

LAPPEENRANTA UNIVERSITY OF TECHNOLOGY
School of Energy Systems
Department of Environmental Technology
Sustainability Science and Solutions
Master's thesis 2018

Assi Häkkinen

**IMPROVING THE YIELD AND QUALITY OF
TURPENTINE IN SUPERBATCH COOKING**

Examiners: Professor, D.Sc. (Tech) Risto Soukka
Laboratory engineer, Lic.Sc. (Tech) Simo Hammo

TIIVISTELMÄ

Lappeenrannan teknillinen yliopisto
LUT School of Energy Systems
Ympäristötekniikan koulutusohjelma
Sustainability Science and Solutions

Assi Häkkinen

Tärpätin laadun ja saannon parantaminen syrjäytyseräkeitossa

Diplomityö

2018

123 sivua, 59 kuvaa, 7 taulukkoa ja 2 liitettä

Työn tarkastajat: Professori, TkT Risto Soukka
 Tekniikan lisensiaatti TkL Simo Hammo

Hakusanat: Tärpätti, SuperBatch, Saanto, Laatu, Tärpättitase

Tämän diplomityön tarkoitus oli selvittää keinoja tärpätin laadun ja saannon parantamiseen syrjäytyseräkeitossa. Tärpätin saanto ja laatu on ollut Metsä Fibrellä Raumalla pitkäaikainen ongelma. Saanto ja laatu ovat ajoittain heitelleet ja selviä syitä heittelyille ei ollut löydetty ja näitä syitä haluttiin selvittää. Tämän tavoitteen saavuttamiseksi työssä kerättiin teoretietoa aiheesta, luotiin Metsä Fibre Rauman tehtaiden tärpättitase laboratorionkokeiden avulla ja kerättiin laatu, saanto ja prosessidataa riippuvuussuhteiden löytämiseksi.

Tuloksena huomattiin, että suurin osa tärpätistä menetetään mäntyöljyn ja hajukaasujen mukana. Huomattiin myös, että suurin osa talteen saadusta tärpätistä on peräisin likaislauhteiden kuorinnasta. Toisaalta keittimien ja lipeäakkujen paineistuksen ja lämpötilan noston huomattiin vaikuttavan positiivisesti tärpättisaantoon. Laatutekijöihin vaikutti positiivisesti tärpättilauhduttimen, hajukaasupesureiden ja tärpätin lähteiden lämpötilan nostaminen. Johtopäätöksenä voidaan sanoa, että tärpätin saantoon ja laatuun on mahdollista vaikuttaa dekanterin, tärpättilauhduttimen, hajukaasupesureiden, keittimien ja lipeäakkujen lämpötilan optimoinnilla.

ABSTRACT

Lappeenranta University of Technology
LUT School of Energy Systems
Degree Programme in Environmental Technology
Sustainability Science and Solutions

Assi Häkkinen

Improving the Yield and Quality of Turpentine in Batch Cooking

Master's thesis

2018

123 pages, 59 figures, 7 tables, 2 appendices

Examiner: Professor, D.Sc. (Tech) Risto Soukka
Laboratory engineer, Lic.Sc. (Tech) Simo Hammo

Keywords: Turpentine, SuperBatch, Yield, Quality, Turpentine material balance

Aim of this master's thesis was to find solutions how to improve the yield and quality of turpentine in the SuperBatch cooking. Yield and quality have been varied at Metsä Fibre Rauma and the reasons to these changes haven't been found. To find reasons to the changes theoretical information was collected, material balance of the turpentine in Metsä Fibre Rauma was formed according to the laboratory analysis and the yield, quality and process data was collected and analyzed to find dependencies between the three. Most of the turpentine is lost with the tall oil and odorous gases. It was noticed that largest amount of the recovered turpentine is from the foul condensate skimming. Pressure and temperature of the cooking digester and the liquor accumulators seem to effect on turpentine yield. Quality of the turpentine is better when the temperature of the surface condenser, gas scrubbers and turpentine sources was increased. Turpentine yield and quality can be improved by optimizing the temperature of the decanter, turpentine condenser, gas scrubbers, cooking digester and liquor accumulators.

ACKNOWLEDGEMENTS

I would like to thank everyone at the Metsä Fibre Rauma for all the help I've got and for accepting me as part of the work community. Thanks to my co-workers, I really enjoyed my time in Rauma far away from home and family.

Special thanks I would like to give my supervisor at Rauma, Timo Saarinen. He gave me the opportunity to complete my thesis at Rauma and gave me a lot of his precious time, effort and advices. I would also like to thank my examiners from the school, Risto Soukka and Simo Hammo who advised me when I needed help.

I would like to thank Anne Penttilä from Eurofins and Hilton Tyre from DRT for lending me lavishly the equipment for the turpentine analysis. Hilton Tyre I would also like to thank for the several advises and efforts. I also want to give my thanks for the Dominique Mayaux and Emmanuel Cazeils for the information and help.

Thank you Erkki Kivekäs, Henri Kesseli, Mikael Svedman, Hannu Mäkitalo, Jari Kotoneva and Pertti Hietaniemi for memorizing the old times for me. I would also like to thank Lari Lammi and Bjarne and Thomas Holmbom for the advices I got.

I would like to give my thanks for Kari Kovasin, Petri Halme and Kari Peltola for the advices and knowledge. I would also like to thank all the staff from control rooms and laboratory for the help and guidance.

In Rauma,

Assi Häkkinen

TABLE OF CONTENTS

	LIST OF SYMBOLS.....	7
1	INTRODUCTION	9
2	CRUDE SULFATE TURPENTINE IN GENERAL.....	11
	2.1 Chemical properties of CST	11
	2.2 Physical properties of the CST	12
	2.3 Safety and environmental issues related to CST	16
	2.4 CST markets and price development	19
3	PRODUCTION OF CRUDE SULFATE TURPENTINE AS A BY-PRODUCT OF PULP MANUFACTURING	20
	3.1 Transportation and storing.....	21
	3.2 Wood handling.....	21
	3.3 Cooking	23
	3.3.1 Stages of displacement batch cooking	26
	3.4 Pulp washing	27
	3.5 Evaporation plant.....	28
	3.6 Turpentine recovery	28
	3.7 Turpentine losses during the process	30
	3.8 Aspects affecting yield and quality of turpentine	34
	3.8.1 Metsä-Botnia Ab, Kaskinen turpentine research	36
	3.8.2 UPM-Kymmene, Metsä-Rauma, Enso and Sunds Defibrator Pori Oy Black liquor expansion tests.....	38
	3.8.3 Terpenes emitted to air from the kraft pulp process in Värö and Gruvön	42
	3.8.4 Change of average sulfur content in Union Camp - BBA Jacksonville Terpene and aromatics plant	43
	3.8.5 Turpentine Recovery at Champion International Courtland Mill	44
4	CASE METSÄ FIBRE RAUMA	47
	4.1 Wood storing	48
	4.2 Cooking	49
	4.3 Turpentine system.....	51
	4.4 Yield and quality problems	52
	4.5 Safety issues	52
5	LABORATORY ANALYSIS TO DETERMINE THE MATERIAL BALANCE OF TURPENTINE IN METSÄ FIBRE RAUMA.....	53
	5.1 Chip samples	53
	5.2 Pulp samples	55
	5.3 Condensate samples	56
	5.4 Other samples	57
6	DATA ANALYSIS	58
	6.1 Yield of CST.....	58
	6.2 Quality of CST.....	61

6.3	Process data	62
7	RESULTS AND ANALYSIS	64
7.1	Results of the laboratory analysis and material balance of turpentine in Metsä Fibre Rauma 64	
7.2	Results of data analysis	72
7.3	Possible changes to the current system to improve the turpentine recovery	96
7.3.1	Chip bin steaming	96
7.3.2	Creating liquid-vapor interface to the top of the digester	98
7.3.3	Changes to the venting	99
7.3.4	Black liquor flashing or expanding	100
7.3.5	Turpentine collecting system from the dilute odorous gases	101
7.3.6	Turpentine stripper to the foul condensate stream	102
7.3.7	Raising decanting temperature	102
7.4	Result analysis	103
8	CONCLUSION.....	112
9	SUMMARY	114
10	REFERENCES	116

APPENDICES

Appendix 1. Components of crude sulfate turpentine

Appendix 2. Temperatures and pressures of the most important components of crude sulfate turpentine

LIST OF SYMBOLS

Roman symbols

<i>A</i>	Characteristic constant of each compound	[-]
<i>B</i>	Characteristic constant of each compound	[-]
<i>C</i>	Characteristic constant of each compound	[-]
<i>m</i>	Mass	[kg]
<i>P</i>	Pressure	[Bar, mmHg]
<i>p</i>	Percent	[%]
<i>T</i>	Temperature	[°C, °F]
<i>V</i>	Volume	[l]

Greek symbols

ρ	Density	[kg/m ³]
--------	---------	----------------------

Subscripts

T, t	Turpentine
S	Steam

Abbreviations

CST	Crude Sulfate Turpentine
HBL1	Hot Black Liquor Accumulator 1
HBL2	Hot Black Liquor Accumulator 2
NaOH	Sodium Hydroxide
Na ₂ S	Sodium Sulfide
NCG	Non-Condensable Gas
RDH	Rapid Displacement Heating

TRS	Total Reduced Sulfur
VOC	Volatile Organic Compound

1 INTRODUCTION

Turpentine is a volatile oil that is produced from soft wood. It can be used as a solvent, in the pharmaceutical industry and in the production of resins, oils and varnishes. It can be used also as a raw material of other products like tall oil and turpentine. Crude sulfate turpentine is separated from the wood chips during the pulp making process. (Wansbrough, 1977) Turpentine is an important by-product for the forest industry as already 10 % of turnover of a pulp mill is from tall oil and turpentine (Metsä Group, 2018a). Yield of pulp and by-products is important, so the utilization rate of the raw material would be as high as possible. It is also important to recover the turpentine since when released to the air it is a hazardous air pollutant. (Lin, 2005) Turpentine is also flammable and it has to be handled in the way that the safety risks are minimized. (Drew et al, 1971, 8)

Two main types of pulp cooking processes are continuous cooking and batch cooking. Continuous cooking is the most common method of cooking. This thesis is concentrated to the turpentine production in the pulp mill that uses SuperBatch cooking method, which is one type of batch cooking. Pulp is produced in several separate digesters in batch cooking. Each digester completes five stages and usually there are at least four digesters to guarantee enough and homogenous production. (Know Pulp, 2016) SuperBatch method offers some benefits in comparison with other methods but for turpentine recovery it causes challenges. SuperBatch method causes changes to the compounds that are formed in the cooking process and some compounds and gases are formed in unexpected locations. For the turpentine recovery and mill safety it is important to be aware in which flows the turpentine is. (VTT Kemiantekniikka 1998)

Metsä Group is an international forest industry company in Finland. Metsä Group includes Metsä Forest, Metsä Wood, Metsä Fibre, Metsä Board and Metsä Tissue. (Metsä Group, 2018b) Metsä Fibre includes pulp and sawmill industries. (Metsä Fibre, 2018a) Metsä Fibre Rauma produces ECF-bleached soft wood pulp, biochemicals and bioenergy. Metsä Fibre Rauma uses 3,4 cubic meters of wood to produce 650 000 tons of ECF-bleached pulp in one production line. (Metsä Fibre, 2018b)

During past years the yield of turpentine has been low in the Metsä Fibre Rauma mill. The other problem is that the quality of turpentine has been varied since the yield of the heavy fractions and the sulfur content have been high from time to time. Time periods when the quality was up to standard has occurred but clear reason why the quality is varied hasn't been found. Partly the reason to the quality problem is that the some of the turpentine is collected from the foul condensate. The quality is significant problem since the buyer of turpentine can't utilize the heavy fractions. High sulfur content decreases the flashpoint of the turpentine and causes problems in transportation.

The aim of this thesis is to find reasons to the low yield and quality problems of the turpentine in Metsä Fibre Rauma and suggest solutions to the problems without negative effects on the pulp production. Safety risks caused by the changes in the process must be assessed and minimized. The theory section of this thesis describes turpentine as chemical component, the production of turpentine as a by-product of the pulp manufacturing and the aspects affecting to the quality and yield of turpentine. The goal of the thesis is achieved by utilizing the information of the theory section, by laboratory analysis and by data analysis. Some tests at the mill are completed.

In laboratory analysis several samples from the chips, cooking liquors, pulp, condensates and gases are analyzed. Samples are chosen according to the theory part and information achieved while conversations with experienced employees of Metsä Fibre Rauma. Some of the analysis are done at the Metsä Fibre Rauma mill and some are analyzed by Eurofins. Analysis determined the amount of turpentine in the samples. According to these samples the amount of turpentine in different flows was calculated and the material balance of turpentine was formed. Material balance of turpentine shows where the turpentine ends up when it is not recovered.

Data analysis aims to find some dependence between the changes in the yield and quality of turpentine and the differences in process parameters. Quality information of turpentine is collected from the quality reports from the client who buys the turpentine. Yield information is calculated from the information collected about the weight of leaving turpentine trucks. Data from the process is collected by Savcor Wedge program. Parameters monitored from

Wedge are chosen according to information of the theory section and information achieved by interviewing experienced employees from the mill and other expert contacts.

When the reasons to the problem have been recognized suggestions are made on how to change the process to improve the quality and yield of turpentine. Depending on how the changes would affect to the main process some mill trials are completed.

2 CRUDE SULFATE TURPENTINE IN GENERAL

Three kinds of turpentine exist, and they are usually sorted by their origin. Types are gum turpentine, crude sulfate turpentine and wood turpentine. Gum turpentine is steam distilled from the resinous exudate of wounded pine trees. Crude sulfate turpentine (CST) is condensed while pulp making from the vapors produced during the alkaline digestion of soft wood chips. Wood turpentine is obtained by the solvent extraction and steam distillation of waste wood. (Weston, 2006) This Master's thesis is concentrated to the production of the crude sulfate turpentine. Turpentine is colorless, odorous, flammable liquid that consist mostly isomers of pinene. (Yang, 2001) It's boiling point is at 149-180 °C and autoignition temperature is 220-255 °C. (IPCS, 2002) In this chapter the physical and chemical properties of turpentine that are relevant for the goal of the thesis are presented. Then some information about the turpentine markets and price development is outlined. Information about safety and environmental concerns regarding to the turpentine are described.

2.1 Chemical properties of CST

Turpentine is formed from the volatile agents in resin. In softwoods these volatile agents are mono-, sesqui- and diterpenes. Hardwoods don't include these substances therefore it's impossible to produce turpentine from hard wood. Most important volatile agents are monoterpenes, α -pinene is the most common one of them. It is the major particle of commercial turpentine. (Know Pulp, 2016) Volatile agents of turpentine are presented in appendix 1. Chemical formula of turpentine is $C_{10}H_{16}$ (pinene). (Yang, 2001) Structural formula of alpha pinene, beta pinene and monocyclic terpenes are presented in figure 1.

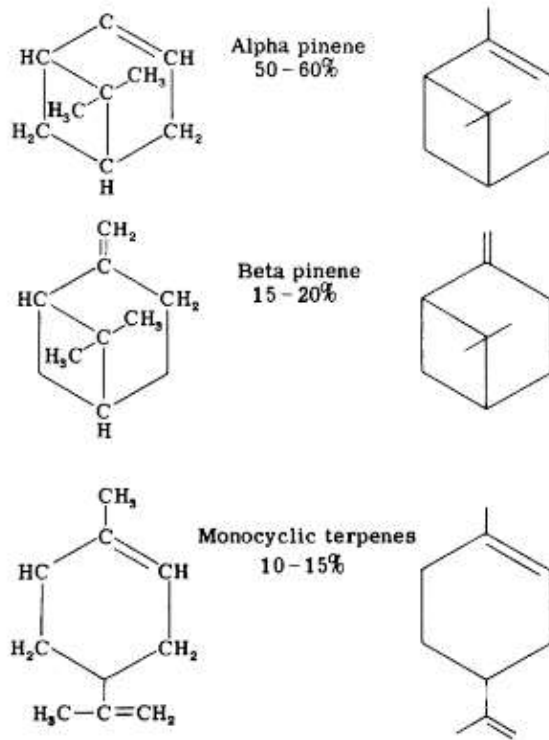


Figure 1. Figure presents the composition of sulfate turpentine. (Wenzl, 1970)

2.2 Physical properties of the CST

Vapor pressure of terpene compounds can be calculated with Antoine equation, equation 1. Antoine equation is valid at temperatures from -18-204°C (0-400 °F) (Drew et all. 1971, 31)

$$\log(P) = A - \frac{B}{t+C} \quad (1)$$

In which,

P = Vapor pressure [mmHg]

t = Temperature [°F]

A, B, C = Characteristic constants of each compound

Characteristic constants used in Antoine equation for each compound are presented in table 1. The thermodynamic properties of the turpentine compounds, calculated in method described above, are presented in appendix 2.

Table 1. Characteristic constants for each compound are shown in the table. (Drew et al. 1971, 32)

Compound	Normal boiling point [°F]	Normal boiling point [°C]	Antoine A	Antoine B	Antoine C
α -pinene	313,7	156,5	6,8459	2609	344,2
Camphene	317,6	158,7	6,8462	2622	343,5
β -pinene	330,9	166,1	6,8471	2665	341,0
Δ -3-carene	341,5	171,9	6,8477	2700	339,0
Dipentene	354,2	179	6,8486	2741	336,7
Alpha-terpineol	426,2	219	7,5676	3512	323,2

Figure 2. represents the partial pressure of turpentine and water vapor as function of temperature. In figure P_T is partial pressure of dissolved turpentine and P_S partial pressure of water vapor. (Tinnis & Kinnula, 1981)

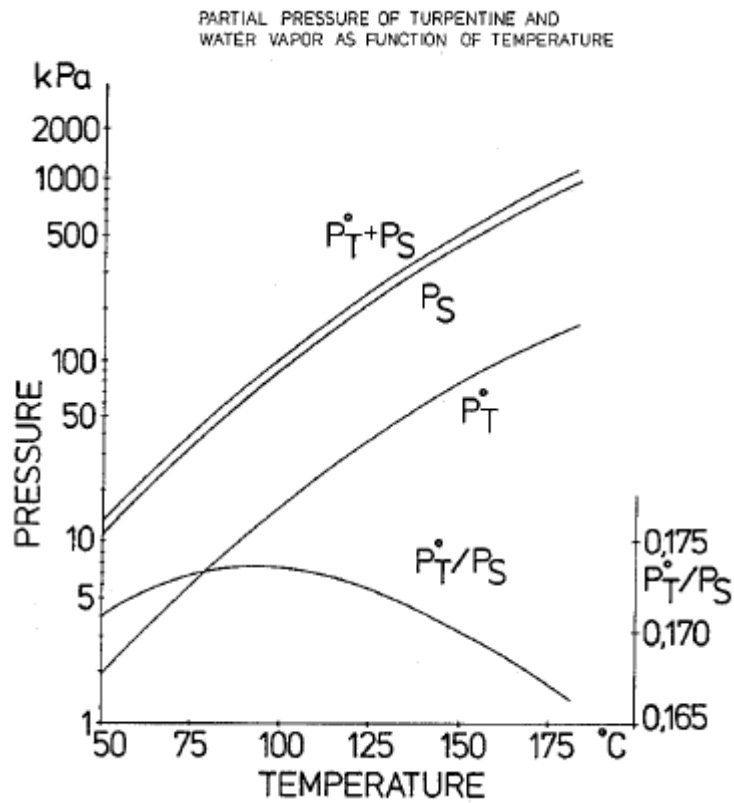


Figure 2. Partial pressure and water vapor as function of temperature. P_T is partial pressure of turpentine and P_S is pressure of steam.

Solubility of turpentine to the water can be seen from the figure 3. As can be seen from the figure turpentines solubility decreases when the temperature rises. Especially solubility of alcohols decreases fast when temperature is increased.

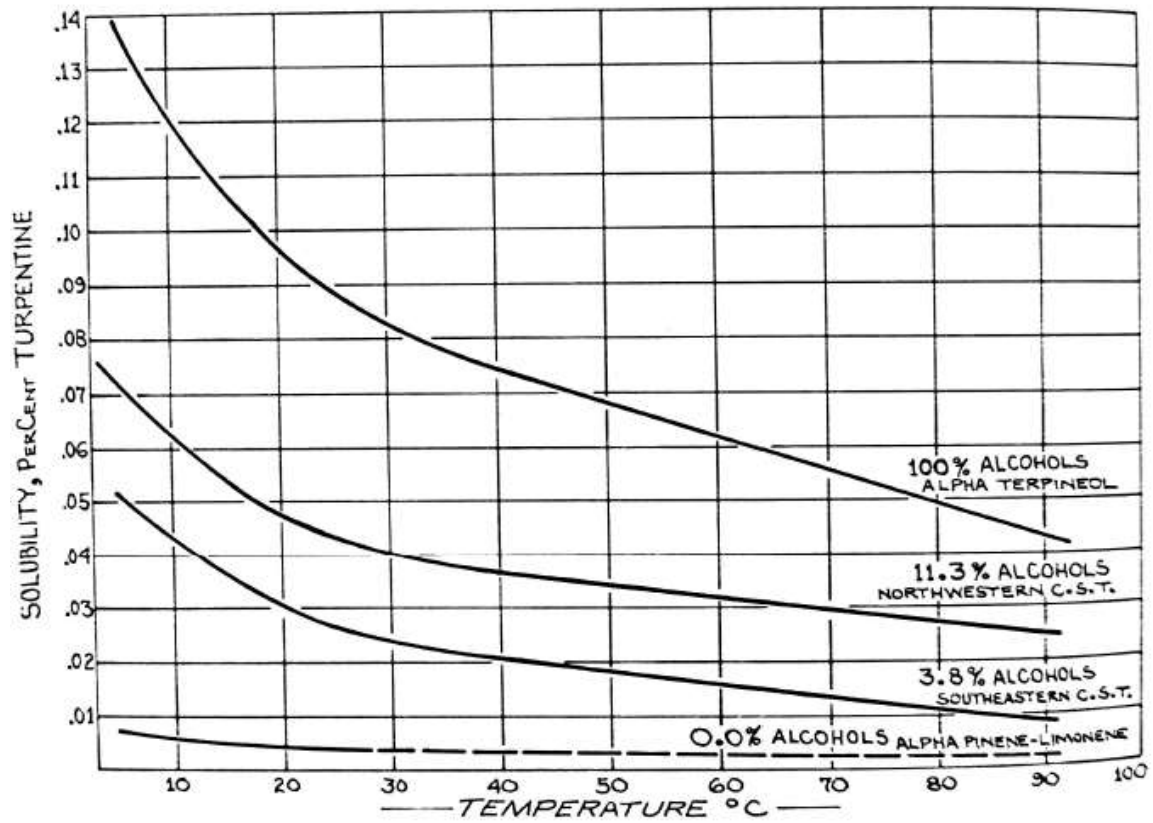


Figure 3. Solubility of the turpentine to the water is presented in the figure. (Drew et al. 1971, 42)

Flash points of commercial factors and pure components are presented in table 2. As can be seen from the table the flash points of turpentine components are low. Exact flash point is dependent on the composition of the CST since it can be varied.

Fraction	Flash point [°C]
Crude sulfate turpentine	34,4
Refined turpentine	37,8
Pine oil	79,5
Alpha-pinene	37,8
Camphene	37,8
Beta-pinene	37,8
Myrcene	45,0
Dipentene	46,0
Methyl chavicol	93,0
Terpineol	96,0
Terpinolene	96,7
Anethole	107,8
Dimethyl sulfide	-34,4

Table 2. Flash points of some commercial factors and pure compounds of the crude sulfate turpentine are presented in table. (Drew et al. 1971, 32)

2.3 Safety and environmental issues related to CST

Turpentine recovery process produces not only revenue as a saleable product but also lowers the steam demand by warming the cooling water in condenser, reduces the waste treatment costs and safety hazards of sewage streams containing turpentine. (Morgan, 1988) One of the most important reasons to recover turpentine is that if not removed from the process it

may cause hazardous situations because of its flammable nature. Its lower explosive limit is 0,8 volume percent and upper 6,0 volume percent. Flame speed is 150 m/s. (Tikka, Kovasin & Laxen, 2002) Explosions caused by turpentine can be catastrophic because of its fast flame speed. Turpentine amount in the non-condensable gas system should be minimized. If turpentine enters to the non-condensable gas system, for example if the turpentine condenser suffers from the lack of cooling water the turpentine might condense to the piping. In the pipe the turpentine and water will decant and if the interface between the two immiscible liquids is exposed to a shear force the friction between the two liquids can generate a static spark and ignite the turpentine. Shear force can occur if the liquids enter a fan or if they cascade from a horizontal pipe run down to a vertical pipe run down. (Frederick & DeMartini, 2017)

In displacement batch cook, where steaming in digester is not possible the turpentine is contained in off-gases from warm and hot accumulators. Even if the turpentine is collected from the gases, a lot of turpentine can be found from the non-condensable gases collection system. This is serious problem and several accidents have occurred in these systems. Turpentine also attaches to the soap micelles in black liquor and it might volatilize in unexpected places. Forming the turpentine balance of the mill can help in designing improved turpentine collection system. (Tikka, Kovasin & Laxen, 2002)

Inefficient turpentine recovery may cause turpentine dissolving to the cooking liquors. A high content of turpentine in spent liquors may cause odor problems in cooking and washing plant. It may also cause safety risks in the collection of weak odorous gases as turpentine may vaporize in black liquors in atmospheric tanks. During washing the weak odor gases may be problematic to handle. (Uusitalo et al. 2008)

Turpentine vapors and liquid must be handled in a manner that minimizes the risks to the fire explosion. Good ventilation, approved diking, flame arrestors, emergency vents and proper grounding must be provided in the storage areas. Electrical equipment in the storage area should be explosion proof type. (Drew et al, 1971, 8-14) Concentrated non-condensable gas should never be added to dilute non-condensable gas especially if it contains turpentine. (Frederick & DeMartini, 2017)

Turpentine reacts aggressively with oxidizing compounds. Crude sulfate turpentine includes organic sulfur components like methyl mercaptan. Turpentine is harmful for breathing and if in touch with skin. Turpentine might be lethal if drunk or if it affects in the respiratory organs. Turpentine irritates eyes and skin and it might cause allergic reaction to the skin. Main components alpha- and beta-pinene are toxic for the aquatic organisms and might cause long term adverse effect. (TTL, 2017)

While handling turpentine protective gloves, glasses and clothing should be used. Protective clothing should be prepared from fluorocarbon rubber, butyl rubber, silver shield, Tychem Responder or poly vinyl alcohol. Respirator mask A2 should be used if needed. Fume hood should be used in laboratory work. (TTL, 2017)

Turpentine is volatile compound and if released to the environment it mostly evaporates to the atmosphere. In atmosphere the main fraction, alpha-pinene, decomposes after impact of hydroxyl radicals and ozone. (TTL, 2017) If turpentine is released to the air it is one of the most offensive pulp mill odors. (Foran, 1992) From the ground turpentine evaporates quickly. Alpha-pinene bonds into the ground and its evaporation is partly prevented. In the ground turpentine is dissolved in aerobic conditions. Some of the components emanate but alpha pinene doesn't emanate aggressively. As described above solubility of turpentine is weak. Density of turpentine is lower than waters and it floats on top of water. Information about the enrichment of turpentine doesn't exist but alpha-pinene most likely enriches in environment. Turpentine is classified to be dangerous to the environment because of the toxicity to the aquatic organisms and long decay time. (TTL, 2017) Turpentine is problematic in the waste water treatment plant since it represents a BOD₅ load of 2 kg/l (16-20 lb/gal). (Foran, 1992)

Strömvall and Petersson have researched impacts of most important components of turpentine, monoterpenes, on the atmosphere. According to their research terpenes react rapidly in the atmosphere and form photo-oxidants. Phytotoxic photo-oxidants that are formed might contribute significantly to forest decline within 50 km of mills that are located along coasts. (Strömvall & Peterson, 1993)

2.4 CST markets and price development

Most important fractions that can be separated from CST are alpha pinene, beta pinene, delta-3-carene, camphene and limonene. They can be used in aromatic chemicals, adhesives, paints, printing inks and camphor for example. CST markets are dependent on the factors like increasing demand for fragrance ingredients. Increasing usage of personal care products like fragrances and cosmetics that include turpentine derivatives, will fuel the market growth of CST. The demand of CST is growing since there is increasing demand for these products in countries like Brazil, India and China. (Rohan, 2016) Most of the turpentine is used in U.S. and Europe. Figure 4. presents the regional turpentine usage.

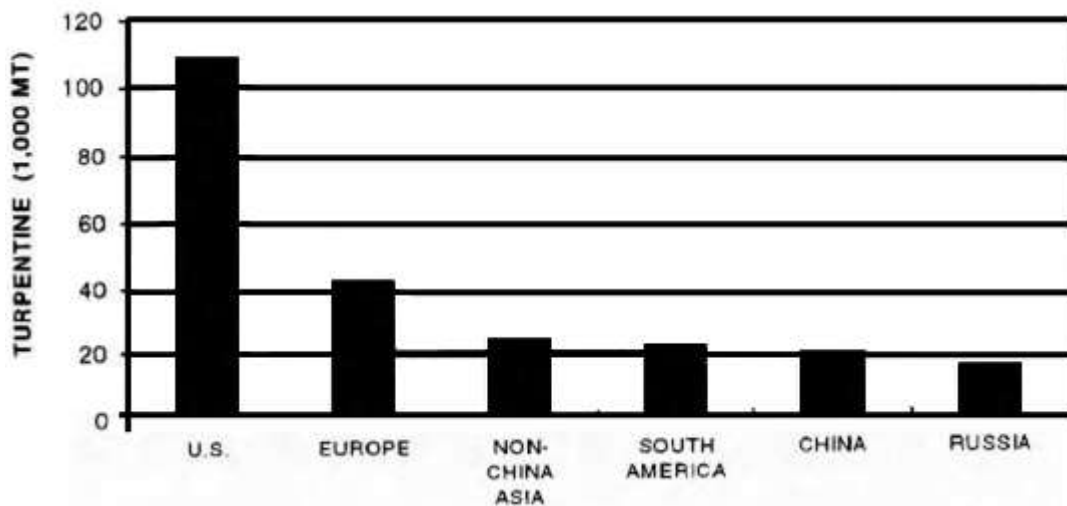


Figure 4. Turpentine usage amounts globally. (Gurkin, 1996)

For 30 years the CST prices have followed cyclic pattern. At highest CST price was at 1989 when it was around 0,49-0,50 €/l (2,10-2,20 US dollars per gallon). After the high point prices fell to under 0,11 €/l (50 cents per gallon) in 1993. Prices revived again to 0,40 €/l (1,75 US dollars per gallon) in 1998. (ICIS, 2003) Figure 5. shows the price development in the years 1998-2005 as US dollars per gallon. (ICIS, 2005)

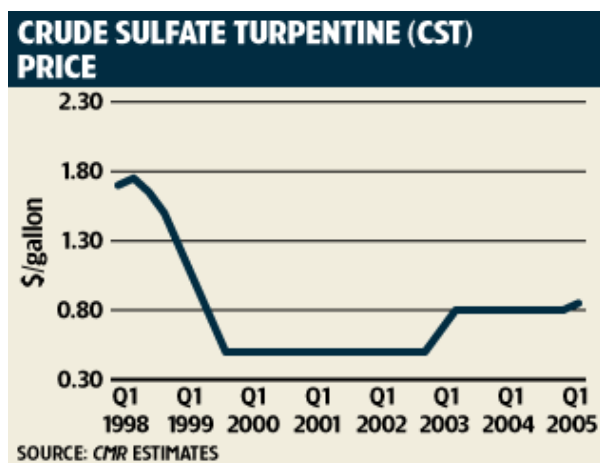


Figure 5. Crude sulfate turpentine price development at 1998 to 2002 in US dollars per gallon. (ICIS, 2005)

History of turpentine price development has been varied. Price of turpentine has been high and low depending on the demand of the chemicals that can be prepared from CST. Since turpentine is a by-product of pulp industry, pulp mills have even burned the turpentine as a fuel when the price of CST has been low and natural gas price has been high. This method gives some pressure to the market and in long term rises the price of CST. Burning CST is not recommendable since its hazardous nature and the strict permitting policy. (ICIS, 2005) Minor attention has been paid to turpentine recovery since it has played a minor economical role to the mills. In batch digesters the yield of turpentine has been lower than in other digesters and hence turpentine recovery has gained even less attention than in general. (Uusitalo et al. 2008)

3 PRODUCTION OF CRUDE SULFATE TURPENTINE AS A BY-PRODUCT OF PULP MANUFACTURING

50 % of the content of wood is something else than cellulose and can't be utilized as pulp in pulp production. These other fractions need to be utilized with other methods, as by-products or as fuel. Crude sulfate turpentine is one of the by-products of pulp production. It is recovered from the odorous gases formed while cooking. (Hase et al. 1990, 150-151)

3.1 Transportation and storing

As earlier mentioned the raw material of turpentine is soft wood, especially pine tree. The pine specie that grows in Finnish nature is Scots Pine, *Pinus Sylvestris*. (ITIS report, 2018) Life cycle of pine tree starts from the forest. After the pine tree is harvested it will be transported to the pulp mill with trucks (80 % of the total transportation), ships (5 % of the total transportation) or trains (15 % of the total transportation). (Seppälä et al, 2005, 20-21) Turpentine yield from wood starts to decrease from the day the tree is cut. (Tate, 1967)

When the wood arrives to the pulp mill it is measured either based on the volume or the weight of the wood. Wood is stored either after land transportation on asphalt fields on piles that are sorted by the tree species or after floating transportation in the water storage. Size of the inventory depends on the mill and the trend is to have smaller and smaller inventories to minimize the storage expenses and to improve the quality of the wood. (Seppälä et al, 2005, 21-22) Normally the storage is enough wood for 1-7 days of production. (Know Pulp, 2016) Storage losses of terpenes are most significant at the summer time and best way to avoid them is to keep the storage times as short as possible. Terpene losses from ground wood can be minimized by using underwater storages. (Strömvall et. Peterson, 2000, 90) Funguses and insects have also an effect on the wood in storage at the summer time and they decrease the yield of the pulp and tall oil. In mechanical pulp production water storage is recommended because moistness of the wood is a requirement for the production. Cold storing is also one possibility to avoid the pest damages. (Seppälä et al, 2005, 21-22)

3.2 Wood handling

At the winter time in the wood handling the wood is de-iced with warm water or steam on the debarking drum infeed conveyor before being debarked. Debarking of the wood is done at the debarking drum. The loose bark is removed from the drum through bark slots. Rest of the bark, stones and short wood is removed from the wood flow. Bark is shredded and directed to the energy production. Debarked logs are washed under water showers. (Know Pulp, 2016)

After debarking the logs are chipped. Chipper infeed line takes the logs from the debarking drum to the chipper. Chipper infeed line removes the bark at the bark removal rollers, and the stones and sand are separated from the logs and logs are washed. Metals are also removed, oversized logs and short wood are picked out and logs are spread before the chipper. With high capacity it is recommended to separate the short wood and chip them separately with the short wood chipper. Aim of chipping is to produce homogenous chips with the minimum number of pins and fines. (Know Pulp, 2016)

After chipping the chips must be screened. In screening oversized chips are cut into accepted size pieces and returned to the main chip flow. The smallest fractions are separated and usually burned with the bark. Screening doesn't improve the chip quality, it just separates wrong sized fractions. Over thick chips are undesirable since they do not cook thoroughly in the sulfate cooking, they also impair the quality, homogeneity and yield of the pulp. (Know pulp, 2016) Wood chips are stored either outside as a pile or in the silos. Mill can store more wood as chips than it can store as logs. (Seppälä et al, 2005, 35) Chip storing times should be as short as possible to minimize the turpentine losses during storing this can be seen from figure 6.

