in Figure 6. it's possible to calculate variables that describe washing operation's performance such as wash ratio, weight ratio, dilution factor, displacement ratio and washing yield. Formulas that define these variables shown next as formulas 1-5 (Gullichen, 2000, p. 314).

Wash ratio

$$W = \frac{V_1}{L_0} \quad (1)$$

Weight ratio

$$W_R = \frac{V_2}{V_1} \quad (2)$$

Dilution factor

$$W_{DF} = V_1 - L_0 \quad (3)$$

Displacement ratio

$$W_{DP} = \frac{(x_0 - x_1)}{(x_0 - y_2)} \quad (4)$$

Washing yield

$$W_Y = \frac{V_1 y_1 - V_2 y_2}{L_0 x_0} \times 100 = (\quad)\% \quad (5)$$

Washing efficiency E is defined as equation 6 when V_2 and L_1 flows are not equal but in case of equal V_2 and L_1 flows equation 6 is simplified into equation 7

$$W_E = \frac{\ln \frac{L_0(x_0 - y_1)}{L_1(x_1 - y_2)}}{\ln \frac{V_2}{L_1}} \quad (6)$$

$$W_E = \ln \frac{L_0(x_0 - y_1)}{L_1(x_1 - y_2)} \quad (7)$$

As an example of washer Figure 7. shows a drum displacer (DD) washer and main stages of operation.

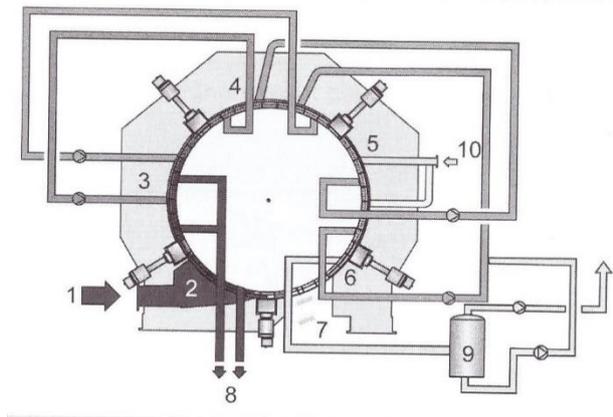


Figure 7. Operating principle of three-stage DD washer: 1 pulp inlet, 2 cake formation, 3 first washing stage, 4 second washing stage, 5 third washing stage, 6 vacuum stage, 7 cake discharge, 8 liquors out, 9 vacuum stage liquor and 10 wash filtrate inlet (Carlsson et al. 2000, p. 584).

3.2.3 Chlorine Dioxide Bleaching

As all ready previously mentioned typical chlorine dioxide bleaching sequence can be in D0-E-D1-D2 configuration. D0-stage or chlorination is more a delignification process than actual bleaching. Chlorine dioxide is mixed into the pulp stream and fed into bleaching tower after which a washing takes place. D0-stage process conditions are pH=1-1.5, t=30-80 min, T=40-60°C and P=atmospheric (Bokström et al. 2000, p. 641-642). During chlorination problematic organic chlorinated compounds like chloro-lignin are formed. In bleaching sequence like this chapter covers most of chlorinated compounds are formed during D0- and E-stages (Gulichen, 2000, pp. 771-772,777).

E-stage or alkaline extraction is used to remove chloro-lignins that are formed during D0-stage and it is carried out with sodium hydroxide. Process performance can be improved with additional feeds of oxygen and/or peroxide (EO or EOP). Some reasons to use oxygen and peroxide are decrease of production costs, improvement of bleaching capacity, defective capacity of chlorine dioxide plant and improvement of pulp properties (purity/brightness) (Klemetti et al. 2005, p. 125).

Oxygen doesn't have effect on bleaching performance because it's used for delignifying. Peroxide is added as bleaching aid. Instead of just one it's also a possibility to have second extraction stage between D1 and D2 stages. E-stage process conditions are pH=10-11.5, t=60-90 min, T=60-90°C and P=2.5-5bar (Bokström et al. 2000, pp. 643-644).

Final bleaching with chlorine dioxide is often done in two stages of D1 and D2 with a washing between them as seen in previous Figure 5. D1-stage process conditions are pH=3.5-5, t=2-4h, T=55-75°C and P=atmospheric. D2-stage process conditions are pH=3.5-5, t=2-4h, T=60-85°C and P=atmospheric. Long reaction times are necessary because of low reactivity of chlorine dioxide with low residual lignin content (Bokström et al. 2000, pp. 642-643).

3.2.4 Requirements for Wash Waters of Bleaching

Use of secondary condensates as wash water is mostly depended on contaminants they are containing and their effect on washed pulp. Beside the chemical remains or odor effects on pulp most important properties such as brightness, KAPPA number or viscosity must not be compromised. Sebbas (1987) brought up how condensates with sulfur compounds must be treated somehow like with steam stripping for sulfur removal to enable their use.

Eriksson et al. (2009) studied washing of unbleached and bleached pulps using condensates and they concluded that washing results were normal when using condensates with relatively low level of COD. Condensates with higher COD levels were found not to be suitable because of their odorous sulfur bearing compounds. (Eriksson et al. 2009, p. 427)

Alakaila et al. (2004) studied use of secondary condensates as process water in D0 bleaching with two sets of experiments. In the first one volatile organic compounds that are found in secondary condensates were added to the pulp before bleaching.

Amount of added VOC was based on so that experiment had COD load of 10 or 30 kg/bdtp. The second experiment used actual different condensates from mill. Interesting find was that most compounds didn't have major effect on pulp properties unlike actual condensates. An assumption was that the difference was caused by sulfur and terpene compounds in condensates. When condensate contained dimethyl sulfide and dimethyl disulfide larger decrease in the pulp brightness was observed compared to a cleaner condensate without them. (Alakaila et al. 2004, pp.113-117).

Table 4. The VOCs used, their COD loads for each experiment and pulp properties used in bleaching (Alakaila et al. 2004, p.114).

Exp. No	Formic Acid kgCOD/tp	Acetic acid kgCOD/tp	Propionic acid kgCOD/tp	Methanol kgCOD/tp	Ethanol kgCOD/tp	Acetone kgCOD/tp	Kappa number	ISO brightness [%]	Viscosity [ml/g]
1	10	10	10	10	10	10	6.3	52.2	900
2	30	10	10	10	30	10	6.2	52.9	900
3	10	30	10	10	30	30	6.2	52.5	910
4	30	30	10	10	10	30	6.1	53.1	890
5	10	10	30	10	30	30	6.4	52.1	900
6	30	10	30	10	10	30	6.2	52.6	900
7	10	30	30	10	10	10	6.1	52.7	910
8	30	30	30	10	30	10	6.1	52.7	880
9	10	10	10	30	10	30	6.3	52.7	880
10	30	10	10	30	30	30	6.2	52.6	890
11	10	30	10	30	30	10	6.2	53.3	910
12	30	30	10	30	10	10	6.1	52.9	930
13	10	10	30	30	30	10	6	52.5	870
14	30	10	30	30	10	10	6.1	52.6	900
15	10	30	30	30	10	30	6	53.2	900
16	30	30	30	30	30	30	6	53.2	910
17	20	20	20	20	20	20	6.1	52.4	900
18	20	20	20	20	20	20	6.1	53.1	890
19	20	20	20	20	20	20	6.1	52.9	890

