Characterization and methods for extraction of extractives in spent sulphite liquor

Master of Science Thesis

Erik Golander

Supervisor: Hans Grundberg, Domsjö Fabriker, Örnsköldsvik
Examiner: Krister Holmberg

Department of Chemical and Biological Engineering
Division of Applied Surface Chemistry
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden, 2011

Characterization and methods for extraction of extractives in spent sulphite liquor

Erik Golander

Department of Chemical and Biological Engineering
Applied Surface Chemistry
Chalmers University of Technology
SE 412 96 Göteborg
Sweden
Telephone +46 (0)31 772

The work was carried out at:
Domsjö Fabriker, DomInnova
Hörneborgsvägen 14
SE-891 86 Örnsköldsvik
Telephone +46 (0)660 756 00
www.domsjoe.com

Abstract

Wood extractives are substances found in the tree that works as a protection against bugs, decay and fungus attack among other things.

In these studies a characterization of wood extractives in the various process streams has been made at Domsjö Fabriker which is a biorefinery with special cellulose as one of the main products.
Methods like soxhlet extraction, GC-ÅBO and ^{13}C NMR have been used and liquid-liquid extractions on pre-evaporated spent liquor with different organic solvents have been tried to extract these extractives.

From five samples/streams five groups of extractives could be determined, fatty- & resin acids, sitosterols, sterylesters and triglycerides but analyses shows that there are also a lot of unknown extractives in the streams.

Chemical analyses showed that almost 100% of the determined groups of extractives follow the cellulose from the digester. These extractives finally assemble in filtrate 3, which is used as one of the washing liquids of the dissolving pulp in the diffuser. In that way, much of the extractives return in the process once again, but to avoid pitch problems enough extractives are removed.
Most efficient liquid-liquid extraction of pre-evaporated spent liquor was made with ethyl acetate as organic solvent.

Today, the removed amount extractives are burned as fuel.
In other countries wood extractives are used in different products as paints, adhesives, road marking, food additive etc.
In the future extractives from Domsjö Fabriker may be a profitable complementary product.

Keywords: Extractives, spent liquor, cellulose, liquid-liquid extraction

Table of contents

1 Introduction

1.1 Background

Domsjö Fabriker in Örnsköldsvik is today a biorefinery. The traditional pulp mill with paper grade pulp as main product has become an advanced biorefinery. Here, the renewable wood raw material is refined into products with a strong environmental profile. The meaning of the concept of biorefinery is to utilize as much as possible of the wood raw material constituents, to make more of the tree.
Only softwood, spruce and pine, are used in their process were the cellulose is sublimated to special cellulose, hemicellulose to ethanol and the lignin to lignosulfonate. Around 1,4 million cubic meters are annually being used and it's both domestic and imported wood. The wood is transported either by boat, truck or railway.
Theirs unique process also gives the possibility to produce complementary products such as carbon dioxide, energy in form of steam, biogas (methane gas) and bioresin. The company has approximately 370 employees in Sweden and 25 more in the Baltic States. The annual turnover amounts to roughly SEK 2.0 billion.

In general a tree consists of sapwood and heartwood. This two tissue types consists mainly of cellulose, hemicellulose, lignin [13] and table 1.1 describes roughly how they are distributed in spruce and pine.

Table 1.1 *Chemical constituents and their approximate percentage in spruce and pine [14].*

Tree species	**Cellulose %**	**Hemicellulose %**	**Lignin %**	**Extractives %**	**Other %**
Spruce	39.5	30.6	27.5	2.1	0.3
Pine	40.0	28.5	27.7	3.5	0.3

The tree also consists of extractives like fatty acids, resin acids and glycerides that are used mainly for protection against insects, microorganisms decay, and fungus attack if the protecting bark is injured [23,24]. Another very important thing is that the extractives are used as nutrition and are stored inside the tree.

Today only a part of the extractives that are present in the incoming biomass to Domsjö Fabriker are extracted. Some of extractives continue with the liquid phase after cooking and some is adsorbed to the cellulose and follow it into the washing and bleaching stages. An overview of the process can be seen in figure 1.1. The fraction that comes with the cellulose can today be valued and can further be sublimated, the other fraction is just following the spent liquor and the energy is recovered in the recovery boiler. One problem with this is that these extractives are toxic to the yeast culture when making ethanol, which ferments the released monosaccharide during cooking. They also negatively affect the quality of the lignosulfonate, which is picked out and sold to the concrete industry.

The extractives are complex in many ways. It's difficult to analyze them because much of the content is hard to determine.
Potential profits that this project can lead to in the future are optimization of the main process; one gets rid of unwanted extractives. Another potential profit is a future product made from the extractives which can be attractive on the market.

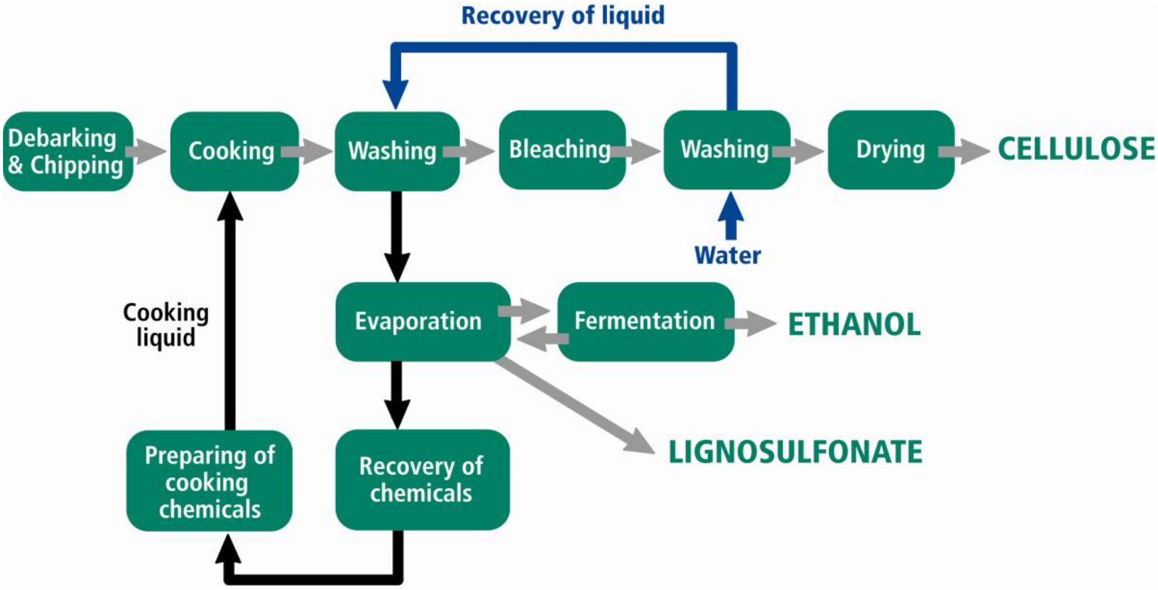

Figure 1.1. *A schematic picture of the process*

1.2 Extractives

Extractives, resin, are a heterogeneous group of different compounds and constitute between 1-4 % of the tree's total dry matter but still they are necessary for the survival of the tree. They are intractable in acidic environments. Some of these extractives are volatile and in general nonpolar (polar extractives can also be present), low molecular weight compounds with different chemical behaviors [1].
Extractives in wood chemically belong to widely separated types of groups like aliphatic hydrocarbons, alcohols, acids, waxes, fats, terpenoidic substances, phenols, glycosides, quinones, protein and carbohydrates [12].
Some of these substances also give each type of wood their characteristic properties as color and permanency [14]. Depending on the wood species, wood age, seasoning and location in the tree the amount of the extractives varies [6].
The extractives found in parenchyma cells are storage of energy and is rich in fats. The extractives which have the primary function of preserve the wood are found in the resin canals and adherent epithelial cells [24].
There are often more amounts of extractives in the dark heartwood compared to the lighter sapwood because the sapwood converts into heartwood when the tracheids (cells in the xylem) are filled with extractives [2]. This gives the heartwood with all the dead cells a natural protection due to the high amounts of extractives while the living parenchyma cells in the sapwood remain quite unprotected.

