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## **Feasibility study for acidic biorefinery concept**

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## **ABSTRACT**

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The integration a recovery process for spent sulfite liquor from a sulfite cooking process with a kraft pulp mill was studied in this thesis work. The process includes a fermentation process for the production of biofuel. The calculation for three cases was done. The three cases considered were with a spruce sulfite pulp production of 100, 250 and 1000 Adt/day corresponding to 10, 25 and 100% of the total pulp production. A kraft cooking process with prehydrolysis was taken in consideration as reference. Compared to kraft cooking with prehydrolysis a bigger amount of ethanol can be produced by sulfite cooking. In the kraft prehydrolysis case 40 t/day of ethanol and 1000 Adt/day pine pulp is produced and in the sulfite case the production is 113 t/day of ethanol and 1000 Adt/day of spruce pulp. The energy consumption in the sulfite process is assumed to be slightly higher than in the kraft prehydrolysis process. The recovery system for spent liquor mix was studied. The evaporation of the spent cooking liquors should be done separately. The approximately composition of melt was calculated.

A comparison of all four cases was done and profitability was estimated

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## List of symbols and abbreviations

CJ	gigajoule	GJ
pH	potential of hydrogen	-
$T$	temperature	°C
T	time	hour
Adt	air dry ton, ton of pulp at 90 % dryness	
BOD	biochemical oxygen demand	
$C_0$	investment cost	
$CF_t$	annual cashflows	
COD	chemical oxygen demand	
DS	dry solids	
HW	hardwood	
IRR	internal rate of return	
LS	Lignosulfonates	
Odt	oven dry ton, ton of pulp or other material at 100 % dryness	
SS	suspended solids	
SSL	spent sulfite liquor	
SW	softwood	
T	investment time horizon	

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Apendicies

# 1 Introduction

The first motor was created a many years ago and it worked by using ethanol as fuel. However, it was not interesting because price of oil was lower. In history the development of ethanol and petroleum had a competitive relationship all the time.

Nowadays the opinion is that exhaustible resources are imminent to expire, price for oil rise every time. Therefore, people from all over the world are interested in new types of fuel – biofuel. The history of biofuel at the world market has begun a few decades ago. Usually biofuel originates from agriculture lands, but this way has many negative feedbacks. Sometimes it happens that harvest is not so good and using it for producing biofuel is not correct. In some countries people are still starving.

Consequently, research projects in the field of biorefinery have been started in the world. People would like to produce biofuel from waste or other substances which already came to the end of their life cycle, but can be regenerated to biofuel. The biofuel can be produced from lignocellulosic materials that are not wastes but not food products either.

The very good source for this purpose is a pulp and paper mill. Wood is raw material for these enterprises. Wood consists of cellulose, lignin, hemicelluloses, pectin substance, mineral matter and a small amount of fats, volatile oils and etc. The main product of pulp and paper production is cellulose pulp and paper. Other products are combusted and regenerated chemicals from it. Nevertheless, the wood components are very good source which contain hemicelluloses and also can be converted to ethanol and others products.

There are two types of chemical pulping processes in the world:

- Kraft (sulfate process);
- Sulfite process.

Now Kraft process predominates, because of stronger properties of end-product and pulp from this process is much better than pulp from sulfite cooking. [1]

In order to receive biofuel from kraft pulp there are several different ways such as:

- Pretreatment of wood chips before cooking, with the target to separate hemicelluloses from other components. This method has a drawback - an acidic pretreatment stage before sulphate process requires more alkaline in cooking process than cooking without acidic pretreatment. During the alkaline cooking at high temperature the wood lignin reacts with alkaline generating plenty of chromospheres compounds which darken the pulp. Also now the influence of chips pretreatment on properties of pulp and paper is unknown.
- Black liquor gasification. From this process getting methanol or hydrogen production is possible.

In the sulfite process ethanol can be derived from spent black liquor, because a big amount of hemicelluloses is dissolved in the cooking liquor. Moreover, spent cooking liquor is a good raw material for manufacturing other products such as nutrient yeast, antibiotics, organic solvent, organic acid, furfural and lignosulfonates. Lignosulfonates have a wide field for application. [2].

For a pulp and paper mill, it is profitable to make other products besides the main products – cellulose pulp and paper. If there is a good biofuel market in the country, so there is less dependence from which is oil imported from other country. This fact means economical profit and political relaxation. Also it is good for environment – decrease emission greenhouse gases to atmosphere.

In present time people need new ecological bleaching technologies. Now it is necessary to launch unchlorine technology for bleaching pulp and the high response of sulfite cellulose to bleaching is valued.

The aims of this work are to make a feasibility study for sulphite process in the new situation of forest industry in Finland. The targets is determination the best available technologies for ethanol production from spent sulfite liquor, determine possible products and their value, estimate a combine regeneration of black liquors from kraft and sulfite mills. By these data it is real to estimate feasibility current work and profitability of project.

## **2 Sulfite process**

### **2.1 Description of whole process**

In this section the basic principle and parameters sulfite process is considered.

#### **1.1.1 Historical part**

The sulfite pulping process was introduced into the pulp industry in the period of 1853-1884, during the industrial revolution in Europe and North America [3]. This process is based on production of cellulosic fiber for paper making in pressurized equipments at high temperature. Step by step pulping methods which were based on using sodium, magnesium, and calcium bisulfate, and ammonium solution were developed. The first commercial sulfite mill was built in Bergvik, Sweden in 1874 and it was based on magnesium base. In 1882 the first sulfite mill was built in America, Rhode Island and in 1878 it was introduced into Canada and the first sulfite mill was founded in 1885 in Ontario. In 1885 first sulfite mill was built in Finland. In 1960 there were 20 sulfite mills in Finland. [4] Thus the whole field of sulfite pulping was explored and opened up technologically within the last 130 years, as the result the potential and capabilities of the four bases at various pH levels are known and used. Sulfite cooking is suitable only for wood with low resin content. Therefore started development of Kraft process with the ability process to accept a wider variety types of wood and produce stronger fibers. [3] This process can convert almost any wood to the pulp. The invention of the recovery boiler by G.H. Tomlinson in the early 1930s [5] allowed Kraft mills to recycle almost all of their pulping chemicals. This made the Kraft process the dominant pulping process at the beginning of the 1940s. [6]

At the present time the most used method of pulping is the alkaline sulfate process (Kraft process), that can be used for most kinds of wood and allows easier recovery of the used chemicals.[7]. Only a minor part of pulp mills in the world use the older sulfite process, which usually is applicable to low-resin woods.

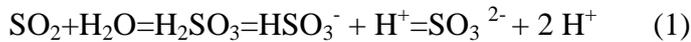
However, currently there are some research projects focused on renewal sulfite cooking process with generation ethanol and other important products.

### 1.1.2 General description of the sulfite process

The sulfite cooking process is mainly a treatment of wood by appointed temperature and appropriate pressure of sulfite acid. This process involves sulfonation and dissolution of lignin, also dissolution and hydrolysis of hemicelluloses. Cellulose remains in solid phase because sulfite acid does not dissolve it to a considerable extent. [2]

The share of sulfite cellulose in the whole world pulp production was 5,3% in 2000 [3]. Four cations are usually used in sulfite cooking: calcium, magnesium, sodium or ammonium. Choosing of cation depends on the solubilities of various sulfite solutions. [8]. The Table I gives information about varying composition of cooking liquor and basic characteristic of cooking process. Also, in this table the approximate positions of the characteristic limiting pH for each base are presented. [9].

Sulfite cooking solution is a complex system; compounds depend on pH and temperature. Following equilibrium reactions exist in the solution [9]:



Following reactions occur during the time of preparation solution:

Solution on Magnesium base:



Solution on Ammonium base:



Solution on Sodium base:



Table I Basic characteristics of sulfite cooking [9]

Name of sulfite cooking	pH	Cation	Reagent	Maximum Temp., °C	Pulp yield, %	Applications
Acid sulfite cooking	1-2	Ca <sup>2+</sup> , Mg <sup>2+</sup> , Na <sup>+</sup> , NH <sub>4</sub> <sup>+</sup>	H <sup>+</sup> , HSO <sub>3</sub> <sup>-</sup>	125-145	40-50	Dissolving pulp, tissue, printing paper, special paper
Bisulfite cooking	3-5	Mg <sup>2+</sup> , Na <sup>+</sup>	H <sup>+</sup> , HSO <sub>3</sub> <sup>-</sup>	150-170	50-65	printing paper, tissue
Neutral sulfite cooking	5-7	Na <sup>+</sup> , NH <sub>4</sub> <sup>+</sup>	HSO <sub>3</sub> , SO <sub>3</sub> <sup>2-</sup>	160-180	75-90	Corrugated medium, semi-chemical pulp
Alkaline-sulfite cooking	8-13	Na <sup>+</sup>	SO <sub>3</sub> <sup>2-</sup> , HO <sup>-</sup>	160-180	45-60	Kraft-type pulp

A scheme of the basic sulfite process is represented in Figure 1. This process involves: [9]

- Preparing of sulfite cooking liquor
- Cooking of chips. In the digester with treatment chips cooking liquor, there is a temperature of approximately 130-180 °C and a pressure of 0,6-1,5 MPa and it involves the operations of regenerating sulfur dioxide and washing of cooked cellulosic mass
- Screening of brown stock from undercooked pulp and mineral spot
- Dehydration and drying of cellulose

- Regeneration of spent liquor.