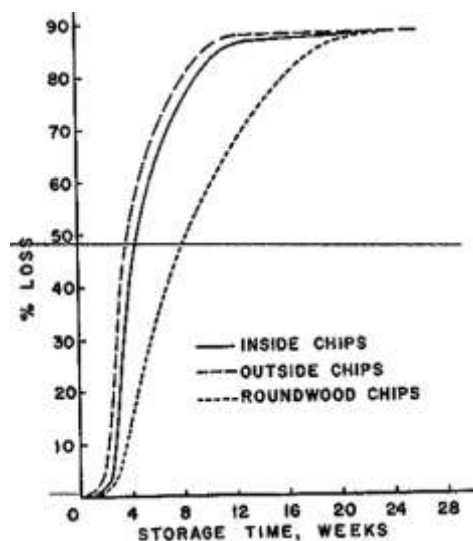


Figure 6. Picture presents the effect of storing to the yield of turpentine. (Thornburg, 1963)

As seen from figure 6. round wood retains turpentine best during the storing. Inside chips of the pile store turpentine a little bit better than outside chips but the difference is not

significant. Wood stores the turpentine well for the first two weeks of storing but after that the turpentine losses are increasing significantly. If storing is longer than 8 weeks already more than 88 % of turpentine content is lost. (Thornburg, 1963)

Resin of wood changes in chip storing fast because of the activities of micro-organisms and their decomposition increases the temperature. Increase of the temperature in chip pile increases the loss of extractive substances of the wood. (Seppälä et al, 2005, 35) If the chips are stored from four to eight weeks or longer, depending on the reference, the yield of turpentine and tall oil is significantly decreased. (Know Pulp, 2016) (Seppälä et al, 2005, 35)

3.3 Cooking

The aim of cooking is to separate the lignin with the heat and chemicals so the chips defibrate easily. Fibers that contain cellulose are to be kept as long, unbroken and strong as possible while cooking. Cooking chemicals dissolve as much lignin as possible and as little cellulose as possible. Wood extractives that can cause foaming and precipitants are attempted to be removed. (KnowPulp, 2016) The cooking process also separates raw turpentine, raw soap and other organic components from the chips. (Seppälä et al, 2005, 75)

Sulfate process utilizes a mixture of sodium hydroxide (NaOH) and sodium sulfide (Na₂S) or more commonly known as white liquor. Sodium hydroxide degrades the lignin and sodium sulfide speeds up the process and decreases the dissolving of the cellulose. Reaction temperature is normally between 150-170 °C. Several variations of cooking process exist which are based on various liquid changes during the cooking. The purpose of changing the reaction conditions is to improve pulp quality and decrease energy consumption. (Know Pulp, 2016)

In the beginning of the cooking terpenes are distilled with the gassing vapors. Terpenes evaporate when the temperature arises above 70 °C so they are already vaporizing on the beginning of pre-steaming phase of the chips or in the beginning of cooking during the temperature arising phase. The terpenes evaporate in a chip bin or in the digester gas

processes together with steam and non-condensable odorous gases. (Know Pulp, 2016) Optimizing the digester heat-up rate and vent relief rate is very important for the turpentine recovery. (Fletcher, 1989) Typical problem of the displacement batch digester for the turpentine recovery is that the digester has high starting temperature in the actual cooking phase and the digester is heated up to the cooking temperature faster than in conventional cooking. The other problem is that the time at gas-off is short and during chip pretreatment no gas-off occurs. (Uusitalo et al. 2008)

Cooking process can be completed either with the batch method or with the continuous method. (Seppälä et al, 2005, 75) This thesis is concentrated on the batch method. Batch method can be divided to traditional batch cooking and displacement batch cooking. Traditional batch cooking is rarely used anymore in mills, but it is still used actively in laboratories. (Seppälä et al. 2005, 84) Displacement batch cooking is based on the recovery heat utilization from the previous batches in the heating of the next batches. The remaining chemicals of the black liquor, mainly the high sulfidity, are utilized. Hot black liquor is stored to the high-pressure accumulator tanks and fed to the impregnation and heating steps of the following cooks. In displacement batch cooking the cooking is interrupted by pumping cooler washing filtrate to the bottom of the digester that displaces the hot black liquor. (Know pulp, 2016) Other difference of the displacement batch cooking to other methods is that the digester is operated with higher liquor-to-wood ratio and this is the other reason why the turpentine dissolves in the black liquor and recovery rate decreases. (Uusitalo et al, 2008)

In displacement batch digesters the digester is either degassed to a pressurized spent liquor accumulator and from there to the turpentine recovery or the digester is degassed straight to the turpentine system. Some combinations of the two also occur. When applying degassing to the pressurized spent liquor accumulator the turpentine recovery is based on pressure control. The target is to retain overpressure in the spent liquor accumulator because it forces the liquor through heat recovery system to the atmospheric tank and controls boiling of the liquor. Little vaporization of volatile compounds occurs in the accumulator. The turpentine solubilizes in the black liquor and this will decrease the yield of turpentine because the pressurized accumulators are constantly held at a significant overpressure. Turpentine that

is not recovered may cause process disturbances. (Uusitalo et al. 2008) Figure 7. presents the gasification system from the digesters in the older type SuperBatch cooking process.

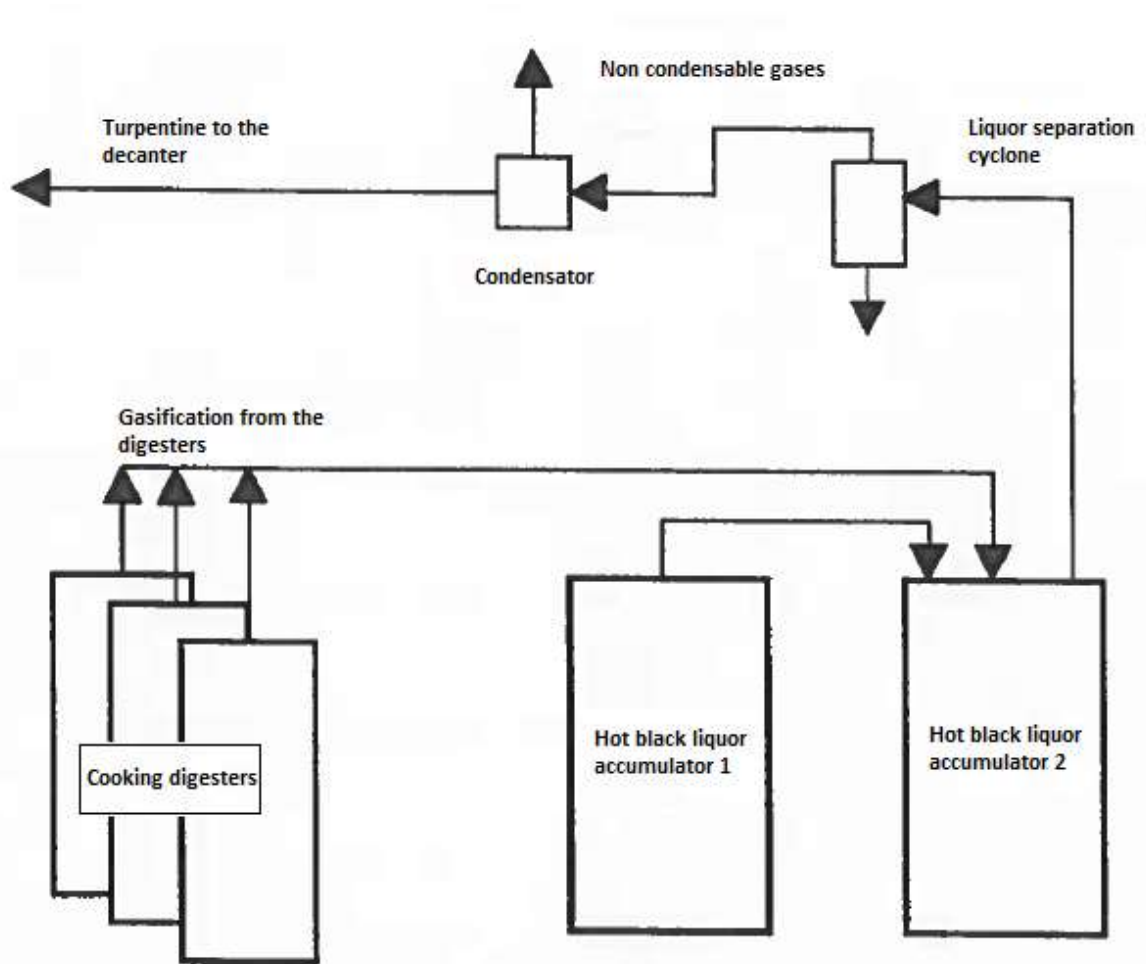


Figure 7. Vapors from the cooking digester are vented to the hot black liquor accumulators and from there they are directed to the turpentine recovery system. (VTT-Kemiantekniikka, 1998)

Four different types of displacement batch cookers exist; SuperBatch, RDH (rapid displacement heating), Enerbatch and Cold Blow. SuperBatch is the most common version of batch cooking. In the SuperBatch method the chips are impregnated with washing filtrates. The chips first encounter impregnation liquor that is cooled down to 90 °C degrees. Low temperature is better for the strength of the pulp and it decreases the need of alkali in impregnation stage. Modern SuperBatch-cooking systems include only one hot black liquor accumulator, white liquor accumulator, a displacement liquor tank and black liquor tank. The liquor accumulators are laying horizontally. In the first SuperBatch cookers were two

high pressure storing tanks, also known as the hot black liquor tanks 1 and 2. (Know Pulp, 2016)

3.3.1 Stages of displacement batch cooking

Displacement batch cooking system has six stages. The first stage of batch cooking is the chip filling. Steam is used to enhance the packing of chips. Steam stabilizes the moisture of chips and removes air from them. The washing filtrates impregnate better to the chips because of this. Terpenes evaporate while steaming and in the beginning of cooking. (Paper Asia, 1997) If a large amount of steam is used in chip filling the turpentine losses might occur. The problem is that the gases from first stage are not recovered. (Drew et al. 1971 67-68)

Second stage is warm liquor filling. Digester is filled from the bottom with warm black liquor, leftover black liquor is returned to the warm liquor tank and back to the evaporation plant. Digester is full of fluid until the end of the cooking. Pressure of the digester is increased with the liquor pump. During impregnation the temperature arises up to 80-90 °C. (Paper Asia, 1997)

The third stage is hot black liquor and hot white liquor filling. Warm liquor is displaced with the hot black liquor. When hot black liquor is pumped the hot white liquor is introduced with the hot black liquor. The replaced liquor comes out the digester and it is divided according to temperature. The liquor that is under 100 °C is pumped to the warm liquor tank and the liquor that's temperature is above the 100 °C is directed to the colder hot liquor accumulator. (Paper Asia, 1997)

The fourth stage is heating and cooking. While using two hot liquor accumulator the heating is completed by directing the mid-pressured steam to the circulation pipe. Circulating pump of the digester is started and kept running through the cooking. (Paper Asia, 1997)

The fifth stage is evaporating of the turpentine and heat transferring. Evaporating of the turpentine is completed as the fluid travels from the hot liquor accumulation to the turpentine

system. It is also possible for turpentine to evaporate from the warmer accumulator to the colder. The fluid starts to evaporate when the temperature reaches 125 °C. The gases are directed from the evaporation sieve to the colder accumulator and from there to the turpentine recovery. From the colder hot liquor accumulator, the liquor is pumped through the heat transfer unit to the warm liquor tank. The recovered heat is used to heat the white liquor and to production of hot water. White liquor needs to be heated with the mid-pressured steam to achieve a temperature of 170 °C. (Seppälä et al. 2005, 86)

The last stage is displacing and the emptying of the cooker. Cooking filtrate is displaced with the washing filtrate which can also be called displacement liquor. Cooking filtrate is directed to the warmer accumulator and when the temperature decreases to 155-160 °C the filtrate is pumped to the colder accumulator. Rest of the filtrate, that's temperature is less than 90 °C, is guided to the warm liquor tank. The digester can be emptied with pressurized air or with centrifugal pump. Dilution liquor is pumped to the bottom of the digester. (Seppälä et al. 2005, 86-87)

3.4 Pulp washing

After cooking and brown stock washing (pre-oxygen washing), sodium hydroxide/oxidized white liquor and magnesium sulfate is added to the soft wood pulp and the pulp is handled with oxygen. Purpose of handling is oxidation reaction of lignin, so lignin dissolves with liquor. After this the pulp is washed. Purpose of pulp washing is to recover the cooking chemicals and wood material from the fibers. After pulp washing it is important that pulp contains the least amount of black liquor as possible, and the cooking chemicals are recovered as efficiently as possible. (Seppälä et al. 2005, 98-101)

Ineffective turpentine recovery can cause problems in washing. Pulp is challenging to de-water and wash. Problems in washing can cause increased demand of chemicals, lower quality of pulp due to high wash losses in bleaching. High turpentine content has a negative effect on soap separation from spent liquors. High content of turpentine in pulp is environmental harm and safety risks might occur if the volatile compounds may evaporate

in washing plant. Efficient pulp production, high quality pulp and high recovery efficiency of turpentine often go hand in hand. (Uusitalo et al. 2008)

3.5 Evaporation plant

The black liquor from cooking is directed to the evaporation plant. After cooking the pulp is directed to the pulp washing. There the black liquor is washed out from the pulp and guided to the evaporation plant. The black liquor from the pulp washing is called washing liquor. The evaporation plant includes several heat transfer units. Inputs of the evaporation plant are black liquor, hot steam and cooling water and the outputs are primary condensate, strong black liquor, secondary condensate and warm water. Aim of the evaporation plant is to evaporate water efficiently from the black liquor, so it can be burned in the power plant. (Seppänen et al, 2005, 147-148)

The recovery of the by-products such as methanol, turpentine and tall oil soap should be considered in the evaporation plant. Turpentine is usually separated from the cooking condensate. (Know Pulp, 2016) If the venting is ineffective the turpentine can be found from the liquors. (Uusitalo et al. 2008) The gas, that has evaporated from the liquor in the evaporator, is directed to the mist eliminator. Mist eliminator removes the liquor drops from the gas. Stripper separates the vaporous substances from the condensate. Stripper system includes several heat transfer units, condensers and stripping column. The gas is separated from the condensate in stripper. (Seppänen et al. 2005, 152-153) Turpentine rich streams from the evaporation plant are usually directed to the foul condensate tank and turpentine recovery from this stream can be handled with the stripper added between the cyclone separator and surface condensers. (Tyre, 2018 a) This system is described more specifically in the next chapter.

3.6 Turpentine recovery

After the venting from the cooking digester or accumulators the turpentine and other gases are directed to the liquor separator. Vapor is directed to the two-staged turpentine condenser

where it will release the heat and condensate. From the first stage the condensate can be guided to the turpentine scrubber, where the strong odorous gases are separated from the condensate. (Seppälä et al. 2005, 86) Surface condenser separates turpentine, water and non-condensable gases. Turpentine condenses easily to separate fluid when temperature is decreased. Non-condensable gases are directed to the strong odorous gases stripping. Turpentine is separated from the odorous non-condensable gases to avoid explosion danger. The condensate includes turpentine and water. The condensate from the surface separator is collected to the decanter and there turpentine raises above the water because it is lighter than the water and poorly soluble. The raw turpentine can be removed from decanter with overflow. Water is guided to the condensate stripping system. (Pulp and Paper, 2018) Typical batch systems turpentine recovery system flow sheet is presented in figure 8.

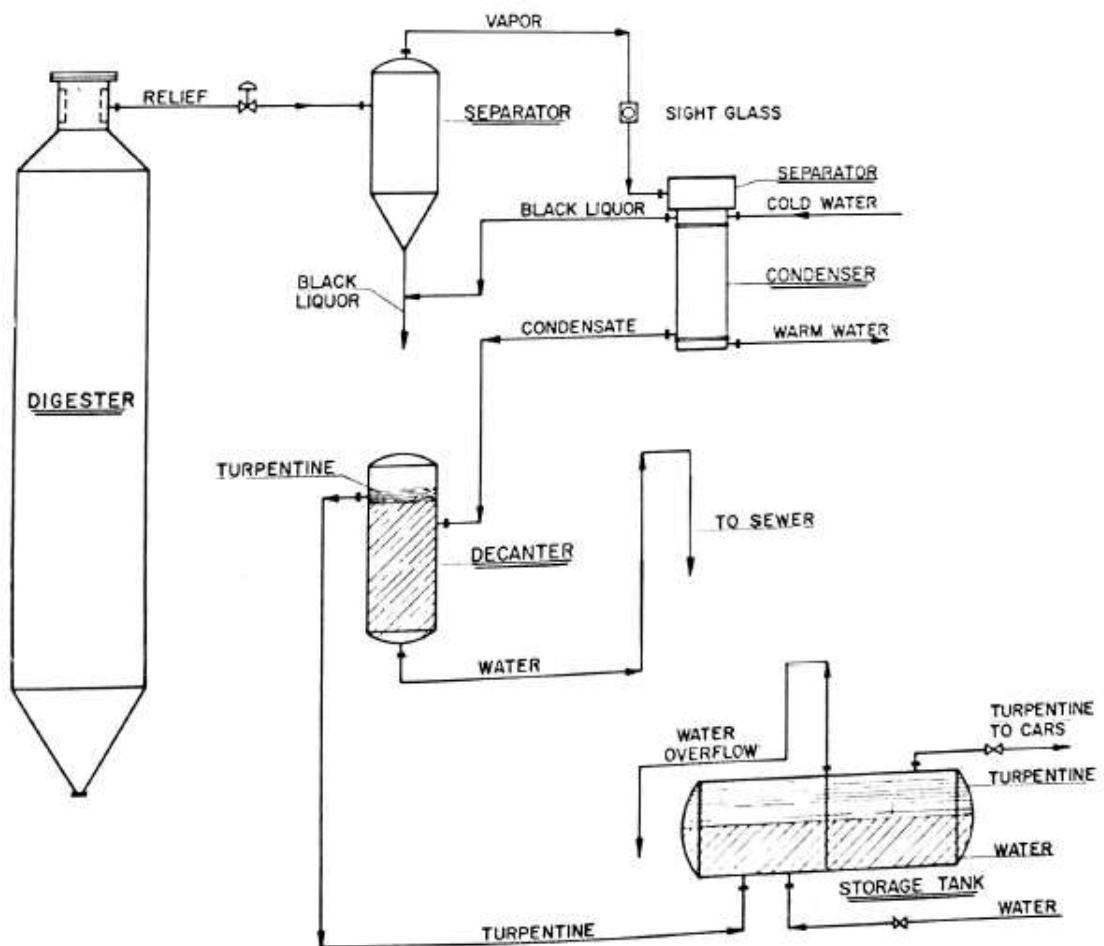


Figure 8. Typical flow sheet of the batch cooking system in crude sulfate turpentine production. (Smook, 1994, 157)

According to several references turpentine that is not decanted in the turpentine recovery system can be stripped from stock and liquor streams. If turpentine is not separated in the digester it ends up to the foul condensate tank and decants on the top of the tank. To reduce the amount of foul condensate loading to the stripper and turpentine decanter the digester condensate can be segregated with its own stripper. Turpentine strips easily and it goes through the stripper off gas system. It causes problems at the incineration point usually a high temperature trip. Turpentine can be avoided to build up to the storage tanks with several methods. The first method is to send the decanter underflow straight to suction of the stripper feed pump. The second method is to make sure that the condensate is agitated. Agitation prevents the turpentine condensing on the top of the storage tanks. Turpentine can also be skimmed. It can be done periodically by returning the turpentine into the stripper feed condensate. (Lin, s.a.), (Frederick & DeMartini, 2017) Turpentine system that includes the stripper is described in the figure 9.

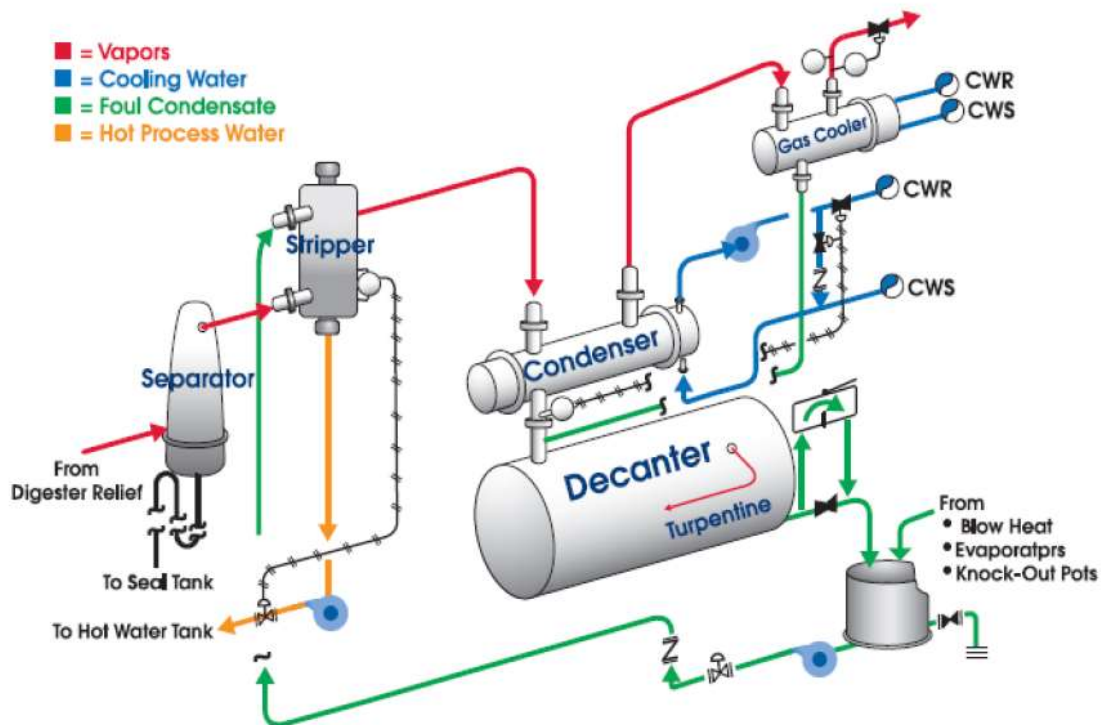


Figure 9. Turpentine separation from the foul condensate with stripper. (Morris, 2015)

3.7 Turpentine losses during the process

As mentioned before the raw material of the turpentine is pine tree. After the wood is harvested it is transported, stored, debarked and chipped. Wood chips are stored in the chip pile and they are cooked in cooking digester. As can be seen from the figure 10. several turpentine losses occur during the process.

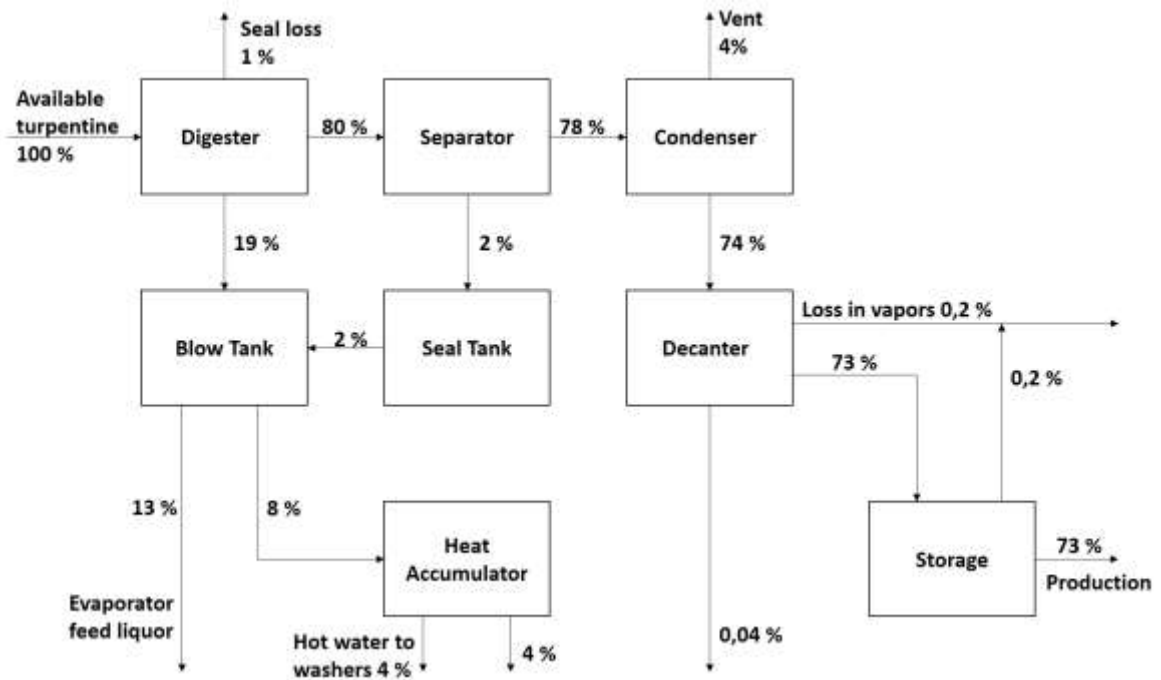


Figure 10. Figure presents typical turpentine production material balance in batch cooking process. (Drew et al. 1971, 67)

Displacement batch systems are problematic for the turpentine recovery and often the turpentine can be found from the pulp discharged from the digester, spent liquors or non-condensable gas system. In black liquor the turpentine causes problems to the soap solubility and it changes the behavior of the soap. (Uusitalo et al, 2008)

Tate has done a lot of work in determining the turpentine losses from the turpentine system already in 1967 and he noticed that turpentine can be lost through leaky head closures, particularly in the gate valve type of closure. Hydraulically operated gates leak always, and they are covered with some water. Turpentine water and steam condense, and the condensate is discharged to the sewer. It has been shown that it is economical to change the gate valve type of closure to another type of automated closure. Turpentine emulsifies extensively in

the seal water because of the presence of black liquor, which has also leaked through the closure during the cook. A de-emulsifier can be applied to the collected turpentine emulsion stream and turpentine can be separated from effluent. Separated turpentine can be directed to the turpentine decanter. De-emulsifiers are expensive and because of that the content of turpentine in the effluent needs to be high enough to cover the expenses. On the other hand, the process produces environmental value since the turpentine is removed from the effluent stream instead of releasing to the nature. (Tate, 1967)

Safety relief valve is placed in turpentine separator line in most mills. If the pressure gets high enough turpentine and water mixture is blown outside air and lost to the atmosphere thorough this valve. The relief pressure should be adjusted higher pressure than that needed to blow the seal to avoid unnecessary turpentine losses through the safety relief valve. So, if the pressure gets high first safety relief would be thorough liquid seal leg and only if the liquid seal leg is also plugged the turpentine would be blown to outside. (Tate, 1967)

Terpene gas from cooking digester includes also other volatile substances, steam, drops of liquor and fibers. Drops and fibers are separated in cyclone separator before the condensing. (KnowPulp, 2016) Efficiency of the next step, surface condenser, depends on the cyclone separator and the separation is referred to be most important single operation of the system. If the fiber and black liquor are not separated properly, they will upset the system regardless of the condenser design. Fiber and liquor harm the process, fiber fouls the tubes and black liquor emulsifies the condensate. These components reduce turpentine yields if they remain in the process. (Marks, 1967) Black liquor can form an insulating scale. (Drew et al. 1971, 75) Thermometers should be installed right before the cyclone separator and in the cyclone separator itself. These temperatures should be checked regularly in order to determine if there are losses occurring. (Tate, 1967)

According to Foran, the turpentine condensing systems, that are used to collect the turpentine from the condensates, are mostly not working properly in batch digester systems. Turpentine bearing condensates are condensed often in two stages and this is done to minimize the stripper size. The problem with batch systems is unstable condensate temperature. The condensate should be kept above 98 °C because below that temperature turpentine

condensation starts to occur. The temperature should be above 102 °C because of the localized sub cooling. The problem is that the sudden swings in condensing load can't be handled quickly enough by using feedback temperature control. (Foran, 1992)

Turpentine can be lost from the surface condensers if the condensers are under sized or fouled. In this case the turpentine is lost as a vapor through the condenser vent. Temperature of the condensate leaving the condensers should be measured regularly and if the temperature is less than 49 °C the condensers require maintenance. Preventive maintenance is possible if the mill has enough of experience. Turpentine losses from the condenser vents will always occur and these losses can be recovered in a vent scrubber system. (Tate 1967)

After condensing the turpentine is directed to the turpentine decanter. Turpentine decanter separates the turpentine from the water by gravity. Horizontal tank as a decanter is more effective than the vertical tank. Most of the turpentine losses are through the emulsions. Normally turpentine and water don't emulsify but presence of black liquor causes emulsion that is hard to break. If emulsion is formed in the decanter the first thing to check is the cyclone separator. If the cyclone separator is not working properly the black liquor carryover might be the reason to the emulsion forming. Emulsion can be broken with caustic or white liquor and in some cases sulfuric acid can be used. (Drew et al. 1971, 79) Some of the turpentine system losses can be seen from the table 3.

Table 3. Turpentine losses in the batch and continuous digesters from the digester accumulators, decanter underflow and evaporator condensates. (Frederick & DeMartini, 2017)

Source		Turpentine [kg/t]
Batch digester	Digester accumulator over flow	0,5
	Turpentine decanter underflow	0,5
	Total evaporator condensate	0,25
Continuous digester	Turpentine decanter underflow	0,5
	Total evaporator condensate	0,5

Some turpentine is lost through the vents to the atmosphere. The turpentine from the gases can be recovered by directing all the vapors to a scrubber system. Turpentine from decanter underflow water can be recovered by pumping it through a heat exchanger. Heat exchanger cools the underflow water and the underflow water can be used to scrub out the vapors in a packed scrubber column. Water and condensed turpentine are returned to the decanter. (Tate, 1967)

Yield of turpentine as by-product of pulp production is 4-12 kg per ton of pine pulp or 2-15 kg per tons of pulp depending on the reference. (Seppälä et al, 2005, 145) (Know Pulp 2016) As earlier explained, turpentine is collected from the cooking with other volatile substances and can be collected from the foul condensate from the evaporation plant. (Know Pulp, 2016) Foul condensate can contain 1-2 kg/ADt of turpentine. (Frederick & DeMartini, 2017) If the turpentine could be collected while steaming, quality of turpentine would be the best. Displacement batch cooking doesn't have steaming stage and this effects on the quality of the turpentine. The turpentine from other stages than steaming includes more sulfur because of the reactions with the liquors. (Know Pulp, 2016)

3.8 Aspects affecting yield and quality of turpentine

Several aspects effect on the yield and quality of the turpentine from the quality of the wood to the collecting methods. Yield of turpentine from the pine tree is from 2-15 kg of turpentine per ton of pulp and for spruce 2-3 kg per ton of pulp (Know Pulp, 2016). Industrial yield of turpentine from Scots Pine round wood is 13,3 kg per metric ton of dry pulp and from chips 10,2 kg per metric ton of dry pulp. (Störmvall et. Peterson, 2000)

According to the theoretical yield of turpentine can be noticed that increasing amount of spruce in the pulp decreases the yield of turpentine. The theoretical yield of turpentine depends on growing conditions of the tree. Yield of turpentine is larger from the trees that have grown in north than from the trees that have grown in south. (Hall, 2000) In pine trees content of the oleoresin is bigger in the heart wood than in the sapwood. The content of the terpenes and yield of turpentine in the wood from the sawmills is smaller because the chips from the sawmill include more the sapwood than heart wood. (Störmvall et. Peterson, 2000)

The age of tree effects also on the yield of turpentine. Older trees contain more turpentine than juveniles. (Hall, 2000)

One of the displacement batch cooking types is rapid displacement heating (RDH). In displacement batch cooking digesters venting is completed through liquor accumulators. The potential turpentine recovery may be significantly below the conventional batch cooking because of this method and turpentine is lost in liquor carry over. (Foran, 1992) In sulfate cooking process the yield of turpentine is significantly lower than in the kraft process. Conventional batch type was the best method to get high yields of turpentine, but modern mills are using other designs, and this reduces turpentine yields. (Anon, 1990)

In the conventional batch process the turpentine is removed from the chips by steam distillation. Experiments have shown that turpentine should be removed early in the cook to reach maximum recovery of turpentine. Turpentine starts to release from the chips when the pressure of the digester is about 4 bar (60 psig). Rapid digester heat up rate is better for the turpentine and the optimum vent relief profile consists of restricting the vent relief until 4 bar is reached in order to conserve steam then relieving rather rapidly until almost all of the turpentine has been removed which is about the same time when the cooking temperature is reached. (Anon, 1990) If the temperature rise is longer turpentine starts to form in higher pressure. It might be caused by the reaction between turpentine and other organic components in the cooking liquid. (Drew et al. 1971, 69) In most continuous processes the digester is hydraulically full. There is no vapor space and turpentine can't be removed by venting the digester. Instead the turpentine is removed from black liquor by flash evaporation. This method is not very effective and some of the turpentine is lost in the evaporation where it is ultimately lost in the condensate or to atmosphere. (Anon, 1990)

Quality of turpentine from the beginning of the cooking is usually better than the quality of turpentine from the end of the cooking because of the lower temperature. In lower temperatures the sulfur compounds haven't formed yet. Difference between SuperBatch and conventional cooking is that the cooking temperature is higher in the beginning of the cooking. (Ranua & Stenlund 1983, 1359) After cooking the pulp is directed to the blow tank

and from the blow steam it is possible to recover turpentine. Sulfur content of this turpentine is usually high. (Foran, 1995)

If the turpentine doesn't evaporate during the cooking and stays in the digester until the end of cooking, it is lost to the blow tank. Part of turpentine might steam-distill in the blow tank and condense in the heat accumulator, but it will be lost. If there are larger amounts of turpentine in the liquor it is lost in the condensate from the evaporators. It is possible to control the amount of the turpentine left in the liquor by regulating the flow rate of the vent vapor relief. Rate should be great enough to ensure the removal of all the turpentine but should be as small as possible in order to conserve steam usage in cook. Turpentine amount in the pulp should be checked regularly to ensure complete turpentine removal while using a minimum amount of steam. (Tate, 1967)

3.8.1 Metsä-Botnia Ab, Kaskinen turpentine research

Background of research at Kaskinen was that the mill started to cook only hard wood except the soft wood sawdust cooks. After this the yield of turpentine was low and its reactions were not known well enough. They wanted to do the research in the Kaskinen mill because of this. In the beginning of the research they noticed that while cooking aspen the yield of turpentine was larger. Aim of the research was to make turpentine separation more efficient but not at the cost of safety or the productivity of other processes. The work was completed by collecting and analyzing liquid samples. Goal of the research was to clarify production of turpentine during cooking, turpentine separation, black liquor evaporation, foul condensate stripping and methanol liquifying. (Niemelä, 2004)

Several samples were taken to clarify the situation. Chip samples of aspen and birch and fresh and 1-2 weeks old sawdust. Each of these samples were cooked in sodium hydroxide (NaOH) and the turpentine formed was caught with the device included to the system. Hard woods didn't transpire turpentine and the fresh sawmill transpired more turpentine than the old one. (Niemelä, 2004)

Samples from the turpentine decanter system were from the sawmill digesters condensate, flow from the turpentine scrubber, in coming water to the turpentine decanter, brine, turpentine from top of the turpentine decanter and turpentine from the turpentine tank. Thick solid material formed on the top of the turpentine decanter. This material was mixed up with the turpentine. Sample was taken from this material. It was analyzed with a microscope, but they couldn't clarify what this material was. In coming water to the turpentine decanter and brine were analyzed and their turpentine content was clarified. The methanol content and some other compounds were also analyzed. According to results some alcohols were separated with the turpentine. (Niemelä, 2004)

Samples from the evaporation plant were from the feed liquor, intermediate liquor, heat treated gas coolers condensate, foul condensate, methanol and methanol column. Turpentine evaporates from the liquor with the steam and after that the evaporated turpentine and steam are condensed. The liquor was analyzed because there wasn't possibility to take sample from the condensate. Liquor samples didn't include a lot of turpentine. The foul condensate included a lot of monoterpenes, monoterpene alcohols, sesqui-terpenes and several other compounds. In the foul condensate, unlike in the turpentine, was more of monoterpene alcohols than monoterpenes. (Niemelä, 2004)

Key results of the test were that there is produced 1,6 kg of turpentine per pulp ton and 1 kg of turpentine per pulp ton is lost with the foul condensate. A turpentine phase is not formed on the top of the methanol tank and it seems that the turpentine is dissolved to the methane. Very small amounts of turpentine was found in the feed liquor and intermediate liquor. (Niemelä, 2004)