Following Table 5. shows properties of three used secondary condensates (SC) (SCA,SCB,SCC)

Table 5. Properties of secondary condensates used in the bleaching experiments (Alakaila et al., 2004, p.116)

	SCA	SCB	SCC
pH	6.43	7.22	8.91
Conductivity ^a , [mS/m]	7.6	5.7	54.3
Colour ^b , [mg/l Pt]	5	15	30
COD, [mg/l]	1,400	2,200	51,100
Na, [mg/l] ^c	0.2	5	16
K, [µg/l] ^c	35	890	4,950
Ca, [µg/l] ^d	57	450	345

^a SFS-EN 27888, Temperature 25°C

^b SFS-EN ISO 7887, Part 4; filtration throw 0.45 µm membrane
(In SCC white precipitation was observed even after filtration)

^c SFS 3017, Measured with Perkin Elmer 4100 FAAS (filtration 0.45 µm)

^d SFS 3018, Measured with Perkin Elmer 4100 FAAS (filtration 0.45 µm)

Like with VOCs experiments, the amounts of secondary condensates was based on COD loads they affect when replacing part of process water. For SCA COD levels were 2 and 5kg/bdtp, for SCB 5 and 10kg/bdtp and for SCC 10 and 30kg/bdtp. Following Table 6. shows the compositions of the original condensates and filtrates after bleaching (Alakaila et al. 2004, p.116).

Table 6. Chemical compositions of the original condensates and filtrates after bleaching experiments (Alakaila et al. 2004, p.116).

Sample^a	Formic acid^b mg/L	HS mg/L	MM mg/L	DMS mg/L	Acetone mg/L	Methanol mg/L	Ethanol mg/L	DMDS mg/L
Blank	53 (±6)	n.d	n.d	n.d	24	16	<8	<10
A2	59 (±11)	<0.4	n.d	n.d	16	n.d	8	10
A5	48 (±12)	<0.4	n.d	n.d	16	n.d	n.d	20
B5	68 (±2)	<0.4	n.d	n.d	16	n.d	n.d	<10
B10	50 (±4)	<0.4	n.d	n.d	16	n.d	n.d	10
C10	49 (±6)	<0.4	n.d	n.d	16	n.d	n.d	n.d
C30	65 (±26)	<0.4	n.d	n.d	24	24	n.d	<10
SCA	n.d	<0.4	n.d	<8.5	n.d	n.d	8	160
SCB	174 (±1)	<0.4	n.d	n.d	n.d	<80	n.d	110
SCC	576 (±211)	ref.	ref.	6,490	n.d	11,760 ^c	n.d	4,240

^a A2, A5 = 2 and 5 kgCOD/bdtp SCA; B5, B10 = 5 and 10 kgCOD/bdtp SCB; C10, C30 = 10 and 30 kgCOD/bdtp SCC

^b Confidence interval from two analyses is in brackets

^c Measured with HPLC

n.d. = no detection

ref. = references

All three condensates showed remains of dimethyl disulfide. SCA and SCC also had remains of dimethyl sulfide. SCB and SCC showed values of methanol and formic acid. Generally, it can be observed how SCC has many times higher values compared to other condensates, underlining it being foul condensate. Filtrates A, B, C taken after each bleaching experiments corresponding to used condensate and specific COD load used. All filtrates had acetone and formic acid in them. Sulfur bearing compounds analyzed were HS [hydrogen sulfide], MM [methyl mercaptan], DMS and DMDS. All filtrates also had small quantities of HS in them and values suggest bleaching had no detectable effect on it.

A and C filtrates showed no traces of DMS suggesting it was oxidized or released during experiments. Blank filtrate from ionized water experiment contained formic acid, acetone, methanol, ethanol and DMDS. Interestingly all filtrates that had DMDS traces had fairly similar values despite of differing initial values or total lack of it.

4 PULSED CORONA DISCHARGE TREATMENT

4.1 Radicals and Advanced Oxidation Processes

Radicals are defined as molecules or atoms that have unpaired amount of electrons. High-reactivity of radicals makes them important for many industrial processes. Generally small radicals are short lived and when colliding with other molecules a reaction leads to a pairing of their unpaired electrons. Reactions involving homolysis of covalent bonds produces free radicals with unpaired electron counts. When created radicals abstract atoms from other molecules to get a paired electron count new radicals are created at the same time (Fryhle & Solomons, 2006, pp. 427-428).

Oxidation treatment of organic contaminants usually aims to creation of hydroxyl (OH) radicals that that have very high oxidation potential. Typically OH radicals oxidize organic compounds by hydrogen abstraction as can be seen in equation (8). When molecular oxygen is added to organic radicals produced in equation (8), peroxy radicals are produced as can be seen in follow up equation (9). These initial reactions start chain of oxidation reactions that in the end lead to carbon dioxide, water and inorganic salts. Alternative reaction possibility is in equation (10) that shows electron transfer to hydroxyl radicals (Braun et al. 1993, p. 675).



Processes that utilize creation of OH radicals are generally called advanced oxidation processes (AOPs). AOPs utilize chemical or photochemical processes in creation of OH radicals. Chemical processes utilize chemicals such as ozone (O₃), hydrogen peroxide (H₂O₂) or different catalysts in creation of OH radicals. Photochemical processes use different combinations of ultraviolet light (UV) with chemicals like ozone, hydrogen peroxide or titanium oxide (TiO₂) (Munter, 2001. p. 62). Following Table 7. shows oxidation potentials of different oxidants and also relative potentials of ozone in comparison.

Table 7. Oxidation potentials of different oxidants and relative potential of ozone compared to them (Fernando, 2004. p.8)

Oxidant	Oxidation potential (V)	Relative Potential of Ozone
Fluorine	3.06	1.48
Hydroxyl radical	2.80	1.35
Atomic oxygen	2.42	1.17
Ozone	2.07	1.00
Hydrogen peroxide	1.77	0.85
Hydroperoxide radical	1.70	0.82
Oxygen	0,40	0,19

Previous Table 7. Shows that hydroxyl radical has second highest potential expect the fluorine. Also ozone and atomic oxygen that are essential oxidation chemicals in different AOPs are also in high on the list. Oxygen itself has relatively low potential compared to other ones.

4.2 Pulsed Corona Discharge Phenomena

Main elements of pulsed corona discharge (PCD) configuration are wire discharge electrode and grounded opposite electrode. Main regions that radiate starting from the wire are corona plasma region and unipolar ion region, which are separated by ionization boundary. When a positive pulsed high voltage is applied to the wire electrode, the free electrons that are formed between electrodes are accelerated toward positive wire electrode. In plasma region colliding electrons and neutral gas molecules produce positive ion pairs. Electrons that are freed in the process are accelerated by electric field and produce more ionization.

Alternatively, they can also attach to electronegative gas molecules or recombine with positive ions. Outside the ionization boundary in the unipolar region, electric field strength is not anymore able to produce electrons and unipolar ions emanate towards grounded electrode. Following Figure 8. shows a model of positive direct current corona discharge and reactions in it (Chen & Davidson, 2002, pp. 200-201).