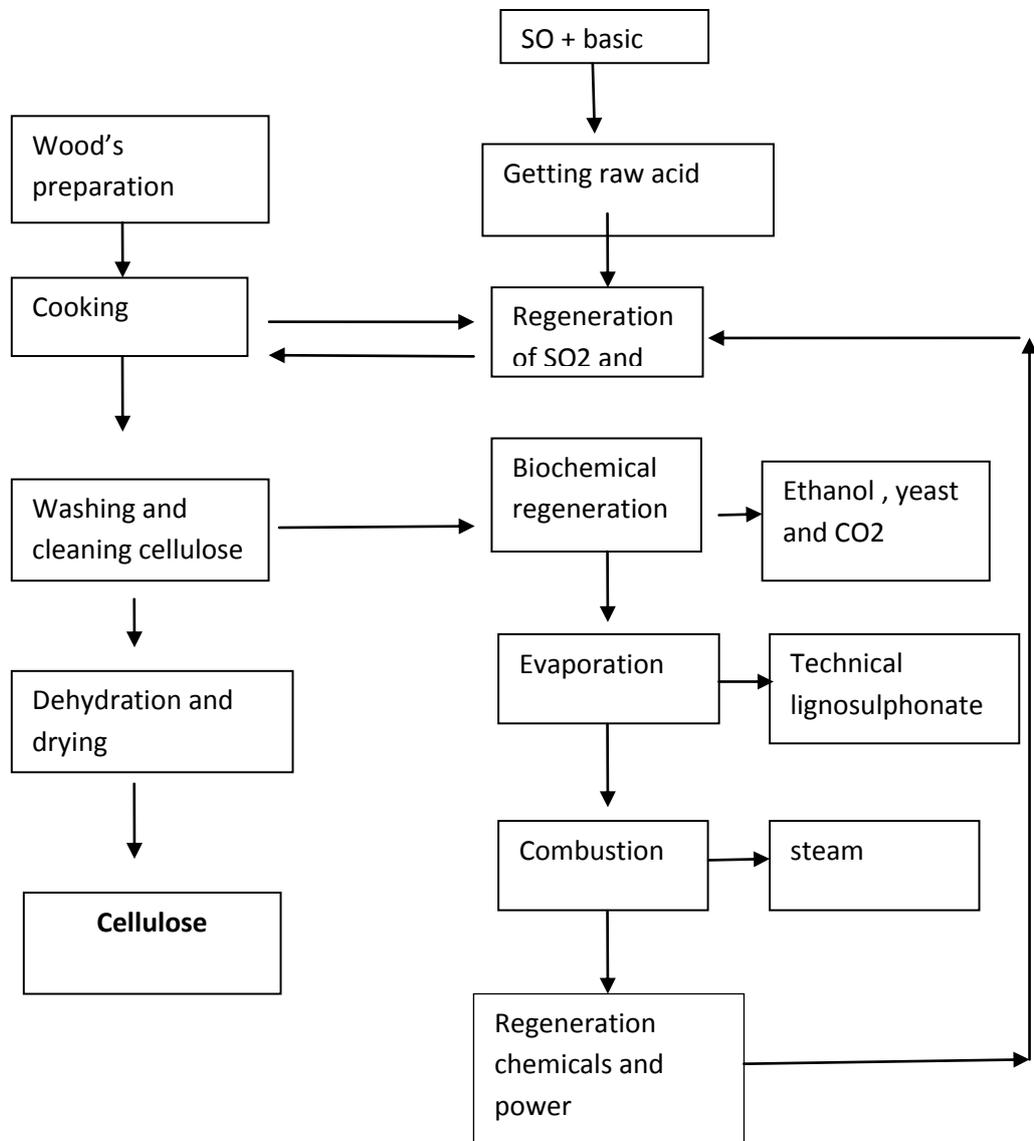


Figure 1. Scheme of the basic sulfite process [2]

Also multistep cooking exists, that modifies processes of single stage cooking.

Of course, sulfite cooking has some disadvantages compared to sulfate cooking, such as:

- Sulfite cooking has higher demand for raw material, than sulfate;

- Concentration of evaporate liquor is not more than 60% which decreases amount of heat (thermal energy), available from combustion. For comparison, concentration of kraft black liquor is about 75% and more; [2]
- “Resins problem”, regulation of pH in the time of evaporation condensates, emission minimization of sulphur and etc. These parameters require extra costs; [2]
- In the wood lignin bounds with hemicelluloses, therefore reactions of dissolving these components progress at the same time.[2]

Theoretically, known composition of easily hydrolyzable fraction of hemicelluloses of spruce wood by sulfite cooking it is possible to get yield of sugars about 24% from wood mass. At that case production of hexatomic sugars must be 75% from whole amount of sugar. But, in the practice yield of sugars is just 14-14, 5% from mass of wood, that is significantly lower. Thus destruction of sugars is about 40% in cooking process. [10]

In the sulfite cooking bypass liquor is used instead of part of cooking acid, which gives a considerable effect to prevent the sugar destruction. [11]. The impregnated chips contain enough liquid to dissolve lignosulfonates. Therefore it is possible to cook in the steam-to-gas phase. In this condition the amount of sugars in the liquid in the vessel can be raised to 5%. [11].

### **1.1.3 Reactions of extractive components**

Components of extractive substances are steady enough in acid and neutral conditions. When concentration of hydroxyl-anion increases solubility of organic acid, which is in ionic form, increases, presence of high fatty acid and resin acids, also fat, undergo hydrolysis; already don't have any negative influence on the process. Therefore pine wood also can be used for cooking by high pH. [9]

## 2.2 Sulfite Pulp quality

Sulfite cooking has an advantage over sulfate cooking – it is possible to use different process options. Parameters of sulfite cooking and processes provide flexibility of given lignocellulosic material, the pH of the cooking liquor and the pulp yield from the different effects of added by choosing of the type and concentration of four bases. One of the most important characteristics is yield of cellulose. Cooking yields for different pulping processes are shown in Figure 2. “Stora” is a two-stage sulfite cooking process, by this process it is possible to achieve very high yields.[8]

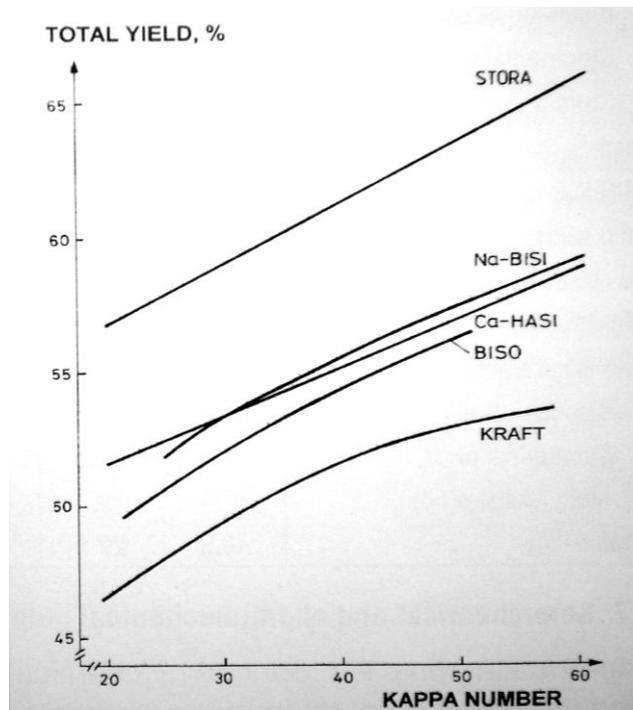


Figure 2. Cooking yields for different pulping processes applied to the same wood species [12]

Some typical properties of unbleached and bleached sulfite pulps in comparison with sulfate (Kraft) pulp are represented in the Table II. Spruce was taken as an example, because in this work it is one of the most important wood types.

It can be understood from this table that sulfite cooking has a higher yield than Kraft cooking and usually the Kappa number is lower in sulfite cooking.