Suggestion to improve the turpentine recovery is that while cooking hard wood, condensate is not directed to the turpentine separation but to the foul condensate tank. If the condensate from the saw dust cooking is only taken into the turpentine separation, turpentine content in the input should increase and methanol content in input should decrease. The retention time in the decanter will increase and the fiber content decrease. The turpentine separation should be more effective and also the amount of monoterpene alcohols in foul condensate should decrease because of these. (Niemelä, 2004)

3.8.2 UPM-Kymmene, Metsä-Rauma, Enso and Sunds Defibrator Pori Oy Black liquor expansion tests

In the tests content of turpentine in the different liquor flows was determined and the discharge of turpentine from the liquor flows by expanding black liquor. Study was completed at Metsä-Rauma and it was part of cooking plant development co-operation between UPM-Kymmene, Metsä-Rauma, Enso and Sunds Defibrator Pori Oy. Expansion tests were completed with the liquors from hot black liquor accumulators 1 and 2 and liquor of the cooking cycle. Figure 11. presents the test arrangements and the sampling points. (Hietaniemi & Saine, 1999)

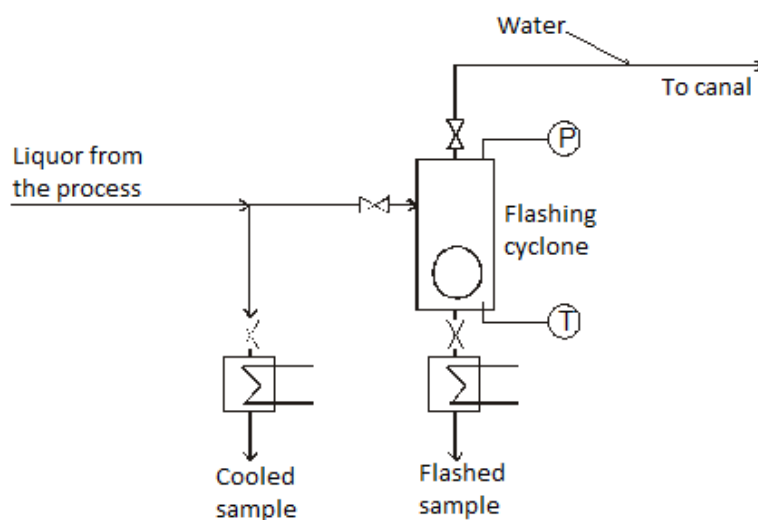


Figure 11. Figure shows black liquor flashing test arrangements and the sampling points. (Hietaniemi & Saine, 1999)

The turpentine content of the liquor was 74 mg/l from the sampler of hot black liquor accumulator 1 and 47 mg/l from the cyclone after the pump. Figure 12. shows the effect of liquor expansion in hot black liquor accumulator 1 on the turpentine content. (Hietaniemi & Saine, 1999)

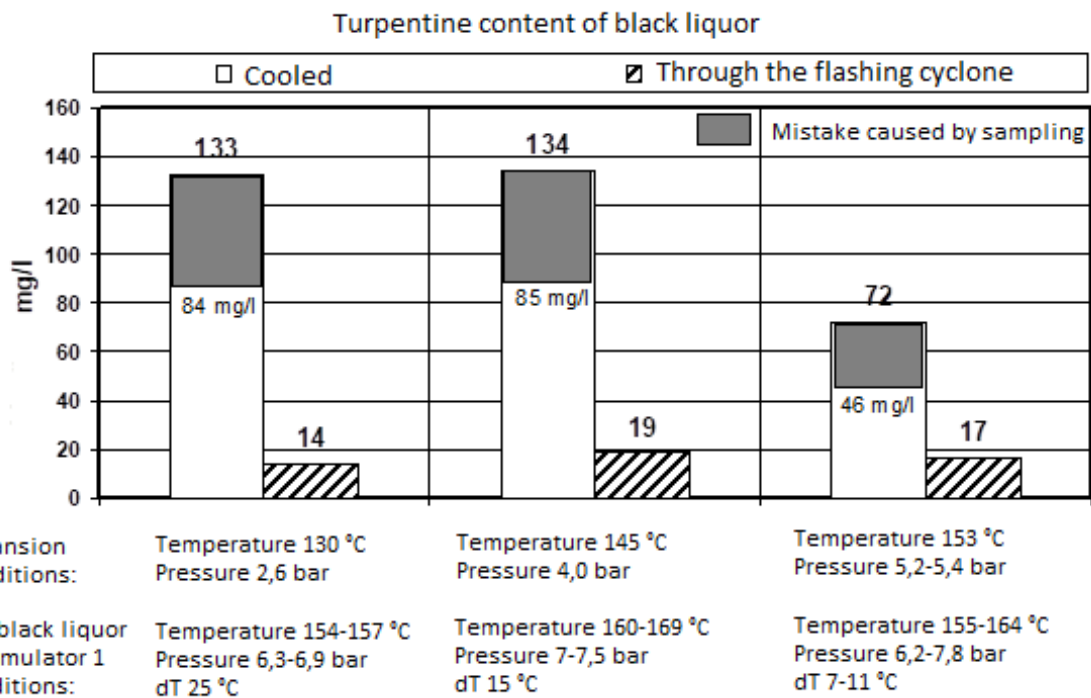


Figure 12. Effect of different conditions while black liquor flashing. (Hietaniemi & Saine, 1999)

As can be seen from the figure increasing the temperature from 130 °C to 153 °C didn't affect the turpentine content of the liquor from the expansion cyclone. Changes in the turpentine content of liquor through the flashing cyclone are caused by the different amounts of tall oil in the liquor samples. This makes the results difficult to compare to each other. Turpentine content of the black liquor after expansion was significantly lower than the turpentine amount of the cooled sample. The quality of the turpentine obtained was planned to be determined but the liquor foamed very easily and because of foaming the quality couldn't be determined. Foaming could have been avoided if cyclone separator was used. Turpentine and tall oil profiles of cooking liquors were determined. (Hietaniemi & Saine, 1999)

Figure 13. shows the results of the tests that researched minimum temperature difference in hot black liquor accumulator 1 (HBL1). The initial level was determined in the liquor run through the cyclone in the beginning of the test before the expansion. Aim of the minimum temperature test was to determine the effect of black liquor expansion on the turpentine content of the liquor in accumulator. (Hietaniemi & Saine, 1999)

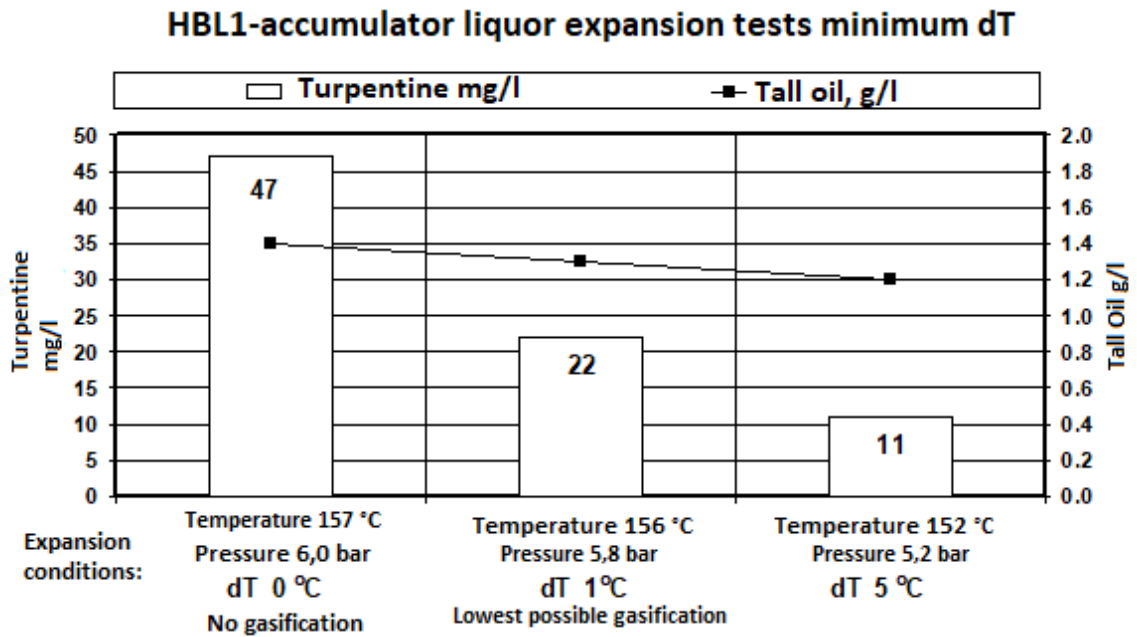


Figure 13. Results of the minimum temperature difference tests completed with the hot black liquor accumulator 1. (Hietaniemi & Saine, 1999)

Figure 14. shows the result of the minimum temperature difference test in hot black liquor accumulator 2 (HBL2). The expansion test was completed at a temperature of 110 °C and the temperature difference between accumulator HBL2 and the cyclone was 5-8 °C. As can be seen from the figure, the turpentine content of the liquor was significantly smaller than the cooled, total amount of turpentine. The turpentine concentration in HBL1 was higher than in HBL2. (Hietaniemi & Saine, 1999)

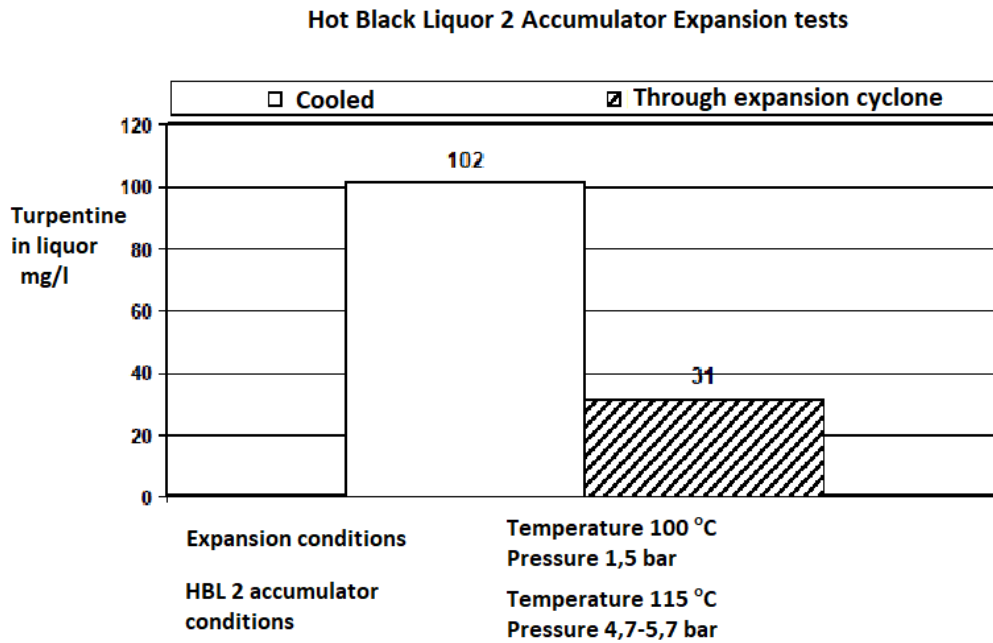


Figure 14. Results of the hot black liquor expansion test in HBL2. (Hietaniemi & Saine, 1999)

Figure 15. shows the results of the minimum temperature expansion test in HBL2. Problems occurred regarding to the variations in temperature and consistency of the liquor coming to the cyclone and because of these problems figure 15. shows only one temperature difference. (Hietaniemi & Saine, 1999)

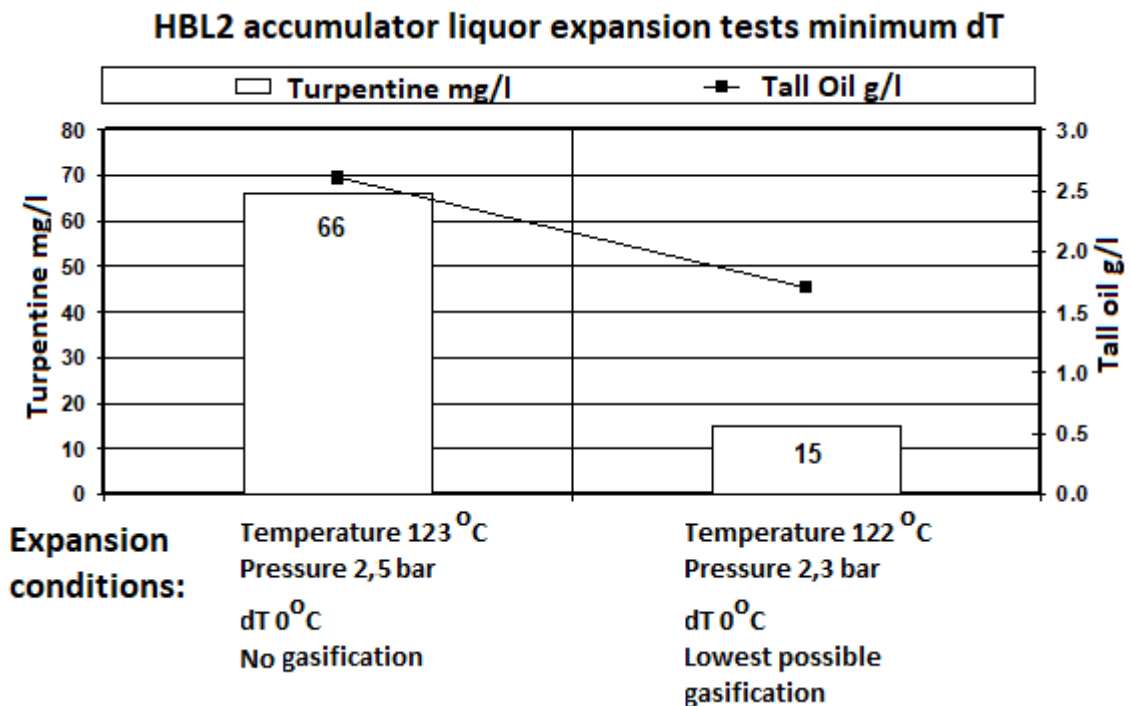


Figure 15. Effect of minimum temperature difference test in HBL 2. (Hietaniemi & Saine, 1999)

The tests show that the turpentine recovery from the black liquor circulation can be significantly improved with small temperature changes. In all tests the content of turpentine in the liquor was smaller after gasification. (Hietaniemi & Saine, 1999)

3.8.3 Terpenes emitted to air from the kraft pulp process in Värö and Gruvön

Terpenes should not be released to the atmosphere not only because they cause losses in the turpentine yield but also because they are regarded as air pollutants. Test was completed to clarify the amount of terpenes emitted to air from the kraft mills in Sweden. The tests were completed in two different kraft mills in Värö and Gruvön. (Strömvall et Peterson, 1993)

Plume samples were taken in the kraft mills. Some samples were taken outside two kraft mills. Three of the samples were taken at different heights above ground from the digesters and the high venting pipe for collected terpene-rich and mal-odorous gas streams. The first near-ground sample represents streams emitted to air during chip loading and steam pretreatment of the chips before digestion. The second sample reflects the gas streams from

the blow tank during blowing after a complete cook. The third sample corresponds to the composition of a collected steam from several process steps like digester loading, pulp washing and black liquor treatment. The fourth sample, that was taken while the pulp process was closed down, reflects the emissions from the pulpwood wood chips. In this sample the amount of volatile monoterpenes were highest of the four. The fifth sample reflects emissions from kraft mill with continuous digester and integrated paper production. (Strömvall et Peterson, 1993)

The biggest difference between the three samples is a higher proportion of the volatile monoterpenes in the low-temperature sample and higher amount of the less volatile compounds in the second sample. This confirms the influence of the process temperature to the forming of sesquiterpenes. Terpenes evaporate in various process steps, but the monoterpenes evaporate mainly from digester gases vented in the beginning of the cooking before the digester has reached its maximum temperature and they pass through the process unchanged. After the tests some terpene-rich streams at the mill have been collected for destruction by burning. (Strömvall et Peterson, 1993)

3.8.4 Change of average sulfur content in Union Camp - BBA Jacksonville Terpene and aromatics plant

Average sulfur content of the turpentine was increasing from 4400 ppm at 1989 to 7000 ppm 1993 in Terpene and Aromatics plant in Union Camp Jacksonville. Process and operating conditions were compared at several hot blow batch mills to clarify the reasons of this change. As a result, several methods to decrease the sulfur content of the crude sulfate turpentine were found. (Foran, 1995)

It seems that with simple adjustments in digester steaming practice could reduce 25-30 % of sulfur content from the current levels without effect on the yield of turpentine. The most important method to decrease the sulfur content is to increase use of chip bin pre-steaming. Another method, that may also reduce the sulfur content, is to increase decanter temperatures. Stripper foul oil shouldn't be returned to the turpentine decanter since its sulfur content is high. (Foran, 1995)

Cold blow batches don't have vapor space at the top of the digester during turpentine evolving. Turpentine starts to evolve before the cook begins. The turpentine bearing liquors are vented to liquor accumulators during the process and from these accumulators the turpentine evaporates and is recovered. In this kind of system, it is almost impossible to pre-steam the chips effectively. Best option to reduce sulfur content in these systems is to increase the decanter temperature. (Foran, 1995)

Condensate strippers are used to reduce the odor and BOD content in many mills. The condensate streams that are directed to the condensate stripper often include evaporator condensates, blow heat condensates and turpentine decanter underflow. Foul or red oil can be produced depending on the stripper design. This foul oil contains a substantial portion of terpenes and because of this, many mills recycle the foul oil to the turpentine decanter. This method drastically increases the sulfur content of the turpentine and degrades its quality. The nature of the reduced sulfur compounds also changes dramatically. The foul oil odor is more offensive than typical crude sulfate turpentine because of the increased sulfur content. (Foran, 1995)

The foul or red oil is heavily contaminated by TRS compounds. If turpentine is disposed of through incineration the red oils can be directed to the turpentine recovery system but if the turpentine is sold the red oils should be processed separately because their high TRS content will degrade the quality of regular turpentine. (Lin, s.a.)

3.8.5 Turpentine Recovery at Champion International Courtland Mill

Champion International produces turpentine as a by-product of pine pulp making. Their turpentine recovery system was more effective than most processes in their time. Reason for this increased level of turpentine was that their recovery system collected the vapors that are richest in turpentine and their equipment was operated effectively in optimal process conditions. Their chip quality was also good because they used very few purchased chips and the storage time of the chips was minimized. (Morgan, 1988)

Their chips are stored on a pad with an underground turntable that removes the chips from the bottom of the chip pile. Chips are conveyed to the chip bin and then to the chip meter, low pressure feeder and to the digester. Digester cooks the chips in 11 bar (165 psig) and 157 °C (315 F). Stock is washed on a two-stage counter-current drum washer and then it is screened. Before bleaching the stock is directed to the decker. The water used in second stage washer is preheated with turpentine condensers and steam. Black liquor formed in cooking goes through a two-stage flash before being sent to the weak black liquor storage tanks. The flashed steam from the first flash tank provides steam to the steaming vessel. Steaming vessel exhaust and the second flash tanks flashed steam are combined and directed to the cyclone separator and then to the turpentine condenser. The vapors from the brown stock washer filtrate tanks are also collected and condensed in secondary turpentine condenser. Non-condensable gases (NCG) from the condensers are collected and blown to the gas-fired odor incinerator. Turpentine condense flows to the horizontal turpentine decanter and vertical storage tank. This system collects 5,7 kg/ADt (1,7 gallons of turpentine per air dry ton of pulp). (Morgan, 1988)

Secondary condenser was installed to the Courtland Mill afterwards since they noticed that they lost turpentine 760-1140 l (200-300 gallons) per day to the washer filtrate tank and from there to the atmosphere. Most important thing to do while installing the turpentine recovery system is to install it there where it is needed. Position of the secondary condenser wasn't considered carefully enough in Courtland Mill. After the installation of the secondary condenser in Courtland Mill the turpentine yield didn't improve. In 1982 an explosion happened in the NCG pretreatment system for the odor incineration and it led to the major re-evaluation of the condition of the turpentine recovery system. In re-evaluation they noticed several problems in the system that needed corrective action. Washer filtrate tanks were over pressurized and the seal legs at the bottom of the overflow lines were blowing through vapors. In the area the odor of turpentine was very noticeable and liquid turpentine was found from the area sewer and caused serious fire hazard. They noticed that in secondary condenser the NCG vent leaves the bottom of the condenser and exits through the building wall to outside air. They determined that as the gases exited the building in a non-insulated line and there occurred additional condensation. Elbow outside the building was flooding and prevented the flow of NGC. The condenser didn't work properly, and the turpentine

yield was low because of this. In 1983 they installed a drain at outside of the elbow and connected to the product line and it allowed the condensate to be removed. This increased the yield significantly. (Morgan, 1988)

One of the most important operational parameters is the condensing temperature in the main condenser. In Courtland Mill they completed a measurement where they measured losses of turpentine from the main condenser as function of temperature. Vapor flows were measured and sampled in various temperatures. This data was used to calculate the turpentine loss from the vent and the information was compared with losses calculated from concentrations based on vapor pressure data for turpentine at the condensing temperature. The results of this study can be seen from figure 16. (Morgan, 1988)

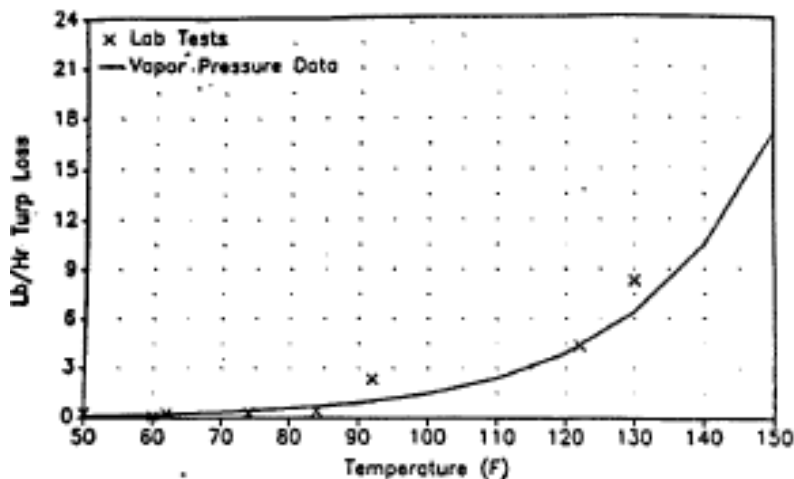


Figure 16. Results of the temperature and turpentine loss study in Courtland Mill. (Morgan, 1988)

Figure 17. shows the underflow loss and vent loss of the Courtland mill in the same picture. The minimum total loss occurs at around 43 °C (110 F) and this was chosen as the operating temperature. In Courtland mill they were able to increase the average turpentine recovery 4,01-5,90 kg/adbt (1,18 to 1,73 gal/adbt). If temperature of turpentine product from the main condenser exceeds 49 °C (120 F) the system will alarm operator. If the temperature exceeds 54 °C (130 F) the NCG vapors are diverted from the blower conveying gases to the odor incineration. When the temperature in the NCG-system arises to 54 °C the turpentine concentration increases sufficiently and the potential for the explosion is unduly high. (Morgan, 1988)

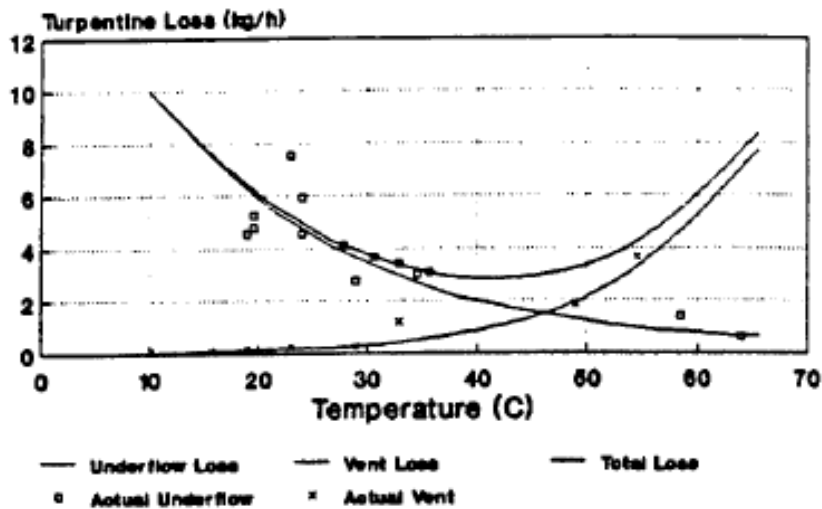


Figure 17. Turpentine loss from the underflow and venting while temperature of turpentine decanter arises. (Foran, 1992)

They also noticed a difference between the summer and winter season. In the summer season the turpentine yield was significantly lower. One of the reasons is the temperature of mill water during the summer time. Temperature arises up to 32 °C (90 F) at the summer time. Other reason is capacity of booster pump. It supplies the water to the turpentine condensers. Capacity and need of elevation cause problems with maintaining steady control of the turpentine system and sometimes lack of sufficient volume of cooling water occurs. (Morgan, 1988)

4 CASE METSÄ FIBRE RAUMA

As mentioned earlier Metsä Fibre Rauma is a pulp mill that produces ECF-bleached pine- and spruce pulp, biochemicals and bioenergy. (Metsä Fibre, 2018a) In this thesis the empirical part focuses on the turpentine production issues at Metsä Fibre Rauma. As explained earlier the issues are related to the yield and quality of the turpentine. Metsä Fibre Rauma wants to research what could be the reason for the decreased yield and varied quality and if possible, solve the problem without affecting on the pulp production significantly and safety risks minimized. This chapter introduces the current process and problems at Metsä Fibre Rauma.

4.1 Wood storing

Metsä Fibre Rauma mill uses mainly wood chips produced by their wood handling and approximately 1/3 of the total amount of wood used is bought from saw mills. Maximum storing time of the round wood is a few weeks at the summer time and a couple months in the winter time at the saw mills. The saw mills don't have chip storing possibilities, so the chips are transported to the Rauma mill as fast as possible. Saw mills are closed during the holiday season at the summer and because of this the stored amount at this season is bigger at Rauma mill. The chips that are stored for this time stay longer in the storage, up to 2-3 months. Amount of this longer stored chips is maximum 10 % of the chips from the saw mills. (Numminen, 2018)

Round wood from which the chips are produced at the Rauma mill are stored longer. Age of the round wood varies according to the wood supply situation and season. Age of the wood varies from 1-4 months depending on the year. Most of the wood is chipped right after arrival but small amounts are stored 1-2 months after arrival before chipping. Wood chips are stored max 1 week in the chip pile depending on the producing program. (Numminen, 2018)

2010-2018 changes in wood storing haven't occurred at Rauma mill. Differences appear between summer and winter seasons, but these differences are similar between the different years. Winter 2017-2018 was challenging for wood supply as the weather was very warm and because of this the wood is fresher during the summer 2018 than in general. (Numminen, 2018)

Amount of turpentine in the incoming chips varies since amounts of spruce and pine chips differ. High amounts of spruce lower significantly the turpentine amount in incoming stream as described earlier. Metsä Fibre Rauma uses approximately 60-80 % pine and rest is spruce depending on the demand. Amount of turpentine in the chips coming to the cooking is expected to be low because of the previous studies. This is assumed to be caused by the high spruce content and southern location. (VTT-Kemiantekniikka, 1997)

4.2 Cooking

Metsä Fibre Rauma uses older type SuperBatch displacement cooking method. The process stages are presented in figure 18. As can be seen from the figure there is two hot black liquor accumulators.

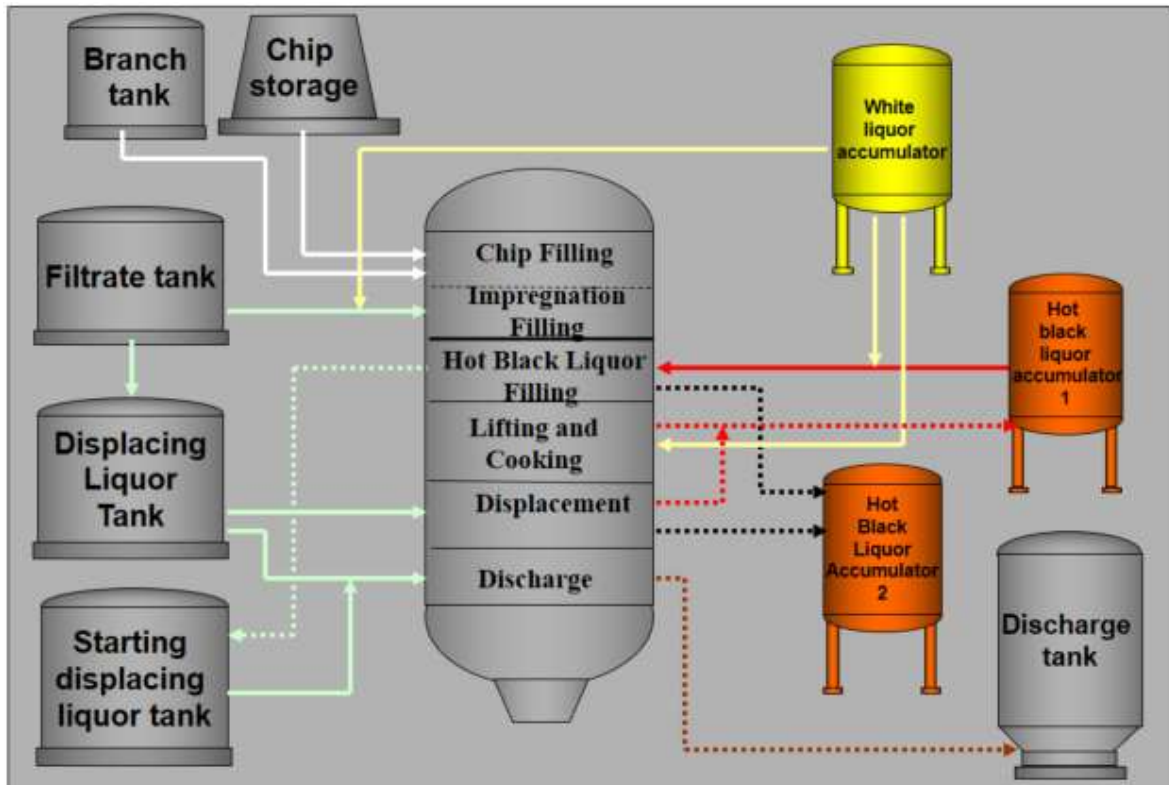


Figure 18. The displacement batch cooking process stages of Metsä Fibre Rauma. Picture is translated from the original version. (POL, 2001)

The first stage is chip filling. In chip filling the digester is filled with chips, branch mass and rejected branch mass from the fourth stage screening. 3 bar low pressure steam is used to spread the chips. Gases are collected from the top of the digester to the dilute odorous gases. (POL, 2001)

Second stage is impregnation liquor filling. Impregnation liquor is a mixture of filtrate from the pulp washing and white liquor from the white liquor accumulator. Impregnation liquor is filled from the bottom of the digester. Impregnation liquor warms the chips and removes air from them. (POL, 2001)

Third stage is hot black liquor filling. Some more white liquor is filled from the white liquor accumulator and some hot black liquor from the first hot black liquor accumulator to the digester. The impregnation liquor is displaced, and the first part of the displaced impregnation liquor is directed to the displacing tank. Rest of the impregnation liquor is guided to the second hot black liquor accumulator. Aim of the third stage is to increase temperature close to the cooking temperature. In the end of the filling some space is added for gasification by pumping some of the liquor back to the first hot black liquor accumulator. (POL, 2001)

Fourth stage is temperature increase and cooking. Temperature is increased to the cooking temperature with mid pressured steam and this temperature is kept during the cooking. Liquor circulates during cooking because it is absorbed from the middle of the digester and then fed back from the top of the digester. White liquor is added from the top of the digester at the beginning of the cooking. Displaced liquor is directed to the first hot liquor accumulator. Strong odorous gases are directed either through the gasification accumulator or the second hot liquor accumulator to the turpentine separator and lime kiln. (POL, 2001)

Fifth stage is displacing. Cooking liquor is displaced with the displacing liquor. The aim of the displacing stage is to finish the cooking reactions and decrease the temperature of the mass to less than 100 °C. The displaced liquor from the beginning of the fifth stage is directed to the hot black liquor accumulator 1 and the displaced liquor from the end of the stage is directed to the hot black liquor accumulator 2 and from there to evaporation plant. Sixth and the last stage is discharging. Pulp is diluted with the liquor from the displacing tank and the digester is emptied to discharge tank. (POL, 2001)

In Metsä Fibre Rauma mill the gasification is completed with the method described in chapter 3.3 and figure 7. System is older type of SuperBatch and the digester vents the gases first to the hot black liquor accumulators and from the black liquor accumulators to the gasification cyclone. During 1998-2005 gasification accumulator was used to improve the turpentine separation but it was omitted at 2005. (Liias et al. 1998) (Prosessikehitysryhmä, 2005)

4.3 Turpentine system

After gasification turpentine is directed to the separation cyclone and from there to the turpentine condensers. Turpentine condenser 1 condensates the turpentine and water with warm water. After turpentine condenser 1 the gas is directed to turpentine condenser 2 which uses cold water for the condensing. Condensate from the turpentine condensers is directed to the turpentine condensate cooler that uses also cold water. The gases from condenser are guided to the scrubber that circulates water and aims to separate rest of the turpentine from the gas stream. (Peltola, 2005)

At Metsä Fibre Rauma mill the turpentine recovery is shared between two different departments. The system described above is located in the cooking plant and rest of the turpentine system is at evaporation plant. This means that turpentine system is operated from two different operating units. Turpentine is separated from water with a turpentine decanter. Turpentine decanter is first unit that is located at evaporation plant. After the turpentine decanter the turpentine is directed to the turpentine tank. From the turpentine tank the turpentine is either directed to the tank truck or pumped to the malodorous gases burning and to the lime kiln to be burned. Conductivity of turpentine is measured and if the turpentine conductivity increases the turpentine is guided to the liquor pump. (Peltola, 2005)

Condensate separated from the turpentine during turpentine recovery is directed to the foul condensate tank that is located at the evaporation plant. (Peltola, 2005) Turpentine that forms on the top of the foul condensate tank is collected and pumped to the turpentine decanter. Foul condensate is collected to foul condensate tank from the evaporation plant, malodorous gas system and turpentine recovery system. Some foul condensate is also collected from the vacuum sewer and weak malodorous gases. Foul condensate is pumped to the stripping column from the foul condensate tank. Turpentine enrichment to the stripping system is avoided by returning some condensate to the turpentine decanter. (Alamaa & Pekkola, 1998) Turpentine skimming from the foul condensate is not automatized but it is done occasionally.

Some turpentine is also recovered from the evaporation plant through a small heat exchanger. Turpentine comes to this heat exchanger from the condensers located after the stripper and from the foul condensate of evaporator 2. This flow goes straight to the turpentine decanter. Purpose of this system is to remove turpentine and other impurities from the stripping system. (Halme, 2018)

4.4 Yield and quality problems

One of the problems in Rauma mill is low yield. Yield has been varied and usually low even for displacement batch digester systems, even if sometimes it has arisen to decent level. Since the yield of turpentine is low it means that the turpentine is not collected to the recovery and it might cause issues elsewhere.