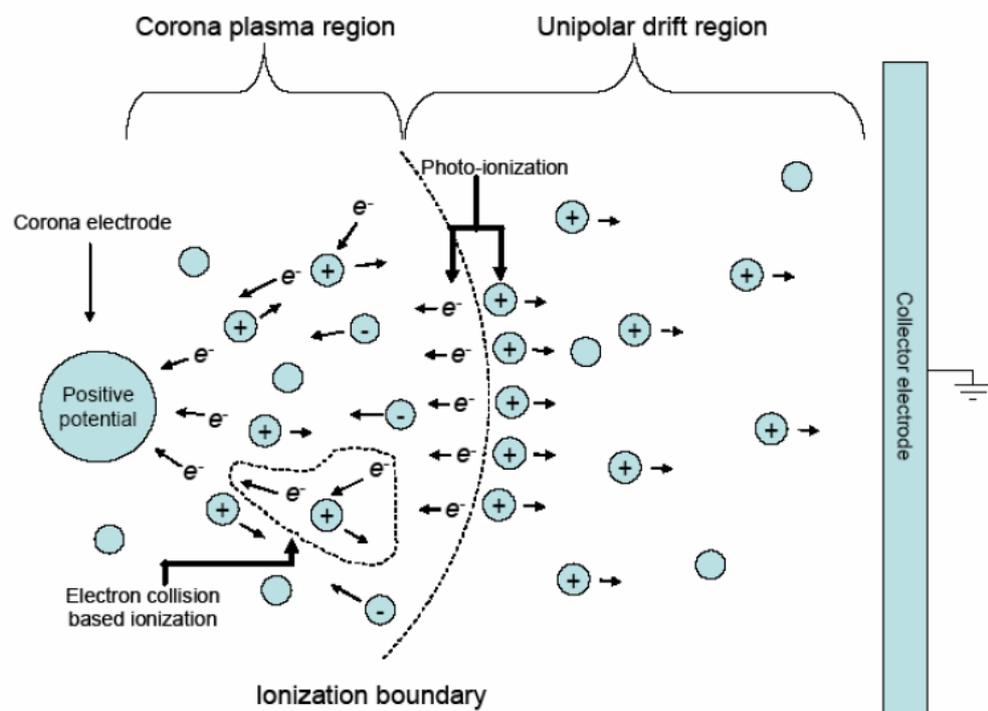


Figure 8. Model of positive direct current corona discharge (Chen, 2002).

In negative PCD configuration as the name implies a negative voltage is applied to the wire electrode and the collector electrode is earthed. Secondary electrons that sustain the negative corona are mainly produced by photoemissions from surface of the discharge electrode. Like in the positive corona discharge, the secondary electrons drive the electron creation ionizations. Unlike in the positive corona discharge the ionization and the plasma region boundaries differ. In the negative corona discharge electrons just outside of the ionization boundary are energetic enough and in sufficient numbers to drive electron impact reactions. Boundary of the corona plasma region marks the region inside which has corona enhanced chemical reactions and in the negative corona discharge, it extends outside the ionization boundary. Following Figure 9. presents a model of negative current corona discharge reactions (Grassi& Tessi, 2009 pp. 379-380).

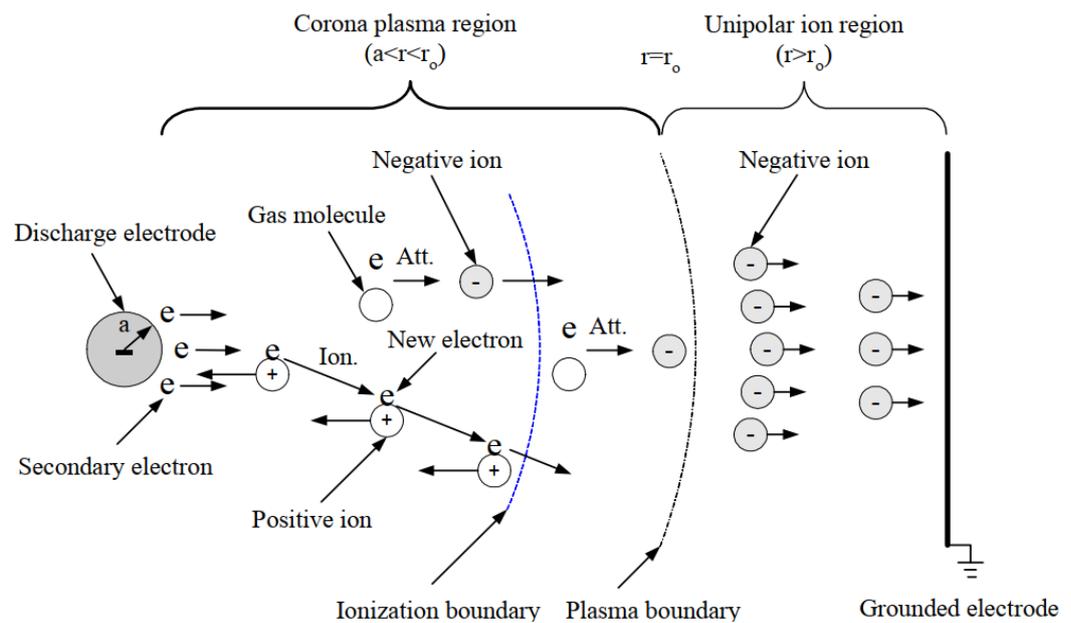


Figure 9. Model of negative direct current corona discharge system (Chen & Davidson, 2003).

4.3 Configurations

PCD can be used for treating both gases and liquids. When treating gases the two main types of PCD are dry “normal” and wet configurations. In the wet ones water is fed to top of the reactor where it is dispersed evenly to flow down the reactor and treated gas flows from bottom to the top. Adding of water aims to create hydroxyl radicals to help a treatment. Following Figure 10. shows an example PCD set up for gaseous effluents that has furnace around reactor for temperature control and analyzer (Lock et al. 2006, p. 529, p.531)

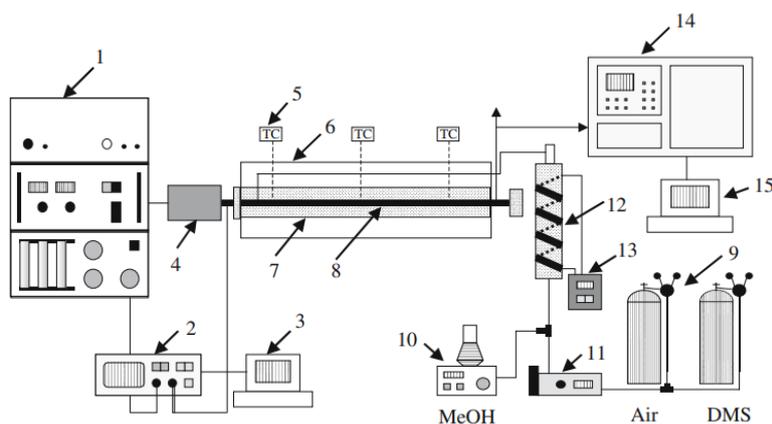


Figure 10. Example of dry gaseous PCD treatment experimental setup: 1 pulsed power supply, 2 oscilloscope, 3 computer, 4 connection box, 5 thermocouple, 6 reactor oven, 7 aluminum jacket, 8 pulsed corona reactor, 9 air and DMS supply cylinders, 10 syringe pump, 11 mass flow controller, 12 mixing and evaporating chamber, 13 temperature controller, 14 gas chromatograph, 15 computer (Lock , Saveliev & Kennedy, 2006, p. 529).