Table II The comparison of unbleached pulp properties of pulps made with different pulping methods from the same softwood sample and beaten in the same beater [1]

Cooking	Unbleached			Bleached at Tensile index 80 Nm/g			
	Yield, %	Kapp a	Bright. Scan., %	Yield, %	Beat. Minute s	Tear index Nm <sup>2</sup> /g	Opacity, %
Spruce							
Acid sulfite	52.5	23.2	62.1	48.5	25	11.3	62
Na-bisulfite	52.8	23.4	71.4	50	26	10.8	61
Mg- bisulfite	55	26.6	69.3	51.1	25	10.5	61
Kraft	48.9	29.7	25.7	46.4	18	19.1	72

In the Figure 3 the pulp yields from spruce by different cooking methods are shown.

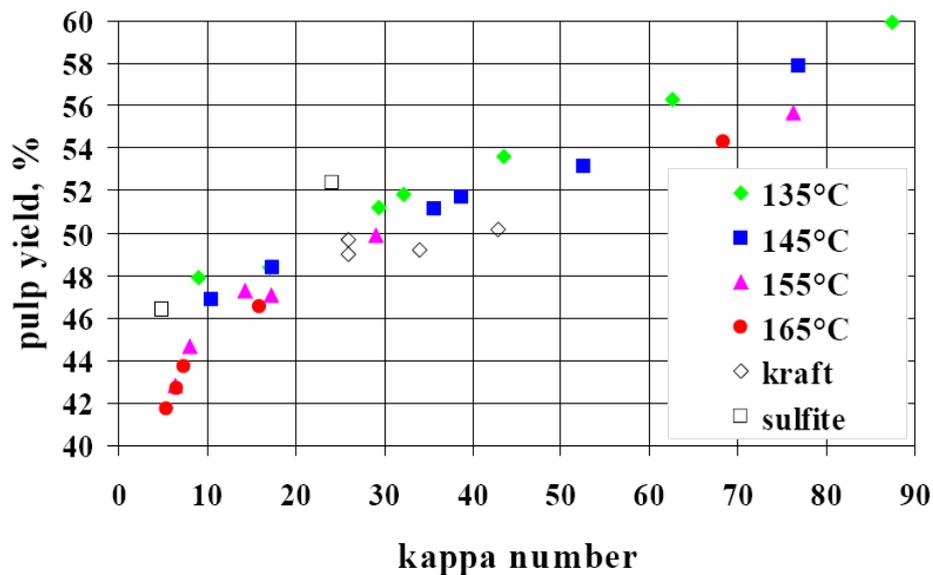


Figure 3. Pulp yield of spruce by different cooking process. [13]

It is obvious from this figure that pulp yield of sulfite cooking is higher than pulp yield of Kraft cooking. But the latter has better strength properties.

The most important parameters of cooking processes influencing process duration, yield and quality of cellulose, also saccharides from its liquor [3]:

- Temperature of cooking;
- Composition of acid, that is composition of free sulphur dioxide and base;
- Type of base;
- Quality of chips and type of wood.

### **2.3 By-products**

Besides celluloses it is possible to get a lot of different products from sulfite spent liquor. The organical (non cellulose) components from sulfite liquor allows obtaining important products, such as proteins yeast, ethanol, carbonic acid gas and carbonic acid snow, spirit and organic acids, vanillin and lilaceous aldehyde, tannins, glue materials, dispersers, organic fertilizer etc. When soluble bases (bisulfite Na, Mg and  $\text{NH}_3$ ) are used for cooking it is possible to regenerate chemicals from spent liquor or from distillers. [9]

### **2.4 Basic knowledge about spent liquor and its regeneration**

About 50% of organic matter exists in spent liquor, which is calculated from initial mass of wood unspent sulfurous acid and its salt and also another sulfur compounds are in ones besides organic matters. Group composition of organic matter is shown in the Table III. [1]

Table III Composition of organic components in sulfite liquor, % [1]

Components	Sulfite cooking		Bisulfite cooking		Monosulfite cooking
	Softwood	Hardwood	Softwood	Hardwood	Hardwood
Lignosulphonate	55-60	30-37	65-66	55-56	45-49
carbohydrates (dilution matters)	28-32	38-42	16-17	17-19	12-14
Organic acid	11-12	23-26	16-18	24-25	36-38
Extractive matter	1	2	1	2	3

Carbohydrates of sulfite liquor generally are compounds from monosaccharides (Table IV) with a little amount of oligosaccharide. Carbohydrates in oligomers and polymers types exist in spent liquor after bisulfite and sulfite cooking.

By sulfite cooking of spruce, 5 monosaccharides are found in the spent liquor in this correlation:

Hexoses: mannose – 50%, Galactose – 15%, glucose 5%;

Pentoses: Xylose – 25%, Arabinose – 5%. [2]

Fermentable components are called hexose sugars. From this ethanol can be produced biochemically. Pentose sugars do not make ethanol. They are therefore called unfermentable components. But nowadays pentose sugars also can be fermented by special type of yeast.

Volatile acids (formic acid and acetic acid), with predominance acetic acid (85-92 %) are created during the cooking process. When spruce wood is cooked, outlet of volatile acids is approximately 70 kg/t, calculated from initial wood. [2]

Table IV Components monosaccharides in sulfite liquor, % [1]

Compound	Sulfite cooking		Bisulfite cooking	Monosulfite cooking
	Soft wood	Hardwood	softwood	Hardwood
Mannose	48	3	50	2
Xylose	22	80	19	82
Galactose	10	2	11	5
Glucose	9	10	15	4
Arabinose	6	3	3	5
Rhamnose	5	2	2	2

Changing sugars composition in sulfite liquor by deepening fusion/penetration is shown in Table V. The composition was taken from spruce sulfite cooking (yield 69, 6%, lignin content 0, 95%). [2]

Content of general fermentable components increases along with increasing of fusion/penetration stage, but content of no invert oligosaccharides in liquor decreases. In some cases when cooking vicious cellulose declining content of dissolved components curve in the end of cooking, as result of particular decomposition of saccharides, conspicuous.

Besides denoted compounds, carbonyl compounds (furfural, 5-methylfurfural, and formaldehyde) exist in spent liquor. They affect negatively biochemical regeneration and utilization of organic components. [2]

Table V Sugars composition in sulfite liquor [2]

Types of saccharides	Composition saccharides in liquor			
	Cooking time by T= 135°C, h			
	4	6	8	10
General dissolved components	8.25	11.15	13.07	14.03
Unfermentable components:				
Xylose	1.80	2.68	3.48	3.75
Arabinose	0.27	0.28	0.21	no
Methylpentoses	0.36	0.34	0.30	0,21
Uronic acids	0.49	0.46	0.33	0.25
Total Unfermentable components	2.92	3.76	4.32	4.21
Fermentable components(hexoses)				
Mannose	3.64	5.63	6.76	7.40
Galactose	1.31	1.50	1.05	0.92
Glucose	0.30	0.14	0.85	1.33
Total fermentable components	5.25	7.27	8.66	9.65
General dissolved components	8.17	11.03	12.98	13.86
% fermentable components from general components	64.2	65.9	66.7	69.6

Basic technological scheme of spent liquor preparation for biochemical conversion usually includes following operations: [9.]

1. Separation of celluloses fiber

2. Desulfitation and removing volatile components
3. Oxidation of sulfites and phenols
4. Neutralization
5. Injection nutrients
6. Defecation and cooling
7. Microbiological conversion.

Strong spent liquor from the digester after washing of cellulose is not suitable for biochemical conversion, because it contains too high amounts of components which have negative influence on biochemical processes (phenols furfural, formaldehyde and etc). Also a part of carbohydrates contains in aldehydebisulfite combinations, which cannot be utilized by microorganisms. [2]

### **3 Environmental issues**

In the sulfite process, large amount of water is necessary for the washing process of spent sulfite liquor, but this water can be regenerated in the evaporation process SSL.