The other problem is high content of heavy fractions. Wanted fractions in the turpentine are the monoterpenes (Strömvall et Peterson, 2000, 78, 81-82). Heavy fractions are considered to be all the components with higher molecular mass than monoterpene hydrocarbons. (Mayaux, 2018a) One of these heavy fractions are sesquiterpenes. They are naturally emitted to air and they have 100 °C higher boiling point than monoterpenes. Amount of sesquiterpenes and terpenoids in turpentine depends especially on the upper distillation temperature and the distillation procedure. (Strömvall et Peterson, 2000, 78, 81-82) Content of heavy fractions should be less than 15 % of the crude sulfate turpentine for it to be considered good quality. (Metsä Fibre, 2017)

Other quality problem is high sulfidity. Crude sulfate turpentine usually includes a lot of sulfur compounds like organic sulfides and mercaptans. The sulfur compounds distillate with the turpentine and they have an effect on the quality and usefulness of the turpentine. (Gantz et Nelson, 1972) Content of the sulfur should be less than 3,5 % in good quality crude sulfate turpentine. (Metsä Fibre, 2017)

4.5 Safety issues

At the end of year 1997 after Christmas shut down an explosion occurred in the dilute odorous gas system at Metsä Fibre Rauma mill. According to the accident inspection, one of the possible causes to the accident was high content of volatile gases in the system. The suspected gases were methyl mercaptan, dimethyl sulfide, dimethyl disulfide and turpentine. Concentration of the gas mixture that caused the accident had to be higher than lower explosion limit and turpentine has lowest explosion limit of the gases suspected. No one got bodily injuries in the accident and after the accident some changes were applied to the process. (Pekkola, 1998) After the accident several methods to dilute the gases and to enhance turpentine recovery were planned and some of them were completed. (Liias et al. 1998)

Other safety issues related to turpentine have been avoided except few times the turpentine has leaked to the waste water treatment plant, but these accidents didn't cause any serious damage. Some odor problems occurred in near-by neighborhood but leakage to the sea was avoided by directing the waste water to the safety reservoir. (Salo, 2003) (KKo & AMe, 2002)

5 LABORATORY ANALYSIS TO DETERMINE THE MATERIAL BALANCE OF TURPENTINE IN METSÄ FIBRE RAUMA

To determine the turpentine balance of Metsä Fibre Rauma mill laboratory analysis was completed. Laboratory tests were completed in three parts. In the first part the chip samples were taken, and the amount of turpentine was determined in these samples. In the second part other samples were taken while cooking pulp that has higher spruce content and in third part same samples were taken while cooking pulp that has higher pine content. While taking the second samples most of the samples from evaporation plant were taken. Some samples were taken afterwards to fulfill the previous samples and to control dispersion if occurred.

5.1 Chip samples

Chip samples were taken from five places to determine the amount of turpentine in the wood. First two samples were taken from the pine and spruce chips from the sawmills. Third sample

was from the pine chips chipped in the Metsä Fibre Rauma mill straight from the chipper before storing. Even if chip piles are named as pine pile and spruce pile at Metsä Fibre Rauma mill the pine pile is not homogeneously just pine. Pine pile includes also small amounts of spruce, but spruce pile is homogenous. Small amounts of fresh spruce are chipped with pine but sample that would include only spruce wasn't sampled. Rarely low-quality spruce is brought to the mill and it is chipped and cooked but sample from these chips wasn't available. Amount of these chips is small, and the quality is low, so it is not considered to be remarkable source of turpentine. Last two chip samples were taken from the in feed of cooking digester. Metsä Fibre Rauma mill produces two types of soft wood pulp, other has higher pine content and other higher spruce content.

To achieve decent quality of the samples three samples were taken during few hours from the same place and these three samples were mixed to form one sample that was analyzed. Purpose of this method was to eliminate the differences in the wood. Samples were collected to the plastic bag that was kept closed in the refrigerator until the sample was analyzed. The equipment used for the analysis followed standard ASTM D889 and the analysis was completed in the method that is described by Drew in his book *Crude Sulfate Turpentine* (Drew et al, 1971, p. 57-59). Figure 19 presents the analyzing equipment described in standard. (ASTM D889, 2017)

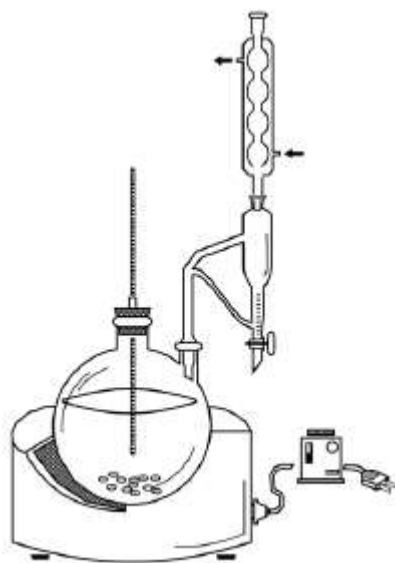


Figure 19. Equipment used to analyze the chip and pulp samples.

During analyzation of chip samples, a defoamer is needed. If oil based defoamer is used in analysis the defoamer dissolves to the turpentine. This makes the turpentine amount in the sample seem larger than it really is. The silicone based defoamer should be used instead because it doesn't distil with the turpentine. (Kotoneva & Hietaniemi, 1998)

500 grams of chips were added to the reactor with 2000 ml of water mixed with 40 grams of sodium hydroxide. The mixture is heated with the heating mantle and when the mixture starts to boil it is let to reflux 2 hours. After 2 hours the system is cooled down and after cooling the amount of turpentine in the trap can be measured. (Drew et all, 1971, p. 57-59.) When the mixture starts to boil turpentine, water and other gases evaporate and they are directed to the cooling unit. Cooling water runs inside the cooling unit and the cooling unit cools the gases. Water and turpentine condense, and they are captured to the trap. Turpentine decants on the top of the trap and trap returns the water to the reactor from the bottom to the trap.

5.2 Pulp samples

Pulp samples are taken after cooking and after washing. Sample from the washing liquid is also taken. Aim of these samples is to determine how much turpentine is drifted with the pulp and how much turpentine is separated from the pulp during washing. The amount of turpentine in pulp can be determined with the same equipment as chip samples (Drew et all, 1971, 58).

Pulp samples are taken to 1 l plastic containers. Entire sample is analyzed, and the sample needs to be refrigerated instantly after the sampling. The sampling should be done from the mass flow without diluting. If diluting water gets to the sample, it will cause an error to the result of analysis. (Kotoneva & Hietaniemi, 1998)

Pulp sample is analyzed by diluting the 1-liter sample to 2500 ml of water. Mixing needs to be completed quickly to avoid the evaporation of the turpentine. Defoamer used needs to be silicone based because of the reasons described earlier. The mixture is heated with a heating

mantle. After cooking the pulp is dried and weighted to determine the dry matter of pulp. (Kotoneva & Hietaniemi, 1998) After this the turpentine amount per ADt can be calculated.

5.3 Condensate samples

Condensate samples are collected from the washing liquid, dilute odorous gas scrubber liquids, foul condensate from the evaporation plant, secondary condensates from the evaporation plant, the foul condensate from foul condensate tank to the stripper and tall oil drying tank. These streams were chosen because it seems that in those streams might be large amounts of turpentine.

Sampling position is important while taking condensate samples. Sample must be sampled from the vertical pipeline or well mixed from the pressurized side of the pump. Turpentine decants to the top of the condensate and because of this the sample can't be taken from the bottom of the tank or horizontal pipe. Sample bottle should be made of glass. (Kotoneva & Hietaniemi, 1998) If the sample has vapor coming out the sample it should be cooled with cooling coil before collecting to avoid turpentine vaporizing from the sample. (Tyre, 2018 b.)

Condensate is analyzed with the device presented in the figure 20. Entire sample is used for the analysis and the sample is heated with the heating mantle. When the sample starts to evaporate the turpentine and water condense to the trap and the sample is let to reflux for 10 minutes. (Hilton, 2018) After this the turpentine amount is measured and collected from the trap.

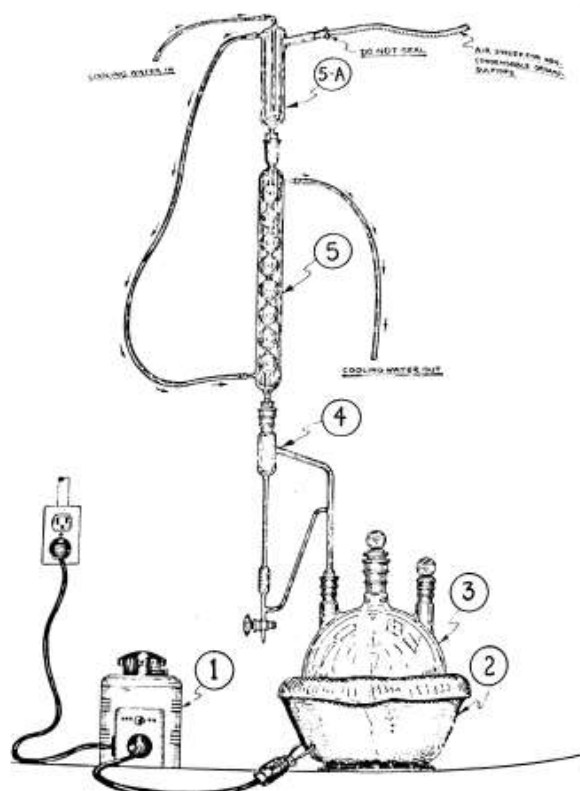


Figure 20. Equipment used for analyzing amount of turpentine in the condensate samples. (Drew et al. 1971, 62)

5.4 Other samples

Liquor samples were taken from the impregnation liquor, displacement liquor and two different places of the hot black liquor. Hot black liquor samples were taken after cooking before heading to the accumulators and after accumulators while heading to the evaporation plant. The goal of the analysis is to find out the amount of turpentine in the liquors from the cooking. These samples are analyzed by Eurofins by Agilent headspace-GC/MS method.

While sampling the liquor it is important to realize that the sample needs to be used entirely in the analysis. It is important that the sample is not taken with the overflow method, but all the liquid and foam is captured in the sample bottle. Sample needs to be refrigerated.

Tall oil sample and two gas samples were also taken. Tall oil is sampled to the glass bottle and it is analyzed with the gas chromatograph. One of the gas samples was from the dilute

odorous gas stream and the other from the strong odorous gas stream. Tall oil sample is also analyzed by Eurofins with GC/MS method.

Gas samples are taken from dilute odorous gases main line, dilute odorous gases from the cooking plant and stripper gases. The amount of turpentine in these samples represent the turpentine losses. The samples are taken from the lines which are burned in the recovery boiler. These analyses are completed by Eurofins. Gas samples are diluted before sampling. Sample is analyzed with headspace-GC/MS method.

6 DATA ANALYSIS

Quality and yield of turpentine has been varied at Metsä Fibre Rauma. Metsä Fibre Rauma wants to increase the yield of the turpentine and decrease content of heavy fractions and sulfur in the turpentine. Metsä Fibre Rauma has data about the turpentine yield and quality that needs to be collected and compared to the data from the process controlling programs and it is analyzed with Savcor Wedge calculation program. Purpose of this is to find similarities in the aspects that have changed in the process while the quality or the yield has changed.

6.1 Yield of CST

Yield of turpentine has been low in Metsä Fibre Rauma mills. In this analysis the period of observation was from the beginning of the year 2006 to spring 2018. Before this time period, 2004-2006 the turpentine has been burned and from this time period all yield information doesn't exist. Reliable and specific yield information from the yield didn't exist, so it needed to be calculated. Yield of turpentine was calculated from the weights of the transportation containers. Metsä Fibre Rauma had the weight and leaving date information of the trucks. The exact time when turpentine was formed in the process couldn't be determined. The yield was calculated from the weights of the trucks as an average from the next three months because of this. For example, yield of January was calculated as a sum of the weights of the trucks left in January, February and March and divided with three. This minimized the error caused by the irregular transportations. The trucks are ordered to the mill when the underflow

water is removed, and the turpentine tank is still full enough. The yield of turpentine has been varied the trucks arrive very irregularly. The three-month system is supposed to stabilize the changes between the months.

Yield differences between the winter and summer seasons were compared. The winter season was determined to be half year period from October to March and the summer season was the period from April to September. It was assumed that the yield at the summer time would be lower than in winter time according to the theory part.

Several time periods when the yield has been good and when it has been significantly low are needed for the analysis. These time periods are wanted to be as short as possible to make following the process conditions easier, but they need to be long enough to minimize the error from the delay of the process. The period is chosen to be one month because of these reasons. In best case the amount of turpentine has been stable for longer time than a month, so the turpentine yield really is increased at this time and not just more actively transported.

As described in theory section the storage temperature is one of the most important factors affecting on the yield of turpentine. To clarify the effect of temperature the average temperature of the month was compared to the average yield of the month. The temperature information was collected by Ilmatieteen laitos. There was no information from Rauma available so the data from Pori, closest city available, was used. (Ilmatieteen laitos, 2018) Figure 21 shows the dependence between the temperature and yield of one year. Recovery rate of turpentine means the share of turpentine recovered from the total amount of turpentine coming to the process. Total amount of turpentine coming to the process is determined in the laboratory analysis and the amount of turpentine recovered is calculated from the weight of transportation trucks. Recovery rate represents the yield of turpentine in comparison with the amount of turpentine coming to the process. As can be seen from the figure, when the outside temperature is high the yield is lower.

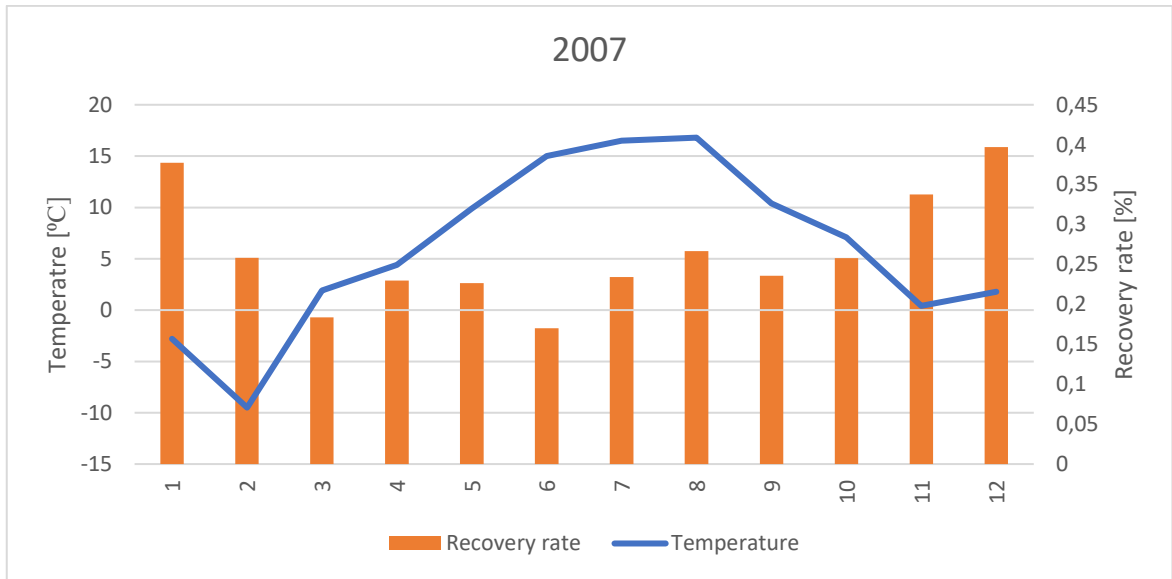


Figure 21. Figure presents the dependence between the temperature and yield.

In years 2009 and 2013 yield seemed also to follow temperature changes. Other years didn't follow the pattern as clearly as the year presented in figure. These years are more interesting for the research because in these years the recovery process had more effect on the yield than the temperature had. The other obvious reason to the yield differences is the dependence between yield and the wood species used. In Rauma pine and spruce are used as a mixture and the pine content is varied. Figure 22 presents the dependence between the turpentine yield and the pine content of the incoming chips in one year.

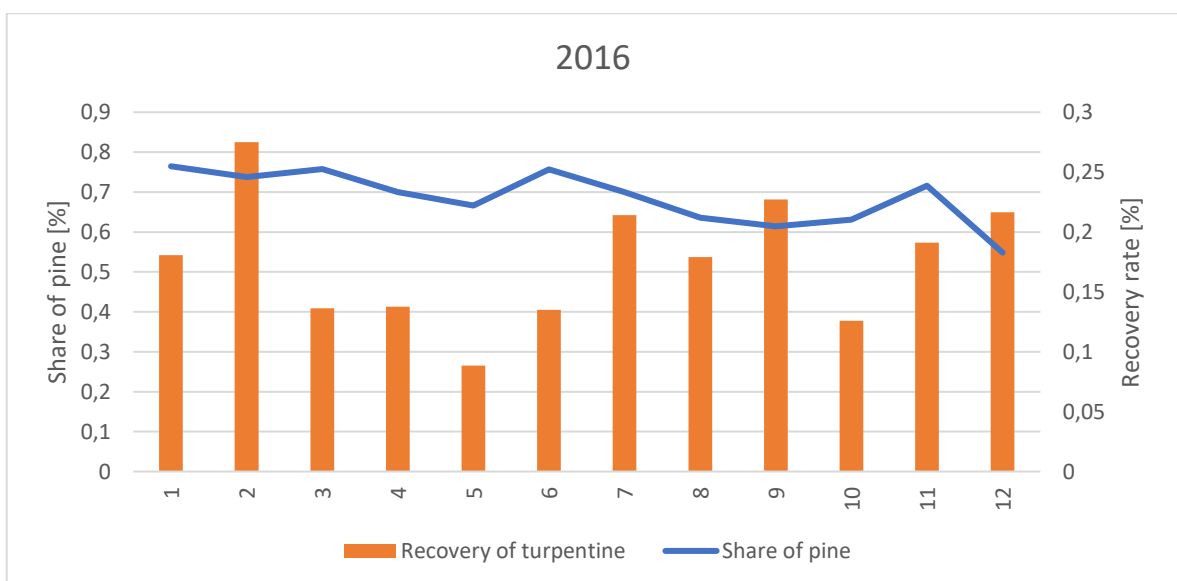


Figure 22. Affection of pine percent to the yield of turpentine can be seen from the figure.

The dependence between the pine content and turpentine yield is not as sharp as the dependence between the yield and temperature but yield seems to follow the pine content as well. Dependence between the two was visible more or less throughout all of the years that were analyzed.

6.2 Quality of CST

Turpentine quality information is from the client, who buys the turpentine. Turpentine is transported to the client and the client analyses the turpentine with gas chromatograph when it arrives. In Metsä Fibre Rauma the turpentine is not analyzed but all the information comes from the client. Client analyses which fractions turpentine includes. Wanted fractions are monoterpenes, especially alpha pinene and δ -3-carene. Their amount should be as high as possible. In Metsä Fibre Rauma mill the problem has been high content of heavy fractions and sulfur. Heavy fractions are components of turpentine that have higher molecular weight than monoterpenes. (Mayaux, 2018b)

Quality information is not as comprehensive as the yield information since some time periods are missing. Quality information from the year 2007 is not available so the time of observation is from beginning of 2008 to spring 2018. Some periods are also missing from the middle of the time of observation. Quality information from the year 2013 and from the end of the year 2012 is missing. Information about heavy fractions is missing also from the year 2012. This might cause errors to the analysis.

It seems that in earlier years of the observation time the quality was better than later years. In first two years problems with quality didn't occur. At the end of year 2010 the problems with heavy fractions started. The quality information from years 2012-2013 is missing but also after that in years 2014-2016 the problems continued, and only short breaks occurred when the content of heavy fractions was low. Lately in 2017-2018 the content of heavy fractions has been mostly low.

Sulfur content was low until the year 2012. The information of year 2013 is missing but it seems that it was the changing point for the sulfur. After that the sulfur problems have occurred regularly. Some periods were better but mostly the sulfur content was high until 2016 when the sulfur content was under control until August. After that sulfur content kept high again until the end of the year with one exception period in April and May. After that the problems returned but the year 2018 has started with the low sulfur content.

Assumption was that the high amount of problematic fractions, heavy and sulfur rich components, came from the foul condensate recovery system. Already in the years when the problems didn't occur turpentine was collected from the foul condensate, so the recovery system itself can't be the reason to the quality problems. Problem can be the increasing amount of the turpentine collected from the foul condensate. Unfortunately, the process data from the early years is missing and because of that the amount of turpentine collected from the foul condensate can't be found.

While comparing the quality and yield was noticed that the years 2011 and 2016 were lowest in the yield from the observation time. These two years were also the only two years when the sulfur content was low but the amount of high fractions was high. Other clear dependences between the yield and quality changes couldn't be found.

6.3 Process data

Process data was collected to the Savcor Wedge program. Data is based either on the online measurements or on measurements completed in the laboratory from the samples. Aim of the analysis was to find changes from the process that would match the time when the yield or quality of the turpentine has changed. If clear dependences between the parameters and yield or quality of turpentine are found index values can be changed if they don't have a significant effect on the production of pulp and don't cause safety issues. While analyzing parameters the focus is in the moments when either yield or quality has changed. All parameters weren't followed in every year because differences occur when the measurements have been installed and at what time the measurement data is available.

The parameters were chosen according to the information gained from the theory section and through conversations with experienced employees in the mill. Followed parameters related to raw material followed especially from which chip pile the wood is from. This is supposed to represent the share of each wood specie. The species are mixed in the piles, but the spruce pile includes more spruce than pine and pine pile include more pine than spruce. Cooking process is followed only from one digester out of ten. This is done because the digesters have same setting values and differences between the digesters are assumed to be small. Chosen digester to the evaluation is digester 1. Both, setting value and real value are followed if possible. From the cooking plant the temperatures and pressures of the cooking digester, liquor accumulators and steam are followed. Temperatures of the liquors in cooking and venting pressures are also checked. Sulfidity of the cooking process is followed.

Temperature of the pulp leaving the digester is checked. Temperatures of the input and output streams of the dilute odorous gas scrubber are monitored. Temperatures of the strong odorous gases vented from the black liquor accumulators to the gasification cyclone are determined. Temperatures and pressures of the surface condenser of the strong odorous gases scrubber is assessed. Temperatures, pressures and liquor flows in the evaporation plant are followed. Temperatures and pressures of the steam to the evaporation plant are also checked. Temperatures, pressures and streams of the stripper are assessed. Temperatures of incoming and outgoing stream of the gas scrubber of the evaporation plant are also evaluated. Temperatures of tall oil and soap are followed. Foul condensate pumping to the turpentine system is followed because flow of this line is not measured. Under flow of the turpentine tank and the conductivity of the under flow are followed.

Several parameters of the gasification accumulator and turpentine to burning were also found but values for these parameters weren't found from the Wedge so these parameters weren't utilized in the analysis.

Yield, sulfur content and amount of heavy fractions in turpentine were all analyzed in their own analysis. For the analysis, that compared yield and process data 13 time periods between the years 2012 and 2018 were chosen. These periods included significantly low and high

yields but also some average yields. Longer time periods, from one year up to three years were used to test the dependences.

7 RESULTS AND ANALYSIS

This chapter presents the results of the laboratory analysis and the turpentine balance collected according to the laboratory analysis. The results of the data analysis are also presented. All the results are analyzed, and the errors are described. The possible changes to the current turpentine system are also described in this section.

7.1 Results of the laboratory analysis and material balance of turpentine in Metsä Fibre Rauma

Material balance of turpentine in Metsä Fibre Rauma was formed based on the laboratory analysis. Sampling positions and analyzing methods have been described earlier. Aim of forming the material balance was to determine the biggest losses of turpentine during the process. Results of the laboratory analysis are presented by comparing them to the amount of turpentine in the chips from the cooking infeed conveyer coming to the Metsä Fibre Rauma mill. Metsä Fibre Rauma mill produces two kind of pulp, one has higher pine content the other has higher spruce content. Total amount of turpentine coming to the digester is calculated from the two analysis results, by multiplying the amounts of turpentine in mainly spruce chips to the cooker and in mainly pine chips to the cooker with the percentage amount of each chip sort from the total production. Table 4 presents the results of chip analysis.

Table 4. Table presents average results of two identical chip analysis.

Turpentine coming to the cooking	100 %
Chips to the cooking digester while cooking mostly pine	121 %
Chips to the cooking digester while cooking mostly spruce	61 %
Fresh pine chips from the debarking	94 %
Pine chips from saw mills	104 %
Spruce chips from saw mills	61 %

As can be seen from the table the results of chip analysis weren't quite as expected. The effect of the storage time was expected to be seen from the results, but the samples of fresh chips from debarking and chips from the saw mills included less turpentine than the samples from the cooker infeed conveyer. Reasons to these differences between analysis results and expectations are discussed more in the result analysis chapter.

Aim of the liquor analysis was to determine the amount of turpentine in the liquor in different stages of cooking. Purpose of samples taken from the displacement liquor from the end of the cook and black liquor from the accumulators to the evaporation was to determine how much turpentine is recovered in the accumulators and how large amount of turpentine ends up to the evaporators. All the samples were taken after the cooking digester so the turpentine amount coming to the cooking digester with the liquor is not determined. In SuperBatch process the liquors circulate in the process for several cooks and because of this determining the amount of the turpentine in only one cook is not possible. Results of the liquor analysis are presented in table 5.

Table 5. Results of the liquor analysis are presented in table.

Impregnation liquor while cooking mostly pine	37,9 %
Impregnation liquor while cooking mostly spruce	39,0 %
Black liquor from beginning of the displacement while cooking mostly pine	74,9 %
Black liquor from beginning of the displacement while cooking mostly spruce	13,1 %
Displacement liquor from the end of the displacement while cooking mostly pine	163,4 %
Displacement liquor from the end of the displacement while cooking mostly spruce	136,6 %
Black liquor from the accumulators to the evaporation while cooking mostly pine	174,4 %
Black liquor from the accumulators to the evaporation while cooking mostly spruce	37,9 %

All the pulp samples were planned to be analysed in the laboratory of Metsä Fibre Rauma but the pulp from the cooker caused problems. When analysed in the method described earlier, the pulp formed thick layer on top of the cooker. This layer caused pressure developing in the bottom of the digester. When pressure increased enough the pulp layer broke and the pulp over boiled and the sample was impossible to analyse. Lowering the amount of the pulp sample didn't affect on the issue. Water amount was also increased but problem still occurred. Since other solution wasn't found with the equipment available the samples were sent to the Eurofins. Other samples were possible to analyse but the measurement wasn't accurate enough. Table 6. presents the results from the pulp sample analysis.

Table 6. Results of the pulp samples are presented in the table.

Pulp with higher pine content from cooker before the washing	7 %
Pulp with higher spruce content from cooker before the washing	2 %
Pulp with higher pine content from the washing	0 %
Pulp with higher spruce content from the washing	0 %

Condensate samples were analyzed with the method described earlier. Condensate samples are taken from several locations to determine different things. Amount of turpentine in the pulp washing filtrate was determined as part of the turpentine material balance of the washing plant. Filtrates of the dilute odorous gases scrubbers were defined to determine the amount of turpentine condensed from the dilute odorous gases. Amount of turpentine in the foul condensate was determined to find the share of turpentine recovered from the cooking plant and through foul condensate. Amount of turpentine in foul condensate to the stripper was determined to represent the amount of turpentine lost from the foul condensate. Turpentine in secondary condensate was determined in order to find where the turpentine from the liquor ends up in the evaporation plant. Decanter underflow was analysed in order to determine the recovery efficiency of the decanter. Condensate of the tall oil drying tank was determined to find the amount of turpentine in the stream and find out wheather it would be efficient to recover or not. Table 7. presents the results of the analysis of condensate samples.

Table 7. Results of the condensate samples are presented in table.

Pulp washing filtrate while cooking mostly pine	0 %
Pulp washing filtrate while cooking mostly spruce	0 %
Filtrate from the dilute odorous gases scrubber of the cookin plant	8,2 %
Filtrate from the dilute odorous gases scrubber of the evaporation plant	0,18 %
Filtrate from the dilute odorous gases scrubber of the caustizicer	0,04 %
Foul condensate from evaporators before foul condensate tank	12,1 %
Foul condensate from the foul condensate tank to the stripper	15,4 %
Secondary condensate 1	5,8 %
Secondary condensate 2	0 %
Secondary condensate 3	0 %
Decanter under flow	0,004 %
Condensate from the tall oil drying tank	0,5 %

Filtrate from the pulp washing didn't include any turpentine, at least not a share big enough to be measured with the method used in analysis. Filtrate from the dilute odorous gases was expected to include significant amounts of turpentine since several gas measurements

completed earlier included a lot of turpentine. Dilute odorous gases to the cooking plant's scrubber come from the cookers and from several storage tanks. Scrubber lowers the gas temperature from 82 °C to 50 °C. This temperature change should condense the turpentine to the filtrate that is condensed in the scrubber. Samples from this stream didn't include any turpentine that could be measured with the method used. Temperature of scrubber output flow was lowered to 45 °C. After this lowering two samples were analysed and a significant amounts of turpentine wasn't found. First two sets of samples were taken from the bottom of the scrubber. Last set of samples were taken from a little bit higher from the scrubber. The first samples weren't taken from here because of the complicated position of the sampler. From this sampling point the samples did include turpentine and only results of this successful analysis were used in the material balance.

Foul condensate samples from the evaporation to the foul condensate tank and from foul condensate tank to the stripper were analyzed to clarify how much of the turpentine from the foul condensate tank is from the evaporators. Secondary condensates were analyzed and only one of them included turpentine. Secondary condensate 1 is from evaporators 2-4 and it was the one that included turpentine. Secondary condensates 2 and 3 didn't include any turpentine.

Condensate from the tall oil drying tank included a large content of turpentine. Only issue with this flow is that the volume flow of this condensate is not large. Even if volume flow is small it included significant amount of turpentine. This turpentine is not recovered but directed to the alkaline sew.

Tall oil sample and gas samples were analyzed by Eurofins. Results of the analysis can be seen from the table 8. Aim of these samples was to determine turpentine lost with tall oil and gases.

Table 8. Results of gas samples and tall oil sample are presented in table.

Dilute odorous gases	0 %
Strong odorous gases from the cooking plant	3 %
Stripper gases	33 %
Tall oil	54 %

Turpentine content of tall oil seems to be bigger than in the earlier analysis but it is possible that tall oil would include large amounts of turpentine. In earlier analysis turpentine content of tall oil was 30 % but the yield of tall oil has increased significantly since this analysis (Kotoneva & Hietaniemi, 1998).

Dilute odorous gases didn't include enough turpentine to be measured in the method used. Stripper gases include strong odorous gases from the stripper. Strong odorous gases from the cooking plant include the gases from the turpentine condenser. It seems that strong odorous gases include more turpentine than dilute odorous gases. This differs quite radically from the previous measurement (Enwin, 2009). In other measurement the amount of turpentine has been bigger in the dilute odorous gases and smaller in the strong odorous gases. Strong odorous gases did include turpentine as well but only half of the amount of the turpentine in the dilute odorous gases. Turpentine to the strong odorous gases came from stripper gases and cooking plant. (Enwin, 2009)

From figure 23 can be seen that the turpentine can be lost in many ways. When the turpentine comes to the cooking digester, it is recovered from the strong odorous gases. It is also recovered from the foul condensate tank. Depending on how and when the turpentine, that is not recovered, reacts it is either burned or released to the atmosphere. Turpentine might also be absorbed to the pulp and tall oil.

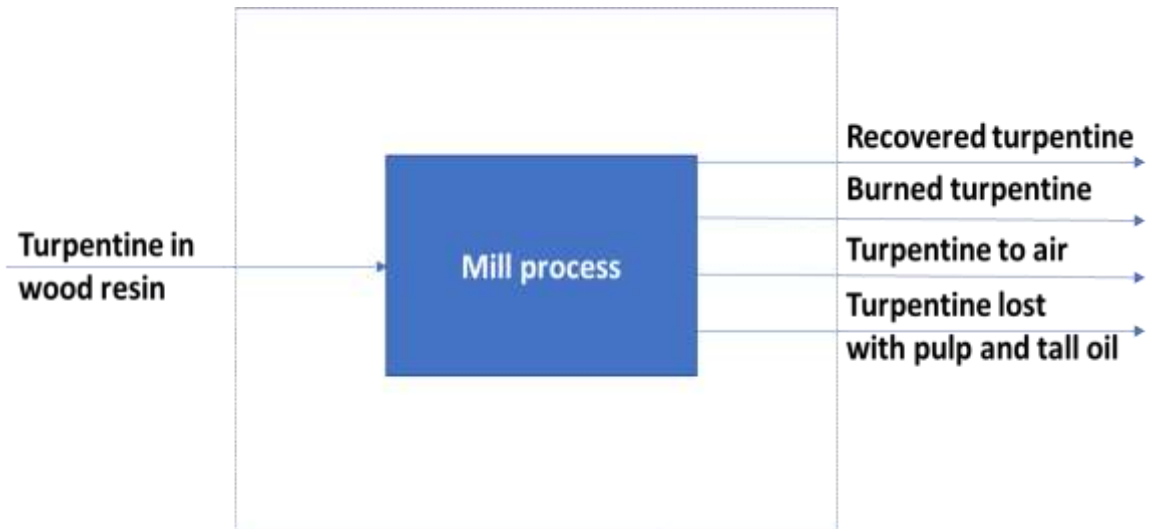


Figure 23. Figure presents turpentine recovery balance.

Some of the turpentine is released to the air from the wood and chip storages. The gas flows that are usually burned include turpentine, that is not removed from the process before. If problems occur in process these flows might end up released to air if burning is not possible (Lahtinen, 2018). Some streams that include turpentine do also end up to the sewers and through the sewers to the waste water treatment plant.

The turpentine is not burned with the black liquor in recovery boiler. Amount of turpentine in the liquor that ends up to the recovery boiler was measured and the liquor didn't include any turpentine. (Torniainen, 2018) Turpentine that is not successfully separated from the dilute and strong odorous gases ends up being burned. Recovery efficiency from these streams could be improved by optimizing the gas scrubbers and turpentine condenser temperatures and by directing the condensate from the scrubbers to the foul condensate tank where the turpentine is skimmed from the top of the tank.

VOC-project was completed 1997-1998 VOC-project. Volatile organic compounds (VOC) and total reduced sulfur (TRS) compounds were analyzed. In this analysis one of the mills was Metsä-Rauma nowadays Metsä Fibre Rauma. Content of turpentine in three gas flows were measured in this project. These measurements showed that the turpentine content was low in strong odorous gases and stripper gases but in the dilute odorous gases the content of turpentine was significantly high. Amount of turpentine in dilute odorous gases was 34 times

higher than in strong odorous gases. Analysis showed that turpentine recovery efficiency was dependent on the amount of turpentine in the wood. Kemijärvi was one of the mills that took part in the project. In Kemijärvi the wood included most turpentine and the recovery rate was best. (VTT-Kemiantekniikka, 1998)

New material balance of turpentine is formed according to the laboratory analysis completed 2018 and the result is presented in figure 24.

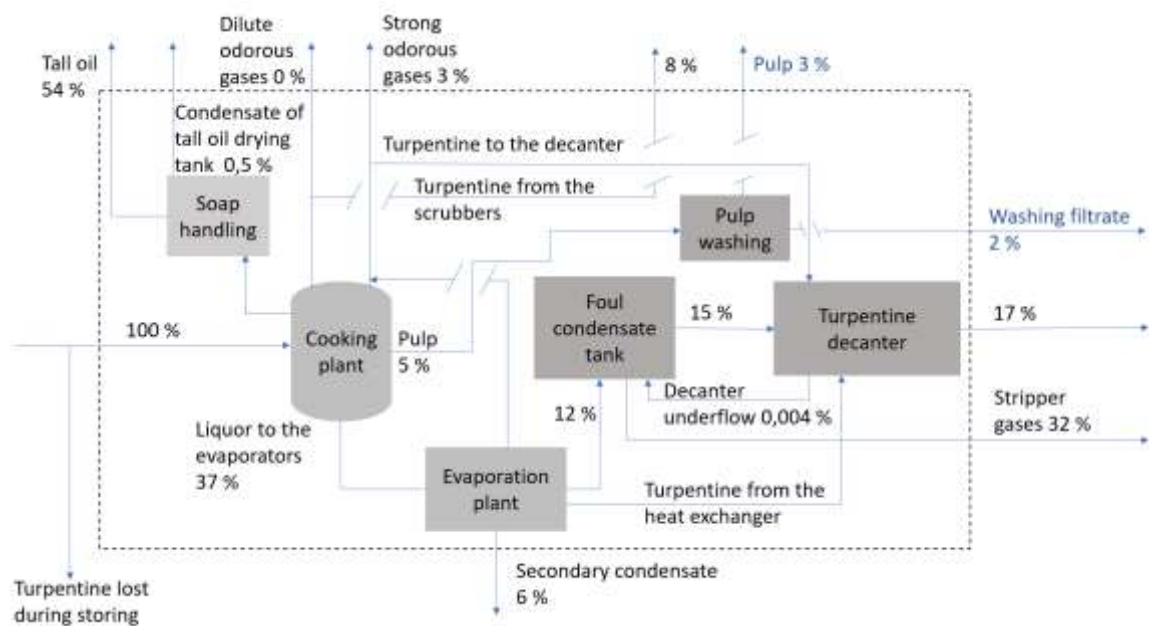


Figure 24. Material balance of turpentine in Metsä Fibre Rauma is presented in the figure. Streams marked with blue are estimations others are based on laboratory analysis.