When treating liquids the treated fraction can be fed to the top of the reactor where it flows down through the reactor. Collection/reservoir tank is located under the reactor and a feed pump is used to circulate the liquid back to the top. Following Figure 11. shows an example of PCD set up for liquids (Preis et al. 2013, p. 1537).

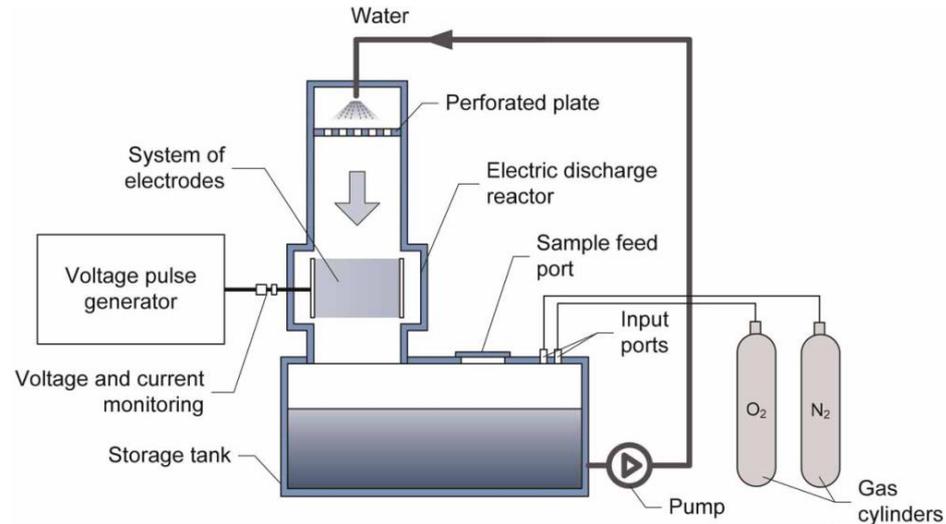


Figure 11. Example of PCD set up for liquids (Preis et al. 2013, p. 1537).

4.4 Treating Volatile Organic Compounds

4.4.1 Introduction

There has been research of using PCD to treat pulp mill VOCs and those have concentrated mainly to gaseous VOC streams. Destruction and Removal Efficiency (DRE [%]), Specific Energy Input (SEI) and Energy Cost can be used to characterize treatment process performance. DRE can be calculated from ratio of initial and final concentrations. SEI is derived from ratio of used power and volumetric flow rate under stable conditions (Lock , Saveliev & Kennedy, 2006 p. 530).

4.4.2 Methanol & Ethanol

Fridman & Gutsol (2008, p.119) researched PCD treatment in a pilot plant scale for VOCs from brownstock washer's vent stream. Pilot plant utilized water scrubber before actual PCD wet treatment. Their observations of methanol oxidation in plasma without byproducts supports prior findings (Sobacchi, 2003. Sobacchi, 2004). Methanol oxidation was also noted to be rather energy depended process as previously also shown by (Sobacchi et al. 2003 Sobacchi et al. 2004).

Following Figure 12. shows how DRE of methanol increases as plasma power of the treatment increases. Low volumetric flow rate with low concentration achieved over 90% DRE with relatively low power level compared to other results. Water scrubbing was carried out by directing gas stream through a backed bed with water flowing from up to down. With 500m³/h and 12ppm a lot more power is required to achieve total removal and it can be seen increasing steadily as power is increased. With the same flow rate and 26ppm with the water scrubbing activated a lot less power is required to achieve over 90DRE and about 1,5kW less power to achieve total destruction.

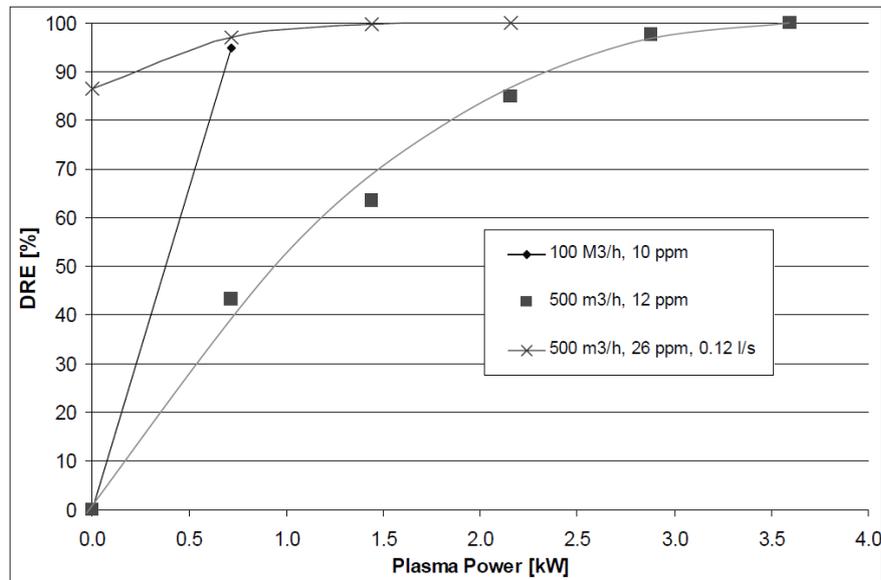


Figure 12. Methanol DRE dependence of plasma power in different flow rates and concentrations with and without water scrubbing of 0,12l/s [Outer electrode was a stainless steel tube with the length of 1.20m and internal diameter of 22,2mm. Inner wire electrode was 0,5mm Inconel[®] wire.] (Sobacchi et al., 2004). (Fridman & Gutsol, 2008, p.119).

4.4.3 Acetone

Sobacchi et al. (2004) researched treatment of gaseous VOC compounds with both dry and wet PCD configurations. Treated compounds were methanol, acetone, α -pinene and dimethyl sulfide and they were chosen to represent a typical composition of brown stock washer's vent stream gas. Acetone oxidation efficiency is strongly link to initial concentration and applied power/frequency. This can be observed from following Figure 13 in four different concentrations.

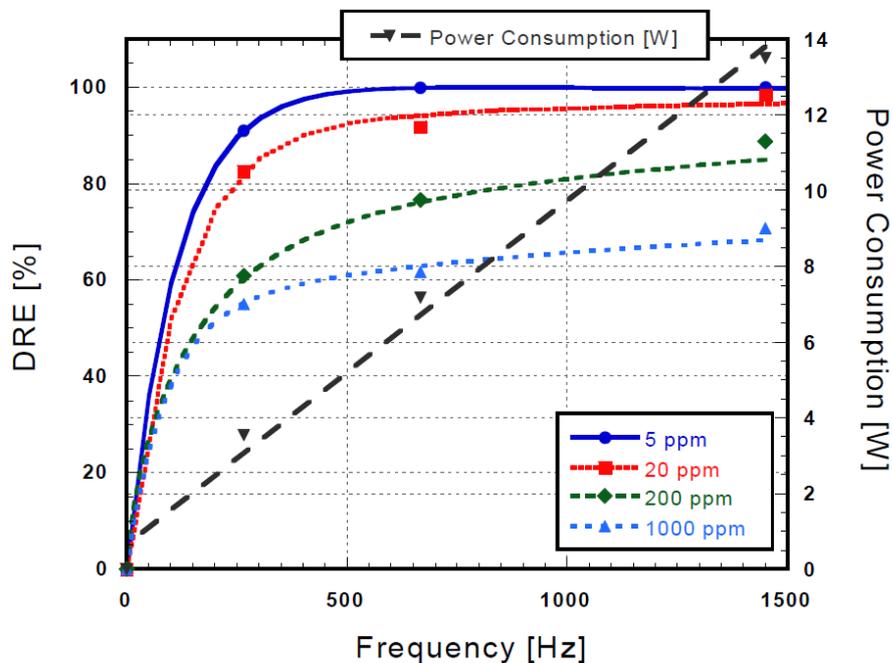


Figure 13. DRE and PCD power consumption as a function of pulse frequency for acetone [T=200°C, Outer electrode was a stainless steel tube with the length of 1.20m and internal diameter of 22,2mm. Inner wire electrode was 0,5mm Inconel® wire.] (Sobacchi et al., 2004).