Resin acids, fatty acids, triglycerides, sterols and their esters are the main lipophilic groups of extractives in spruce and pine.
Triglycerides dominate the sapwood in both spruce and pine while the amount of resin acids is higher in the heartwood of pine [3]. In pine it's around two times more resin acids in the heartwood compared to the sapwood.
There are almost no triglycerides in the heartwood of pine, instead there's a large amount of free fatty acids [4].
If you compare chips from spruce- and pine thinning three to five times more extractives are found in pine than in spruce, that's because the pine have a greater average size of the parenchyma cells which makes it possible for more storing of extractives [3].

1.2.1 Resin acids

Resin acids have a lipohilic carbon skeleton and a hydrophilic carboxyl group. This basic skeleton, a 3-ring system, is shared by almost all the acids. They are tricyclic compounds of abietan- or primaran type. In figure 1.2 the molecular structure of abietic acid is shown.
High amounts of the acids are located in the canal resin of the wood.
It's a very sticky material and can lead to pitch problems in a process.

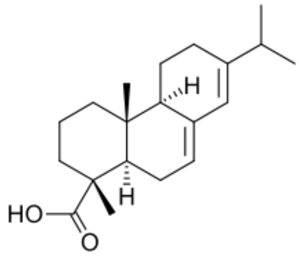

Figure 1.2. *The molecular structure of abietic acid [25]*

1.2.2 Fatty acids

Fatty acids are long chains of aliphatic monocarbon acids with chain lengths of 10-24 carbon atoms. They can be either saturated or unsaturated. The saturated ones are chemically very stable compounds while the double bonds present in the unsaturated fatty acids makes them susceptible to oxidation- and addition reactions. In figure 1.3 two fatty acids are shown.
Fatty acids often come esterified in the wood extractives [3,12].

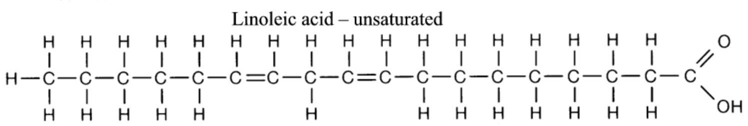

Figure 1.3. *The molecular structure of palmitic acid (saturated) and linoleic acid (unsaturated) [26]*

1.2.4 Triglycerides

Triglycerides are a type of fat composed by one molecule of glycerol and three fatty acids. Ester bonds are formed when the carboxyl groups of the fatty acids connect to the hydroxyl groups of the glycerol [17].
When heartwood is formed the triglycerides are hydrolyzed to free fatty acids. Large amount of these are found in the heartwood and it's highly likely that some of these fatty acids metabolizes to heartwood-phenols like pinosylvin and pinosylvin monomethylether [5].

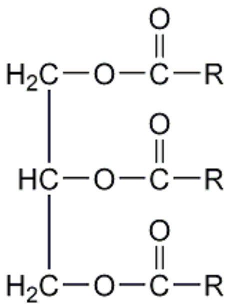

Figure 1.4. *The molecular structure of a triglyceride [27]*

1.2.5 Sterols

Sterols are ordinary oxygenous compounds. Hydroxyl groups are usually a part of their structures. Sterols are difficult to chemically modify in order to make it easier of the removal from the pulp. The most common sterol in wood is β-sitosterol, see figure 1.5 [12].

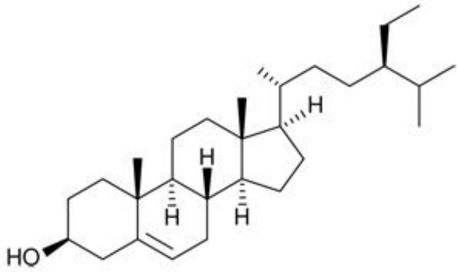

Figure 1.5. *The molecular structure of β-sitosterol [28]*

1.3 The process

As mention earlier only softwood are used in the process. In the figure 1.6 you can follow the log to bale and were the five samples (1-5) were collected. After the wood is debarked it is chipped and fed to the digesters together with the cooking chemicals which have sodium as a base. During the sulphite cooking the individual fiber is released as well as lignin and hemicellulose. The bark is sold to Övik Energi were it is burned and energy is recovered as steam.
Typical for dissolving pulp that are processed at Domsjö Fabriker is a two-step-cooking, longer cooking , low content of lignin and hemicellulose and lower yield compared to paper pulp [9].

After cooking the cellulose is washed with different washing liquids in the diffuser. The purpose with the washing is to clean the pulp, take charge of burnable substance, remove and recycle cooking chemicals and minimize the environmental effects. An impure pulp might cause spillage in later steps of the process. Also the cooking chemicals would be lost in an impure pulp and that will cost money to replace [10].
The cellulose is then bleached with hydrogen peroxide in the closed-loop bleaching unit, then wash and dried. The advantage of bleaching the cellulose is more than to get a high brightness. Bark- and wood substance is removed and substances that can cause bad odour are eliminated [11]. The cellulose is delivered in bales and the whole process from log to bale takes ca 40 hours.

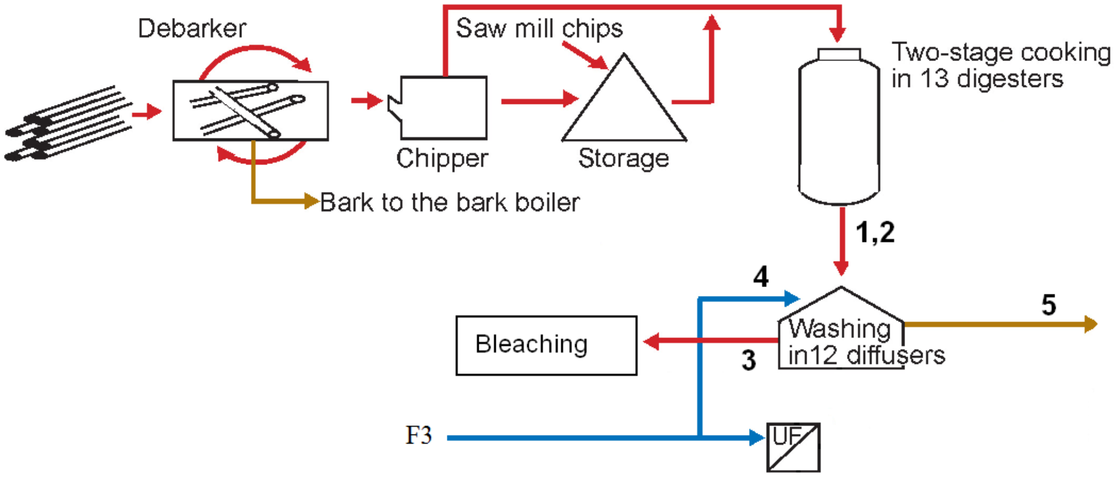

Figure 1.6. *The number 1-5 correspond to sample points in a simplified schematic picture of the process.*

1.4 Purpose

The purpose with this master's thesis can be divided into two parts.