One outlet value is missing, turpentine lost during storing. As described earlier the chip analysis was unsuccessful and because of that the turpentine lost during storing was not determined. The inlets and outlets of the balance don't match. If all the outlets are calculated, it makes 125 % while there is only one inlet 100 %. This error can be caused by several reasons. These reasons are analyzed in the result analysis chapter.

7.2 Results of data analysis

In data analysis the yield of turpentine was determined during years 2006-2018. The average yield of observation period was low, as expected, 23 % of the amount of turpentine arriving to the cooking digester of Metsä Fibre Rauma mill. Amount of turpentine arriving to the cooking digester of Metsä Fibre Rauma mill is achieved in the laboratory analysis completed. Best average yield year was 2010 and it was the only year when the average yield was 30 % of the turpentine arriving to the cooking digester of Metsä Fibre Rauma mill. 2011 on the other hand had the lowest yield and the yield was only 57,8 % from the yield of year 2010 and 76 % of the average yield of observation period.

Difference between the average summer time and winter time was 31,6 % and average yield of July was 38,7 % smaller than the average yield of January. This difference can be assumed to be caused from the temperature differences between the winter and summer time. Best half year period was at winter season 2012-2013 and the best summer season was summer 2015. Average yield of winter 2012-2013 was 42 % bigger than the average yield of the winter seasons. The yield of summer 2015 was 32 % bigger than the average summer time yield.

Yield criteria for the good period is more than 27 % of turpentine recovered from the amount of turpentine coming to the cooking digester. On the other hand yield criteria for low yield is less than 16 % recovered from the amount of turpentine coming to the cooking digester. In only two years when the average yield of the month was always more than 27 %, years 2007 and 2012. In 2017 the yield was never above 27 % and in 2016 the yield was more than 27 % only in February. The differences between the summer and winter seasons can be seen in the periods chosen to the more specific observation as assumed. Most of the best periods are at winter season and most of the lowest yields have been at the summer season.

Low or high yield periods that had lasted several months were chosen for the process data analysis. Average values of each parameters during the time periods were compared to each other and dependences between the average values of parameters and turpentine yield were analyzed. Ten time periods during years 2012-2018 were chosen for this analysis.

Several dependences were found during the analysis that compared yield and process data. Some dependences were hard to prove, and they weren't linear, but it seemed that the values changed equally more often than would be logical if they weren't dependent. All the parameters didn't include data during all time periods chosen and the analysis had to be made from a limited number of values.

First parameter tested was the dependence between the yield and amount of spruce chips from the total. Dependence was clear, yield was higher when the spruce content was lower. Only one exception during 8 periods, when the parameter included values, occurred. This exception was the highest yield period.

From cooking several parameters were followed and few seemed to affect significantly and clearly to the amount of turpentine. Pressures of the digesters and all accumulators seemed to affect more to the yield than the temperature even if the temperature had affection as well. In general, it seems that when pressure was high the yield was high. Figure 25 presents the dependence between the pressure of the digester and yield of turpentine. Figure of dependence between gasification pressure and turpentine yield was similar to the dependence between the pressure of the digester and turpentine yield. Sieves are placed between the two measurements and this causes small difference between the two pressures, but this difference wasn't visible in the figure. Start point of the gasification was at 10 bars and end point 2 bars and there weren't any changes during the time of observation.

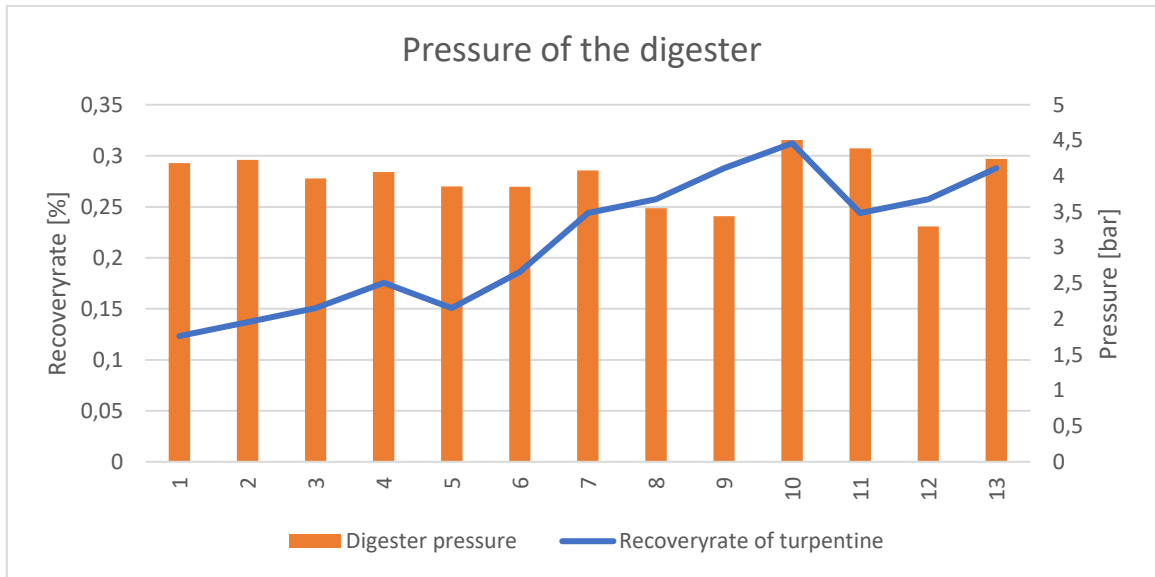


Figure 25. Dependence between the digester pressure and the turpentine recovery can be seen from the figure.

Temperature seems to affect most to the sulfur content of the turpentine. It seems that sulfur content is lower when the temperatures in general are higher. Pressures don't seem to effect on sulfur content as much even if they do affect as well. Sulfur compounds evaporate already in low temperatures and if the temperature is higher the sulfur compounds don't foul recovered turpentine. Dependency between the cooking digester upper circulation temperature and the sulfur content can be seen from figure 26 and dependency between the vacuum circulation temperature and sulfur content is presented in figure 27.

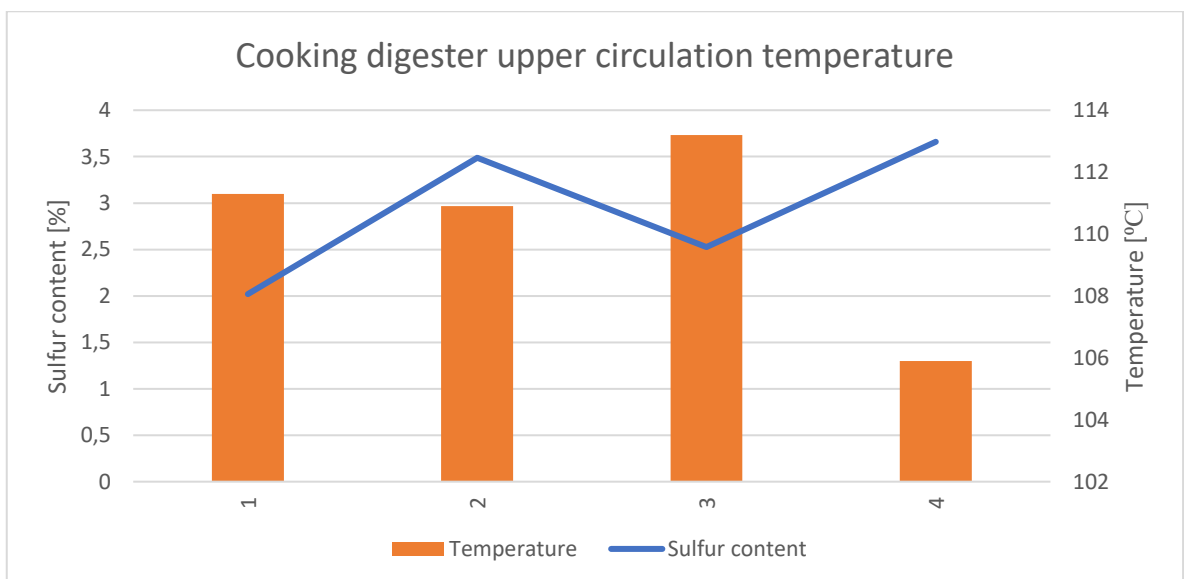


Figure 26. Dependence between the sulfur content and temperature of the upper circulation temperature.

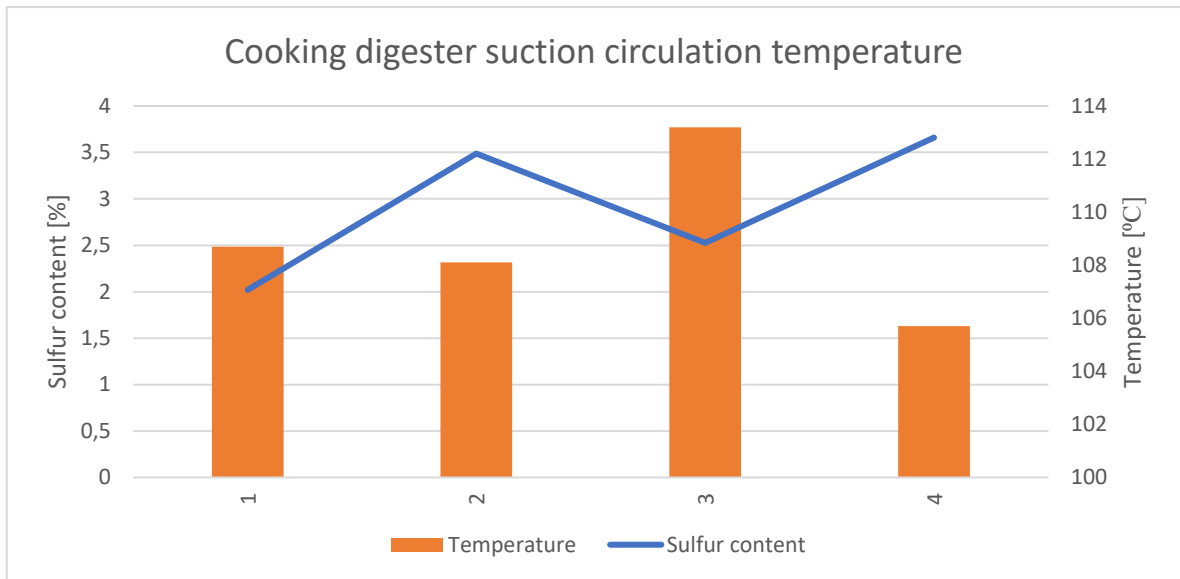


Figure 27. Dependence between the cooking digester suction circulation temperature and sulfur content.

While analyzing heavy components and process parameters problems occurred. Time of observation was shorter than while analyzing dependencies between sulfur content, yield of turpentine and the process data because of the inaccuracy in the quality information. Observation time was 2014-2018 and because of shorter time period the analysis is not as reliable as the other analysis.

Pressure of black liquor accumulators seems to have an effect on the yield of turpentine as well. Higher pressure causes more gas flow through the accumulators that could gain more turpentine (Kovasin 2018). More pressure on the accumulators also means increasing demand of steam (Kovasin 2018). Temperature increase also seems to have a positive effect on the yield of turpentine. Dependence between the turpentine yield and pressure and temperature of black liquor accumulator 1 can be seen from the figures 28-29.

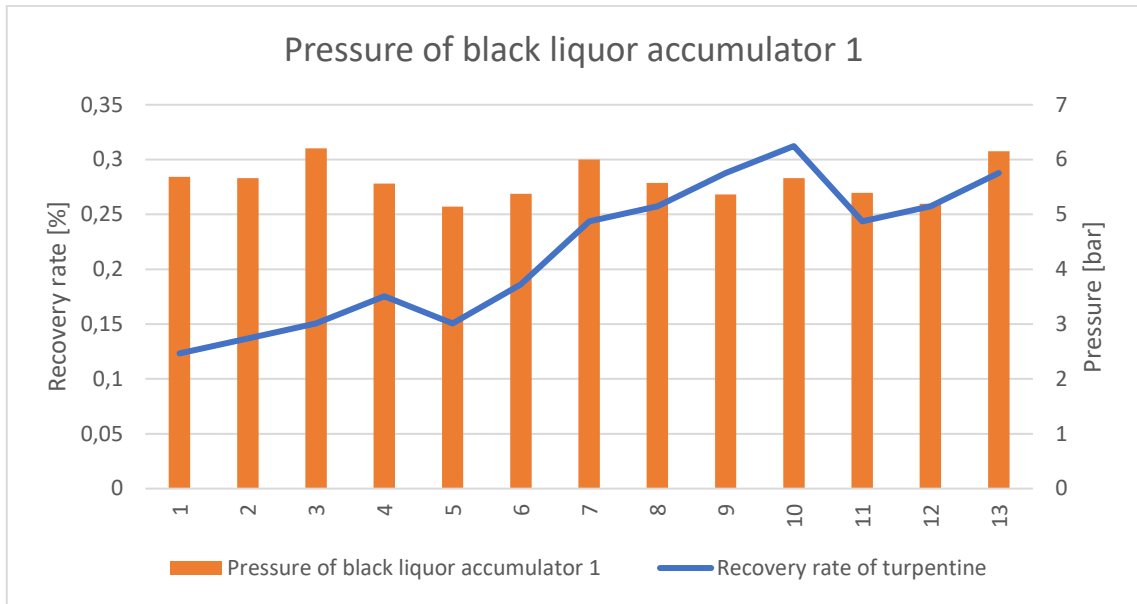


Figure 28. Effect between the turpentine yield and pressure of black liquor accumulator 1.

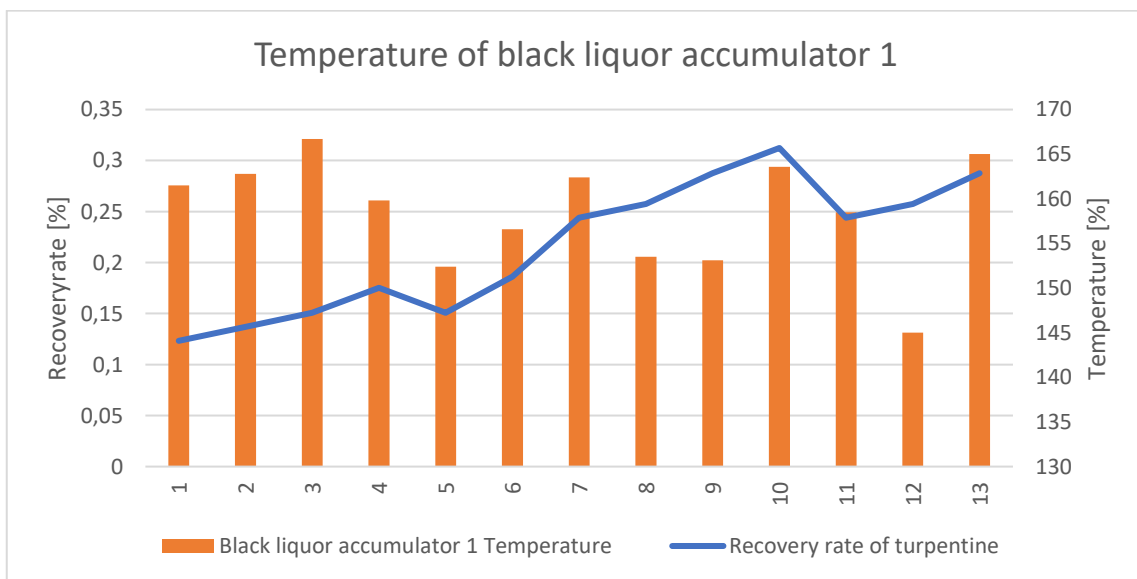


Figure 29. Dependence between the turpentine yield and temperature of black liquor accumulator 1.

Dependence between the pressure of the black liquor accumulators and the sulfur content seem to be that when the pressure is higher also the sulfur content is lower. Pressure of black liquor accumulator 1 and sulfur content can be seen from the figure 30. It seems that higher temperature of the accumulators would also obtain lower sulfur content. This can be seen from figure 31.

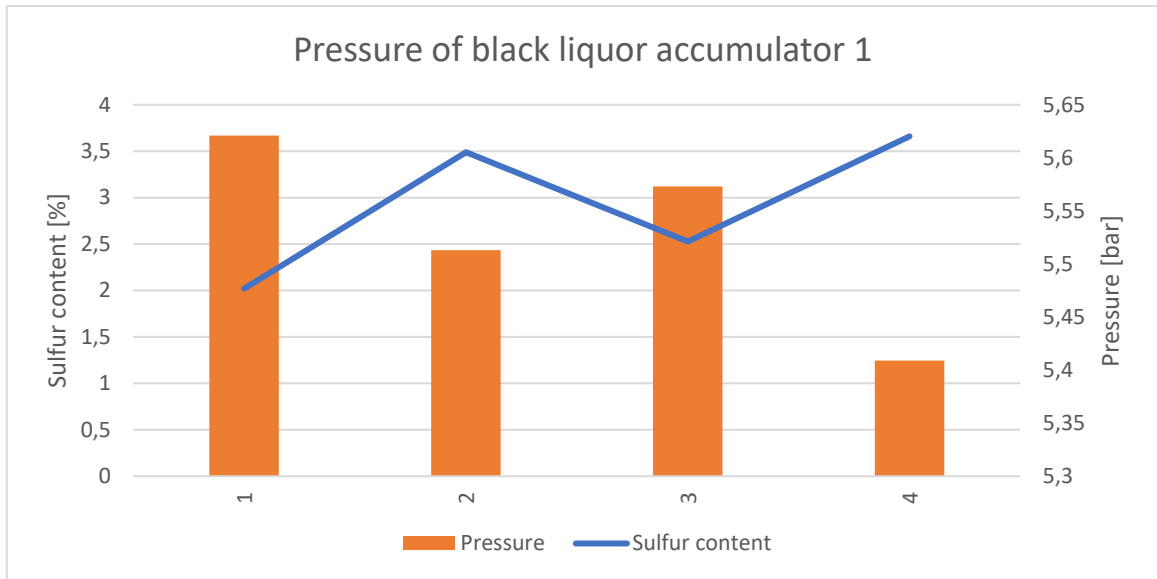


Figure 30. Dependence between the sulfur content and pressure of black liquor accumulator 1.

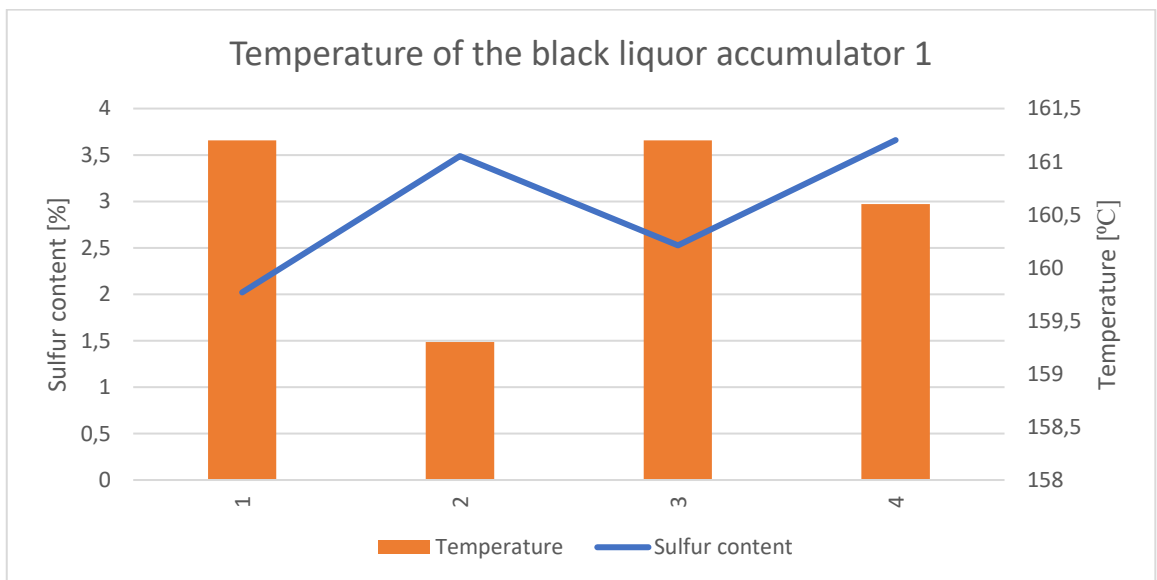


Figure 31. Dependence between the sulfur content of turpentine and temperature of the black liquor accumulator 1.

Effect of pressure and temperature of black liquor accumulator 2 to turpentine recovery can be seen from figures 32-33. As can be seen from the figures 32-33 effect of conditions inside black liquor accumulator 1 seems to be bigger than effect of conditions in black liquor accumulator 2 even if all the dependences seem to be quite similar.

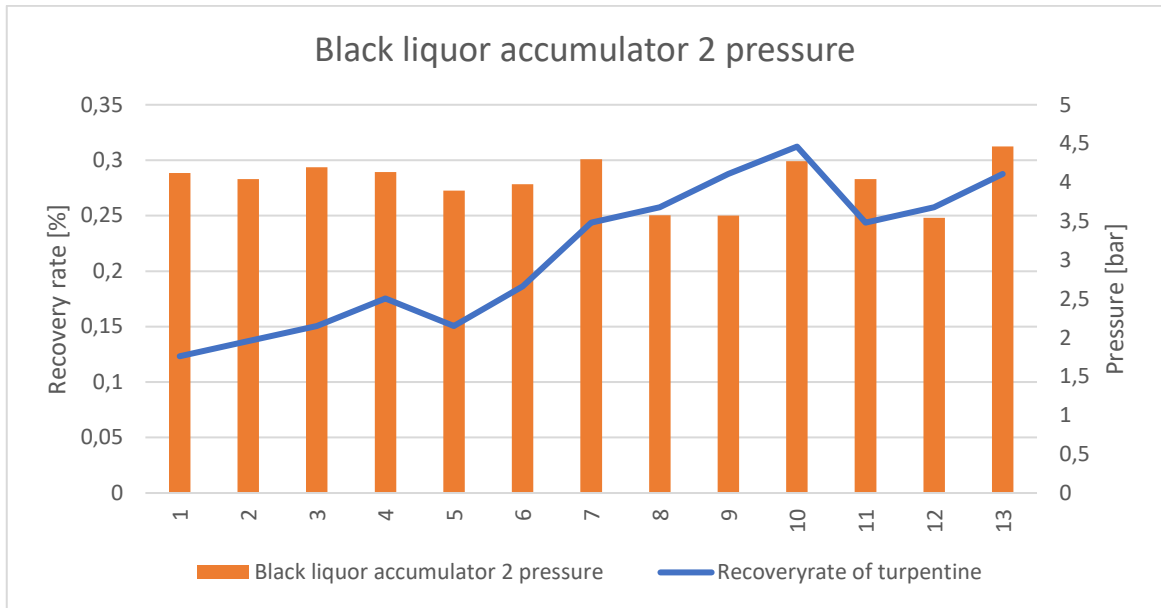


Figure 32. Dependence between the pressure of the black liquor accumulator 2 and recovery rate.

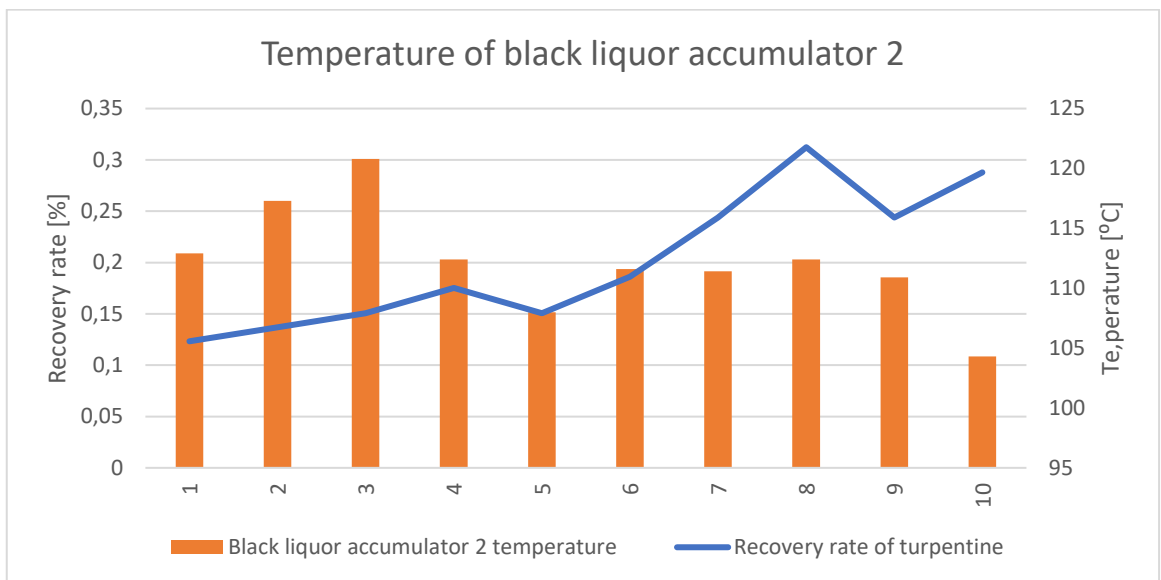


Figure 33. Effect of temperature in black liquor accumulator 2 to the turpentine yield.

Dependency between the pressure of the black liquor accumulator 2 and sulfur content can be seen from the figure 34. It seems that conditions of black liquor accumulator 1 have a bigger effect on the turpentine quality and yield than other accumulators.

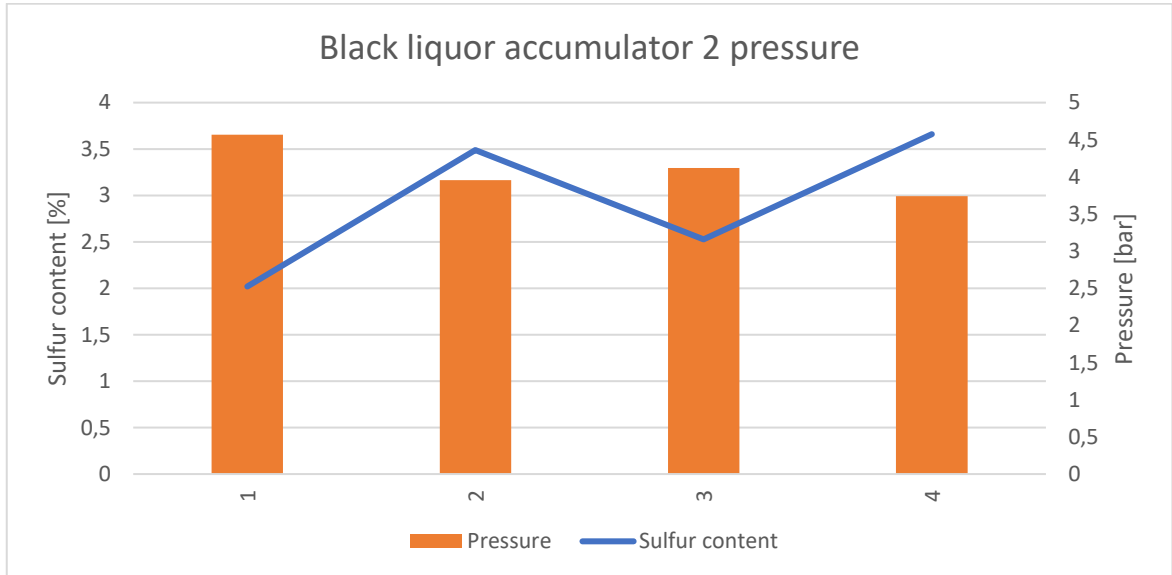


Figure 34. Dependence between the pressure of the black liquor accumulator 2 and sulfur content.

Temperature and pressure of white liquor accumulator also has an effect on the yield. Figure is similar, and dependence is visible but not as sharp as with the black liquor accumulators. Older values couldn't be found for the research and because of this there is less measurement points. Figure 35-36 presents the dependencies between the recovery rate and the pressure and temperature of white liquor accumulator.

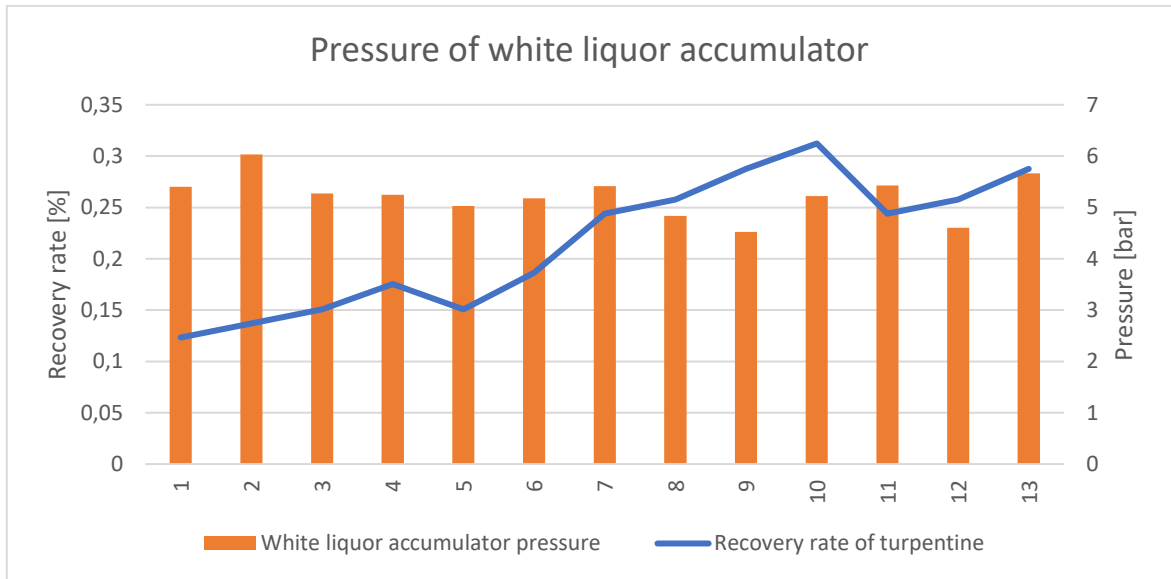


Figure 35. Dependence between the pressure of white liquor accumulator and recovery rate of turpentine.

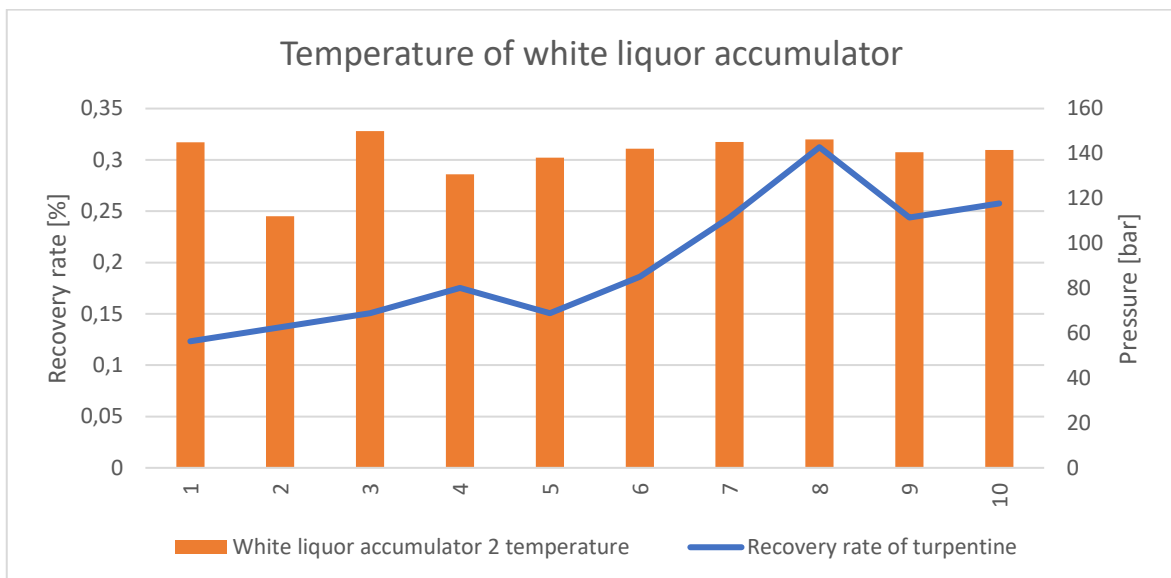


Figure 36. Dependence of temperature of white liquor accumulator to recovery of turpentine

Dependence between the conditions of white liquor accumulator and sulfur content of the turpentine can be seen from the figure 37. Temperature of the white liquor accumulator follows same pattern that the dependency between the conditions of other accumulators and the sulfur content does. Pressure doesn't follow same pattern. It seems that the lower the pressure the less the sulfur in turpentine.

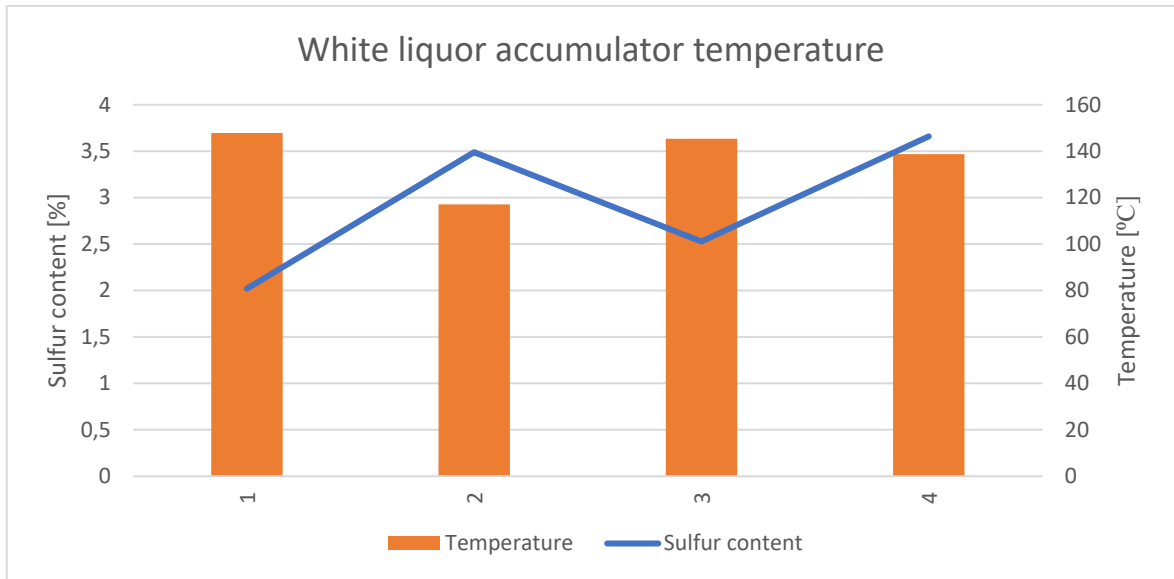


Figure 37. Dependency between the sulfur content and temperature of white liquor accumulator can be seen from the figure.

Temperature of the pulp from the digester didn't seem to have a clear effect on the yield of turpentine but it seems that it would have an effect on the sulfur content. When the temperature has been higher the amount of sulfur compounds has been lower. This dependence can be seen from the figure 38.