As can be seen from previous Figure 13. DRE of acetone decreases as concentration of compound increases. While with the lowest concentration DRE reaches 100% but when moved into higher ones the available increase of frequency and therefore power is not enough (Sobacchi et al., 2004)

4.4.4 Dimethyl sulfide and other sulfur bearing compounds

Fridman & Gutsol (2008, p. 120) also found support for prior research (Sobacchi 2003 Sobacchi 2004) that showed that Dimethyl sulfide oxidizes into two byproducts of methanol and acetone. This creation of byproducts can be seen in the following Figure 14. which uses concentration of total hydrocarbons for dimethyl sulfide measurement.

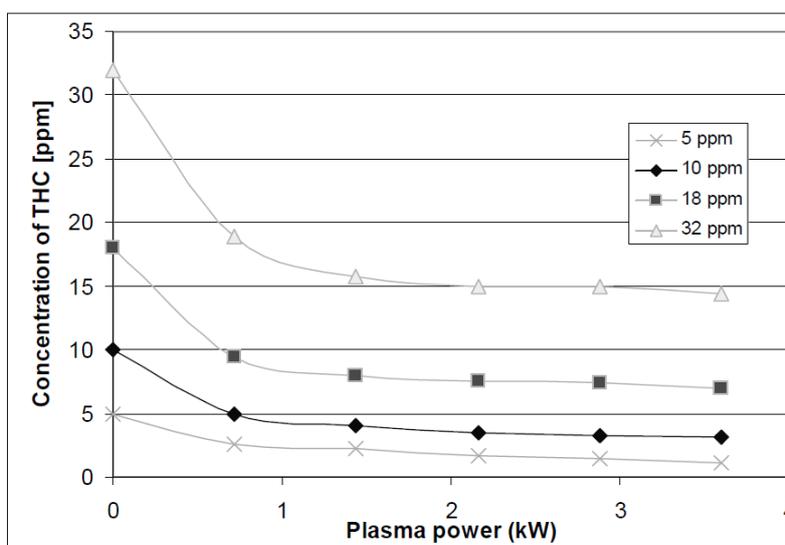


Figure 14. Dimethyl sulfide oxidation using total hydrocarbon measurements in 500m³/h [Outer electrode was a stainless steel tube with the length of 1.20m and internal diameter of 22,2mm. Inner wire electrode was 0,5mm Inconel® wire.] (Sobacchi et al., 2004). (Fridman & Gutsol, 2008, p. 120)

As can be seen in the previous picture initial concentration decreases quickly that is mostly oxidation of dimethyl sulfide itself. After initial drop dependence of power decreases as created byproducts are oxidizing. Reactions of DMS (CH₃SCH₃) and OH radical have many reaction pathways to follow. See the following equations (11)-(14) (Barone, Turnipseed & Ravishankara, 1996A, p. 14695).





In equation (11) M stands for non-reacting molecule. Methanethiol also known as methyl mercaptan (CH_3S) is believed to be intermediate product of DMS oxidation. As can be seen it can be produced by previous equation (14) (Sobacchi et al., 2003, p.361). Alternatively with the presence of oxygen and nitrogen methyl mercaptan can be produced starting from equation (12). Following equations (15)-(19) show this alternate path with oxygen and nitrogen (Turnipseed, Barone & Ravishankara, 1996B, p.14703).



OH and DMS reactions when oxygen is introduced can be seen in equations (18) and (19).



4.4.5 Effects Temperature and Humidity

Lock et al. (2006, pp.527-541) studied PCD treatment of methanol and dimethyl sulfide in dry and humid air streams. The used configuration was dry type with the reactor placed inside a furnace for temperature control. Effects of input power, humidity and temperature were tested on DRE, SEI, actual compounds decomposition and created byproduct formation. Effects of input power were tested by two sets of tests. In the first one the peak pulse voltage of 8kV was kept constant and the pulse repetition rate was changed from 250HZ to 1316HZ. In the second one rate was kept at 250HZ and voltage was changed from 8 to 14kV. Following Figure 14. shows the decomposition efficiencies for input power experiments.

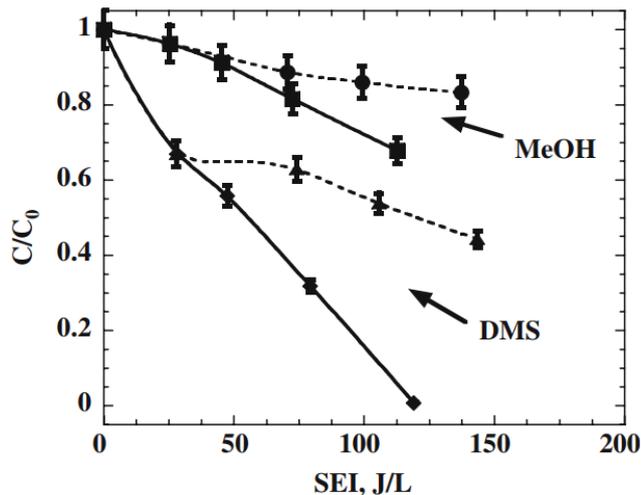


Figure 14. Decomposition efficiencies of methanol and dimethyl sulfide as function of SEI at $T=80^{\circ}\text{C}$ and initial concentrations of 1000 ppm. Dashed line shows changing of repetition rate and solid line is for peak pulse voltage. (Lock et al., 2006, p. 530).

Experiments of DRE under different temperatures showed how rise of temperature also increased DRE on both compounds. Increase of humidity was not as straightforward. Under lower temperatures of 50 and 80°C , a humidity 0,5% gave best DRE results for both compounds. At 180°C methanol achieved 100% removal rate under humidity of 2%. Generally going over humidity 0,5% decreased DRE results in both cases. Water molecules of humidity are main source for creation of OH radicals when treating dry gas streams. However, increasing humidity too much also increases collisions of between water molecules which causes decrease of electron mean energy and process efficiency. Following Figure 15. shows development of DREs under increasing humidity (Lock et al., 2006, pp. 531-532).