Figure 4 provides an overview of the main processes involved in sulphite pulping and the major sources of emissions (to water and air). The emissions to water originate from different processes mainly washing losses, effluents from the bleach plant and condensates from the evaporation plant. They also include accidental spills. [14]

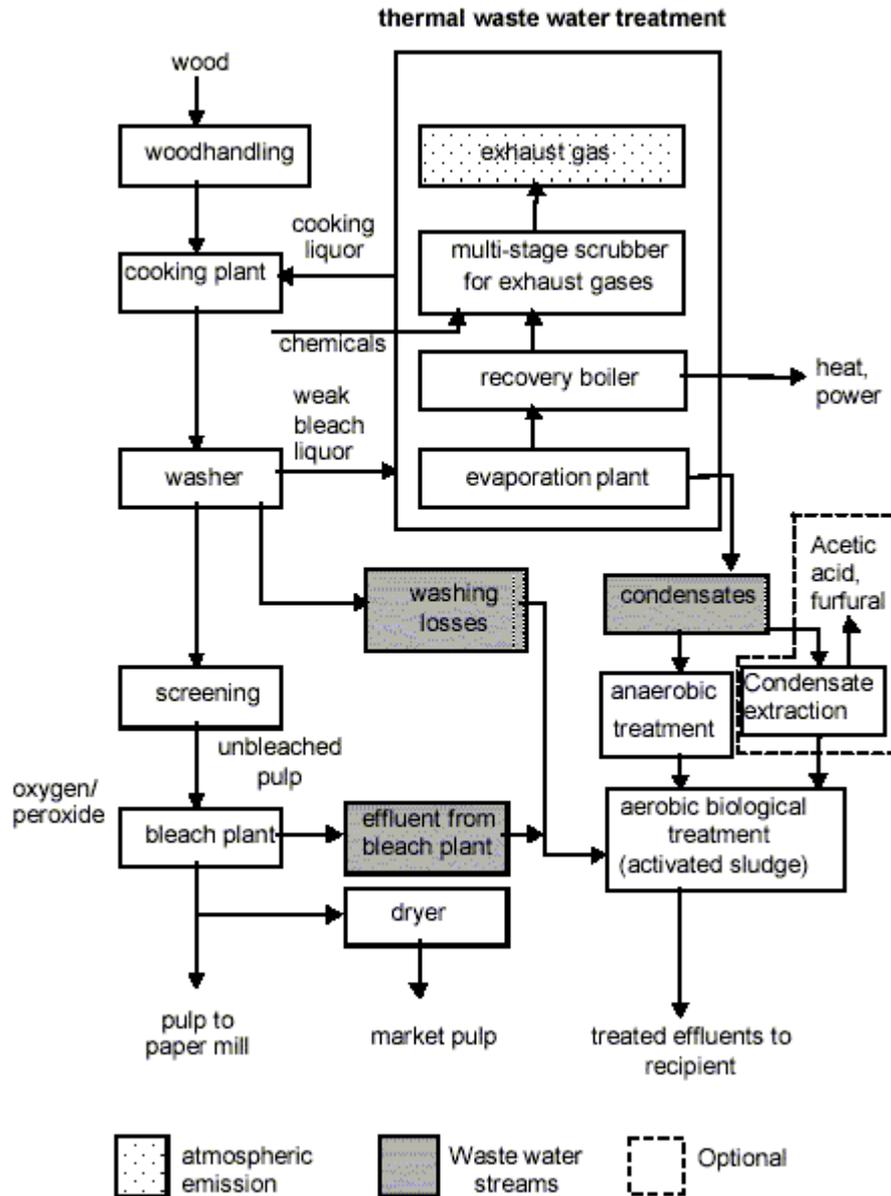


Figure 4. Main processes involved in sulphite pulping and the major sources of emissions (to water and air) [14].

The wood pulping and production of the paper products generate a considerable amount of pollutants characterized by biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS), toxicity, and color when untreated or poorly treated effluents are discharged to receiving waters. [1] Each pulping process utilizes large amounts of water, which reappear in the form of an effluent. The most

significant sources of pollution among various process stages are wood preparation, pulping, pulp washing, screening, washing, bleaching and paper machine and coating operations. Depending on type of the pulping process, various toxic chemicals such as resin acids, unsaturated fatty acids, diterpene alcohols, chlorinated resin acids, and others which are generated during pulp and paper processes. [15]

During cook the delignification is brought down to a kappa number of about 14-22 for softwood and 10-20 for hardwood. The yield of pulp in the cooking process is somewhat higher than for Kraft pulping. As a consequence the amount of wood, mainly hemicelluloses, dissolved out in the open part of the process (after brown stock washing) is comparatively high in alkaline bleaching stages and can be up to 40-50 kg COD/t. The specific waste-water volume of the bleach plant in better performing mills is in the range of 15 - 25 m<sup>3</sup>/Adt. [14]

On each stage different types of pollution are generated. In Table VI the waste-water pollution from individual pulping and papermaking processes are given: [15]

Table VI Typical waste-water generation and pollution load from pulp and paper industry [15]

Process	Wastewater (m <sup>3</sup> /adt pulp or paper)	SS (kg/adt pulp)	COD (kg/adt pulp)
NSSC	20-80	3-10	30-120
Ca-sulfite (unbleached)	80-100	20-50	Not reported
Ca-sulfite (bleached)	150-180	20-60	120-180
Mg-sulfite (unbleached)	40-60	10-40	60-120
Kraft-unbleached	40-60	10-20	40-60
Kraft-bleached	60-90	10-40	100-140

From the data of this table it can be seen, that Ca-sulfite cooking produces the biggest waste-water amount, but it is pretty old technology, which is not suitable for our process. The Mg-sulfite cooking has the same wastewater amount like sulfate cooking.

The better alternative process will be described in the section 5.2 – it is a proceeding by multistep-washing with black liquor decreases consumption of clear water and improves properties of spent sulfite liquor for further fermentation process.

Pollution from pulp and paper mills can be reduced by different processes and management measurements such as the Best Available Technology (BAT). It is any new technology that is more suitable and efficient for reducing harmful influence on environment from pulp and paper mills. Globally the sulfite process pulping is decreased due to environmental issues and also Kraft pulping provides better mechanical properties. However, currently there is a great deal of available technologies for recycling water and eliminating pollutions from water. Consequently sulfite cooking will not make more damages for environment, than Kraft process. Therefore this process can be used broadly without abuse of environment pollution.

## **4 New economical sulfite mill**

### **4.1 World cases**

Forest-based companies usually make other products from by-products at paper mills. A few examples are sulfite cooking with producing by-products which also are very important for customer. Some examples are situated in Canada. The Old Howard Smith Paper mill plant in Cornwall, Ontario produces ethanol from spent liquor and vanillin, also other products. [12]. In present time Tembec Temiscaming mill is located in Canada and produces high purity cellulose, Tembec's Specialty Cellulose, and during sulfite pulping process also lignosulfonates are produced. The mill ferments the sugars in ammonium sulfite spent liquor and sells the leftover lignosulfonates. The Temiscaming produces about 18 million liters of ethanol a year. This mill receives steam and electricity from the mixed biomass waste by burning it in a co-generation boiler and supplies the site with most of its energy requirements. [16]

Nippon Paper Chemicals (NPC) Co., LTD and Cosmo Oil Co., LTD made agreement about project research to develop an efficient ethanol production process using effluent (black liquor) generated from sulfite pulping process as raw material. [17].

The basic principle

Soft wood, mainly spruce, and hardwood (mainly beech) can be used as raw material in the sulphite pulping process. Logging and sawmill residues can also be used. The use of wood and the yield for production of bleached pulp depends on the selectivity in delignification and bleaching. The wood which is required for manufacturing 1 tone of bleached sulphite pulp is normally between 4.2 and 5.2 m<sup>3</sup> unbarbed wood/Adt. [17]

The first important parameter is right chosen base for cooking. For this process was chosen cation Na<sup>+</sup>, because with this base it is possible to make a combined regeneration with kraft pulping, and also this base provides the better result in the fermentation process which direct to obtaining ethanol.

Realization of regenerated sulphur dioxide in the cooking process will be beneficial for economic purpose and it is necessary for further fermentation process, because sulphur dioxide is a strong inhibitor. Also regeneration of sulphur dioxide decreases consumption of raw acid. The two basic principles in regeneration of sulphur dioxide are cold regeneration and hot regeneration.

## **5 Spent sulfite liquor recovery process**

In the Figure 5 all presently known types of regeneration for this base-liquor are shown. The target products for us are cellulose and ethanol. Consequently the regeneration stages were chosen, with by-products and further regeneration chemicals, which should be possible to regenerate with kraft spent liquor.