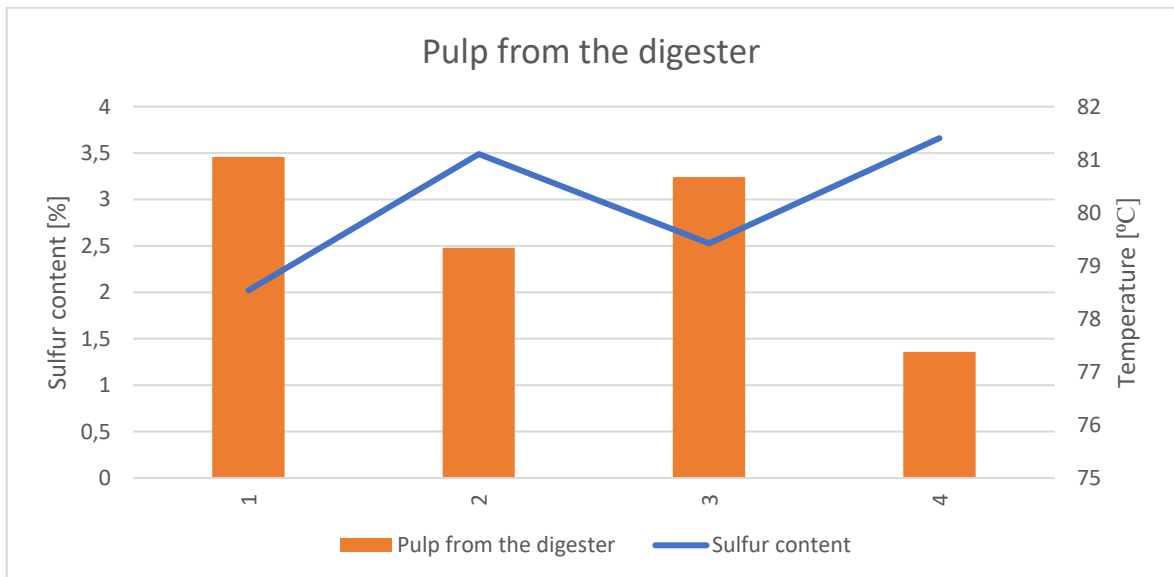


Figure 38. Dependence of the share of sulfur components and the temperature of the pulp can be seen from the figure.

The analysis that compared the yield and process data evaluated the effects of the dilute odorous gas scrubbers. Two temperature measurements were utilized in evaluation of each scrubber. Temperature of the incoming gas stream and outgoing gas stream. Dilute odorous gases come to the scrubber of the cooking plant from the cooking process and several storage tanks. There seems to be a clear dependency between these two flows and yield and quality of turpentine. Higher temperature of the input flow seemed to be better for the turpentine yield and content of heavy fractions. Dependence between the content of heavy fractions and input temperature can be seen from figure 39.

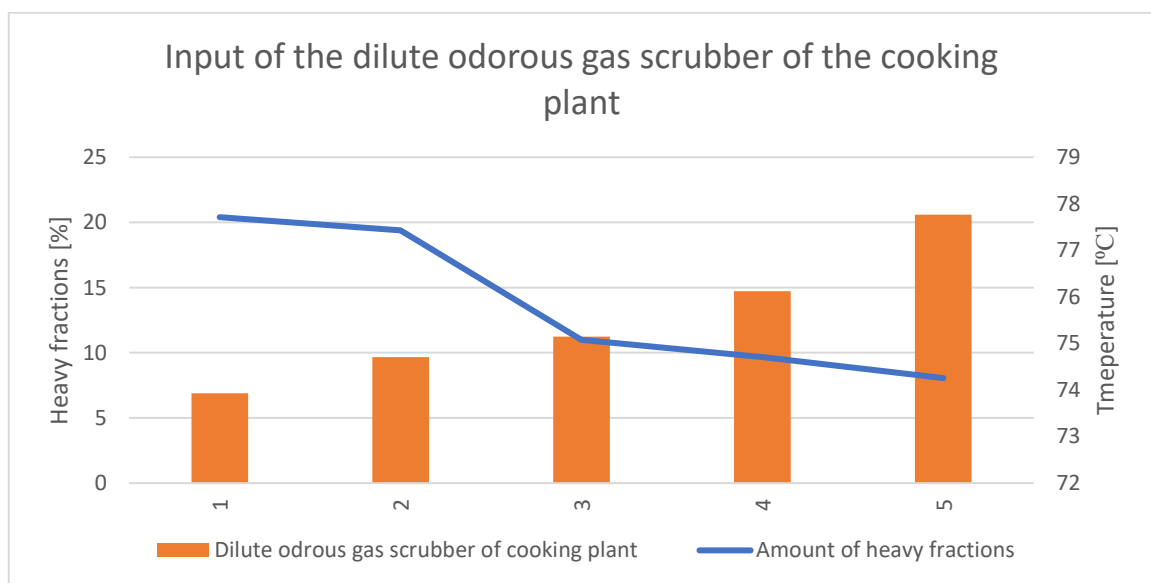


Figure 39. Dependence between the amount of heavy fractions and turpentine quality seems quite clear. Yield also increased when the temperature was higher.

The dependency between the outgoing flow and yield seemed to be more significant than the incoming flow and yield. On the other hand, the temperature of the output didn't seem to effect on the yield. When the temperature has been high the yield has been significantly lower. When the temperature has been lower the yield has been high. This dependence can be seen from figure 40.

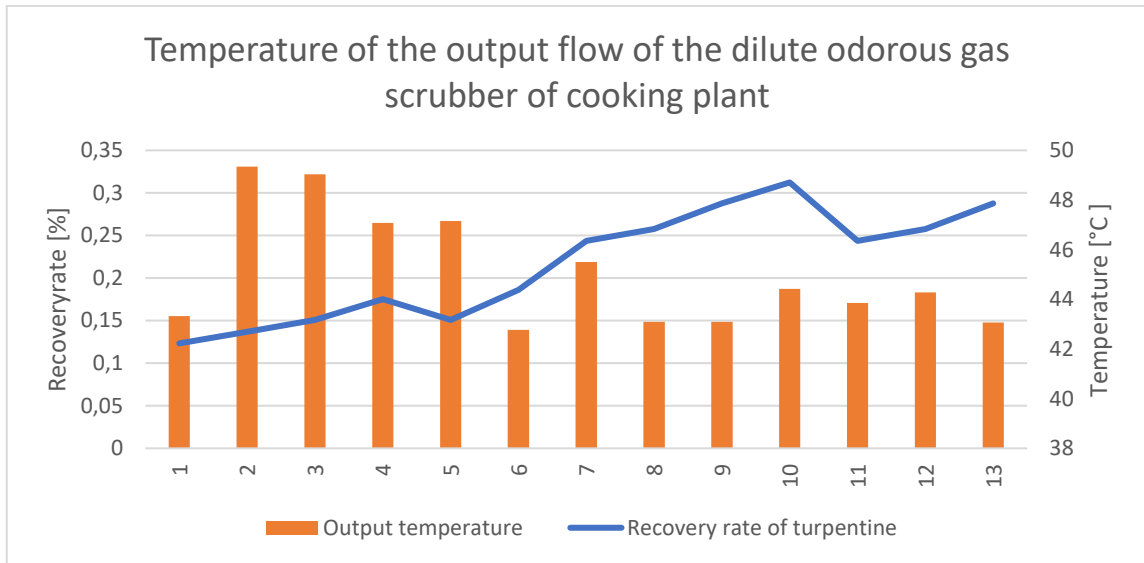


Figure 40. Dependence between output temperature of the dilute odorous gas scrubber and the turpentine recovery rate seems to be significant.

Two other dilute odorous gas scrubbers exist also in the mill, one on the evaporation plant and causticizer. It seems that the incoming temperature of the gas from evaporation plant affects more on the yield than the outgoing temperature of the scrubber. Outgoing temperature doesn't seem to have effect on the yield. Figures 41-42 present the effect between turpentine yield and temperatures of the input and output flows of the evaporation plant's dilute odorous gas scrubber.

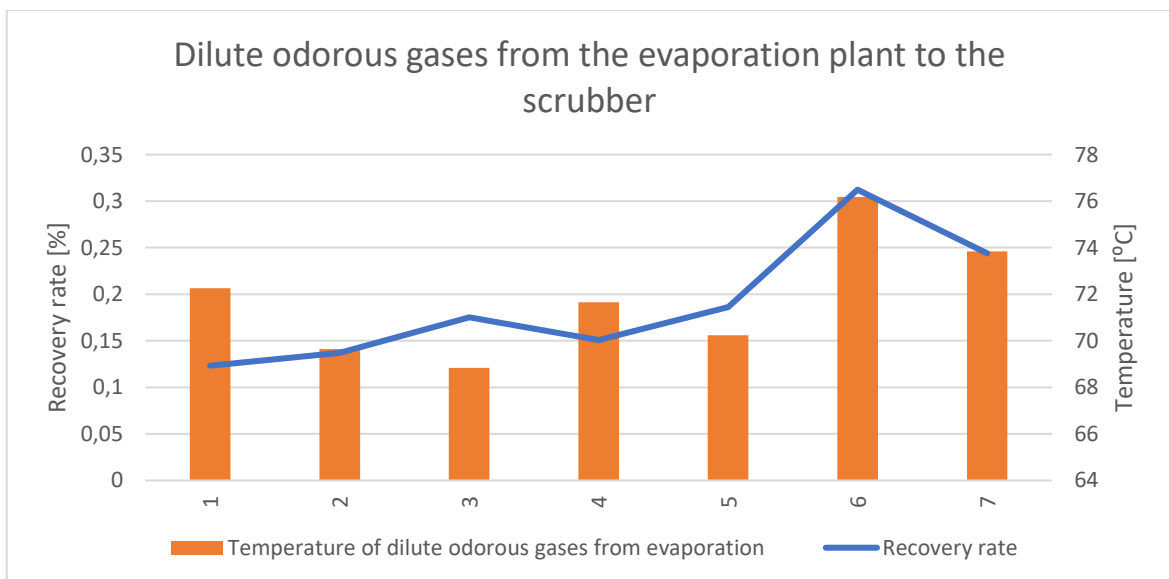


Figure 41. Dependence between the temperature of the dilute odorous gases from the evaporation plant and the yield of turpentine can be seen from the figure.

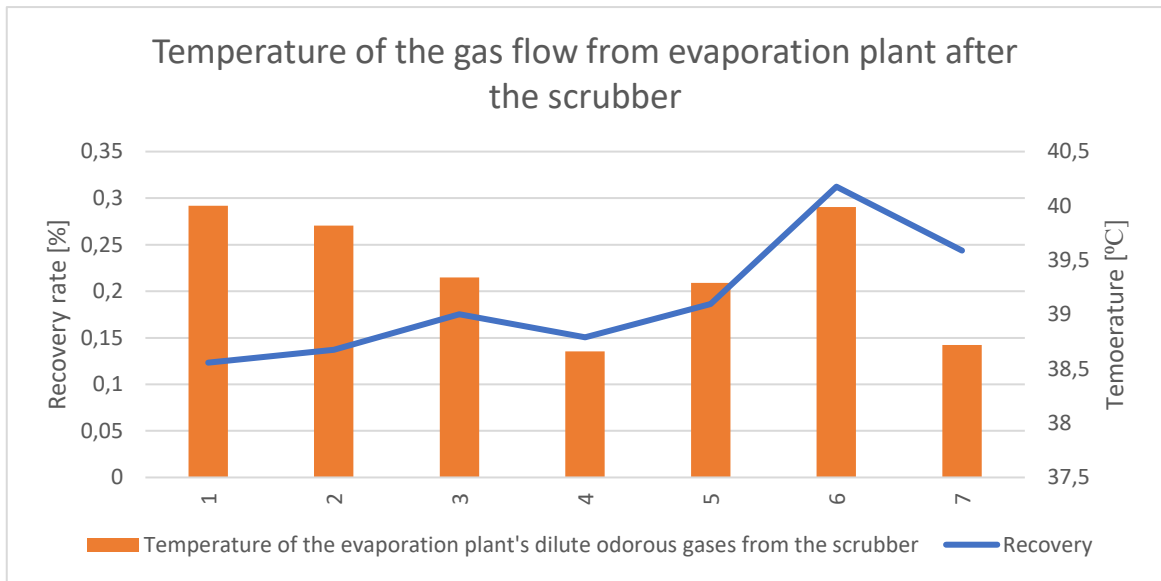


Figure 42. Dependence between the dilute odorous gas scrubber out let temperature and the recovery rate of turpentine.

Temperature of the output flow of the evaporation plant's dilute odorous gas scrubber seems to affect also on the sulfur content. Higher temperature seems to obtain lower sulfur content. This also proves that the sulfur rich compounds are from the evaporation plant. This dependency can be seen from the figure 43.

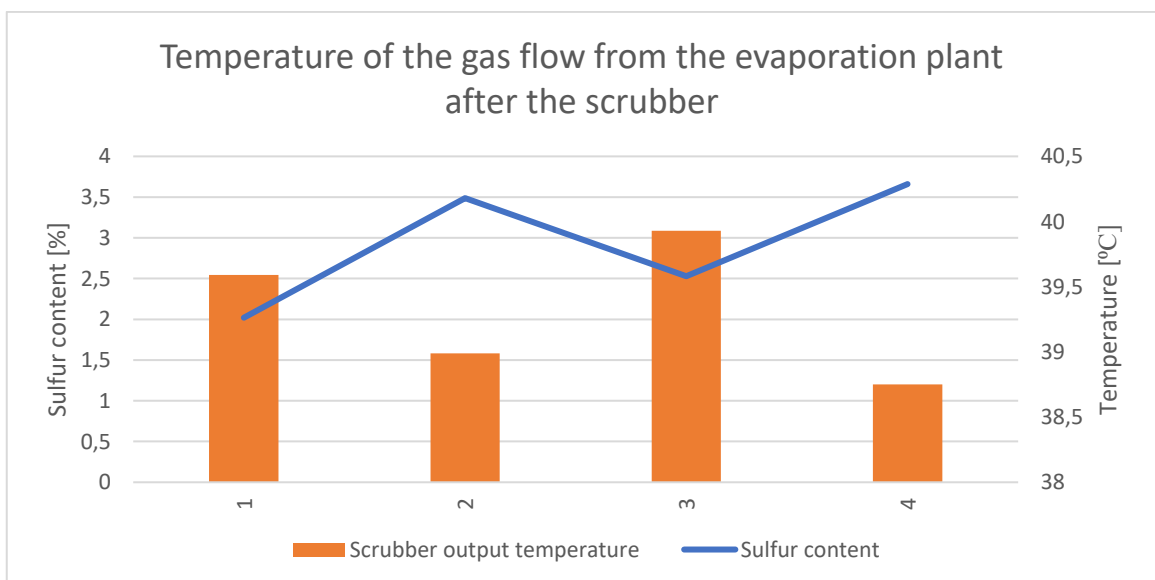


Figure 43. Dependence between the temperature of the evaporation plant's dilute odorous gas scrubber and the sulfur content of the turpentine.

Effect of the temperatures of the dilute odorous gas scrubber from the causticizer is not as obvious as the effect of the temperatures of the input and output streams of the cooking plants scrubber's and evaporation plant's scrubber's but still they seem to follow same pattern as turpentine yield, but it can't be said there would be dependency. The temperature of the input flow seems to have an effect on the sulfur content. This can be seen from the figure 44.

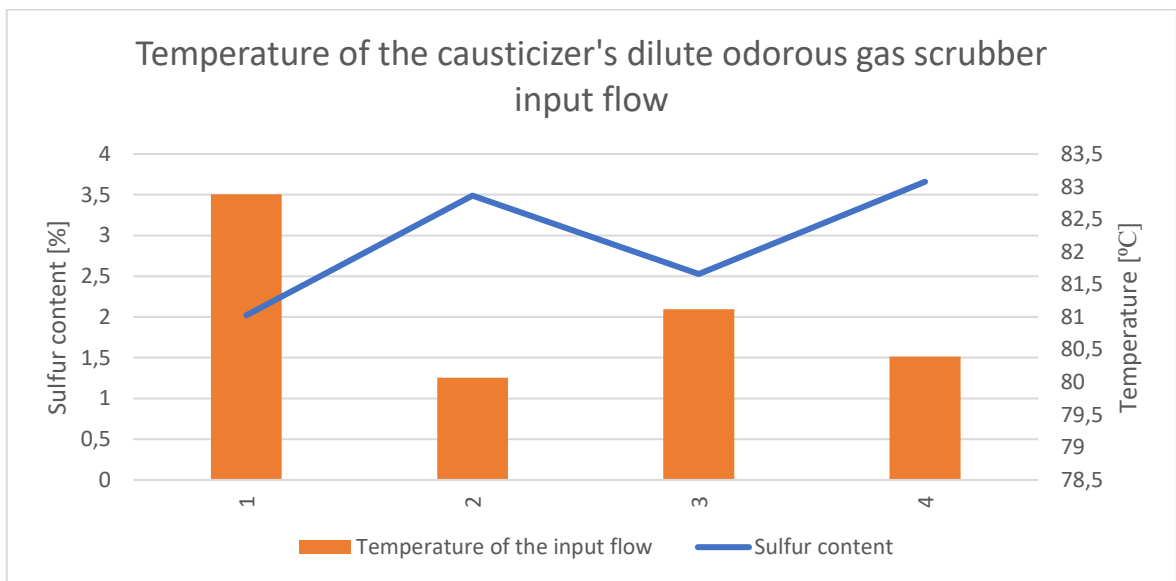


Figure 44. Temperature of the input flow of causticizer effects to the sulfur content of the turpentine.

It seems that the turpentine flow from the strong odorous gases is rather small in comparison with the flow from the foul condensate. It is not a surprise that conditions of the turpentine condenser don't seem to have an effect on the yield much. Temperature of the gas output flow seems to have an effect on the sulfur content of the turpentine. This can be seen from figure 45.

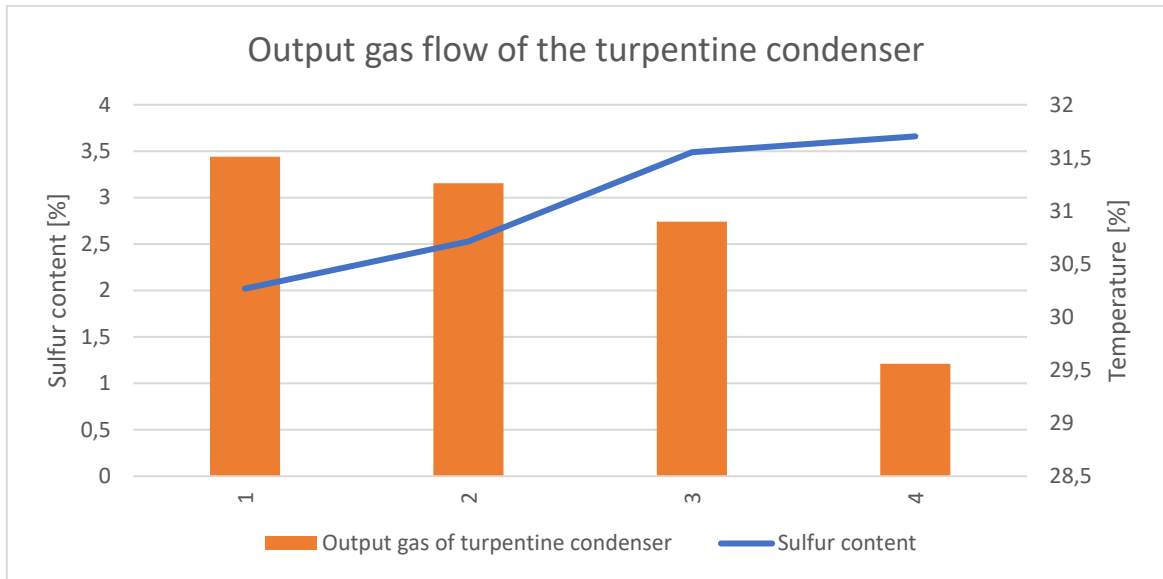


Figure 45. Lower temperature of the output gas flow of the turpentine condenser seems to increase the sulfur content.

Temperature of the strong odorous gases to the lime kiln also seems to have an effect on the quality of the turpentine. When the temperature of the gas is higher the amount of heavy fractions seems to be smaller. This can be seen from the figure 46.

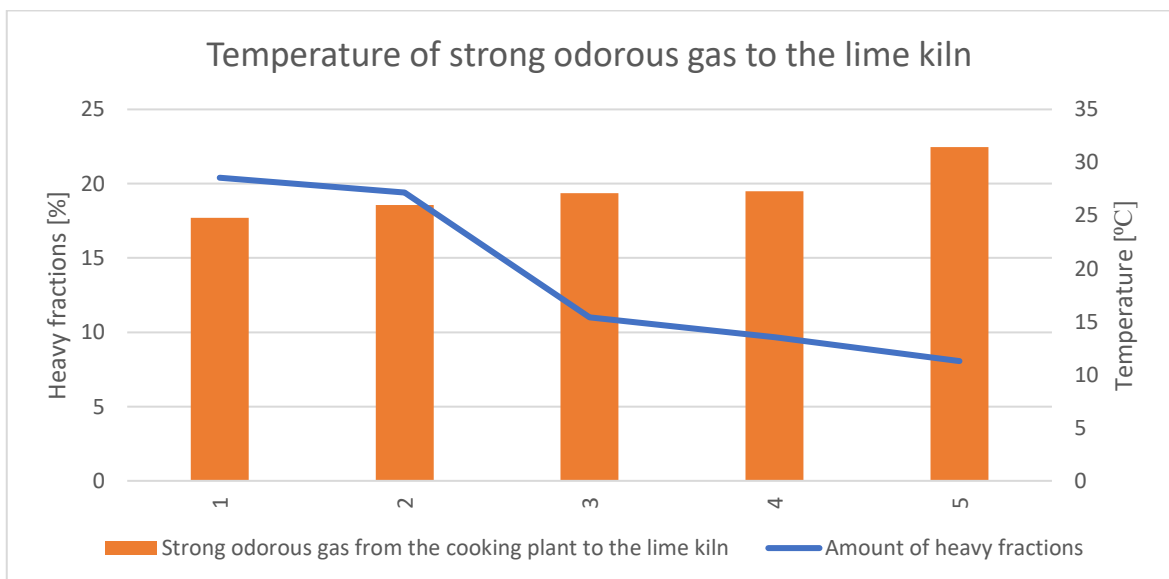


Figure 46. Temperature of the strong odorous gas to the lime kiln seems to effect on the amount of heavy fractions.

Conditions in evaporators also seem to affect the yield and quality of turpentine. Several parameters were followed during the analysis and the paragraph presents the ones which seem to have dependence with turpentine yield. Liquor circulations of the evaporators 1A-1D seem to affect the turpentine yield and especially on the quality of the turpentine. When the temperature is higher the yield and quality have been better. For example, figure 47 presents the dependence between the temperature of the first liquor circulation of evaporator 1B and sulfur content. Figure 48 presents the dependence of the 1. Liquor circulation of the evaporator 1C and turpentine yield. Second liquor circulations also follow same pattern.

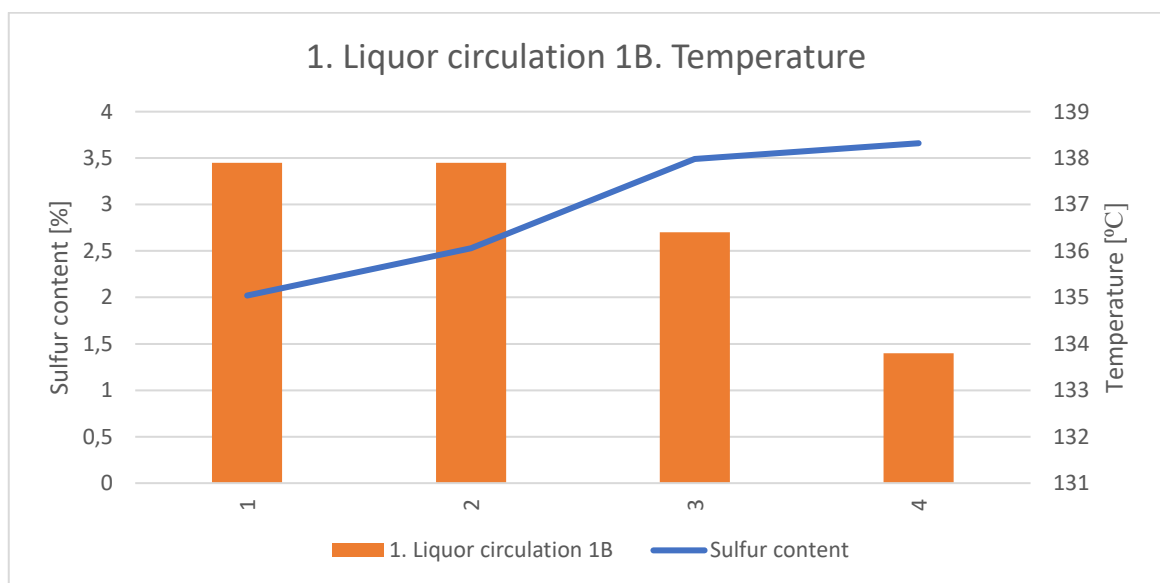


Figure 47. 1. Liquor circulation 1B. and sulfur content seem to be dependent.

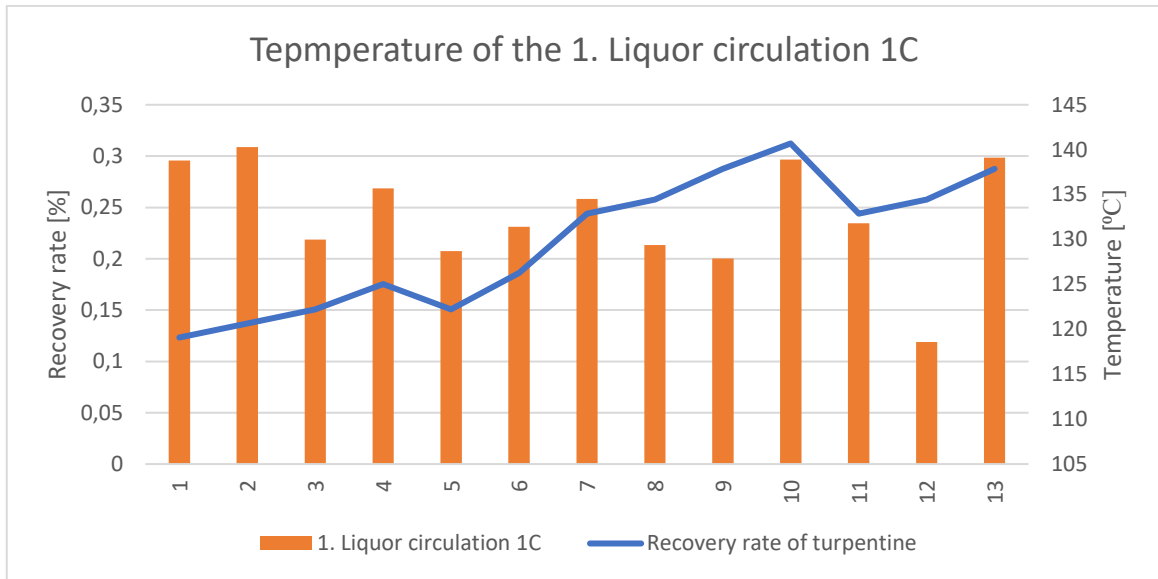


Figure 48. Dependency of the 1. Liquor circulation 1C and recovery rate of turpentine.

It seems that evaporators 1-3 effect more on turpentine yield and quality than the evaporators in the previous stages. It also seems that the evaporators 1A-D effect more on turpentine than evaporators 2 and 3. This can be explained with the fact that the evaporators 1 A-D have higher temperatures than the previous evaporators. Turpentine that would have evaporated in lower temperatures would have evaporated already before the evaporation plant and when the liquor ends up to the evaporation only the fractions with the highest boiling point are still dissolved with the liquor. Sulfur content and yield seems to be better when the temperatures are higher.

Condensate is one of the outputs of evaporators 3-7. Temperature of this condensate seems to affect the turpentine yield and quality. In these condensate temperatures it also seems that temperature of the condensate from evaporators 3 and 4 matters more than the temperature of the condensate from evaporators 5-7. It seems that the higher temperature obtains less sulfur and more yield. Figures 49-51 show the dependencies between the heavy fractions, sulfur content and the recovery rate with the temperature of the condensate from evaporator 3.

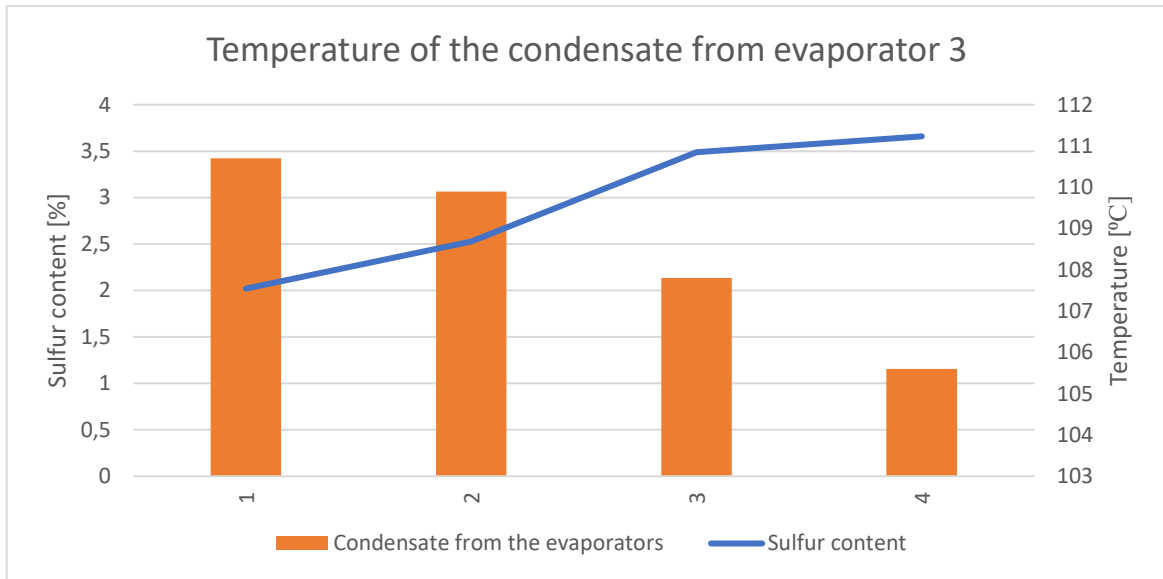


Figure 49. Dependency between the evaporator 3 and the temperature of the condensate from evaporator 3.

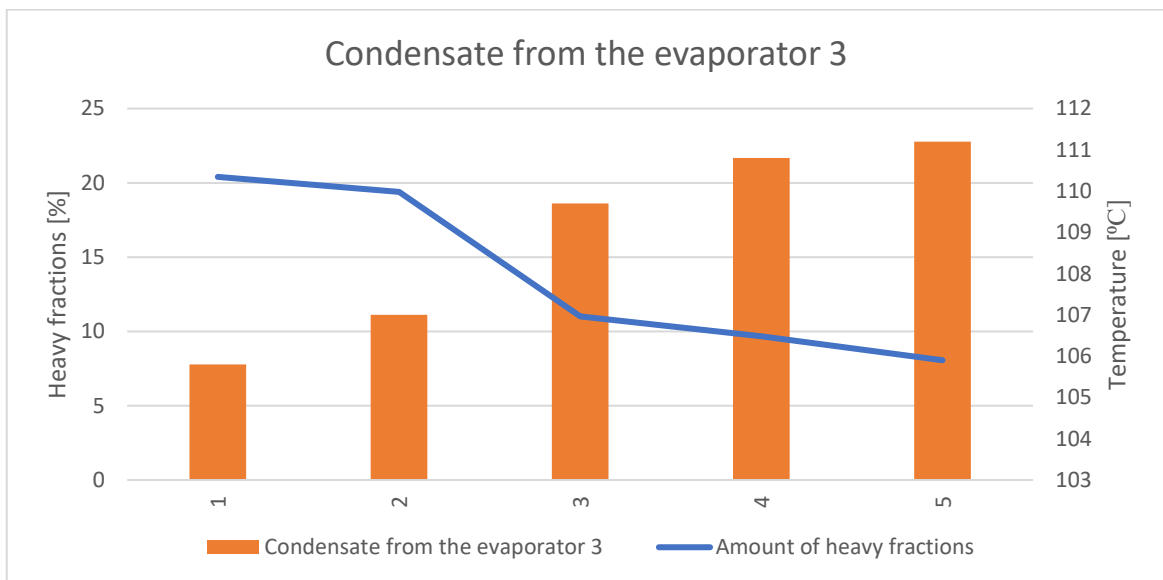


Figure 50. Temperature of the condensate from the evaporator 3 seems to effect on the amount of heavy fractions in turpentine.

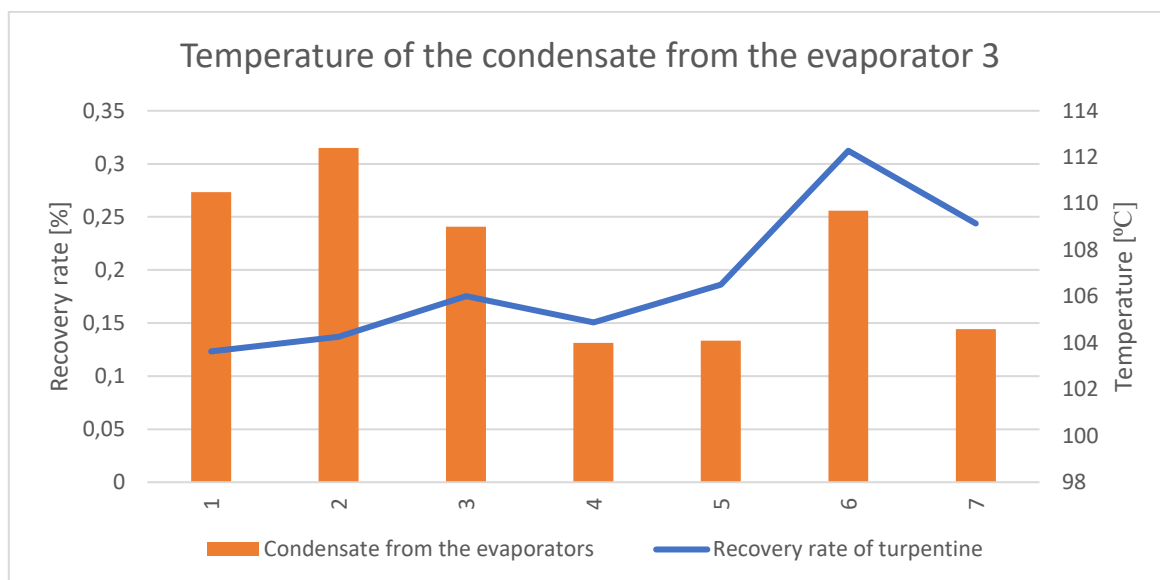


Figure 51. Dependency between the temperature of the evaporator 3 and turpentine recovery rate can be seen from the figure.

Temperature of the steam coming from the evaporators seems to also effect on the yield and quality of the turpentine. Figure 52 presents the dependency between the temperature of the steam coming from evaporators and the sulfur content of the turpentine.

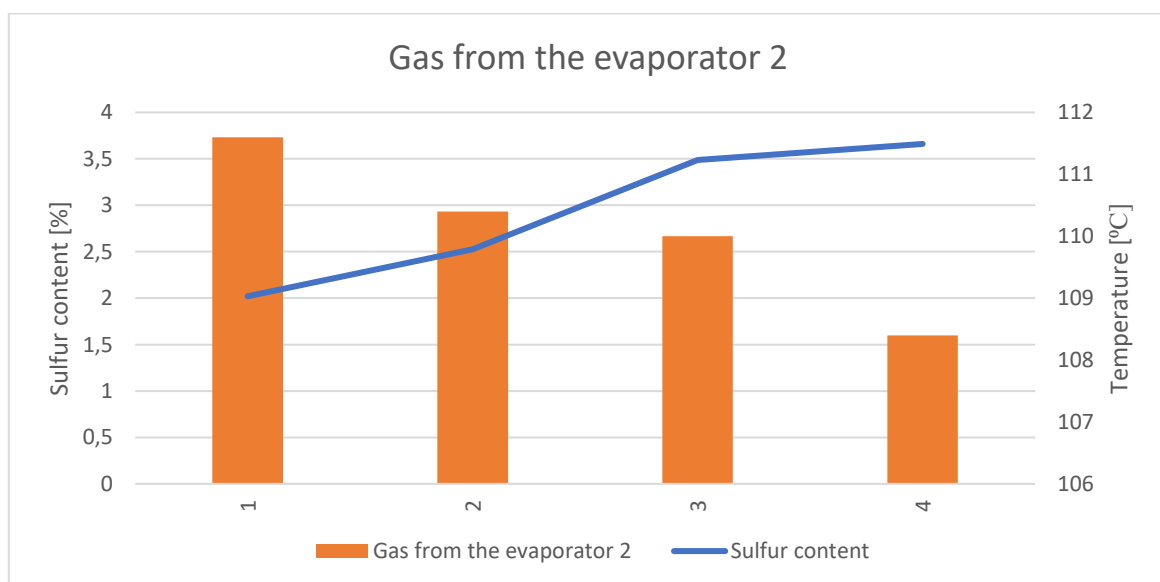


Figure 52. Dependency between the sulfur content of the turpentine and the temperature of the gas from the evaporator 2.