Part 1:
A characterization of the various streams of extractives needed to be done, what different extractives are present and is there any difference in the composition of what goes into the bleach plant compared to what goes into the spent liquor.

Part 2:
It would be extremely interesting if the extractives present in the pre-evaporated spent liquor (sample 5) could be extracted.
Liquid-liquid extraction is a method that will be used with different solvents.

2 Theory

2.1 Soxhlet extraction

The soxhlet apparatus (see figure 2.1) is a solid-liquid extraction technique. With a solvent in this method, the amount of lipophilic extractives of the sample content can be determined.
The solvent is placed in a distilling pot and is then heated. The evaporated solvent travels up through a distillation arm and condenses when it reaches the condenser. It is then dripped into the sample container were the extraction take place. The solvent, containing extracted compounds, passes through the sample container and back into the distilling pot. This cycle is repeated continuously and can continue as long as needed. Finally the wanted compounds are concentrated in the distilling pot. The solvent is then removed leaving the extract [20].

Figure 2.1. *Soxhlet extraction setup.*

2.2 GC-ÅBO

The Gas Chromatography ÅBO method, GC-ÅBO, is a method used in mixtures to separate volatile compounds. It is very similar to a regular GC. Characteristic for GC-ÅBO is a very short column, about five meter, made of 100 % dimethyl polysiloxane and a temperature-programmable-injector of on-column type. The sample needs to be derivatized before analysis because organic acids is not volatile and have a very polas acis moiety. Therefore a silyl ester is synthesized from the acid. with help of a syringe a small amount of the derivatized sample that should be analyzed is injected into a hot injector port of the gas chromatograph. In order for the mixture to evaporate the injector temperature is set higher than the compounds boiling points.

The mixture will evaporate inside the injector, i.e. the compounds will go into a gas phase. Through the injector a carrier gas (mobile phase), helium, flows and the compounds of the sample pushes onto the capillary GC column. Inside the column there is also a stationary phase which is a high boiling liquid. The separation takes place in the column. Due to different chemical and physical properties some of the compounds are slowed down by the absorbent than others so they move through the column at different speeds. After the column the sample components reach a high temperature GC-FID (gas chromatography – flame ionization detector) which sends a signal to a data system that records the signals. The signals will result in different peaks in the chromatogram and the area of each peak is proportional to the number of molecules generating the signal [8,15].

2.3 NMR spectroscopy

Nuclear magnetic resonance spectroscopy, NMR, is one of the most used techniques for determining the structure of a molecule.

When a sample containing hydrogen is placed in a very strong magnetic field and at the same time irradiates by electromagnetic energy the hydrogen nuclei of the compound may absorb energy know as magnetic resonance. The instrument NMR spectrometer measures the absorption of energy by the certain nuclei. Usually they are designed in that way so they irradiate the compound with electromagnetic energy of a constant frequency while the magnetic field strength is varied. When the correct strength is reached of the magnetic field, resonance occurs, i.e. the nuclei absorb energy. A small electrical current develops that flows in an antenna coil that the sample are being surrounded by. The current amplifies resulting in a peak or series of peaks in an NMR spectrum.

In these studies ***^{13}C NMR spectroscopy*** has been used. With a ^{1}H spectroscopy (proton NMR) information about the carbon skeleton of an organic molecule is obtained indirect because most of the carbon atoms have at least one attached hydrogen.

By ^{13}C spectroscopy the carbon skeleton is observed directly and whether the carbons have for example hydrogen-, phosphor- or zinc atoms attached or not peaks are plotted in the spectrum [7].

Every peak corresponds to a carbon atom. A spectrum with for example four peaks means that there must be four different environments for the carbon atoms in the compound [21].

2.4 Liquid-liquid extraction

Liquid-liquid extraction is a method to extract compounds from a liquid using an organic or aqueous solvent. The principle behind the method involves two immiscible liquids, the solution containing compounds one wants to extract and a solvent. These two forms two layers unmixed due to differences in densities, one organic layer and one aqueous layer (see figure 2.2). The specific solute in the solution is soluble with the solvent.

In most extractions water is involved because it is very polar and immiscible with most organic solvents.

During heavily mixing maximum surface contact between the two immiscible liquids is reached in the separatory funnel. This is necessary to allow the solute to be extracted into the organic layer. Too vigorously mixing can however lead to an emulsion.

The organic layer now contains the solvent and the solute. Finally, the solvent is removed by evaporation, leaving the extract [16,22].

If emulsions are formed, one way to break them is with brine which is a saturated sodium chloride-solution.

By changing the pH in the aqueous solution an organic substance can be charged and be a part of a water-soluble salt pair.

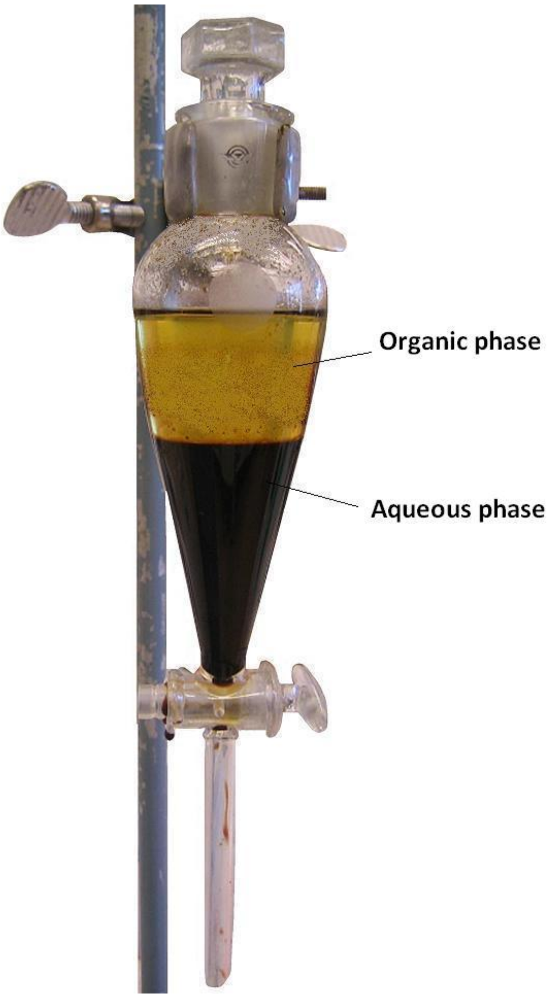

Figure 2.2. *A separatory funnel showing a two-phase liquid-liquid extraction.*

3 Materials and methods

3.1 Materials

Five different sample points from the process streams are described below.

3.1.1 Spent cooking liquor

The dark brown spent cooking liquor is the cooking liquid in the digester (see figure 3.1). This aqueous solution contains active chemicals as sodium sulphite (Na_2SO_3), sodium bisulphite ($NaHSO_3$) and sulphur dioxide (SO_2). The temperature of the spent cooking liquor is around 100°C and the pH is around 1. The boiling temperature determines the reaction rate which in turn is pH dependent.
After cooking, the spent cooking liquor contains the cooking chemicals, the released wood substance, extractives, water from wood moisture and condensate from the steam.

Figure 3.1. *Spent cooking liquor.*

3.1.2 Cellulose from digester

Together with the spent cooking liquor the chip are boiled to release the fiber, remove lignin and extractives to the extent that the following step will be easier.
The sulphite pulp is grey yellow after the cooking (see figure 3.2). The color is due to changes in the rather colorless lignin.
The dry matter of the cellulose is ~15 %.