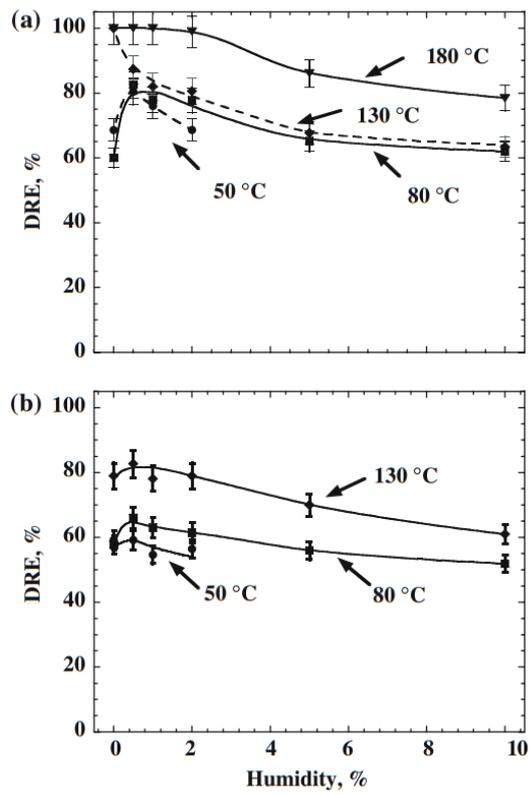


Figure 15. DRE as function of humidity in different temperatures for methanol (a) [12kV and 1000Hz] and dimethyl sulfide (b) [12kV and 250Hz] (Lock et al., 2006 p. 531).

Experiments of Lock et al. (2006, p.532) on humidity's effect on SEI showed how increasing humidity decreased SEI values. Losses in SEI are due to already mentioned increase of water molecule collisions. Increasing temperature also increased SEI values because of increase of electron free energy. Under the same conditions, dimethyl sulfide requires less power than methanol. This can be seen when comparing SEI values for both compounds in the Figure 16.

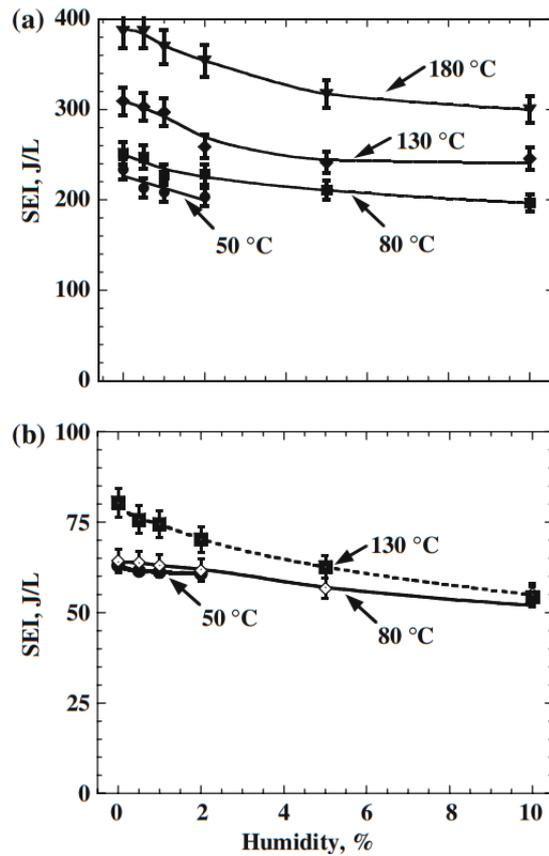


Figure 16. SEI as a function of humidity in different temperatures for methanol (a) [1000ppm] and dimethyl sulfide (b) [1000ppm] (Lock et al., 2006 p. 532).

4.4.6 Byproducts

Lock et al. (2006) also researched formation of byproducts from methanol and dimethyl sulfide. Methanol concentration decreases steadily as SEI is increased. Correspondingly nitrogen dioxide starts to form and concentration increases steadily as power increases.

Profile of carbon monoxide is different initially concentration increases rapidly all the way to 1000 ppm at about 300J/L. After high peak carbon monoxide concentration starts to decrease ending close to nitrogen dioxide. DMS concentration does not decrease as sharply compared to methanol but still it too has steady drop as SEI is increased. DMS produces four different byproducts sulfur dioxide, carbon monoxide, nitrogen dioxide and methanol.

Two most abundant ones are sulfur dioxide and carbon monoxide. Sulfur dioxide reaches highest concentration at the highest SEI like carbon monoxide. Methanol and nitrogen dioxide concentrations grow relatively slowly and stay slow even through whole range of SEI increase. Following Figure 17. shows development concentrations of methanol and dimethyl sulfide and forming byproducts (Lock et al., 2006 pp. 535-536).

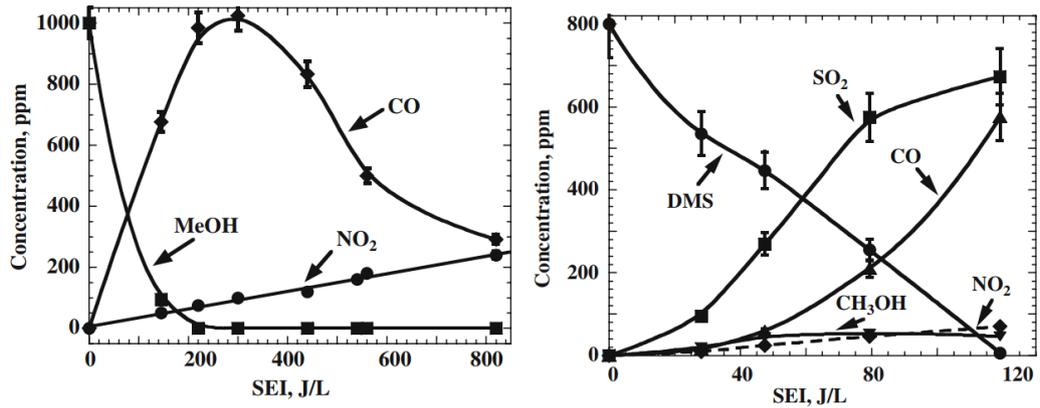


Figure 17. Formation and destruction of byproducts of methanol [1000ppm, 100°C, humidity 1%] and dimethyl sulfide [800ppm, 80°C, humidity 0%] (Lock et al., 2006 p. 535-536).

4.5 Conclusions

PCD treatment on gaseous VOC streams has been area of interest in a limited fashion. Beside the laboratory tests, there has also been pilot scale PCD treatment set-ups. VOCs that have been main interest in literature are methanol, ethanol, acetone and dimethyl sulfide. These compounds are also some of the main components of secondary condensates. Prior research has shown that these compounds can be treated successfully with PCD treatment. Also it has been shown that an increase on compounds concentration decreases destruction efficiency.

To compensate this the power/frequency of the treatment must be increased. One area that is lacking research for this thesis, is the treatment of VOC liquids with PCD method. This makes it hard to predict how well knowledge of gaseous treatments translates for liquid VOC treatments. Secondary condensates have been neither been treated with PCD.

5 Experimental Part

5.1 PCD Set Up and Treatments

Laboratory PCD set up chosen for condensate treatments had five power setting ranging from 33W [400pps] all the way to 277W [840pps]. Minimum treated volume had to be at least 40 liters due the set up layout and any samples taken during treatment had to be taken into account by having initial volume of 50l. There was no heating built in so treatments were carried out in a room temperature. Circulation pump had adjustable flow rate and because of this time required to treat a certain volume once could be changed. The set up also had a sample port and there was no real limit to the sample size except the previously mentioned minimum volume that could not be exceeded. Samples up to 1l were therefore considered possible if necessary. Following Table 8. shows available power levels and corresponding frequencies for the PCD set up.

Table 8. Available power levels [W] and corresponding frequencies [pulses per second, pps] for PCD set up.