Temperature difference between the liquor and condensate seems to affect the yield and sulfur content as well. When the difference is smaller the yield has been better and sulfur content lower. This can be seen from the figures 53-54.

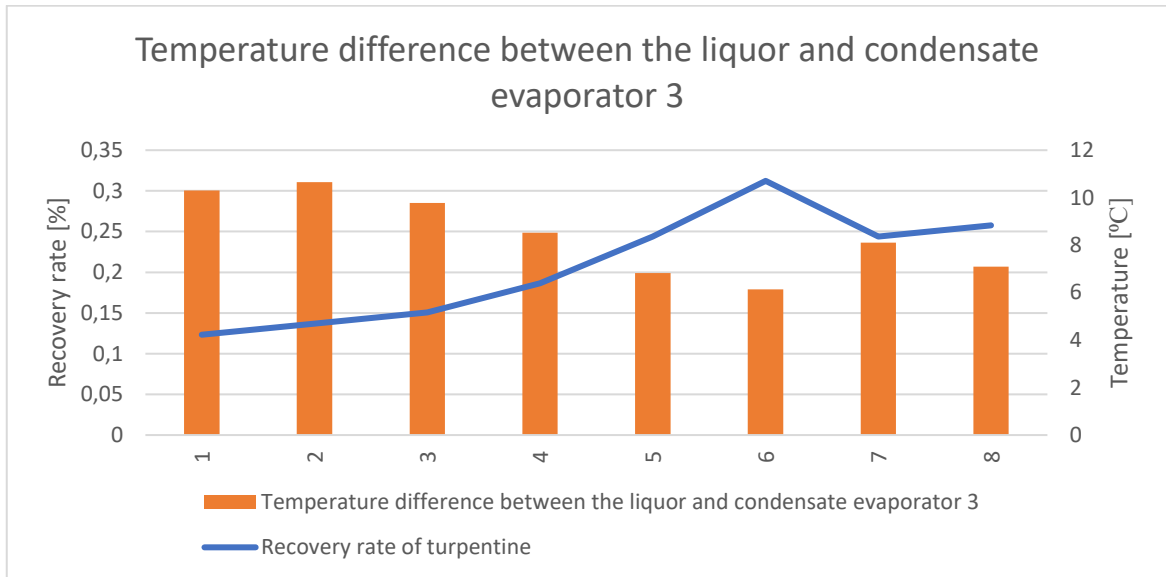


Figure 53. Figure presents the dependency of turpentine recovery rate and temperature difference between the liquor and condensate in evaporator 3.

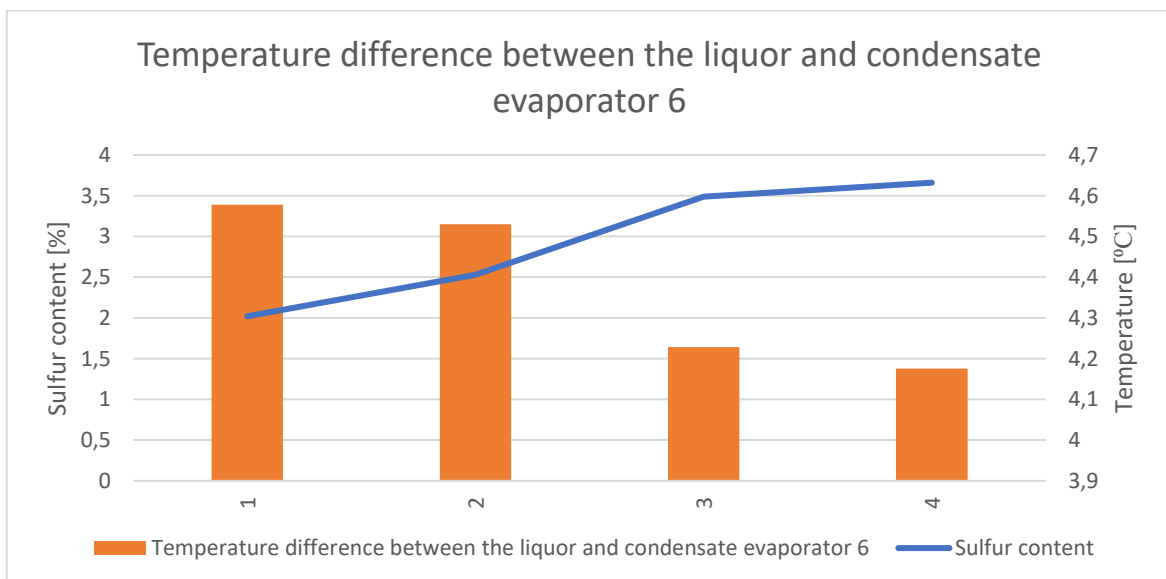


Figure 54. Temperature difference between the liquor and condensate and it's affection to the sulfur content of the turpentine.

Foul condensate is stripped at the evaporation plant. Steam and foul condensate are the stripper inputs and outputs are steam and secondary condensate. Pressure of the steam seems to effect on the yield and quality of the turpentine. This dependence can be seen from figure 55.

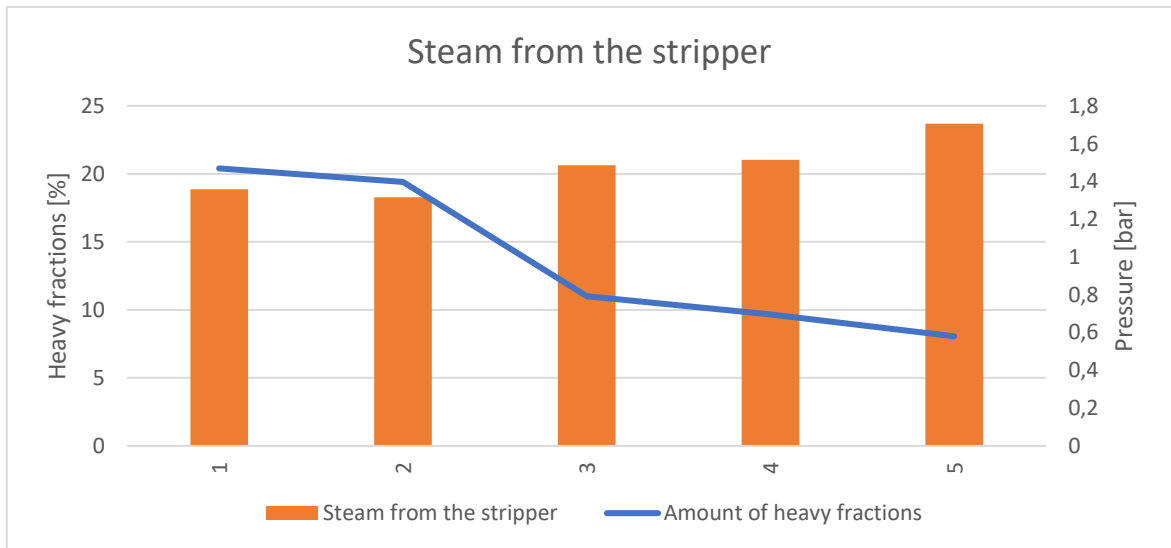


Figure 55. Pressure of the steam from the stripper and the amount of heavy fractions in turpentine.

Temperature of the stripper gas to the recovery effects to the turpentine yield through a heat exchanger that is located to the evaporation plant. It removes the turpentine from the stripper circulation to the turpentine decanter. Effect of the temperature of the stripper gas to recovery to the turpentine yield and recovery can be seen from figures 56 and 57.

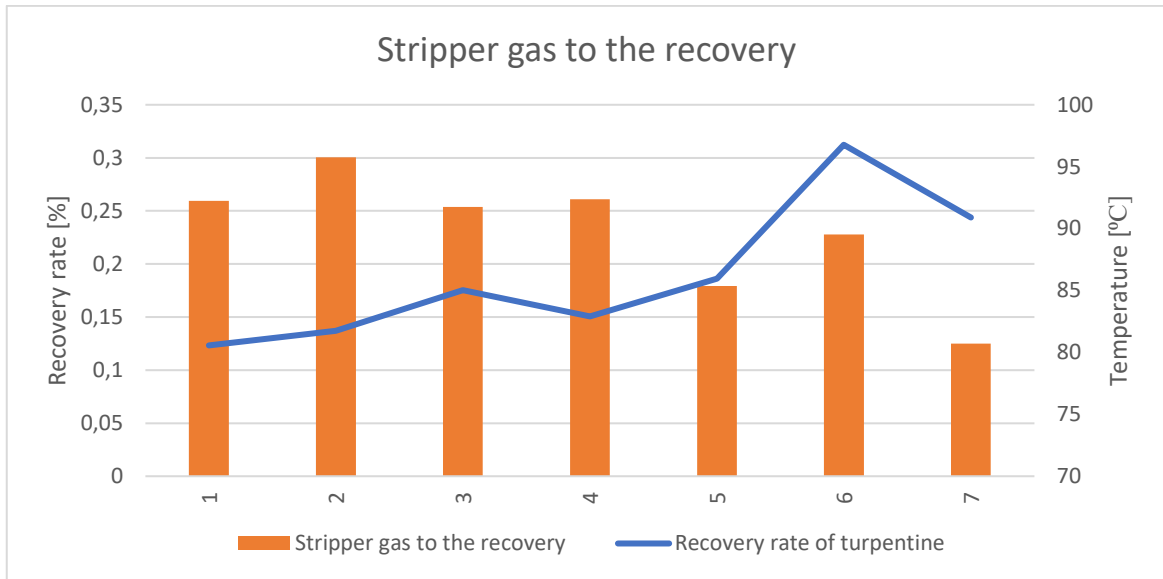


Figure 56. Effect of stripper gases to recovery rate of turpentine is presented in the figure.

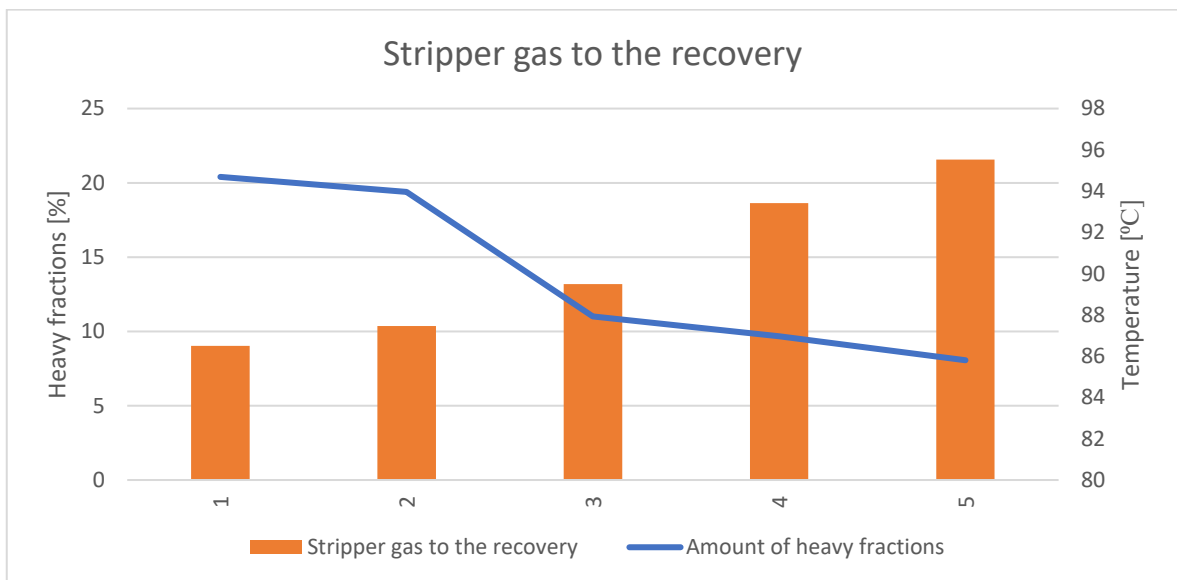


Figure 57. Dependency of the stripper gas to the recovery and heavy fractions.

It seems that big share of the turpentine is mixed with the soap and from soap the turpentine ends up to the tall oil. Relationship between the soap and the turpentine yield was followed through temperature of the soap tanks but the dependence doesn't seem to be clear.

Temperature of the tall oil tank didn't seem to affect either on anything but the temperature of the drying tank of tall oil did. Reason to this might be that the turpentine solved to the water that tall oil includes. The turpentine in this stream is originally from the black liquor.

It seems that when the temperature of the tall oil drying tank is higher the yield of turpentine is higher. It might be caused because the condensate of this tank includes a lot of turpentine, but the turpentine is not recovered through condensate from this tank. When the temperature is higher some of the turpentine evaporates and ends up to recovery through dilute odorous gases scrubber on the evaporation plant. The condensate from this tank is directed to the foul condensate tank and recovered through skimming. This dependence between the turpentine yield and drying tank of tall oil can be seen from figure 58.

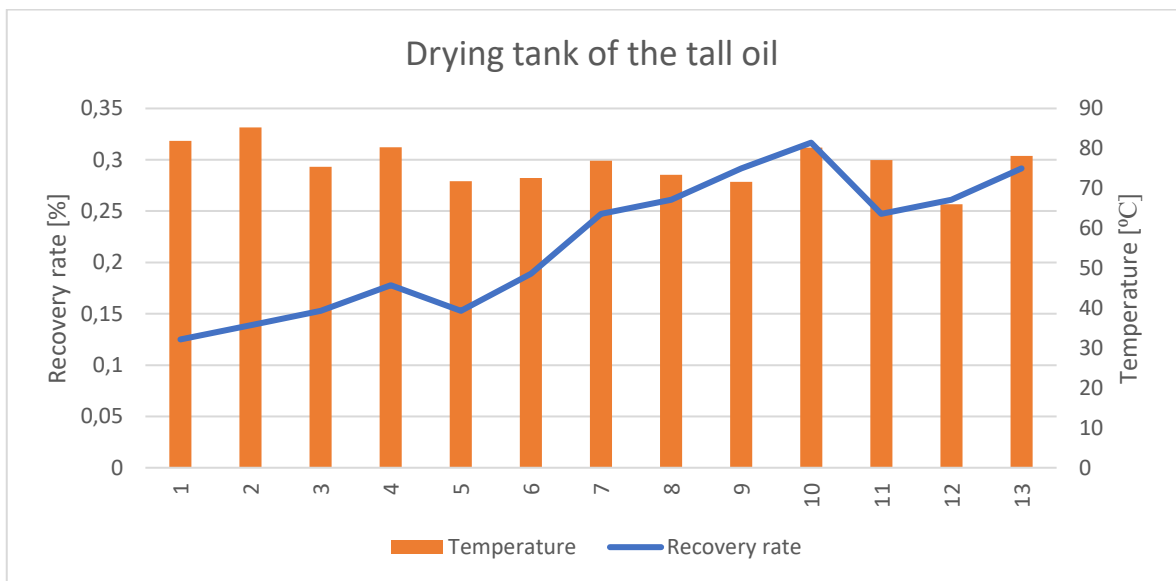


Figure 58. Dependence between the temperature of the drying tank of turpentine and the recovery rate.

Dependency between the sulfur content of turpentine and temperature of tall oil drying tank can be seen from the figure 59. It seems that also sulfur content would be lower if the temperature of the tall oil drying tank would be higher.

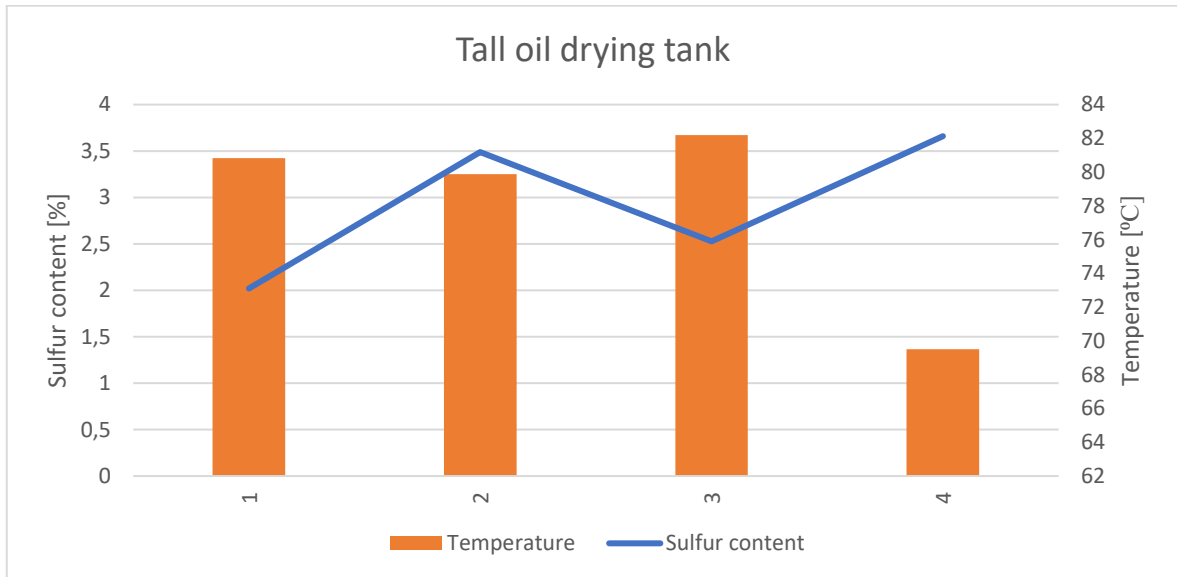


Figure 59. Dependency between the sulfur content and the temperature of tall oil drying tank.

It could be assumed that tall oil tank would have similar effect on yield because of the results of the drying tank of tall oil but no clear dependence occurred between the yield and temperature of the tall oil tank. On the other hand, the sulfur content was lower when the temperature of the tall oil tank was higher. This can also be coincidence.

7.3 Possible changes to the current system to improve the turpentine recovery

The research revealed several methods to improve the recovery system of turpentine occurred. This chapter presents the possible changes to the process, which would improve the yield and quality of recovered turpentine.

7.3.1 Chip bin steaming

One of the limits of the displacement batch system is the lack of time. This problem might be solved by adding the steaming and gas collection system to the chip bin. Chip bin steaming is possible to utilize in Metsä Fibre Rauma, if the mill invests the dilute non-condensable gas collection system. The chip silo already has the steam system and the power plant produces extra steam that could be used for the purpose. The steaming can't be used at the moment because of the lack of gas collection. (Kesseli, 2018)

Non-condensable gases from the chip bin have been defined as a high-volume low concentration source and they are collected with other dilute non-condensable gases. Most of the time these gases are emitted to the dilute non-condensable gas source, but they can reach combustible levels because of turpentine and TRS-compounds. It is common to install a dedicated system for this source. In U.S. the Environmental Regulations require that the non-condensable gases from the chip bins are collected if the steam used is flash steam. On the other hand, if the used steam is fresh steam the collection is not required. Collecting system is described in figure 60. (Frederick & DeMartini, 2017)

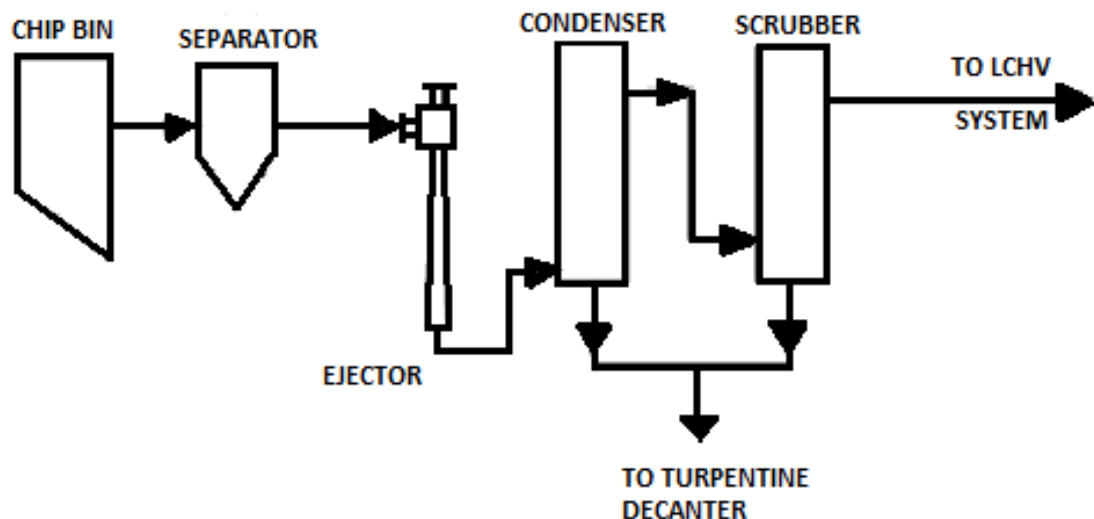


Figure 60. Dilute non-condensable gas from the chip bin can be collected with the system described in the figure. (Frederick & DeMartini, 2017)

In the chip bin the chips are steamed to remove the air before they enter to the steaming vessel. Steaming removes the volatile compounds like terpenes from the chips. Large quantities of turpentine may be present in chip bin gas. One craft mill in US has reported recovering up to 1 kg of turpentine per ADt from the chip bin gas. Especially at softwood

mills the vent stream may also contain high turpentine vapor loadings due to stripping from the raw chips. In locations where a high proportion of softwood is used in the wood supply, like Metsä Fibre Rauma, turpentine liberated in the chip bin and carried out with the non-condensable gases becomes a safety concern if introduced into the main dilute non-condensable gas collection header. The chip bin requires pressure and vacuum protection and fast acting mechanical type devices are preferred. The vent gases from the chip bin are passed through a cyclone separator and cyclone is flushed with hot water or filtrate to prevent fiber hang up. Then the gases are directed to the indirect contact cooler, similar in design to the dilute non-condensable cooler to cool and dehumidify the gases ahead of collection. In softwood mills due to potentially high turpentine levels a direct contact turpentine scrubber is included after the cooler. To recover and remove turpentine from the chip bin gas, the gas is cooled, condensed and scrubbed. Vapor pressure of alpha-pinene is high enough at temperature as low as 30 °C and atmospheric pressure to create an explosive mixture. To avoid safety risks the dilution air needs to be added to ensure a safe mixture. The condensate from the condenser might be too cold to be directed straight to the decanter and it might need to be reheated to avoid problems in decanter. (Frederick & DeMartini, 2017)

7.3.2 Creating liquid-vapor interface to the top of the digester

If chip bin steaming is not possible the optional method is to leave some space for the gases to evaporate. In this method the air is removed from the digester with a vacuum that is placed next to one or several circulation sieves during the chip filling. When the digester is full it is closed and filled with warm and mild black liquor. Black liquor warms the chips and removes rest of the air from the digester. While liquor impregnates to the chips the liquor is circulated. After this some liquid is removed by guiding the circulating liquor to the pipeline that removes the liquid from the circulation. Size of the space is 5-15 % of the digester volume. During this process the pressure is lowered and therefore the gas separation is more efficient. (Pikka & Martikainen, 1999)

Sieves prevent the chips from entering to the venting. Pressure of the digester is adjusted so the efficient gas separation is guaranteed. In the next stage the digester is pressurized with

the steam and the digester is filled with the displacement liquor. Gas removal during the cooking is not compulsory but it is recommended. (Pikka & Martikainen, 1999)

Gas space can also be completed as a separate unit. In this system during the digester filling the vent is closed. After chip filling the gas space is pressurized, and the vent is opened. Gas formed during cooking is directed to the separate gas space and the pressure of the gas space is kept stable. (Pikka & Martikainen, 1999)

In the third method to create the gas space, perforated plate is added to the top of the digester. Advantage of this method is that the digester can be filled with chips up to the plate and the impregnation liquor can be filled to the top of the digester or just above the plate. If the impregnation liquor is filled up to the top of the digester the liquid surface needs to be lowered later. If the surface of the impregnation liquor is left just above the plate the space for gases is left on top of the digester automatically. (Pikka & Martikainen, 1999)

This system was tried with some method at Metsä Fibre Rauma mill years ago, but it didn't seem to improve the yield and issues occurred. Sieves got blocked and it seemed that more issues than benefits occurred. Unfortunately, any written material doesn't exist from these tests and specific timing is not clear. (Peltola, 2018)

7.3.3 Changes to the venting

One of the systems installed to the turpentine system after the explosion in the dilute non-condensable gas system was gasification accumulator. Principle of gasification accumulator was to direct the gases formed in cooking to the gasification accumulator instead of the black liquor accumulators. After gasification accumulator the gas stream is directed to the cyclone separator that separates the liquor from the gases. Gases are directed to the gasification cyclone and black liquor to the evaporation plant. From the gasification cyclone the condense was guided to turpentine separation and the non-condensable gases to incineration. (Kesseli, 1999)

Gasification accumulator was supposed to control the pressure changes during the cooking in the malodorous gas system. Significant improvement didn't occur, and the problem was that the gasification accumulator got contaminated by fibers and pulp. (Mäkitalo, 2018) Gasification accumulator was removed from the process in 2005. (Metso, 2005)

According to the data-analysis the venting pressure could be increased. If the pressures and temperature of the digester and accumulators would increase the turpentine yield would be better as well.

7.3.4 Black liquor flashing or expanding

Uusitalo et al. have planned a system that improves the turpentine recovery rate especially while using displacement batch cookers. It also makes the pulp easier to wash and handle and more odor gases are collected within the plant. The innovation is based on expansion of at least one of the spent liquors directed from the digester to pressurized tanks and directing of released vapor to the turpentine recovery facilities. One of the liquors from the digester conducted to the pressurized tanks expands against a first pressure which is lower than a second pressure equivalent to the boiling point of the liquor before the expansion. The pressure drop represents to 1-5 °C difference in the temperature. Expansion vapor is directed to the turpentine recovery. (Uusitalo et al. 2008)

Several methods to complete the expansion exist. One method to complete the expansions is by heating liquor 1-5 °C above the boiling point at corresponding pressure and letting the heated liquor to flash. The other method is to depressurize the liquor with 1-5 °C temperature drop. The invention can be completed also by expanding the liquor stored in pressurized tanks at temperatures over 100 °C. Preferably the expansion is completed in the pressurized tank that has the highest temperature. One more method to complete the expansion is to feed spent liquor into a tank that holds liquor at saturation pressure in which the temperature of the tank is lower than the temperature of the incoming liquor. The expansion can also be completed by introducing the spent liquor to a tank and the stream of liquor is conducted from tank to a heating device and from there to the gas space that is left above the liquid surface in the tank. The stream of liquor can be directed also from the tank and via heating

device to the expansion vessel and it can be returned from the expansion vessel to the tank. (Uusitalo et al. 2008)

According to the Uusitalo et al the pressure in at least one of the tanks is retsin at or near the saturation pressure of black liquor. Vapors are released in expansion zone from the black liquor stored in tank by adjusting the pressure to or below of the saturation pressure of the black liquor. Pressure is preferred to keep 1 bar under the saturation pressure of the black liquor directed to the expansion zone. The expansion zone is placed inside the tank or outside the tank. The pressure adjustment is corresponding to 1-5 °C difference in temperature. (Uusitalo et al. 2008)

Venting of the displacement liquor digester is done during the cooking phase under liquor circulation and digester temperature adjustment. The best result is achieved when the top liquor circulation conduit is placed in the top of the digester above the gas space or into a vessel above the gas space during the temperature adjustment and cooking phase under liquor circulation. This system is supposed to improve flashing. Pressure control controls the venting from the digester at a pressure bigger than or same as the saturation pressure of the liquor directed to the liquor-vapor interface. The pressure should be kept stable at around the saturation pressure of the liquor directed to the liquor-vapor interface. (Uusitalo et al. 2008)

7.3.5 Turpentine collecting system from the dilute odorous gases

According to previous measurements there is a significant amount of turpentine in the dilute odorous gas system. (Enwin, 2009) (VTT Kemiantekniikka, 1998) Dilute odorous gases are collected from many places but most of them are from the beginning of the cooking and from the tank relief gases. The cooking gases are directed to the gas scrubber that cools the gases from 80 °C to 50 °C. This decrease is enough to condense at least most of the turpentine from the cooking. (DNA Operate Client, 2018) Amount of turpentine in this condensate was measured earlier, after the installation of the scrubber to the dilute odorous gas system and it included a lot of turpentine but also fibers. It seems that if this turpentine would be collected it would need fiber filter and own decanter. (Kesseli, 2018) Tank relieves are also scrubbed in the evaporation plant and causticizer. It seems that also these streams effect on

turpentine yield. Turpentine yield can be improved by optimizing the temperature of these scrubbers.

If it seems that dilute odorous gases include a lot of turpentine that doesn't go through the scrubbers, secondary condenser can be added to this system. According to Foran, sulfur content of this turpentine is higher. (Foran, 1995) To define whether there is need for the secondary condenser or not more gas measurements should be done.

7.3.6 Turpentine stripper to the foul condensate stream

Turpentine stripper is described in the turpentine recovery chapter. In Metsä Fibre Rauma turpentine from the foul condensate is skimmed from the foul condensate tank. The overflow collection system is not automatized but the turpentine is collected irregularly by operators and clear system when or how often the turpentine is collected from the condensate doesn't exist. It seems also that the high amount of turpentine from the evaporators might cause problems to the quality. Turpentine from evaporators is directed to the foul condensate tank.

Turpentine stripper is installed between the cyclone and turpentine condenser. Strong odorous gases come from the cyclone and heat the condensate that will strip to the strong odorous gas stream and continue to the surface condenser. (Morris, 2015) This system reduces foul condensate loading to the stripper and turpentine decanter. It also improves heat recovery. (Frederick & DeMartini, 2018)

7.3.7 Raising decanting temperature

Temperature of the decanter is not measured in Metsä Fibre Rauma mill. Turpentine condense from the surface condensers is measured and the temperature of foul condensate streams before the foul condensate tank are measured. The pipelines from the cooking digesters and evaporation plant where the foul condensate tank is located are long and the temperature of the foul condensate tank is not measured. (Kiuru & Heikkinen, 1995) (Annala, 1994)

Temperature of turpentine decanter was measured with two thermometers. First with thermographic camera and also with the surface thermometer. Both thermometers are used from the outside surface of the decanter, so the temperature inside the decanter might be little higher. Significant differences between higher and lower parts of the decanter couldn't be found. Temperature of the pipelines to the decanter were also measured.

Temperature of the smaller stream to the decanter from the foul condensate tank was higher than from the cooking plant. Temperature of the stream from foul condensate tank was as high as 60 °C and the bigger stream from the cooking plant was only 33 °C. Temperature of the decanter was 31-33 °C depending on the device used and the height of the measurement point on the decanter. Temperature of the overflow stream from the decanter was also measured and it was 30 °C. This pipe line is located higher and the distance between the thermometer and the pipe line was longer. This can effect on the measurement result. Results of the measurements show that the decanting temperature of turpentine is significantly lower than in Courtland mill where the optimal decanting temperature was 43 °C.

As described earlier decanter temperature could be controlled with the amount and temperature of condensate from the foul condensate tank. The temperature should be optimized in the way that the total turpentine loss is minimized. Increasing decanting temperature also decreases the amount of sulfur components in the turpentine. It would be recommendable to add online temperature measurement on the turpentine decanter and follow it with the process controlling system.

7.4 Result analysis

While analyzing results of the laboratory analysis it can be assumed that the amount of turpentine in samples is affected by the outside weather during the sampling. The sampling and analysis were completed in august and after warm summer. According to Drew the amount of extractives in the wood is generally lowest in the end of the summer and highest at the winter. This can be assumed to be caused by the smaller amount of turpentine in the wood due to the warm weather at summer time. A reason to smaller yields in summertime can also be warmer conditions in the mill in general. In data analysis was noticed that

temperatures in general were a bit higher at summer time than in winter time and this might also effect on the process.

The plan at the beginning was that all the samples would have been taken at the same time and from one cook. This wasn't possible because of the timing, dispersion between the samples and because all the samples weren't analyzed in the Metsä Fibre Rauma. This might cause issues to the material balance because of the changes in the raw material, weather and process conditions. For example, the dilute odorous gas scrubber temperature was lowered before the sampling of gases and it should affect positively on the turpentine losses through dilute odorous gases but also increase the amount of turpentine recovered through foul condensate. These changes are visible only in the dilute odorous gas sample but not in other parts of the material balance.

Turpentine material balance is formed during VOC-project at 1998. Turpentine amount in the chips seems to be close to this amount still. Results of the chip analysis were dispersed and the differences between two identical analysis occurred especially while analyzing samples that included more spruce than pine. These differences were expected and an attempt on solving them was done by taking the samples three times during few hours and mixing the sample analyzed from these three samples. At least two identical samples were analyzed and if there was a lot of dispersion between the two, more samples were taken and analyzed.

According to the theory part the amount of turpentine in the incoming chips was expected to be dependent on the wood specie and on the amount of chips from sawmills and chips from the debarking. Chips from the sawmills were expected to include less turpentine than fresh chips from the debarking. It was expected that the results would show difference in turpentine amount between the stored chips and the fresh chips. As can be seen from the results, they don't prove all the expectations. These differences can be caused by the inhomogeneous quality of chips. Amount of turpentine in the pine was significantly higher than in the spruce in all analysis as it was expected to be. Unpredictably all three pine samples had smaller dispersion than both spruce samples. In samples that included mostly pine the difference between two identical analysis was at highest 12,5 % but while analyzing

samples with higher spruce content the difference was up to 75 %. One sample that was supposed to include mostly spruce from the cooker infeed conveyor was abandoned because the turpentine content of this sample was significantly higher than theoretical references assumed to be possible. It seems that this sample included more pine than spruce and it would have caused errors to the material balance of turpentine. Other possible reason to the unexpected results of the chip analysis might be that the chip ages can be varied. It is possible that the wood that was chipped in debarking was older than the wood in the chips that were going to the cooking digester from the chip pile.

Liquor samples were all taken from digester six because it had best possibilities to obtain representative samples. This can affect to the analysis if there are big differences between the digesters. Only one sample from each different liquor was taken and analyzed and this causes issues to analysis results. Liquor samples taken from digester six were cooled before sampling. Liquor sample from accumulators to the evaporators wasn't cooled since cooling system wasn't available. This might cause small changes to the results.

It was expected that all the samples that were taken while cooking mostly pine would contain more turpentine than the samples taken while cooking mostly spruce. Only impregnation liquor samples didn't follow this expectation but the difference between the two was smallest, so the range of the results seems to be correct. The sample from black liquor from the beginning of the displacement seems to have high differences between the two samples. More samples from these streams would be needed to clarify the actual amount of turpentine in these streams. Turpentine amount in displacement liquor from end of the cook seems high but it is possible since the turpentine in this stream is most likely not only from one cook, but it includes also turpentine from the previous cooks.

Results of the liquor samples seem to be reasonable except for one sample that was not utilized in the material balance. This sample was the liquor sample from the accumulators to the evaporation while cooking mostly pine. This sample seems to be too high and it is in totally different scale than the representative sample while cooking spruce. To determine the turpentine amount in this stream more samples should be analyzed. This was not possible in

the time frame available and because of this only the sample while cooking spruce is utilized because it seems more reasonable.

Results of the pulp samples seem reliable. The amount of turpentine in the pulp was assumed to be low and it was. Unfortunately, it was impossible to determine the amount of turpentine in the pulp after washing with the analysis method used but it can be assumed that it includes turpentine less than 3 % of the amount of turpentine that comes to the mill (Kovasin, 2018). Pulp samples were stored longer than two weeks and the sample was warm when taken.

Condensate samples were taken from several positions. These positions were chosen, because they were important part of the material balance or because it was assumed that they would include large amounts of turpentine. Analyzing method used determines the amount of turpentine but not the quality of it. If the content of turpentine in the sample is really low the analysis doesn't determine the amount of turpentine in the sample. This happened with the pulp washing filtrate and the secondary condensates 2 and 3. It is possible that these samples don't include turpentine, or the share of turpentine is extremely low. Even if the share would be low the amount of turpentine in the flow per ADt can be significant if the volume flow of the stream is big.