Figure 3.2. *Dried cellulose from digester.*

3.1.3 Cellulose from diffuser

In figure 3.3 one can see that the color of the washed cellulose is a little bit brighter compared to the cellulose from the digester and the dry matter is ~7 %. This sample was reclaimed from wash press 1 because it’s very difficult to withdraw a sample from the diffuser directly. The cooking liquid that was absorbed by the pulp during the cooking was removed by suppression with different washing liquids.

Figure 3.3. *Dried cellulose from diffuser.*

3.1.4 Filtrate 3 to diffuser

Filtrate 3 (F3) is a light brown aqueous liquid containing a large amount resin (see figure 3.4). It is used as one of the washing liquids in the diffuser.
The liquid derive from the last washing step in the bleach plant. Fresh water is added in the bleach plant and with the principle of “counter-stream”-washing the washing liquid is pushed against the cellulose flow all the way up to the diffuser. Before entering the diffuser a part of F3 is ultra filtrated, i.e. a certain amount extractives is extracted.

Figure 3.4. *Filtrate 3 to diffuser.*

3.1.5 Spent liquor

Spent liquor is a blackish aqueous liquid from the diffuser (see figure 3.5). The content of the liquid is cooking chemicals, released wood substance as lignin and hemicellulose but also residues from cellulose and low molecular resins. The pH is around 2.5.
The meaning of pre-evaporated spent liquor is that highly volatile compounds, such as SO_2, acetic acid and furfurals, already have been eliminated.

Figure 3.5. *Pre-evaporated spent liquor.*

3.1.6 Organic solvents

An organic solvent is a non-aqueous liquid. It can dissolve a solid, liquid or a gaseous solute that results in a solution. As the name indicates the molecular structure of the solvent is based on carbon.
In this case different kinds of organic solvents are used in liquid-liquid extraction. The solvents have different properties as polarity, density, molar mass, boiling point etc. (see table 3.1) that will affect the extractions in different ways [18].
The properties changes when mixing two or more organic solvents and in that way you can get wanted polarity of the solvent.

Polar groups in resin components increase its solubility in polar organic solvents and reduce its solubility in nonpolar organic solvents. The solubility also decreases with increasing molecular weight for resin components. The fatty acids solubility decreases with increasing chain length especially in organic solvent with a higher degree of polarity.
Sometimes resin- and fatty acids can form micelles in nonpolar organic solvents. These micelles can solubilise polar substances like water, carbohydrates and salts that are insoluble in the organic solvent. During an extraction these substances can follow the phase that is being extracted [12].

Table 3.1. *Properties of eight organic solvents that will be used in liquid-liquid extraction and the properties of water [19].*

Solvent	Formula	Molar mass g/mol	Boiling point °C	Density g/mL	Polarity	Solubility in water g/100g
n-Pentane	C_5H_{12}	72.15	36.1	0.626	1.8	0.04
Petroleum ether	-	-	30-60	0.656	-	-
Toluene	C_7H_8	92.14	110.6	0.867	2.4	0.05
Methyl *t*-butyl ether (MTBE)	$C_5H_{12}O$	88.15	55.2	0.741	2.6	5.1
Diethyl ether	$C_4H_{10}O$	72.12	34.6	0.713	4.3	7.5
Dichloromethane	CH_2Cl_2	84.93	39.8	1.326	9.1	1.32
Ethyl acetate	$C_4H_8O_2$	88.11	77	0.895	6.0	8.7
Methanol	CH_4O	32.04	64.6	0.791	33.0	miscible
Water	H_2O	18.02	100	0.998	78.54	-

3.2 Methods

3.2.1 Soxhlet extraction

MoRe Research, a research and development company, performed all the soxhlet extractions. The five samples were extracted using acetone in the soxhlet extraction method. Also soxhlet extraction was made with MTBE but only cellulose from digester and cellulose from diffuser were analyzed.
A weight of 10 g was prepared for samples from pulp. The extractions were run for 4 hours. The solvent could partly be evaporated in the soxhlet apparatus and the rest by a turbo evaporator.

3.2.2 GC-ÅBO

The extract from the soxhlet extraction with acetone and MTBE were analyzed with GC-ÅBO. The analyses were made by the company MoRe Research.
The solid extracts were first reacted with 100 µL BSTFA (N,O-Bis(trimethylsilyl)-trifluoro-acetamid) and 50 µL TMCS (Trimethylchlorosilane).
A volume of 1 µL sample was injected into the gas chromatograph.
The present extractives in the samples were determined as well as the amount of each extractive.

3.2.3 NMR

The ^{13}C NMR measurements were performed at Chalmers University of Technology. Extracts from six samples (see table 3.2) were analyzed at room temperature. One-dimensional spectrums were obtained on a Varian spectrometer at 400 MHz. Each sample was prepared by dissolving 50 – 100 mg sample in 700 µL deuterated chloroform ($CDCl_3$).

Table 3.2. *Sample-extracts that were run in NMR.*

1. Pre-evaporated spent liquor
2. Spent cooking liquor
3. F3 to diffuser
4. Extract from pre-evaporated spent liquor/Ethyl acetate
5. Extract from pre-evaporated spent liquor/ Diethyl ether
6. Extract from pre-evaporated spent liquor/ MTBE

3.2.4 Liquid-liquid extraction of pre-evaporated spent liquor

Eight different organic solvents were tested with liquid-liquid extraction at room temperature to see the ability to extract extractives from pre-evaporated spent liquor.
First, all solvents were tested separated in a separatory funnel at room temperature. In the ratio of 1:1, 25 ml solvent is mixed with 25 ml spent liquor.
The color of the organic phase proves that substances have been extracted into the solvent from the aqueous phase.
The solvent in the organic layer was removed in a rotary evaporator.
To calculate the amount extractives the glass-flask contained the organic layer was weight empty and after the solvent was eliminated.
Three extractions were made with each solvent and the result shows the average values. The values were recalculated from mg/25ml to mg/kg and the calculations were base on 1000 ml pre-evaporated spent liquor with a weight of 1100 g.

Combinations of the organic solvents were also tested in the extraction. The combinations were based on the results from the first extractions when each organic solvent were tested separate.

Also brine was added to extractions to try extracting more extractives.

The three best extractions were analyzed with GC-ÅBO.

MoRe Research made a liquid-liquid extraction with spent liquor, spent cooking liquor and F3 to diffuser with MTBE as solvent. Before analysis pH were adjusted to 3.

4 Results and discussion

4.1 Soxhlet extraction

The soxhlet extractions results with acetone and MTBE can be seen in table 4.1.
The cellulose coming from the digester contained 1,97 % extractives.
Compare the spent liquor results from the soxhlet extractions in table 4.1 and the GC-ÅBO in table 4.2 a large difference can be seen. 2030 mg/kg and 341 mg/kg respectively tell us that there is almost 1700 mg/kg unknown organic compound.
The same thing can be observed with spent cooking liquor. A total amount organic compound of 9,94 g/kg compared to a total amount determined groups extractives of 61 mg/kg.
The values for cellulose from diffuser are incorrect due to no consideration of the mass concentration in the diffuser has been taken.