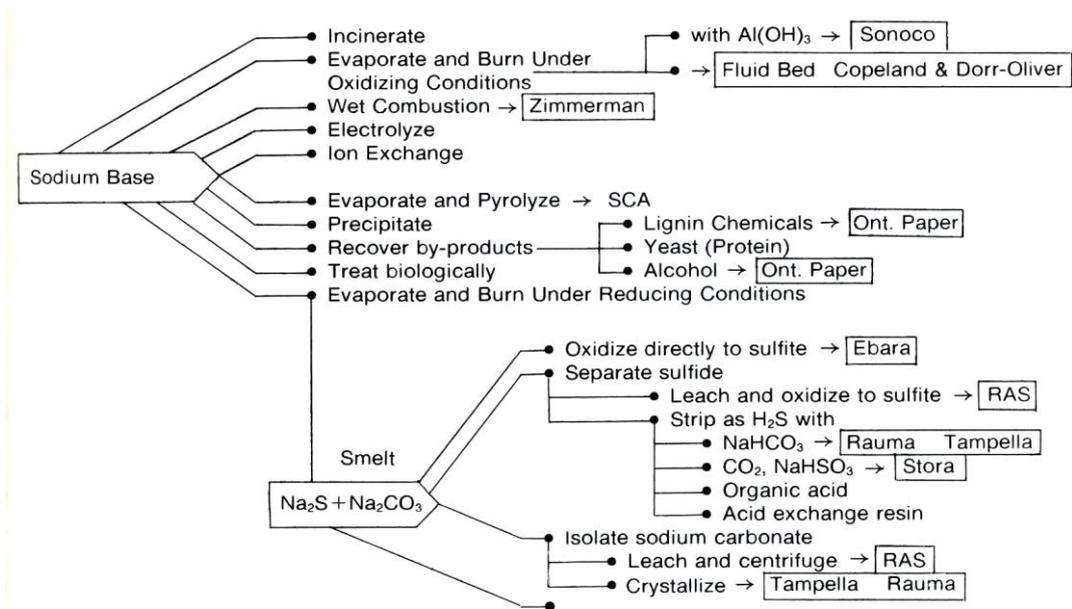


Figure 5. Sulfite recovery system which is considered and currently used (in boxes) [3]

## 5.1 Characteristics of sulfite liquor

Sulfite spent liquor can be considered a solution containing, transferred in the sulfite process, no cellulose components of wood and products of cooking acid. [2]

Nowadays the sulfite liquor is containing carbohydrates, organic acid monosaccharides and acetic acid that are components for biochemical utilization. Due to potential biochemical reserve, oligosaccharides and ox(y)acids are related, for conversion which is necessary adding operation in substrate.[18]

There are sugars, organic and mineral acids and their salts, liginosulfonates complex in sulfite liquor. In addition there is some methanol, extractive components of wood and some other components. Also different cations exist in macro- and micro-amounts in the liquor. [19,2]

Some organic and mineral components from sulfite liquor form a group of inhibitors of biochemical process. Main representatives (chemical agent) are dioxide sulfur and components: phenol substances, formic acid and aromatic acids, furfural, cymene [18].

These compounds in defining dosage render oppressive influence on usage microorganism in biotechnology of sulfite liquors. Also they can be adsorbed on the surface of cells, which disturbs interchange with substrate. [18]

Constitutive part of organic components is lignosulfonates. They determine colloid-chemical behavior of sulfite liquors. [18].

Sugars concentration in spent liquor fluctuates in the limit of determined conditions of cooking process and ways of selection liquor from digester. Consistency of sugars in sulfite liquor of spruce wood is fluctuating between 1,8 to 3,5%. [1] Sugars concentration in spent liquor of aspen is about 2,1%. Of different sugars, the share of pentose in spent liquors is 92 %. [19].

## **5.2 Spent sulfite liquor and its preparation for recovery**

Amount of liquid in the digester towards the finish of cooking process is determined by following factors. [2]:

- Moisture of chips fed into the digester
- Extent of compaction chips in the digester
- Temperature of incoming acid in the digester
- Amount of liquor removed by relief liquor in another digester (or by haul-back in accumulation tank) and by blowdown gas in the end of cooking process
- Amount of condensed steam in the cooking process.

The liquor connects with cellulose in the end of cooking process in the digester: [2] in  $m^3/t$ :

1. Liquor unconnected with cellulose, 1-2;
2. Liquor allocated in space between slivers, bunches and separated fibers 3,5-4;

3. Liquor that contains in cistern of cells 1,5-1,8;
4. Liquor that contain in cells wall 0,3-0,5.

Spent liquor which is allocated between slivers and separated fibers can be separated from mass by pressure about 3 Atm. [2]. For liquor separation in other conditions, water has to be used. Consequently spent liquor concentration is lower, that is not good for recovery. For increasing quality of liquor separation, there are methods of multistep washing with reserve liquor usage [1]. This way can be used for dumping different types of digester. The main point of the method: after part of liquor disconnected with cellulose, reverse liquor (from tank 1) inject into digester for supplanting strong liquor (figure 6). On the stage of selection of liquor, weak liquor injects into the digester (from tank 2) which supplanting mix strong and reverses liquors. This mix is going directly to tank 1. Following hot water injection into the digester and selected solution is going to tank 2. [1]

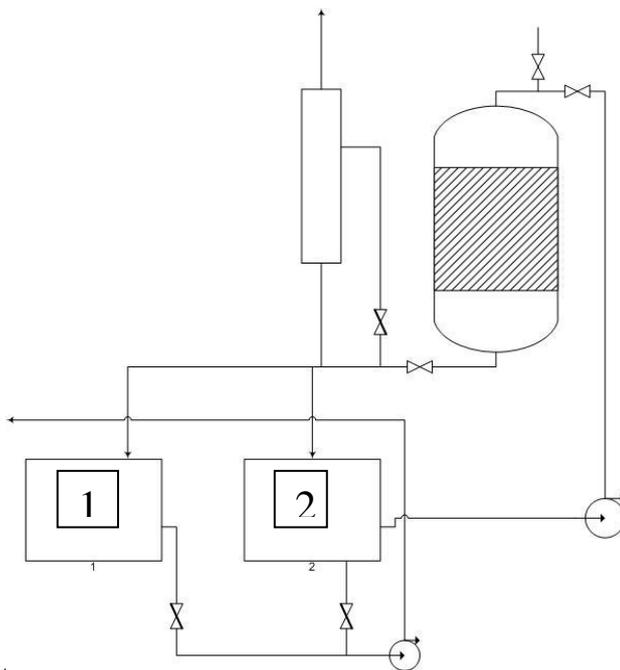
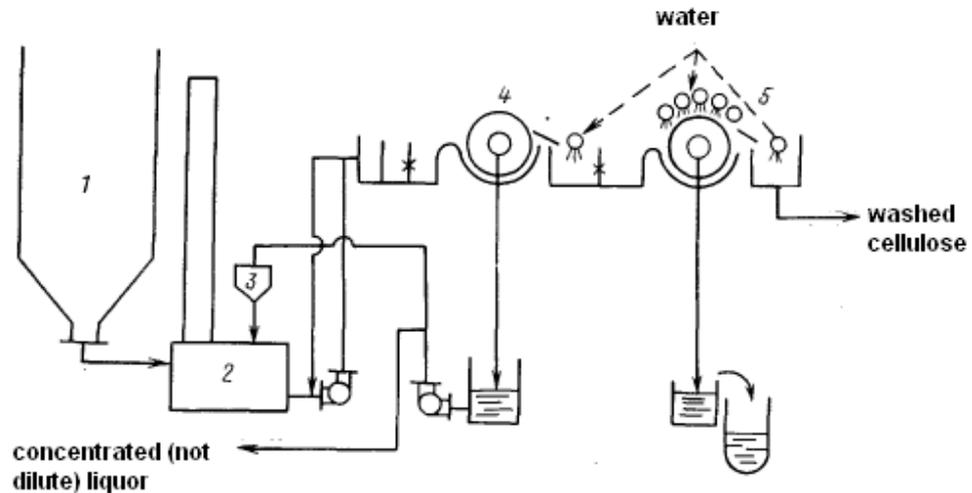


Figure 6. Scheme selected liquor from the digester with using multistep washing. [1]

It is shown in the figure 6 that application of multistep selection raise level of using solids (dissolved matter) in the liquor in 1, 8 by increase concentration in 1, 5 times.

Also Devis M. [21] described utility with thickener high densities which allow concentrating mass from 8 to 25% selection 74% liquor without dilution. Scheme is presented in the following picture



1 – digester; 2- blownvat tank with mixer; 3- tank; 4 - vacuum-thickener; 5- vacuum-wash apparatus;

Figure 7. Scheme selection liquor on vacuum-filter [21]

At the end of the cooking contents of digester (consistency about 8%) blows out to tank with mixer. The mass that is strongly diluted with liquor is concentrated in a vacuum-thickener to a consistency of 25%. Liquor separated from mass at this stage time. Concentrated mass, after thickener, is diluted with water and washed in vacuum-wash apparatus. [2]

By this type of selection of spent sulfite liquors is about 95% of solid (dissolved matter) with a small dilution. This scheme is used at Russian mills. [2]

These types also influence on water consumption. When this type of spent liquor separation is used – water is spare. It is important point for environmental impact.

### 5.2.1 Technology of spent liquor preparation

Preparation of spent liquor for biochemical treatment includes:

- removal of volatile compounds

- neutralization of non-volatile acids and enrichment of nutrients
- clarification of liquor from suspended material
- cooling of liquor until favorable temperature for biochemical treatment.

Liquor becomes wort after these operations. Wort contains the sugars that will be fermented by the brewing yeast to produce alcohol.