Frequency [pulses per second, pps]	Power [W]
100	33
200	66
400	132
600	198
840	277

See the Figure 18. for a picture of used laboratory scale PCD set up.



Figure 18. PCD laboratory set up for condensate treatments

Previous Figure 18. can be compared to earlier Figure 11. of example of PCD set up for liquids. It can be noted how similar they are in their basic layout. It was decided to use initially two frequency settings of 400pps and 840pps for treatments. Later an intermediate setting of 600pps was also used. Each treatment had 7 samples taken: 1 zero sample and 6 treated ones. Sampling was based on delivered energy to the treated condensate. Sample points ranged from 200 Wh/m³ to 5000Wh/m³. After a desired energy input PCD was turned off and liquid was allowed circulated through once to ensure homogeneous composition before sample was taken. Sampling decreased total volume and that had to be taken into account. With the 840 pps the first sample point was achieved before whole volume had flown though once so no sample could be taken. Following equation (20) was used to calculate energy input to the treated condensate.

$$\mathcal{E} = \frac{(GE*t*1000)}{((V-V_s)*60)} \quad (20)$$

Where \mathcal{E} =energy, Wh/m³
 GE=generator power, W
 t=time, min
 V=total treated volume, l
 V_s=extracted sample volume, l
 1000=for liters to m³ conversion
 60=for minutes to hours conversion

Following Table 9. shows calculated sample points for delivered energies and corresponding times.

Table 9. Sample points for delivered energies and corresponding sampling times for all the treatments with different frequencies [pps].

Sample	Energy [Wh/m ³]	400 pps	600 pps	840 pps
0	0	0:00:00	0:00:00	0:00:00
1	200	0:04:32	0:03:01	0:02:10
2	400	0:09:04	0:06:03	0:04:19
3	800	0:18:09	0:12:06	0:08:39
4	1600	0:36:17	0:24:12	0:17:18
5	3000	1:08:03	0:45:22	0:32:26
6	5000	1:53:25	1:15:36	0:54:03

5.2 Analyses

5.2.1 Conductivity, pH, COD and Colour

Conductivity and pH of samples were measured with C3010 multiparameter-analyzer made by Consort. First two measurements were done right after the samples were taken.

COD analyses were done with a method based on DIN ISO 15705 standard. The used Merck Spectroquant reaction cells had measuring COD range of 0-15000mg/l and expiry date of used set was 31.8.2018. In the test, a 20ml of a sample was added into reaction cell containing potassium dichromate ($K_2Cr_2O_7$). Test cells were placed to heated COD reactor at 148°C for 120min. After the heating the cells were left to cool down for 10min before they were mixed and then left for other 30min.

Potassium dichromate reacts with oxidizable organic or inorganic compounds. Concentration of formed Cr^{3+} was then measured with photometrically. Analyses results were measured with DR/2010 spectrophotometer by HACH. COD measurements used in build program P435 that had measuring wavelength of 620nm.

Color changes of samples were measured with Hach DR/2010 spectrophotometer [program P120, 455 nm]. Results were given as a unit of PtCO APHA. First the analyzer was zeroed with a blank sample of filtered deionized water to the wavelength of 455nm. Samples were also filtered with a 0,45µm membrane filter. Then measuring of samples took place.

5.2.2 TOC

TOC (Total Organic Carbon) analyses were done with Shimazu TOC-L analyzer. TOC measurement is based on subtraction ($TOC=TC-IC$) of measured TC (Total Carbon) and IC (Inorganic Carbon) values. Analyzer used a combustion catalytic method where a sample is completely combusted at high temperature. Combustion temperature was 680°C. Combustion happened with the presence of platinum catalyst. TC combustion is done with presence of purified air and during it sample decomposes and converts into carbon dioxide. After cooling and dehumidification carbon dioxide is fed to NDIR (Nondispersive Infrared Detector) detector. IC was measured in a similar manner but after the combustion a sample was sparged with acid. Sparging converts IC to carbon dioxide before sample was fed to detector.

5.2.3 Sulfates & Acids

Sulfate analyses were done with Dionex ICS-1100 ion chromatography. 1000ppm solution was used to make calibration curve. Used carrier fluid or eluent was anionic Na₂CO₃ 45mM/NaHCO₃ 1,4mM. The pre-column was Dionex IonPac AG22 and the primary column was Dionex IonPac AS22. Cation suppressor was CSRS300.

Acid formation in the samples was measured with Agilent 1100 HPLC (High Pressure Liquid Chromatography). Samples were filtered before analyses with a 0,45µm regenerated cellulose syringe filters. The used column was Agilent MetaCarb 87H 300*7,8mm. The eluent was 5mM H₂SO₄. Temperature was 65°C and flow rate 0,4ml/min. The used detector was UV (Ultraviolet) at 210nm.

6 RESULTS

6.1 Conductivity, pH, COD and Colour

Following Table 10. shows measured conductivity values of all the samples and treatments.

Table 10. Development of conductivity in all the treatments.

Sample	Conductivity [mS/m], 400pps	Conductivity [mS/m], 600pps	Conductivity [mS/m], 800pps
0	13.31	19.95	11.88
1	15.41	85.90	15.82
2	14.31	15.75	32.00
3	51.90	61.90	22.00
4	46.70	28.30	19.44
5	34.70	27.80	28.60
6	43.30	39.10	55.30

As can be seen in the previous Table 10. there is no clear development of conductivity. Values differ greatly between samples of same treatment. A small observation is that final conductivity values are higher than zero samples.

Following Table 10. shows the all the measured pH values of the samples.

Table 11. Development of pH in all the treatments.

Sample	pH, 400pps	pH, 600pps	pH, 840pps
0	9.62	9.43	9.52
1	9.14	9.21	9.22
2	9.01	8.87	8.99
3	7.34	7.13	7.82
4	6.05	4.86	4.87
5	4.19	3.78	3.81
6	3.70	3.47	3.51

As can be seen in the previous Table 11 there is a big drop of pH in all the treatments. Remarkable thing is how closely values drop and how close final values are of each other. These drops led to having acid analyses to explain the drop.

Following Table 12. shows measured COD values

Table 12. Development of COD values of samples in all the treatments.

Sample	COD [mg/l],400pps	COD [mg/l],600pps	COD [mg/l],840pps
0	1700	1600	1680
1	1740	1600	1690
2	1720	1600	1660
3	1830	1590	1640
4	1730	1640	1680
5	1730	1690	1640
6	1720	1640	1660

Table 14. shows that COD values didn't have a change one way or other. This is a bit surprising since one would have expected COD to drop as compounds are oxidized during PCD treatment. Following Table 13. shows measured colour values in all the samples and treatments.

Table 13. Development of colour of samples in all the treatments.

Sample	Colour [PtCo APHA],400pps	Colour [PtCo APHA],600pps	Colour [PtCo APHA],840pps
0	37	30	30
1	41	50	39
2	44	30	50
3	42	26	42
4	17	12	24
5	9	8	14
6	6	7	18

As can be seen from previous Table 13. condensate samples brighten towards the end. Initial decrease of brightness is most likely due to proper mixing that was not achieved when condensate circulated before actual treatment. Still trend is after sample two in all the cases towards brighter although in reality difference wasn't possible to observe by eye. Most likely cause of this is decomposition of colored lignin derived compounds still present in the condensate.