Table 4.1. *Amount extracted extractives with soxhlet extractions using acetone*

	Acetone-extract mg/kg	**MTBE-extract mg/kg**	**Acetone-extract %**
Spent liquor	2030		
Spent cooking liquor	2290		
F3 to diffuser	9940		
Cellulose from digester		2380	1.97
Cellulose subtracted	430		

4.2 GC ÅBO

The extracts from the soxhlet extractions analyzed with GC-ÅBO can be seen in table 4.2 as well as the liquid-liquid extraction with MTBE.

Five different groups of extractives could be determined in almost all samples, fatty- and resin acids, sitosterols, sterylesters and triglycerides.

The results in table 4.2 show that almost 100% of the determined extractives in the digester follow the cellulose and only a small part end up in the spent cooking liquor. However, the spent liquor coming out from the diffuser contains a lot more extractives which means that extractives are released from the cellulose and filtrate 3 contribute with a larger amount of extractives.
Total amount extractives of ~14,2 g/kg were measured in the cellulose from the digester.
The straight chain of cellulose is polar, but insoluble in water. On the outside of each chain there is OH-groups distributed forming hydrogen bonds when connecting to other cellulose chains. However the surface of the cellulose is nonpolar and that is

the reason why the nonpolar extractives prefer the cellulose instead of the spent cooking liquor.
As expected fatty- and resin acids made up the major part of the acetone-soluble extractives in all the samples. The cellulose from digester contained ~10,3 g/kg fatty- and resin acids (total amount extractives, 14,2 g/kg).
Cellulose from diffuser compared to cellulose from digester contained around 34 % less extractives and ¾ of these 34 % were constituted of fatty- and resin acids.
F3 to diffuser contained ~6,2 g/kg extractives, but only 0,341 g/kg follows the spent liquor from the diffuser. The majority of the extractives are still on the cellulose.
An extra sample, cellulose subtracted, was also analyzed and as expected it was similar to spent cooking liquor because it's generally speaking the same liquid.

As can be seen in table 4.2 the amount acetone- and MTBE soluble extractives varied. The ability to extract organic substances is due to properties of the organic solvents as polarity, density, solubility in water etc.

Besides F3 to diffuser (~3,4 g/L) the liquid/liquid extraction with MTBE did not give any particular results.

Table 4.2. *Analytical results from GC-ÅBO.*

Extractive	**Spent liquor mg/kg**	**Spent cooking liquor mg/kg**	**F3 to diffuser mg/kg**	**Cellulose from digester mg/kg**	**Cellulose subtracted mg/kg**	**Cellulose from diffuser mg/kg**
Fatty- & resin acids	294	59	5098	10345	38	6725
Sitosterols	12	2	417	374	2	307
Sterylesters	28	0	464	1328	3	1102
Triglycerides	7	0	241	2182	1	1278
Total	*341*	*61*	*6220*	*14229*	*44*	*9412*
All samples above were extracted with the Soxhlet extraction method/**Acetone**						
Fatty- & resin acids				9281		7175
Sitosterols				365		318
Sterylesters				1393		1221
Triglycerides				2424		1430
Total				*13463*		*10144*
The two samples above were extracted with the Soxhlet extraction/**MTBE**						
	mg/L	**mg/L**	**mg/L**		**mg/L**	
Fatty- & resin acids	54	38	2908		10	
Sitosterols	0	0	80		0	
Sterylesters	0	0	255		0	
Triglycerides	0	0	148		0	
Total	*54*	*38*	*3391*		*10*	
Above samples were extracted with liquid-liquid extraction (MTBE) after pH adjustment to 3 before analysis						

The GC-ÅBO analysis showed that my three own extractions of pre-evaporated spent liquor that gave most extracted amount extractives contained fatty- and resin acids, sterylesters and triglycerides.

No sitosterols were extracted from the pre-evaporated spent liquor and that is probably because of to high polarity of the organic solvent.

Table 4.3 shows GC-ÅBO results and the amount extract.

Only a small part of the extract showed to be fatty- and resin acids (~2%) which mean that a whole lot other organic compounds are extracted.

Table 4.3. *GC-ÅBO results of extracts from pre-evaporated spent liquor with liquid-liquid extraction using three different solvents. Also the amount extract from each sample was weight.*

Organic solvent	**Fatty- & resin acids mg/kg**	**Sterylesters mg/kg**	**Triglycerides mg/kg**	**Outweighed amount extract mg**
Ethyl acetate	16000	800	<500	112
MTBE	21000	800	<500	45
Diethyl ether	19000	600	<500	44

4.3 Mass balance

The calculations below describe the mass balance in filtrate 3 and the stream of spent liquor.

F3 to diffuser:

Flow: 400 m^3/h ≈ 400 000 l ≈ 400 000 kg

Amount extractives: 9940 mg/kg (see table 4.1)

$0{,}00994 \times 400\,000 = 3976$

About 4000 kg extractives/h flow into the diffuser. That is just over 95 ton/day.

Spent liquor:

Flow from spent liquor tank towards the evaporation: 212 m^3/h ≈ 212 000 l ≈ 212 000 kg

Amount extractives: 4224 mg/kg (see table 4.4)

$0{,}004224 \times 212\,000 = 890{,}4$

About 890 kg extractives/h flow into the evaporation. That is just over 21 ton/day.

4.4 NMR

Great complexity of the extractives can be observed in the ^{13}C NMR spectrum in figure 4.1-4-6. The many signals in nearly all spectrums tell us that the carbon is located in many different environments.
Samples 1 and 3 prove to be very similar to each other which can be seen in figure 4.1 and 4.3; the content is largely composed of the same compounds though in different concentrations.
The spectrum in figure 4.2 had very few peaks and that's because the majority of the extractives follow the cellulose as mention earlier in the GC-ÅBO results.

Only assumptions can be made for the chemical shifts. Fatty- & resin acids and some aliphatic compounds (12-40 ppm), polysaccharides (42-48 ppm), aromatic compounds (120-150 ppm), free acids and esters and carboxylic acids (180 ppm) among others. The peak at 77 ppm is the solvent $CDCl_3$.

The three extracts from the pre-evaporated spent liquor showed similarities (see figure 4.4-4.6) and as can be seen in figure 4.4, largest amount of organic material were extracted with ethyl acetate.