Firstly, the sulphur dioxide is removed, because this component has an inhibitory effect on the yeast. When concentration of free-  $\text{SO}_2$  is 0,005% in the solution, then yeast ability increases by 10% to form alcohol. Yeast stops ferment sugars when free- $\text{SO}_2$  concentration increases until 0,015% in the solution. [2]. Even if sulphur dioxide will be in the solution such as bisulfite, and then yeast will exist in suppressed condition. The sulphur dioxide does not influence on the yeast, almost. Only in condition monosulfite and concentration until 0,2 %.[2].

The sulphur dioxide present in the spent sulfite liquor slows down or makes impossible the biochemical utilization of sugars. This is because sulphur dioxide connects sugars in sugarbisulfite combination. Having new properties, and also because of aldehydebisulfites components are formed with intermediate products of fermentation. [2]

The main task of preparation liquid for biochemical treatment is to ensure that concentration of easy to sliver  $\text{SO}_2$  is not higher than equivalent concentration of carbonyl compounds. This value is minimum/maximum concentration of sulphur dioxide. [2]

The easier way to reduce free- $\text{SO}_2$  is to blow air into SSL, released in the storage tank. Amount of air should be approximately 5 m<sup>3</sup>/hour on each cubic meter of liquor. Duration of the blowing is 1-3 hours, depending on the parameters of pulping and selection of SSL. [23]

One of the most important parameters in the process of reducing  $\text{SO}_2$  is temperature. The temperature should be not less than 80 °C in the storage tank during the blowing the SSL. [23]

In the scheme of treatment SSL “ethanol-yeast” incoming liquor is concentrated in 1,5-2 time with target lowering of value SSL. Up to 25% of sulphur dioxide (from total content they are components in SSL) removing with evaporation moisture process. But this sulphur dioxide is difficult for regeneration, because its concentration in the condensate is very low. [23]

The highest level of sulphur dioxide removing is achieved by bubble treatment of SSL with steam. This process is carried out in the plate or packed column. By this treatment it is synchronously possible to reach considerable reduction in concentration of SO<sub>2</sub> for removing in the liquor and by specific condition release fully discharged sugars tied with sulphur dioxide. By this way it is possible to remove about 45-55 % combination with sulphur dioxide [23].

When using Na-cation base, the SSL consists significant amount of dissolved sulfite. It can be removed by blowing air, already released from sulphur dioxide in the column. As the result of this treatment sulfites will oxidize by oxygen of air to soluble sulfate, which is safe for further fermentation process. [23]

The unit operation is based on the Somer liquid SO<sub>2</sub> concept development in the forties in Finland. [3]. The system ties together pulp digester blow, sulphur burning, liquid SO<sub>2</sub> production and storage for second pulping stage. [3].

There is also a system called “Cansolv system SO<sub>2</sub> process technology”. This is a process of regenerable sulphur dioxide scrubbing technology, which utilizes a proprietary ammonium solution in a cyclic absorption-regeneration flowsheet shown in Appendix 1. [24]

### *5.2.2 Neutralization of spent sulfite liquor.*

The pH of wort is usually about 4, 5 to create profitable conditions to biochemical treatment of sugars. [1] But pH of wort sulfite liquor usually is necessary bring to higher volume. Because sugarbisulfite compound is depend on pH of solution. In this condition, zone the greatest stability all existed sugars of bisulfite compounds in liquor include profitable pH for fermentation. [18]

Chalk, lime milk and also sulfate sludge can be used as neutralization agents for sulfite liquor.

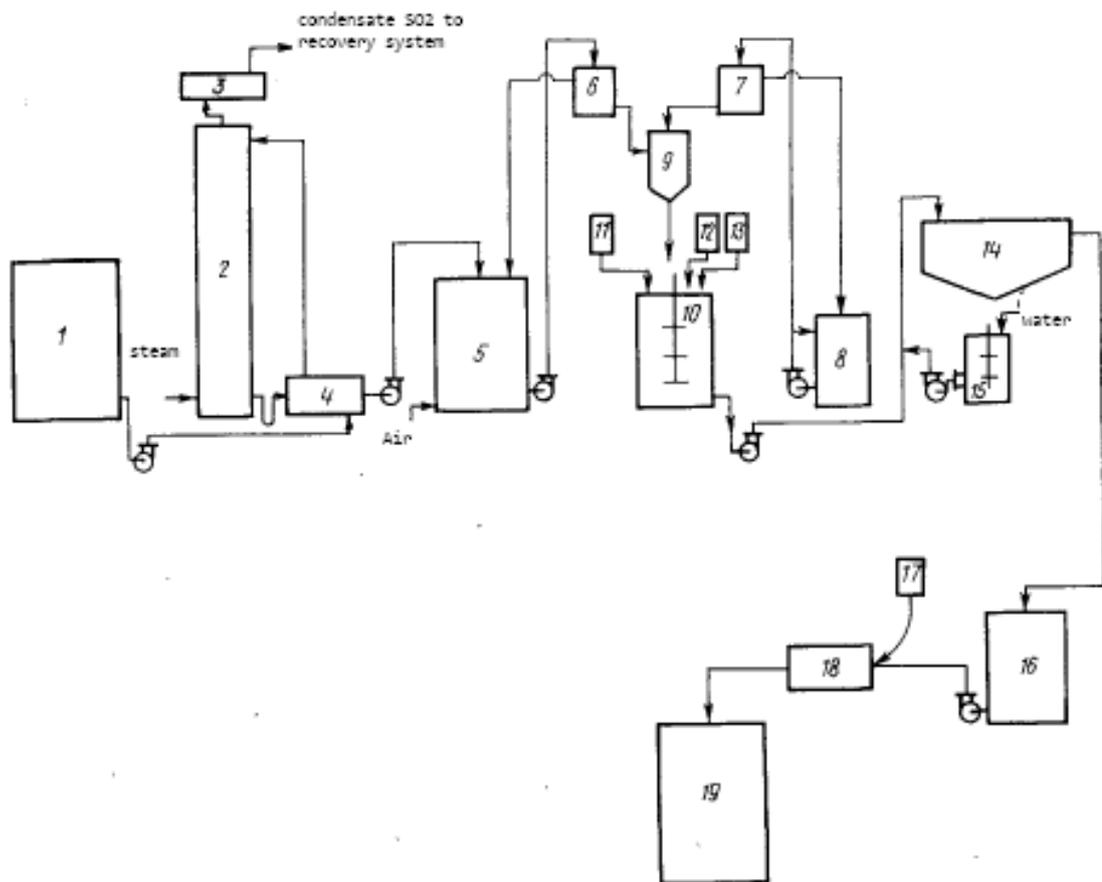
Chalk and sulfate sludge are weak bases. It means that speed of neutralization with these components is lower than this with lime milk. Based on Sapotnickiy's data [2], speed of neutralization spent sulfite liquor by sulfate sludge is about 0, 1 mm/sec. Consequently area of clarifier must be larger.

This process is better led with active mixing. A.Byevskiy [21] determines that active mixing of liquors, in the time of neutralization, makes it possible to decrease degradation of sugars. Sugars disintegration is 15, 6 % in the neutralization process without mixing. But, when speed of mixing is increased, the amounts of disintegrated sugars are decreased. In the table VII experimental data is shown [21]:

Table VII Influence mixing of liquor upon destroying of sugars [21]

Neutralization with mixing, turn(revolution)/min	80	150	300	450	740	2000
Destroying of sugars, %	8.7	7.2	5.6	4.6	2.6	1

In the Figure 8 is presented the main stages of spent sulfite liquors preparation to biochemical treatment.



1- Storage tank for liquor; 2 - Column for blown liquor by air; 3 - Condenser gas-vapor mixture; 4, 18 Heat-exchanger; 5 - Oxidizer; 6,7 - tank with constant level; 8 - tank for lime milk; 9- neutralizer;10- holder; 11-dosimeter for lime; 12,13 - dosimeter for nutrient salt; 14- clarifier; 15 - mix for sludge;16- tank for clarify liquor; 17 - dosimeter for ammonia water; 19 - storage tank for prepared liquor

Figure 8. Principal scheme units for preparation spent sulfite liquor for the biochemical treatment. [23]

The sulfite liquors contain a small amount of bioactive substances, from the viewpoint of biochemical treatment. Usually in this stage the spent liquor include nutritious components for biochemical treatment. [23]

In the next stage favorable neutralization liquor is made for biochemical treatment pH 4,4-4,8. Usually it is made by adding 25% solution of ammonia, which in the same time beneficiate liquor nitrogen. Usually consumption of ammonia (calculation on 100%) is limited 0,6-0,8 kg/m<sup>3</sup> of liquor. [23]

Last stage in preparation of spent sulfite liquor for biochemical treatment – cooling clarified wort to required temperature. For heat saving purposes this process is carried out in heat exchangers.