Analyzing results of condensates didn't have a lot of dispersion, only the amount of turpentine in the foul condensate from the evaporators and filtrate of the dilute odorous gas scrubber of cooking plant had changes but the reasons to these changes were different. It was found that the turpentine didn't form on the top of the trap but drops formed that seemed to be turpentine but they didn't decant on the top of the condensate. The drops floated back to the reactor with the condensate and evaporated again. Sample from the evaporators seems to be red oil and this would mean that at least some of the turpentine that has high sulfur content would be originally from the evaporators. Turpentine from the evaporators was also heavier than condensate since it didn't decant on top of the trap. The turpentine and some condensate from this sample was collected and let to decant. After some time the turpentine formed two phases to the condensate. One layer of turpentine was on the top of the condensate and on the bottom of the bottle was second turpentine phase. Both of the turpentine phases were orange while the condensate was light and blurry.

Foul condensate from the foul condensate tank to the stripper included more turpentine than the foul condensate from the evaporators. This sample also included the heavy drops of turpentine and turpentine that decanted on top of the trap. Turpentine from the foul condensate was bright orange coloured and can be assumed that this condensate included a lot of sulfur since the red colour of the turpentine comes from the sulfur. Heavy fraction that formed drops that didn't decant seems to be red oil. (Tyre, 2018)

Results of the secondary condensates were doubted since it would seem more logical that secondary condensate 2 and 3 would include some turpentine but secondary condensate 1 wouldn't since it is supposed to be the cleanest possible secondary condensate. Afterwards during the annual maintenance, it was found that stripper package of the unit 2 was damaged and stripper gas ended up to the condensate of the unit 3 and from there to the secondary condensate 1. This explains the unexpected results.

Filtrates of the dilute odorous gas scrubber from the evaporators and causticizer also included turpentine. Filtrate from the dilute odorous gas scrubber from evaporation plant is directed to the foul condensate so turpentine from this stream is recovered. Filtrate of the dilute odorous gas scrubber from the causticizer included more turpentine than the evaporators scrubber but the volume flow of this stream is much smaller than the stream from evaporators and because of this it seems smaller. Filtrate of the dilute odorous gas scrubber from the causticizer is directed to the alkaline sew so the turpentine of this stream is not recovered. Turpentine to this flow is assumed to be originally from the secondary condensate that is used in the scrubber. These flows don't have measurement devices so the amount of the volume flow had to be estimated. Estimation was based on the designing values of the pipes with 20 % addition because it was estimated that the volume flow has increased from the time when the designing values are determined. Designing values were found from the flow diagrams.

Filtrate of the dilute odorous gases from the cooking plant had dispersion between the samples because the samples were taken from two different places. First samples didn't include turpentine, but the last samples did. Only the last samples are utilized in the material

balance of turpentine because they seem more reliable. Filtrate was also warm while taking the sample since the cooling system wasn't available. Most effective uncertainty in the analysis was most likely that there wasn't measurement about the volume flow of the filtrate. Designing value was found from the flow diagram was used for the calculations because of this.

Same problem with the lack of volume flow measurement occurred while analyzing the condensate from tall oil drying tank and decanter under flow. Volume flow of the condensate from the tall oil drying tank amount was measured by flowing all the condensate to the bucket and measuring volume of the condensate in the bucket and measuring time of flowing. From the volume of the condensate in the bucket and the time used for flowing the volume flow was calculated. This measurement method is most likely very unreliable, and it would need to be measured with better method to get more reliable results. Decanter underflow was measured by closing the vent that removes the water from the decanter and let the surface rise. Time while doing so was measured and the increase of the liquid in the decanter was also measured. Volume flow was calculated with these values and radiator of the decanter. This measurement is also very unspecific since the condensate comes to the decanter cyclically and the chosen time period didn't necessarily represent the actual volume flow very representatively.

In general, all the samples weren't cooled, and the samples were taken from the positions where it was possible. These locations weren't always in vertical pipeline and in the right side of the pump. Changes in the content of the samples might occur even if at least two samples were analyzed in order to define the dispersion. Timing might cause issues, production wasn't always necessarily optimal and stable, and this might cause that the samples are not representative.

Results of the gas samples differ quite dramatically from the previous measurements. In previous measurements the amount of turpentine was larger in the dilute odorous gases and smaller in stripper gases and strong odorous gases. Two previous measurements had quite similar results, but the newest ones were different. This might be caused by changes in the process since the previous measurements were completed long time ago. The changes in the

process are not possible to evaluate since the process data from the time the samples were taken is not available. More samples should be analyzed to evaluate whether the results are representative or not. Measurement accuracy of the method is 0,1 µg/l which while analyzing dilute odorous gases stream is up to 4 % of the turpentine coming to the process.

Amount of turpentine in tall oil was higher than previous researches but the high content is possible and would explain the lower yield even if turpentine amount in tall oil is significantly bigger than in earlier research. Earlier research was completed at the end of 19th century and from these days the yield of tall oil has increased 25 %. This could explain the increasing amount of turpentine lost with tall oil. Turpentine is possible to separate from the tall oil, but it might not be efficient to do this process at the pulp mill (Kovasin, 2018). Tall oil is made from the soap and soap is skimmed from the liquor (Know pulp, 2018). This seems that the turpentine drifts with the liquor.

Laboratory analysis in general just represent the situation at the moment they are taken and if there is something unusual going on in the process they might not be representative. More measurements would be needed to have more reliable results in general. The turpentine material balance formed therefore represents the balance of the end of summer 2018. Summer 2018 was unordinary warm and the analysis for the balance were taken in the end of summer.

Inputs and outputs of the turpentine material balance didn't match but this was expected to happen. The balance is formed from samples taken different time. The gas samples were taken in the end of September and chip samples in August. Amount of turpentine in the chips was most likely smaller in August than in September since the weather was warmer. Measurement accuracy also causes differences to the balance.

Results of the data analysis seem mostly reliable and consistent. It seems that methods that improve yield improve also quality. Dependencies found during the data analysis seem to mostly have logical reasons for the improving effect. While comparing yield there was 10-13 measurement points. Probability that these dependencies would be just coincidence is lower than while comparing quality of the turpentine and the process data. While comparing

sulfur content and process data, four measurement points were utilized. In this analysis the uncertainty is higher, but the results seemed to follow same pattern that seems logical. While comparing amount of heavy fractions and the process data five measurement points were used. Results of this analysis seemed similar to the analysis which compared sulfur content and process data. While temperature was higher the content of heavy fractions seemed to be lower. Some of the dependencies were found from the same parameters and this also seems to prove that these parameters do effect on turpentine yield and quality.

Delays of the process were tried to minimize by utilizing long time periods while comparing the yield or quality and data. Measurement points are not just one moment but they are average values of few months or even years. This stabilizes the delays of the process and brief unsteadiness in the process. This was also assessed to stabilize the problems with the irregular transport times of the turpentine and the deposition of the turpentine in the storage tank. This also tackles the problems with timing the quality changes on the process.

All the parameters that effect on turpentine are most likely not found and the ones that are presented were the ones that followed the yield and quality most regularly. It seems that there are several parameters that effect but not as strongly as the ones presented and there weren't enough proofs that they would actually have an effect and the similarities weren't just coincidence. Some of the dependencies found can also be coincidence or the values are affected by another parameter that has an effect on turpentine and the dependency seems to be there even if it actually doesn't have significant effect.

Pressures and temperatures of the accumulators and digester most likely do effect on the yield of turpentine. If the pressure is higher, more gas flow to the strong odorous gases will occur. The dependence seems logical but to prove it, more analysis would be required. Temperature increase seems to lower the sulfur content as well. Dependence between amount of heavy fractions and conditions of cooking digesters and accumulators aren't found. Temperature of the pulp from the digester seemed to also effect on the sulfur content. This is caused most likely because the pulp from the digester includes turpentine and the turpentine will evaporate if the temperature is high enough. The turpentine from the pulp includes a lot of sulfur but sulfur content of recovered turpentine seems to be lower if the

temperature is higher. Already small temperature increases seem to decrease the amount of sulfur.

From dilute odorous gases the turpentine is removed with gas scrubbers. From strong odorous gases the turpentine is removed with the turpentine condenser and if the turpentine is not condensed in these systems it is burned. Filtrate from the scrubber is directed to the screening. The filtrate circulates to the screening and back to the scrubber. If the turpentine wouldn't have access out from this circulation safety issues would most likely occur because turpentine would enrich in this process. It seems that even if the route of turpentine isn't clear, it does exit from somewhere perhaps through evaporation. It even seems that at least some of the turpentine ends up to the recovery since the effect of temperature control was seen in turpentine recovery. It would be safer to guide the filtrate to the foul condensate and recovery process. This could result increase in the yield if the temperatures of the input and output flows are optimized. If the temperatures are optimized scrubbers will improve both the yield and quality of the turpentine in more secure way. Increasing amount of turpentine in the dilute odorous gases might cause safety issues that need to be assessed. Filtrate from the cooking plant's scrubber and evaporation plant's scrubber go to the foul condensate tank but filtrate from the causticizer goes to the alkaline sew and isn't recovered. This stream did include some turpentine that is estimated to be originally from the secondary condensate. Secondary condensate from the evaporators 1-4 did include turpentine in the laboratory analysis and all the secondary condensate ends up to the two tanks that are connected to each other so the turpentine spreads to the both tanks.

Amount of turpentine in the strong odorous gases is significantly smaller than in dilute odorous gases. The dependence of the turpentine condenser input and output temperatures wasn't visible in the analysis even if it obviously affects. Instead the effect of the temperature increase was clear to the sulfur content. When the temperature is increased only couple degrees the sulfur content is instantly lower. Temperature of the strong odorous gases seems to effect on the amount of heavy fractions as well.

It seems that the evaporation units 1-3 effect more on the turpentine than the previous units. This result was doubted a lot in the mill. It was assumed that in last units there wouldn't be

any turpentine but according to the analysis it seems the other wise. Some issues have occurred at the evaporation plant and one of them is that the evaporator unit 3 is fouled and it causes some issues with the evaporation process. This might effect on the results as well.

Evaporators 1 A-D and 2 are pressurized but evaporators 3-7 are in under pressure. Temperatures of the units 1-2 are above 120 °C and units 3-7 less than 102 °C. (DNA, 2018) It is possible that some components with higher boiling point would segregate in the higher temperature or the conditions of the units 1-3 effect on some other parts of the process and through them to the turpentine recovery.

Temperature of the stripper gases effects on the turpentine content since some turpentine is recovered from the cooling system that is located after the stripper but before the strong odorous gases are directed to the pipeline that directs them to burning. This turpentine seems to include heavy fractions, but their amount can be controlled by optimizing the conditions of the streams of the stripper. Turpentine from this stream has low quality since temperature increase of the stripper gas to the recovery and steam to the stripper seems to improve the yield but decrease the yield.

Tall oil seems to include a lot of turpentine and it would be logical that conditions of the tall oil handling would effect on the turpentine yield. Temperature of the tall oil drying tank affects to the turpentine yield through the dilute odorous gas scrubber of the evaporation plant. Gases from the tall oil drying tank are directed to the dilute odorous gases and the gases go through the scrubber before they are burned. Filtrate from this scrubber goes to the foul condensate tank and turpentine is skimmed from there. Turpentine from this tank seems to be good quality since the temperature increase of the tank will lower the sulfur content of the turpentine.

8 CONCLUSION

Problems with turpentine recovery system are common while using SuperBatch cooking and these problems have been tried to solve with several methods. Several solutions how to improve turpentine recovery exist. Turpentine recovery would be important to have under

control to avoid safety issues related to turpentines hazardous nature. It is also important to realize where the turpentine is located in the process, so the risks can be assessed.

Biggest losses of turpentine are through the tall oil and strong odorous gases according to the new material balance of turpentine. Only 17 % of turpentine is recovered. Most likely the turpentine comes to the strong odorous gases from the stripper gases. If this measurement results are reliable secondary turpentine condenser could be added after the stripper. The temperature of the condensers should be optimized. Several small streams could be directed to the foul condensate. Turpentine could be also skimmed from the secondary condensate tank.

If turpentine is not removed while cooking process it drifts with the liquor and soap to the tall oil and evaporation system and with other substances. From these substances the liquor evaporates, and it is directed to the dilute odorous gases. If turpentine doesn't condensate while scrubbing it is burned. Tall oil seemed to include large amount of turpentine. More research would be needed to find methods how to separate the turpentine from the tall oil or how to prevent turpentine drifting with tall oil.

Turpentine flows from the dilute odorous gas scrubbers and condensate from the tall oil drying tank could be directed to the foul condensate tank so the turpentine would be recovered from these flows. Problem with directing the condensate from the dilute odorous gas scrubber to the foul condensate is the fibers and other impurities the condensate includes. Some filters are placed in the pipeline, but they were often blocked. If the condensate would be directed to the foul condensate tank where the turpentine would be recovered the problem with the filters would need to be solved. If the condensate would be directed to the foul condensate less safety concerns would occur regarding to the turpentine in the scrubber-screening circulation. Foul condensate skimming could also be automatized. Temperature measurement should be added to the turpentine decanter and temperature of the decanter should be followed and controlled.

Pressure and temperature increase of the cooking digesters and accumulators would probably direct more turpentine to the strong odorous gas system and the turpentine would drift less

with the liquor, pulp and by-products. When the turpentine drifts with other substances it either remains in the substance or it evaporates in the tanks if the temperature is high enough. The tank relieves are directed to the dilute odorous gas system. If the turpentine is not captured from these streams with dilute odorous gas scrubbers, it is burned in the lime kiln. Turpentine drifting causes issues since it might occur in places where it is not expected to be and cause safety hazards or other problems.

In general, it seems that higher temperatures of the gases before scrubbers and lower temperatures after scrubbers improve yield of turpentine and affect positively also on the quality of turpentine. Sulfur content seems to be dependent on the temperature. If the temperature is higher sulfur content is lower. In theory section was described the method to lower sulfur content of the turpentine by raising decanting temperature up to 43 °C. This seems to be good output temperature also for the scrubbers and condensers. It lowers the sulfur content and increases the yield. Heavy components seem to also follow same pattern as sulfur. When the temperature has been increased the amount of heavy fractions has also been under control. Temperature of the turpentine condenser could be optimized. If the temperature of the input flows of the dilute odorous gas scrubbers is increased safety risks should be assessed.

If the changes in the process conditions don't improve the yield as wanted other solution is to invest into the process and add new components to it. Chip bin steaming combined to the black liquor flashing seems to be most effective combination, but it would require big investment and safety issues occur while steaming chip bin that includes only soft wood. Other issues of chip bin steaming are that the fiber filters get blocked and the surface level of the chip bin varies and causes instability to the steaming process.

9 SUMMARY

Turpentine handling is important because it is saleable product but also because it causes safety issues at the mill if the turpentine drifts at the process unconditionally. Turpentine handling starts from the day the wood is cut. Short storing time improves the yield. SuperBatch cooking system is problematic for the turpentine yield since the turpentine

separation is ineffective and the turpentine drifts with the liquors, soap and gases. Biggest turpentine lost is through tall oil but also stripper gases included large amount of turpentine as well.

Other important aspect regarding to turpentine along with the yield is the quality of the turpentine. This interests especially the client who buys the turpentine. At Metsä Fibre Rauma the problem has been the high amount of sulfur and heavy fractions in the turpentine. It seemed that best method to control these problems is by raising the temperature of the turpentine sources and decanter. Input and output temperatures of the scrubbers and the condensers should be optimized to increase the yield and improve the temperature. While optimizing the temperature of the dilute odorous gases the risks have to be evaluated. Yield seemed to improve when the pressure and temperature of the cooking digesters and accumulators was higher. This would probably be the best method to increase the turpentine yield since it would most likely direct turpentine to the strong odorous gases and to the turpentine recovery system where the turpentine is wanted. Black liquor flashing combined with the chip bin steaming would most likely improve the turpentine yield efficiently.

10 REFERENCES

Alamaa, Matti. Pekkola, Marko. 1998. 41 Haihduttamo. Process guide.

Annala, K. 21 Keittämo, Virtauskaavio, Lämmön talteenotto, Tärpätin erotus. [Flow sheet]
[Lisence required]

Anon. 1990. Factors Affecting Yields of Turpentine from Kamyr vs Batch Digesters.
Naval Stores Review. July/August 1990.

ASTM D889-13. 2017. Standard Test Method for Volatile Oil in Rosin. ASTM
International. P.3

DNA Operate Client, 2018. Process handling program. [Requires license]

Drew, John. Russel, James. Bajak, Henry. 1971. Sulfate Turpentine Recovery. 148 p.
ISBN 0-9600416-2-1. Pulp Chemicals Association

Fletcher, David. 1989. By-products recovery. Pulp and Paper Manufacture, volume 5,
Alkaline Pulping. Third edition. p. 609-615. ISBN 0-919893-6.

Foran, C. D. 1995. Impact of recent pulp-mill modifications on sulfur contents in crude sulfate
turpentine, Tappi Journal, vol 78, 1995, no.6 p. 93-101

Frederick, Jim. DeMartini, Niko. 2017. Black Liquor Evaporation. [PDF-document] [Requires
license]

Gantz, Delbert. Nelson, J.M. 1972. Process for removing sulfur from crude sulfate turpentine
or distillate fraction thereof. [Patent application] Applied at 2.5.1972 [Accessed at 20.4.2018]
Available at:

<https://patentimages.storage.googleapis.com/4c/bc/8e/a4a8b9a9b7859b/US3660512.pdf>

Gurkin, Michael. 1996 Turpentine: The Real Story. Naval Stores Review. November/December 1996

Hall, Wayne. 2000. The effect of Mill Chip Handling on Crude Tall Oil and Turpentine Recovery. 2000 Pulping/process and product quality conference. Boston. MA, USA. 5-8 Nov. 2000. TAPPI Press.

Halme, Petri. 2018. Conversations. 21.9.2018.

Hase, Anneli. Komppa, Veikko. Lokio, Ari. Riistama, Kyösti. Vuori, Merja. 1990. Suomen kemian teollisuus. 286 p. ISBN 952-9597-02-9. Länsi-Savo Oy. Mikkeli

Hietaniemi, Pertti. Saine, M. 1999. Final report: Turpentine Study at Metsä-Rauma- Black liquor expansion tests. Published 28.2.1999. Lännen laboratoriot Oy. [Requires licence]

ICIS. 2005. CST prices are creeping upward. ICIS Chemical Business. [Internet article] [Accessed 27.6.2018] Available at:

<https://www.icis.com/resources/news/2005/09/26/2010239/cst-prices-are-creeping-upward/>

ICIS. 2003. Crude Sulfate Turpentine Hanging on Despite Price Stall. ICIS Chemical Business. [Internet article] [Accessed at 27.6.2018] Available at:

<https://www.icis.com/resources/news/2003/01/03/187458/crude-sulfate-turpentine-hanging-on-despite-price-stall/>

Ilmatieteen laitos. 2018. Lämpötila ja sadetilastoja vuodesta 1961. [Internet article] Available at: <http://ilmatieteenlaitos.fi/tilastoja-vuodesta-1961>

ITIS Report. 2018. Pinus Sylvestris. [Accessed 30.4.2018] Available at:

https://www.itis.gov/servlet/SingleRpt/SingleRpt?search_topic=TSN&search_value=183389#null

IPCS. 2002. Tärpätti. [Accessed 8.5.2018] Available at:

http://www.ilo.org/dyn/icsc/showcard.display?p_card_id=1063&p_edit=&p_version=1&p_lang=fi

Kesseli, Henri. 2018. Metsä Fibre Rauman kaasausakku, hakesiilon höyrytys, keittimen vajautus ja laimeiden hajukaasujen dekantointi. [private email] Recipient: Assi Häkkinen. Sent 12.7.2018 at 17.26 (GMT +0200).

Kesseli, Henri. 1999. Kaasausakun toimintakuvaus. OY Metsä-Rauma AB. Published 6.1.1999. [Requires license]

Kiuru, R. Heikkinen, P. 1995. 41 Haihduttamo Virtauskaavio. 900673-34. [Flow sheet] [Lisence required]

KKo. AMe. 2002. Vuorokausiraportti 21.5-22.5.02. [Lisence required]

Know Pulp [pulp and automation e-learning material]. 2016. Prowledge Oy. [Accessed 4.4.2018]. Requires license.

Kotoneva, Jari. Hietaniemi, Pertti. 1998. Osaprojekti 2 Uuteaineet ja VOC Loppuraportti.

Kovasin, Kari. 2018. Conversation. 10.9.2018

Lahtinen, Matti. 2018 Conversation 26.9.2018

Liias, Pirkko. Kesseli, Henri. Hautala, Tuomo. Mäkitalo, Teuvo. Merikallio, Timo. Joronen, Risto. 1998. Keittämön kehityssuunnitelma. [Requires license]

Lin, Ben. 2005. Collecting and burning non condensable gases. [Accessed 30.4.2018]

Available at:

<http://www.tappi.org/content/events/08kros/manuscripts/3-6.pdf>

Lin, Ben. s.a. The basics of foul condensate stripping. [PDF-article] [Accessed 4.7.2018]

Available at:

<http://www.ahlundberg.com/wp/wp-content/uploads/2017/04/AHL-The-Basics-of-foul-condensate-stripping.pdf>

Marks, Robert. 1967. Engineering aspects of Turpentine Recovery Systems. Tappi. Vol. 50. No 4. April 1967

Mayaux, Dominique. 2018a. MATSA: CST Quality and quantity master theses in Rauma [private email]. Recipient: Assi Häkkinen. Sent 14.5.2018 at 20.46 (GMT +0200).

Mayaux, Dominique. 2018b. Manager, Purchasing, DRT. Meeting at Rauma 19.6.2018.

Metso paper. 2005. Kuitulinjan prosessikehitysryhmä 25.8.2005. Appendix of the meeting document.

Metsä Fibre. 2017. Botnia Nordic CST RMA, tärpätin laatutiedot. [Excel document]

Metsä Fibre. 2018a. Metsä Fibre lyhyesti. [Company website], [Accessed 23.3.2018]

Available at:

<https://www.metsafibre.com/fi/yhtio/Pages/default.aspx#Mets-Fibre-lyhyesti>

Metsä Fibre. 2018b. Rauman sellutehdas. [Company website], [Accessed 23.3.2018]

Available at:

<https://www.metsafibre.com/fi/yhtio/Pages/Rauma.aspx>

Metsä Group. 2018a. Sivuvirrat ja jätteet. Monipuolisia biotuotteita sellutehtailta.

[Company website], [Accessed 22.3.2018] Available at:

[https://www.metsagroup.com/fi/kestava-](https://www.metsagroup.com/fi/kestava-kehitys/tehdaspaastot/resurssitehokkuus/Pages/default.aspx)

[kehitys/tehdaspaastot/resurssitehokkuus/Pages/default.aspx](https://www.metsagroup.com/fi/kestava-kehitys/tehdaspaastot/resurssitehokkuus/Pages/default.aspx)

Metsä Group. 2018b. Metsästä maailmalle. [Company website], [Accessed 23.3.2018]

Available at:

<https://www.metsagroup.com/fi/yhtio/Pages/default.aspx>

Morris, Charles. 2015. Is your recovery process up to snuff? Pulp and Paper International.

Vol. 57, Iss 3. March 2015. p. 30-32.

Mäkitalo, Teuvo. 2018 Conversation 2018.

Niemelä, Klaus. 24.6.2004. Tärpättitutkimus, Oy Metsä-Botnia Ab, Kaskinen.

Numminen, Antti. 2018. Hakkeen ikä ja ostohakkeen määrät. [private email]. Recipient: Assi Häkkinen. Sent 3.5.2018 at 14.01 (GMT +0200).

Paper Asia. 1997. SuperBatch cooking: from innovation to experience. Published at March 1997 in Paper Asia. Originally published at SPCI Stockholm, Sweden in June 1996. [Accessed 19.4.2018] Available at:

<http://www.sefs.washington.edu/classes.pse.480/References/pdf/Suberbatch%20Cooking%20From%20Innovation%20to%20Experience.pdf>

Pekkola, Marko. 1998. 27.12.1997 Laimeiden hajukaasujen käsittelyjärjestelmässä tapahtunut räjähdys. Companys inner material. Requires license.

Peltola, Kari. 2005. 21 SuperBatch keittäminen. Process guide.

Peltola, Kari. 2018 Conversations. 7.5.2018

Pikka, Olavi. Martikainen, Seppo. 1996. Menetelmä ja laitteisto massan tuottamiseksi. Patent application 951399. [PDF-document] [Accessed 5.9.2018] Available at:

<https://patentimages.storage.googleapis.com/78/86/47/9be6daaf47a195/FI103814B.pdf>

POL. 2001. Rauma SuperBatch keittokierron toiminta. Companys inner education material. Requires license.

Prosessikehitysryhmä. 2005. Kuitulinjan prosessikehitysryhmä 25.8.2005 kokouksen liite 1.

Pulp and Paper Online. 2018. Turpentine Recovery System. [Internet article], [Accessed 18.4.2018] Available at:

<https://www.pulpandpaperonline.com/doc/turpentine-recovery-system-0001>

Rohan. 2016. Crude Sulfate Turpentine Market Worth 279,5 Million USD by 2022. PR Newswire Europe Including UK disclose, New York. Nov. 15, 2016.

Salo, Mika. 17.06.2003. Tärpättivuoto jätevesilaitokselle 16.06.2003. [Lisence required]

Seppälä, Markku et al. 2005. Paperimassan valmistus, 2-3 painos. Saarijärvi. Opetushallitus. 2005. 196 p. ISBN 952-13-1142-8.

Smook, Gary. 1992. Handbook for pulp & paper technologists. 2 printing 1994. Vancouver. Angus Wilde Publications Inc. p. 419. ISBN 0-9694628-1-6.

Stenlund, B. Ranua, J. 1983. Kemiallisten tuotteiden talteenotto. Puumassan valmistus osa 2. Suomen Paperi-insinöörien yhdistys r.y. 1301-1369. ISBN 951-99117-1-5.

Strömvall, Ann-Margret. Peterson, Göran. 2000. Volatile terpenes Emitted to Air. Pitch Control, Wood Resin and Deresination. 392 p. ISBN 0-89852-519-5.

Strömvall, Ann-Margret. Peterson, Göran.. 1993. Photooxidant-forming monoterpenes in air plumes from kraft pulp industries. [PDF-document], [Accessed 3.5.2018] Available at: http://publications.lib.chalmers.se/records/fulltext/local_72626.pdf

Tamminen, Ari. Tamminen, Tarja. 2009. Hajukaasupäästöjen mittaukset Oy Metsä-Botnia Ab:n Rauman tehtaalla 20-22.1.2009. [PDF-document], [Accessed 28.5.2018]

Tate, Dan. 1967. Turpentine Recovery System for Batch Digesters. Tappi. Vol. 50, No 4. April 1967.

Thornburg, W. 1963. Effect of Roundwood or Chip Storage on Tall Oil and Turpentine Fractions of Slash Pine. Tappi. Vol. 46, No.8. August 1963.

Tikka, P. Kovasin, K. Laxen, T. 2002. Solving soap and turpentine related process problems in softwood kraft mills. Pulp and Paper Canada. 103:6: T149-154 (June 2002)

Tinnis, Valentin. Kinnula, Tuomo. 1981. A method to control the turpentine recovery process of batch kraft pulp digester. Tappi engineering conference proceedings, Tappi press Atlanta p.47

Torniainen, Jorma. 2018. Polttolipeä tulokset 28.3.2018. [PDF-document], [Accessed 28.5.2018] [Requires license]

Tyre, Hilton. 2018 a. Conversations. 19.6.2018.

Tyre, Hilton. 2018 b. Clearance delay on FedEx package. [private email] Recipient: Assi Häkkinen. Sent 1.8.2018 at 16.53 (GMT +0200).

Uusitalo, Päivi. Svedman, Mikael. Vaistomaa, Jukka. Haaslahti, Hannu. 2008. Method for improved turpentine recovery from modern cooking plants. United States Patent. [PDF-document], [Accessed 18.7.2018] Available at:
<https://patentimages.storage.googleapis.com/d3/c2/eb/faba865b8b7cd8/US7384501.pdf>

TTL. 2017. OVA-ohje: TÄRPÄTTI. [Updated 6.11.2017] [Internet document], [Accessed 29.6.2018] Available at:
<https://www.ttl.fi/ova/tarpatti.html>

VTT-Kemiantekniikka. 1998. VOC-osaprojekti 1 Haihtuvien kaasumaisten yhdisteiden määrittäminen - Loppuraportti.

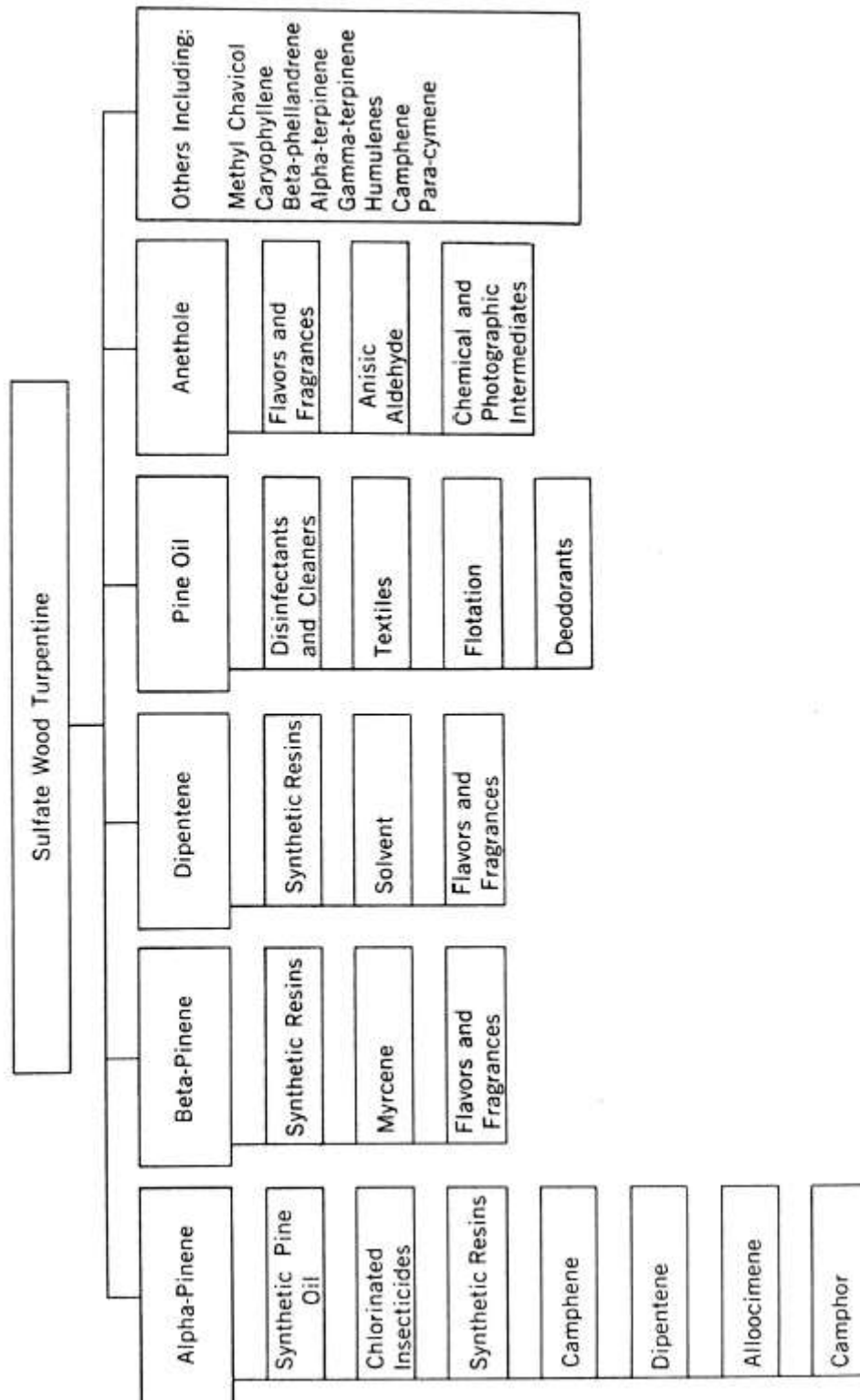
Wansbrough Heather. 1977. Turpentine Production and Processing. [PDF-document], [Accessed 22.3.2018] Available at:
<https://nzic.org.nz/ChemProcesses/forestry/4F.pdf>

Wenzl, Hermann. 1970. The Chemical Technology of Wood. London. Academic press, INC. 650 p.

Weston, Roderick J. 2006. Recovery of turpentine from the production of medium-density fibreboard. Published 12.4.2006. [Accessed 4.4.2018] Available at:

https://www.scionresearch.com/__data/assets/pdf_file/0009/59067/08WESTON371124-1362007.pdf

Components of crude sulfate turpentine (Drew et al, 1971, 20)



Temperatures and pressures of the most important crude sulfate turpentine compounds
(Drew et al, 1971, p. 34-37)

Alpha pinene			
Temperature [°F]	Temperature [°C]	Pressure [mmHg]	Pressure [bar]
0	-17,22222	0,18	0,00023998
50	32,77778	1,57	0,002093155
100	82,77778	9,32	0,01242561
150	132,77778	36,65	0,048862513
200	182,77778	112,05	0,149387301
250	232,77778	283,87	0,378461161
300	282,77778	622,5	0,82992945
350	332,77778	1219,11	1,625341834
400	382,77778	2181,3	2,908152786

Beta pinene			
Temperature [°F]	Temperature [°C]	Pressure [mmHg]	Pressure [bar]
0	-17,22222	0,11	0,000146654
50	32,77778	1,09	0,00145321
100	82,77778	6,43	0,008572605
150	132,77778	26,48	0,035303666
200	182,77778	83,97	0,111950483

250	232,77778	219,09	0,29209517
300	282,77778	492,18	0,65618422
350	332,77778	983,51	1,311235202
400	382,77778	1790,03	2,386503797

Delta-3-carene			
Temperature [°F]	Temperature [°C]	Pressure [mmHg]	Pressure [bar]
0	-17,22222	0,08	0,000106658
50	32,77778	0,87	0,001159901
100	82,77778	5,34	0,007119395
150	132,77778	22,51	0,030010782
200	182,77778	72,72	0,096951758
250	232,77778	192,55	0,256711511
300	282,77778	437,82	0,58371038
350	332,77778	883,75	1,178233175
400	382,77778	1622,25	2,162816145

Camphene			
Temperature [°F]	Temperature [°C]	Pressure [mmHg]	Pressure [bar]
0	-17,22222	0,16	0,000213315
50	32,77778	1,52	0,002026494
100	82,77778	8,6	0,011465692
150	132,77778	33,15	0,044196243

200	182,77778	105,25	0,140321405
250	232,77778	268,33	0,357742923
300	282,77778	591,52	0,788626294
350	332,77778	1163,49	1,551188138
400	382,77778	2089,5	2,78576319

Myrcene			
Temperature [°F]	Temperature [°C]	Pressure [mmHg]	Pressure [bar]
0	-17,22222	0,11	0,000146654
50	32,77778	1,09	0,00145321
100	82,77778	6,43	0,008572605
150	132,77778	26,48	0,035303666
200	182,77778	83,97	0,111950483
250	232,77778	219,09	0,29209517
300	282,77778	492,18	0,65618422
350	332,77778	983,51	1,311235202
400	382,77778	1790,03	2,386503797

Dipentene			
Temperature [°F]	Temperature [°C]	Pressure [mmHg]	Pressure bar
0	-17,22222	0,05	0,000066661
50	32,77778	0,6	0,000799932
100	82,77778	3,86	0,005146229

150	132,77778	16,98	0,022638076
200	182,77778	56,66	0,075540245
250	232,77778	153,93	0,205222555
300	282,77778	357,48	0,476599486
350	332,77778	734,36	0,979063439
400	382,77778	1368,2	1,824111604

Dimethyl sulfide			
Temperature [F]	Temperature [C]	Pressure [mmHg]	Pressure bar
0	-17,22222	68,49	0,091312238
50	32,77778	261,74	0,348957003
100	82,77778	765,74	1,020899883
150	132,77778	1841,02	2,454484684
200	182,77778	3827,03	5,102272937
250	232,77778	7109,14	9,478047631
300	282,77778	12088,79	16,1170166
350	332,77778	19152,74	25,53481602
400	382,77778	28649,41	38,1959664