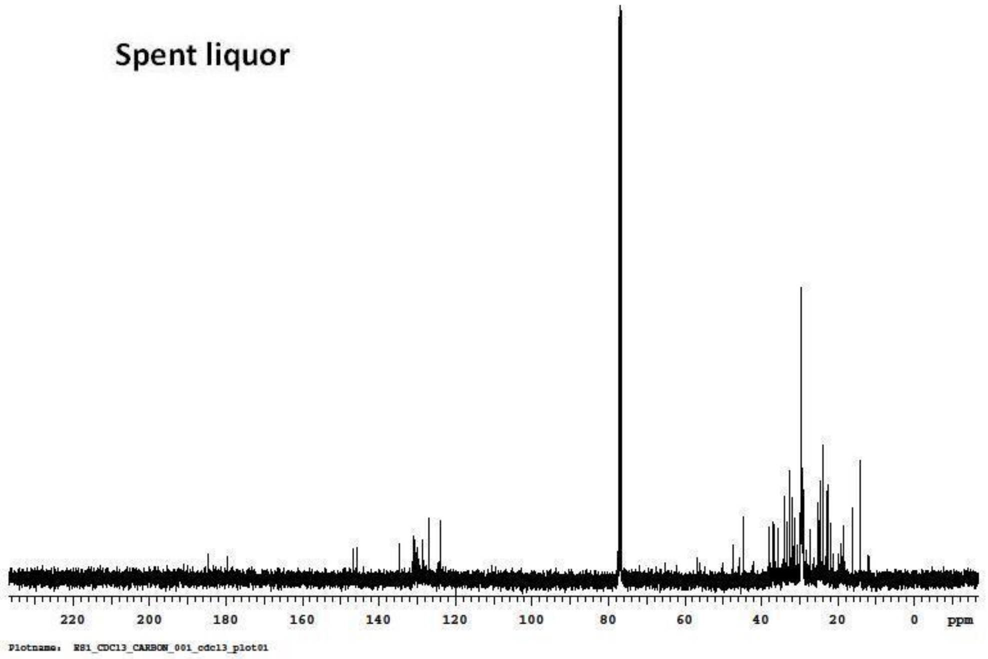

Figure 4.1. *^{13}C NMR spectrum of spent liquor (1).*

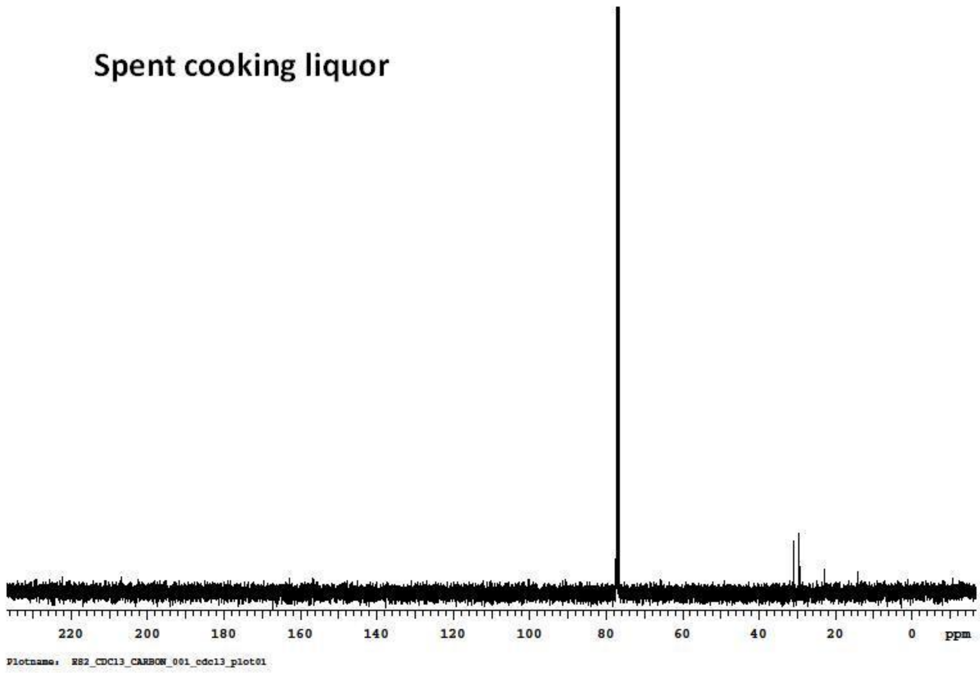

Figure 4.2. ^{13}*C NMR spectrum of spent cooking liquor (2).*

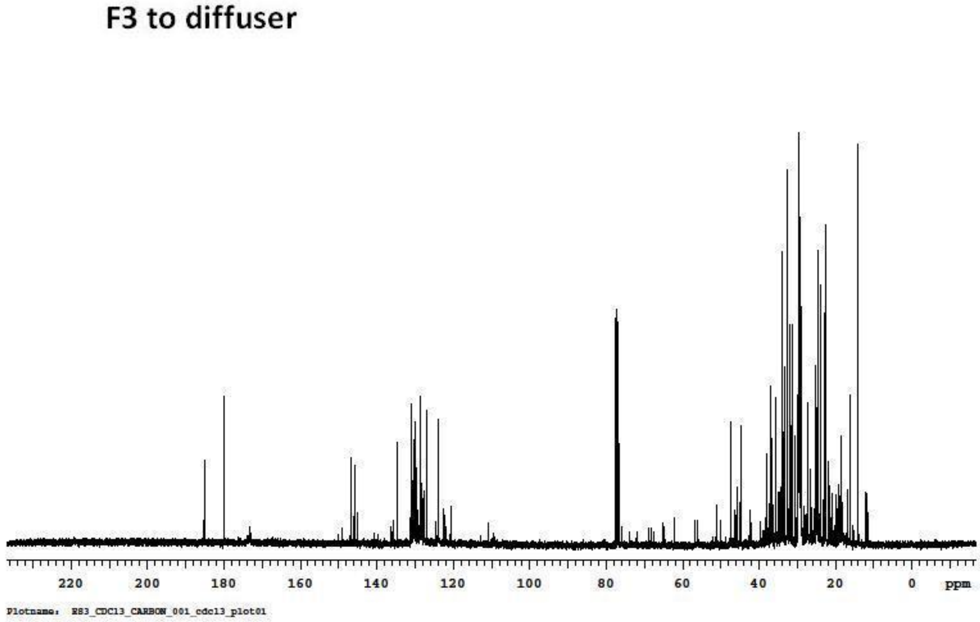

Figure 4.3. ^{13}*C NMR spectrum of F3 to diffuser (3).*

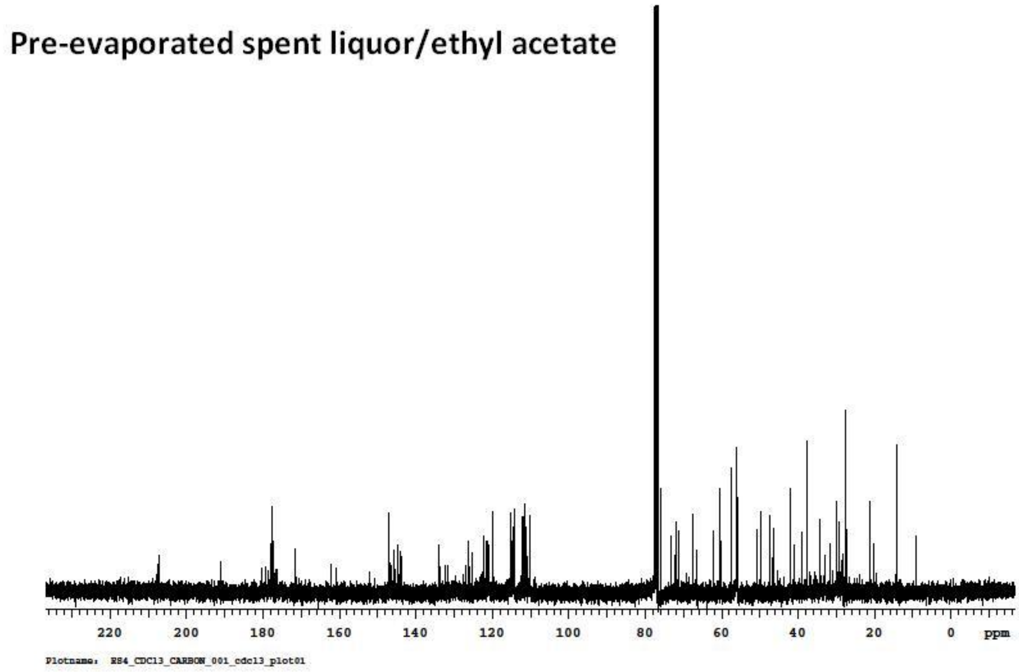

Figure 4.4. ^{13}*C NMR spectrum of extract from pre-evaporated spent liquor/ethyl acetate (4).*