## **6 Usage of the carbohydrate part of sulfite liquor**

### **6.1 Ethanol**

Biochemical treatment liquor is the most important application. This method enables the production of ethanol and yeast. The source is monosaccharides (hexoses and pentoses), and for fermentation yeast the source is acetic acid. So long as only hexoses are utilized by spirit fermentation, a residue is sulfite waste liquor which consists of pentose sugars which can be used for cultivation of yeast. Residue after cultivation of yeast consists of only lignosulfonates and mineral part of liquor. This also can be regenerated.

Spirit fermentation is carried out by ferment zymaze, which macerate sugars to ethanol and carbon dioxide.

A summary reaction for spirit fermentation is explained in Gay-Lussac's equalizing:



Theoretical yield of ethanol by spirit fermentation reaction from spruce is about 51,14 kg from 100 kg fermentable sugar (only hexoses was assumption). Or can recalculated by density absolute spirit 0, 79245 g/cm<sup>3</sup> (15°C) – 64, l. As long as 5-7% sugars are spent on life-sustaining activity and formation by-products, real yield of ethanol is no more than 61 l from 100 kg fermentable sugars. In fact, it is about 4-7% of methanol in the liquor. Fermentable sugars are 62-67% from all amounts of soluble solids from sulfite cooking of cellulose normal yield. [18]. But by their content in common mass of sugars sulfite liquor is 65%, from 100 kg all available sugars:

$$61 \cdot 0,65 = 39,65 \text{ dm}^3 \text{ (without calculation loss on others stages)} \quad (6)$$

Weight content of ethanol in sulfite waste liquor is:

$$2,8 \cdot 0,39 = 1,1\% \quad (7)$$

By an average mass fraction of dissolved solids in liquor 2,8. [18].

Also resin components influence the fermentation process. They adsorb on yeast plant and make it more difficult for plants to contact with substrate.

Yeast *Saccharomyces* and *Shizosaccharomyces* are usually used for fermentation sugars from spent sulfite liquor. Sugar is fermented at different rates by different yeasts.

A lot of studies have been made in the world about fermentation process.

Kitavin G.S [2] has made some studies on this field. His data is presented in the table VIII.

Table VIII Velocity of fermentation sugars [2]

Types of yeast	Glucose		Galactose	
	Start fermentation, h	End of fermentation, h	Start fermentation, h	End of fermentation, h
Sacch.cerevisiae	2	11 <sup>3/4</sup>	26 <sup>1/2</sup>	48 <sup>1/2</sup>
Sacch.exiguus	2	12	4 <sup>3/4</sup>	21

Velocity of fermentation depends on concentration of dissolved-solid (consequently – sugars). When fermentation spent sulfite liquor (SSL) is doubly striped, then velocity of fermentations process and amount of fermentable sugars is higher, than in fermentation process initial SSL. In the case of triple striped SSL fermentation (concentration is 4%) a slight velocity of process was noticed. [2, 21].

By the data of Egara and Mac-Carty [2] the concentration of solid matter of SSL does not influence ethanol yield, but affect the rate of process. Thus fermentation time increases twice by striped from 20% to 50% solid matter SSL.[2]

Other significant problem in fermentation of SSL is xylose as a part of dissolved-solids does not ferment by *Saccharomyces cerevisiae*. Xylose can compose 15% of sugar in softwood (SW) and 50% in hardwood (HW) SSL. [26]

Experimental data [26] showed that a little improvement in xylose fermentation in SSL is necessary under industrial fermentation conditions. From the data the conclusion was made that effectiveness of nutrient addition and lime pretreatment increased yeast growth and biomass yield from wort. Also this study showed that high pH and high yeast concentration are used for fermentation, which can vary with ratio to increase ethanol yield. Ethanol yield is increased by the way of 259 ST types of yeasts usage in interlinking with increases in the biomass yield.

The “Optimization of spent sulfite liquor fermentation” work is directed to determine optimal parameters for xylose fermentation [25]. Usage of 259 ST was reached with lime pretreatment, high initial pH, high concentration of yeast, supplemental yeast extract peptone. The xylose fermentation and growth of yeast were correlated. “Under fermentation conditions where no growth was observed (yeast concentration about 2g/l and pH<5), no xylose was fermented in SSL. Under conditions auspicious for growth (yeast concentration about 6 g/l and pH>5.3), an average of 5.5 g/l ethanol was obtained from xylose fermentation”. [25]

In all cases, 259ST produced at least the same amount of ethanol as the parent strain and the reference strains, implying that hexoses fermentation is not affected by the inhibitors in SSL even if xylose fermentation is affected under certain conditions. Due to the significant amounts of xylose in SSL, utilizing 259ST for SSL fermentation will result in greater ethanol production, 20% (2 g/l) more for SWD SSL fermentation, 85% (8.5 g/l) more for HWD SSL, assuming complete xylose fermentation with a yield of 0.4 g ethanol/g xylose. In order to achieve these results the pH needs to be maintained above 5.3 to minimize inhibition during fermentation, and a high yeast concentration is required due to the low fermentation rates of SSL. [26].

On the ground of described technologies it is possible to make a conclusion that the most important parameters for yield of ethanol are:

- pH of medium 4,5-5,5

- lime pretreatment and addition of nutrient salts is necessary
- active agitation on the stage of neutralization of SSL
- temperature of process 32 -35 °C
- Concentration of dissolved-solids (20-50%)
- amount of free-SO<sub>2</sub> concentration in the process – about 0,005% and not more than 0.015% (stop process).

The better type of yeast, available in present time, is *Saccharomyces cerevisiae* 259 ST that can ferment xylose and hexoses sugars undiluted and non-detoxified SSL.

Fermentation is continuous method by temperature 32-35°C in special system. The system consists usually from two parallel leading tank and one end-fermentation (after-fermentation) tank. For the recovery of carbon dioxide formed in the process a leading tank should be closed. [2]

By fermentation process wort continuously feed from top to leading tank and mix in tanks with yeast suspension which continuously feed to the process. Concentration of yeast is usually about 15-20 g per l (calculated on compressed yeasts). Fermenting wort is continuously fed from leading tanks to after fermentation tanks. In the last tank fermentation process becomes completed. After this wort is fed to separators (it can be membrane) where yeast separates from sulfite-waste liquor. The sulfite-waste liquor consists of alcohol about 1-3% concentration. The separated yeast suspension resets to the leading tanks. The sulfite-waste liquor is directed to distiller. The duration of fermentation process is about 6-8 hours. [27]

Distillation and clarification of alcohol is carried out in distillation section, where distillation column and fracking fractionators are situated. In general case process carries out distillation spirit fraction (ethanol and methanol) by steam in distillation column. Distillery stillage is fed into yeast section, and alcohol concentrate direct to epuration column. In the epuration column esters and aldehydes are removed. After this process alcohol is fed into spirit-fracking fractionator. In these columns methanol

and ethanol are separated from each other, concentrated, and clarified. In this process the outcome may be two marketable products (ethanol and methanol). [27]

## 6.2 Carbon dioxide

In fermentation process carbon dioxide is formed as by-product in amount of 96% from alcohols mass. This gas is caught and after clarification is transformed into liquid or solid carbonic acid. The yield of product is about 50-60% theoretical. The outgoing gas from fermentation tanks is collected in gasholder. Production of carbonic acid includes following operations: clarification, compression, condensation of gas. The gas sequentially passes through series columns for clarification. The gas is sequentially passed through series of columns for clarification. In these columns gas oxidized dilution solution of  $\text{KMnO}_4$ . The volatile organic components contained in the carbonic acid and washing water are dehydrated in layer of char and are making carbon treatment released from swell impurity. [27]

The cleaned gas is compressed in the compressor by 3 stages, sequentially increase of pressure until 490, 1770 and 700 kPa, cooling of gas in the cooler and in addition cleaning gas after each stage of compression. Dry carbonic dioxide is compressed to 7000 kPa and cooled with water and by critical temperature of 27,8 °C is condensed into liquid, which fills bulb. [27]

At the average about 1 m<sup>3</sup> carbonic acid (in the condition of normal temperature and pressure) segregate by distillation of spirit on 1 m<sup>3</sup> sulfite span with temperature 300°C. [27]

The integration of reaction–separation is an attractive alternative for the intensification of fractionation of SSL. The current methods to remove ethanol from fermented broth are showed as follows: [30]

- Vacuum extraction, which can be conducted by coupling of fermented vessel with a vacuum chamber extracting the more volatile ethanol from fermentation broth which allows the partial product removal and the increase of overall process productivity.