6.2 TOC

Following Table 14. shows TOC (Total Organic Carbon), TC (Total Carbon) and IC (Inorganic Carbon) measurement results of 400pps treatment.

Table 14. TOC, TC and IC values at 400pps (pulses per second) treatment.

Sample	TOC [mg/l]	TC [mg/l]	IC [mg/l]
0	338.84	346.72	7.88
1	354.28	361.88	7.572
2	356.08	363.96	7.876
3	328.64	335.92	7.304
4	345.08	352.6	7.516
5	348.96	355.08	6.14
6	325.12	331.28	6.172

Following Table 15. shows TOC (Total Organic Carbon), TC (Total Carbon) and IC (Inorganic Carbon) measurement results of 840pps treatment.

Table 15. TOC, TC and IC, values of 840pps (pulses per second) treatment.

Sample	TOC [mg/l]	TC [mg/l]	IC [mg/l]
0	318.52	328.08	9.572
1	333.68	341.84	8.16
2	334.84	343.16	8.316
3	348.4	356	7.604
4	346.68	354.36	7.704
5	323.32	330.88	7.576
6	315.12	323.16	8.02

Neither of previous Tables 14. or 15. don't show a drop in their TOC values. While in both cases sample six has slightly lower value compared to original sample zero erratic way values differ from sample to sample it's not possible to say that actual decrease has happened.

6.3 Sulfates & Acids

Following Table 16. shows result of sulfate content analyses for all the treatments.

Table 16. Development of sulfate content of samples in all the treatments.

Sample	Sulfates [mg/l], 400pps	Sulfates [mg/l], 600pps	Sulfates [mg/l], 840pps
0	21.08	10.08	19.72
1	23.05	17.88	23.91
2	28.17	27.21	27.54
3	37.08	38.70	38.17
4	42.97	41.16	41.60
5	41.47	42.85	42.27
6	41.78	43.68	43.41

Previous Table 16. shows a clear increase of sulfate concentration that is also quite uniform between different treatments. Increase is most likely due to oxidation of sulfur sulfides to sulfates. This would suggest that goal of treating harmful sulfure sulfides is at least partially met. Following Table 17. shows results of formic acid analyses.

Table 17. Development of formic acid in all the treatments.

Sample	Formic acid [mg/l], 400pps	Formic acid [mg/l], 600pps	Formic acid [mg/l], 840pps
0	-	-	-
1	-	-	-
2	-	-	-
3	-	-	0.5
4	-	4.7	5.4
5	38.1	12.8	16.5
6	97.1	26.6	41.9

As can be seen from previous Table 17. concentration of formic acid starts to show and increase after sample three with the 840pps treatment samples. With the 600pps treatment the first sample to show acid was number four and with the 400pps treatment number five. While more powerful treatment starts to show formic acid first the low power treatment has higher final concentrations. Following Table 18. Shows results of acetic acid analyses.

Table 18. Development of acetic acid concentration in all the treatments.

Sample	Acetic acid [mg/l], 400pps	Acetic acid [mg/l], 600pps	Acetic acid [mg/l], 840pps
0	-	-	0.2
1	-	-	0.1
2	1.1	-	-
3	0.2	-	0.0
4	-	0.2	-
5	-	1.2	-
6	-	2.7	-

Previous Table 18. shows how there is no major increase of acetic acid in any of the treatments. Medium power treatment of 600pps has slight increase in the end. One possible reason there is a difference between formic and acetic acid is that there has been chemical changes of samples between sampling and analyses. This might also wipe away low initial values of formic acid. Taking this into account it is also possible that acetic acid had relatively low values to begin with in the samples. Following Figure 19. shows both pH and formic acid concentration as a function of energy in the same chart.

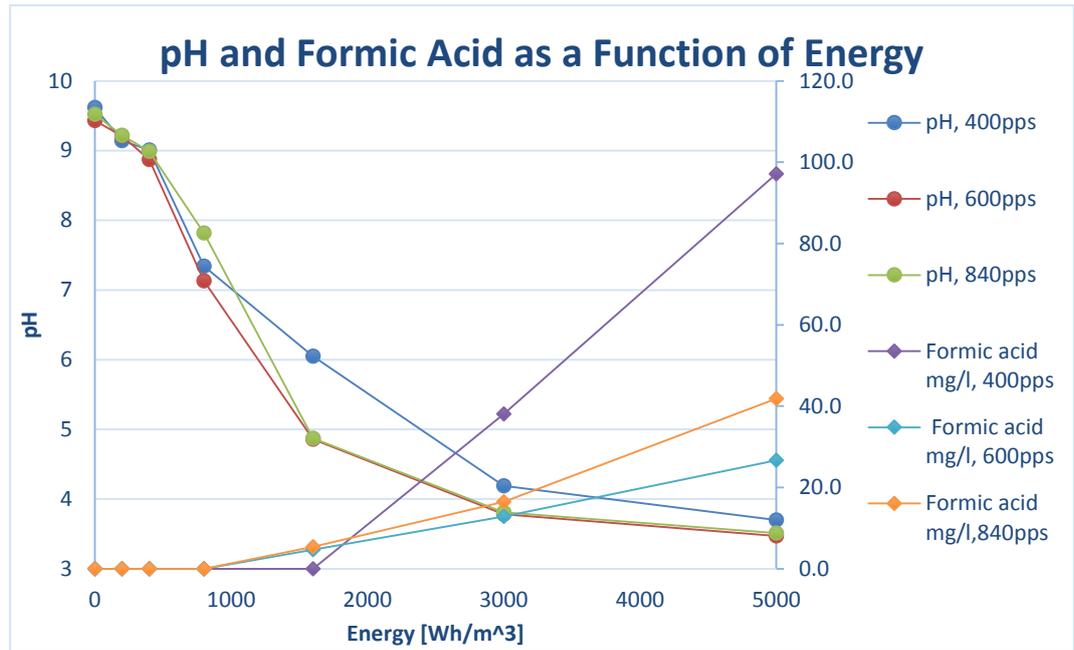


Figure 19. Formic acid concentration and pH as a function of energy, the left side of y-axis shows pH and the right side one shows the concentration [mg/l³] of formic acid. Different treatments are referred by their frequencies in units of pulses per second or pps.

Figure 19. shows that the sharpest drop of pH occurs before energy of 1600Wh/m³ which is also the energy dosage that starts to show increase of acid concentration. Since acids are a one likely cause for pH drop but initially acid concentration does not even register in the analyses so there ought to be also other factors behind it. Interestingly as the acid concentrations increase the decrease of pH slows down in all cases although not completely.

7 SUMMARY AND CONCLUSIONS

The purpose of this thesis was to study treatment of secondary condensates with the PCD method for usage as process water at the pulp mill. Main aim was to enable oxidation of odorous sulfur compounds and other compounds as well at the same time. Based on increase of sulfate content one part of the goal was apparently achieved to some extent.

Sharp drop of pH was unexpected observation that led to the finding of formic acid formation, although it is unlikely the only contributor for the drop. Other unexpected find was that there was no decrease of COD values even at the highest energy dosages.

Based on results of this thesis there are two main areas for further research. First one consist of more detailed composition analyses on how PCD effects on condensates. Besides the sulfur compounds one sub-area of interest should be background of pH decrease and relation of acid formation to it. Second area has bleaching washing tests with treated secondary condensates to determine actual effects on washed pulp.

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