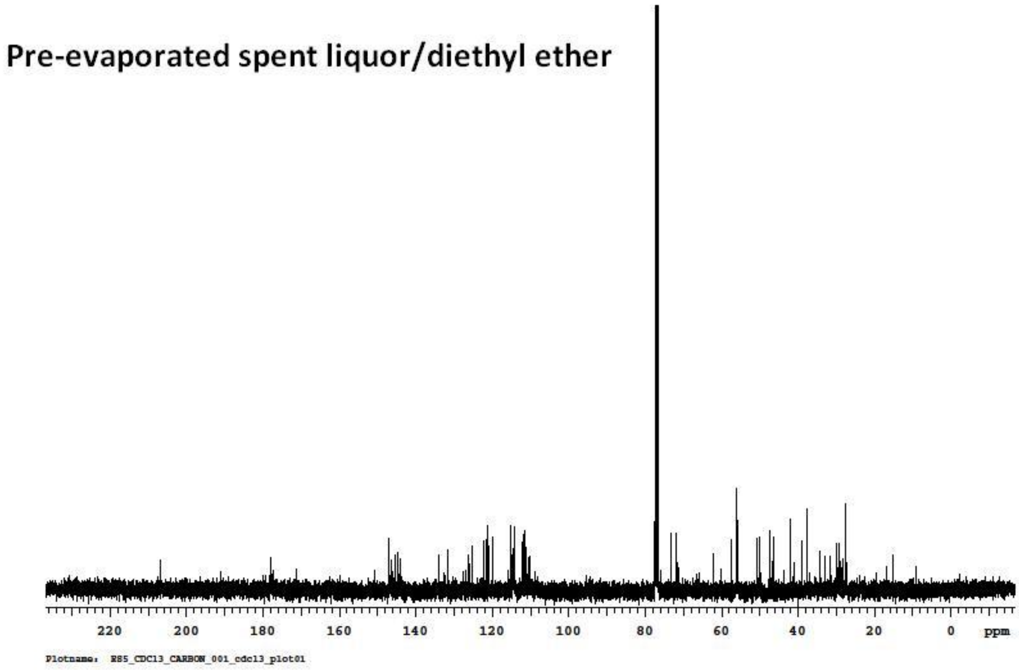

Figure 4.5. ^{13}*C NMR spectrum of extract from pre-evaporated spent liquor/diethyl ether (5).*

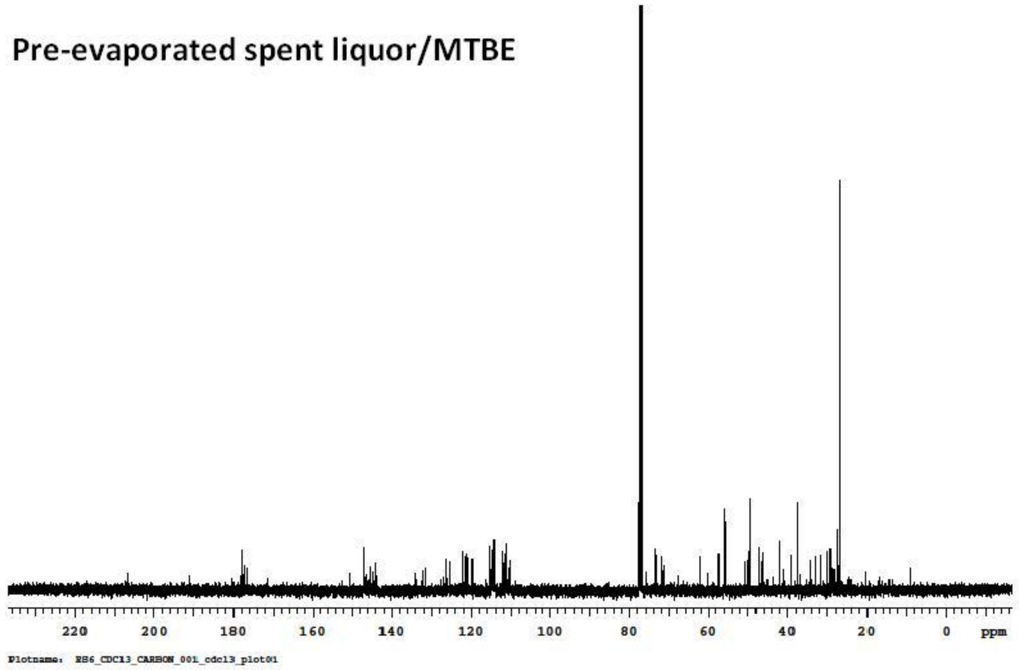

Figure 4.6. *^{13}C NMR spectrum of extract from pre-evaporated spent liquor/MTBE (6).*

4.5 Liquid-liquid extraction of pre-evaporated spent liquor

The results from the liquid-liquid extractions of pre-evaporated spent liquor showed that ethyl acetate is the most effective organic solvent for extraction of extractives. Table 4.4 shows that 4,2 g/kg extractives were extracted. Also MTBE and diethyl ether gave rather good extraction results.

In some extractions, dichloromethane and methanol for example, the separations were of that low quality, the aqueous- and organic phase was difficult to separate. In many of these extractions emulsions were formed.

Both methanol and dichloromethane have a relative high polarity, not as high as water but still high compare to the other organic solvent. Methanol is miscible in water while dichloromethane have very low solubility in water. These factors may be a reason for the emulsions.

Ethyl acetate and MTBE however have lower polarity and a relatively high solubility in water.

When combining different organic solvents ethyl acetate/MTBE proved to be the most effective.

Also ethyl acetate/diethyl ether, diethyl ether/MTBE proved to be quite effective.

The properties of the combinations were similar to the individual solvents and therefore not any big difference of extracted amount.

Adding brine to some extractions gave a negative effect because the existing separations were destroyed. Probably the lignin in the solution was affected by the increased ionic strength and that's why the organic phase became a dark and viscous solution.

It was not any big difference between my own results from extraction of pre-evaporated spent liquor with MTBE compared with those from MoRe Research. MoRe Research reclaimed 2030 mg/kg acetone-extract (see table 4.1) while I extracted 2728 mg/L (see table 4.4).

Table 4.4. *Amount extract from liquid-liquid extraction.*

Organic solvent	Amount extractives extracted mg/kg
Ethyl acetate	4224
Methyl *t*-butyl ether (MTBE)	2728
Diethyl ether	1848
Toluene	748
n-Pentane	572
Petroleum ether	396
Dichloromethane	No separation
Methanol	No separation
Ethyl acetate + Methyl *t*-butyl ether (MTBE)	4004
Ethyl acetate + Diethyl ether	3300
Diethyl ether + Methyl *t*-butyl ether (MTBE)	2244
Ethyl acetate + n-Pentane	1848
Diethyl ether + n-Pentane	1452
n-Pentane + Methyl *t*-butyl ether (MTBE)	836
Diethyl ether + Petroleum ether	660
Ethyl acetate + Petroleum ether	No separation
Petroleum ether + Methyl *t*-butyl ether (MTBE)	No separation
Ethyl acetate + brine	No separation
Methyl *t*-butyl ether (MTBE) + brine	No separation
Diethyl ether + brine	No separation
Toluene + brine	No separation
n-Pentane + brine	No separation

5 Conclusions

In these studies five different lipophilic groups of extractives were determined from the various process streams. Fatty- & resin acids, sterylesters, triglycerides and sitosterols were found in almost all streams/samples though in varied concentrations.
The analyses also show that there are a lot of unknown organic compound in the streams.

From the GC-ÅBO measurements it was obvious that almost 100% of the determined wood extractives follow the cellulose from the digester and only a fraction ends up in the spent cooking liquor.
One can say that the cellulose works as a filter for the extractives in the diffuser. There are extractives on the cellulose coming from the digester and more extractives are added via filtrate 3. Due to a “saturation” of the cellulose occur, not all extractives in the liquid can adhere to the cellulose surface and therefore follow the liquor instead. Extractives are also released from the cellulose in the first wash press.
That are factors why the spent liquor contains a lot more extractives compared to the spent cooking liquor.

The content of the extractives is dominated by fatty- & resin acids. Sterylesters comes second, triglycerides and sitosterols as third and fourth respectively.

Filtrate 3 (F3) contains a lot of extractives and these are coming from the cellulose. As the cellulose is washed several times, subjected to resin ejections extractives are removed from the cellulose ending up in F3. As F3 is used as one of the washing liquids the extractives return to the diffuser and from there taking place in the process again. To prevent pitching problems a certain amount resin is extracted from the process (More about this in 9 Future work).

Ethyl acetate proved to be the most efficient organic solvent in the liquid-liquid extractions.
Based on the mass balance calculations you can <u>in theory</u> extract around 21 m^3 extractives from the spent liquor stream with this method every day.
Today, around 25 m^3 extractives are burned every day.

The NMR measurements confirm that the streams contain much more than the determined groups of extractives.

Extractives have proved to be very difficult to analyze. Heterogeneous and complex composition is one of several reasons.
Due to the sulphite environment, isomerization of some extractives can occur.

6 Complementary work

There are work that should be very interesting to add in this report.
It would have been providing to take a liquid sample from the diffuser. Thus one can be able to calculate the mass concentration and further calculate the amount organic material on the cellulose and to see how much organic material that have been released from the cellulose.
To take advantage of an GC-MS, to see the what specific extractives the groups includes.
A more comprehensive mass-balance calculation of the organic material from log to bale. How much are added in the digester, how much extractives are there in the final products etc.

7 Future work

Today, an enough amount extractives are removed by ultra filtration, flotation and separation from a partial flow from filtrate 3 to prevent accumulation in the process. Approximately 25 m^3 extractives are sublimated to resin oil and burned as fuel in the recovery boiler every day.

The extractives at Domsjö Fabriker may not affect the cellulose in any particular way. But they are toxic to the yeast culture in the fermentation of hemicellulose to ethanol and negatively affect the quality of the lignosulfonate. Earlier, only more yeast was added to keep a steady balance of the yeast, but since a new method was developed no new yeast needs to be purchased.
An elimination of extractives would reduce the breakdown of the yeast culture and improve the quality of the lignosulfonate.

Arizona Chemical in the USA is the world's leading biorefiner of pine chemicals. Extractives are used in several products, fatty acids in paint & coatings, rosins (a solid form of mainly resin acids) in adhesives, road marking and sterols in food additives among others.

Different possibilities have been examined and continue if the extractives can be one of Domsjö Fabriker complementary products instead of just burn it.

8 Acknowledgements

It’s a pleasure to thank those who made this master’s thesis possible.

Thanks to:

Hans Grundberg, my supervisor, for all your support, inspiration and effort making this an interesting time for me.

Kristina Elg Christoffersson, Research and Development Manager at DomInnova, for giving me this opportunity to do my master’s thesis work at DomInnova.

Robert Selling, Claes-Göran Gidlund and Ann-Christine Hammarsten, at MoRe Research, for all help with chemical analyses and questions.

Romain Bordes, at Chalmers University of Technology, for helping me with the NMR analyses.

Roland Agnemo, Maria Lindgren, Magnus Lundmark and Peter Strunk, at DomInnova, for making me feel like a member of your team and taking time to answer my questions.

Krister Holmberg, my examiner at Chalmers University of Technology, for all your support.

9 References

[1] Pai Peng, Jing Bian and Run Cang Sun. (2010)
Cereal Straw as a Resource for Sustainable Biomaterials and Biofuels
Chemistry, Extractives, Lignins, Hemicelluloses and Cellulose, pp. 49-72.

[2] W. E. HILLIS (1971)
Review article formation and properties of some wood extractives.
Forest Products Laboratory Division of Applied Chemistry, C.S.I.R.O, Melbourne, Australia.

[3] Dinesh Fernando, Jonas Hafrén, Jan Gustafsson, Geoffrey Daniel (2007)
Micromorphology and topochemistry of extractives in Scots pine and
Norway spruce thermomechanical pulps: a cytochemical approach
© The Japan Wood Research Society 2007, pp 134.

[4] A. Assarsson, G. Åkerlund (1970) Studier av vedharts – del 6.
Extraktivämnessammansättning i splint- och kärnvedsprover från olika höjd i trädet.

[5] A. Assarsson, G. Åkerlund (1970) Studier av vedharts – del 7. Undersökning av extraktivämnessammansättning samt vedhartsets C^{14} aktivitet i olika områden av splint- och kärnved hos tall.

[6] R.C. Sun, D. Salisbury, J. Tomkinson (2002) Chemical composition of lipophilic extractives released during the hot water treatment of wheat straw,
pp 95.

[7] T.W. Graham Solomons (1988) Organic Chemistry, (4th ed.) USA: John Wiley & Sons.

[8] Manual for GC-ÅBO, Group determination of wood extractives, 4 Method B, Lipophilic wood extractives, pp 13-17.

[9] Internal document from Domsjö Fabriker, Basic education Certification – Domsjö Digestion.

[10] Internal document from Domsjö Fabriker, Domsjö Washing.

[11] Internal document from Domsjö Fabriker, Domsjö Bleaching.

[12] Ingemar Croon (1969), Hartskompendium, Svenska Pappers- och Celllulosaingenjörsföreningens hartskommitté, pp 20-21.

[13] Information\Broschyrer\Vi gör mer av trädet! (2009-10-06)

[14] http://www.paperonweb.com/wood.htm (2011-05-12)

[15] http://www.wfu.edu/chem/courses/organic/GC/index.html (2011-03-08)

[16] http://courses.chem.psu.edu/chem36/Experiments/PDF's_for_techniques/Liquid_Liquid.pdf (2011-03-11)

[17] http://www.scientificpsychic.com/fitness/fattyacids1.html (2011-03-23)

[18] http://www.cdc.gov/niosh/topics/organsolv/ (2011-03-28)

[19] http://www2.onu.edu/~b-myers/organic_solvents.html (2011-03-28)

[20] http://www.erowid.org/archive/rhodium/pdf/soxhlet4dummies.pdf(2011-04-04)

[21] http://www.chemguide.co.uk/analysis/nmr/backgroundc13.html#top (2011-03-08)

[22] http://www.scribd.com/doc/7009722/Liquid-Liquid-Extraction (2011-03-11)

[23] SLU, Inst. För virkeslära (1999) Lagringshandbok för trädbränslen

[24] Magnus Wålinder (2000) Wetting phenomena on wood, factors influencing measurements of wood wettability

[25] http://www.abitabout.com/Resin+acid (2011-05-24)

[26] http://www.greenspirit.org.uk/resources/lifechemistry.shtml (2011-05-24)

[27] http://www.chemryb.at/ckurs/2007/stoff3.htm (2011-05-24)

[28] http://www.prostate-miracle.com/beta-sitosterol.html (2011-05-24)