- Gas stripping to increase the concentration of sugars in the stream feeding the fermenter and improvement of liquid circulation and mass transfer.
- Membrane separation. For example, ceramic and acetate cellulose membranes can be used to filter cell biomass and remove ethanol during the fermentation. The removed ethanol is then distilled and the resulted bottoms are recycled to the culture broth resulting in a drastic reduction of generated wastewater. The coupling of fermentation with the pervaporation is another case to remove produced ethanol and reduce the natural inhibition of the cell growth caused by high concentrations of ethanol product.

The objective of ultrafiltration (UF) is to separate the SSL into two fractions: purified lignosulfonates (LS) and reducing sugars. [28].

LS represent a polydispersed system with a wide range of molecular weight distribution, from 200 to 150,000 Da. [30]. The lignosulfonates during UF become concentrated to about 30% total solids. [28]. The purified sugars are produced for fermentation purpose. The data of the current research demonstrates that cellulose acetate (CA) membranes may be used at temperatures 50-60°C [28]. Moreover, there is no loss in membrane flux rates and rejection rations were noticed to be higher during an operating period of 1100 hr.

The comparison of the UF of SSL by using various polymeric membranes was done. During the “studies on ultrafiltration of spent sulfite liquor using various membranes for the recovery of lignosulfonates”. [30] The affection of different operations was noticed on flux and rejection in the UF of SSL. And it has been observed that high MWCO (GR 100K) membranes are suitable for UF of SSL. [29]

- Liquid extraction by using an extractive biocompatible agent (solvent) that favors the migration of ethanol to solvent phase, a process known as extractive fermentation. [30]

### 6.3 Cultivation of nutrient/fodder yeast

After fermentation ethanol also can be converted into nutrient yeast. If there are necessary nutrients in the solution, then yeast is grown by utilizing sugars.

The hydrolytic yeast includes a high content of good digestible protein, biologically active substances – vitamin, enzymes, and microelements therefore it is used as feed for animals and birds.

For normal life activity of yeast substrate should include besides sugars, organic acid, nitrogen, phosphor, potassium and trace elements.

Consumption of nutrient on the growth 1 t a.d. yeast composes: 90 kg nitrogen or 450 kg sulfate nitrogen; 48 kg phosphor ( $P_2O_5$ ) or 266 kg superphosphate and 27 kg of potassium or 50 kg of potassium chloride. Usually some amount of components is lost during the manufacture, therefore real common consumption rises about 10 % [23],

Technology of nutrient yeast production is divided into the following stages [23]:

- Preparation of nutrient medium
- Growth of yeast
- Concentration yeast suspension
- Evaporation of concentrated yeast suspension
- Drying of yeast
- Storage of yeast.

The process of nutrient yeast growth consumes oxygen. The amount of consumed oxygen reaches 80% from receiving amount of dry yeast. Consequently in order to receive maximum yield of product then growth of yeast should be made by the continuous mixing and intensive blow-through medium by air. [23]

The theoretical consumption of oxygen is 0, 7-0, 8 kg per 1 kg nutrient yeast in average for synthesis biomass of yeast. For decreasing amount of air, consequently

energy is needed to make a maximum spraying air in the medium. It is also important to mix the medium because it provides a good dispersion and solution oxygen. For this purpose the air diffusers are installed in the yeast propagator. [23]

Yeast cultivation process is done at temperature range 32-36°C. The irreversible process happens in the yeast at higher temperature. Acidity of medium limiting pH= 4-5,5. SSL from spruce have pH close to 4, and SSL from SW have pH close to high value. [23]

Rate of biosynthesis process and other parameters depend on concentration of organic matter – sugars and acetic acid which biochemically utilized by yeasts. Concentration of organic matter in SSL from spruce depends on sugar that must to be not more than 1,7-2% (by dissolved-solids). [23]

By technical parameters, finished nutrient yeast should be received in the dry form with 8-10% of moisture content. For this purpose yeast suspension is concentrated, after this evaporated and dried. [23]

#### **6.4 Lignosulfonates**

Lignosulfonates are complex polymeric materials obtained as co-products of wood pulping; they consist of a mixture of sulfonated lignin, sugars, sugar acids, resins and inorganic chemicals. Most lignosulfonates are obtained from the spent pulping liquor of sulfite pulping operations, although some are also produced by postsulfonation of lignins obtained by sulfate pulping (Kraft process). Recovered co-product lignosulfonates may be used with little or without additional treatment or they may be converted to specialty materials with the chemical and physical properties adjusted for specific end-use markets. [31]

Lignosulfonates function primarily as dispersants and binders. Concreted admixtures are the leading market for lignosulfonates, accounting for 38% of world consumption in 2008. They are consumed as binders in copper mining, carbon black and coal is the next largest world market, accounting for 12% of world consumption in 2008. [31]

World production of lignosulfonates is estimated to be about 800,000 tones and of sulfonated lignin 15,000 tones. [32]

The bigger amounts of lignosulfonates are used in the foundry, oil refinery, in the building branch and other process. There are these industries in Finland, but they are not very big industries. The lignosulfonates are added in the technological process in a very small amount. Also lignosulfonates market is unstable. [32]. Therefore it is possible to make a conclusion that there is no demand for lignosulfonates. Consequently it is better to feed the wort after spirit and yeast fermentation process directly to the combined regeneration with kraft black liquor.

## **7 Possible common sulfite and Kraft regeneration**

Very important part for any manufacture is effective regeneration system. In the case with sulfite cooking it is good to make a common regeneration system with Kraft spent liquor. The spent sulfite liquor will be directed to the combined regeneration after ethanol fermentation and yeast cultivation processes.

The first step should include evaporation of spent liquors. This stage can be carried out separately or together for both liquors. If evaporation is made separately, then it is possible to get acetic and formic acids from SSL after evaporation. If evaporation is made together, then SSL is going directly to the mixer with Kraft liquor. It should be evaluated from the standpoint of economical profitability, because evaporation system requires a big amount of energy and also water for process. Also mixtures of formic and acetic acids are corrosive enough. Possibly, it is not profitable to spend energy, consequently money and time on acids production, because they are cheap products.

There are some technologies for regeneration sulfite and sulfate liquors. The first research in this area appeared together with introduction of Kraft pulping process.

The process of combined recovery presented by G.G.Dehaas and L.C.Amos directed to recovering sulfite cooking liquor from mixed liquors with minor additions in kraft recovery system. It involves contacting green liquor with a gas containing CO<sub>2</sub> to convert sulfur to gaseous H<sub>2</sub>S, which is converted to SO<sub>2</sub>. Elemental sulfur can be

recovered by partial oxidation of  $H_2S$  with an aqueous-phase catalyst. Sodium recovery, as sodium carbonate obtained by removing all sulfide from green liquor. Process represent on the figure 9.[33].

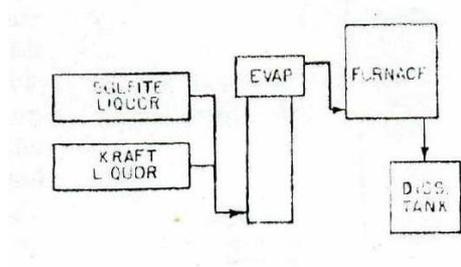


Figure 9. Mixing Kraft and sulfite liquor

The problem in combining regeneration systems is the chemical balance. For a good recovery it is necessary to have a small amount of sulfite liquor and bigger amount of kraft liquor. If big amount of sulfite liquor is added then removal of both sodium and sulfur is required for preservation chemical balance.

The process of recovery of sulfur and sodium from Kraft liquor has following main stages: [33]

- Removal of sulfur from green liquor as  $H_2S$
- Oxidation of  $H_2S$  to  $SO_2$  or to elemental sulfur
- Absorption of  $SO_2$  in makeup caustic or stripped green liquor.

The method “Combined Acid Sulfite and modified sulfate pulping process with recovery cycle” was patented in the USA. [34] In this invention an integrated system having a novel elemental sulfur pulping (“sulfofate”) system operating in conjunction with another process. This process includes a combination of two spent liquors from other processes, evaporating them to concentration of above 50% solids, burning this solution in reducing furnace to obtain smelt and dividing it into two portions and proceeding with its chemical conversion and recovery. [34] The technologic schemes of this process are presented in the Appendix II.

## 7.1 Tampella conversion system

A practical solution for the problem of balancing the recovery of chemicals in integrated kraft/sulfite operations was first demonstrated industrially in 1968 at the Kemi mill in Northern Finland. This method was directed to the recovery of pulping liquor where sulfur is present, such as: [3]

- Conventional sulfite sodium base NSSC;
- Integrated Kraft-sulfite and kraft-NSSC (cross-recovery);
- Conventional Kraft, where a lower sulfidity is desired;
- Polysulfide Kraft.

The principle of the recovery process: separate stock washing and spent liquor evaporation, joint liquor combustion, separate conversion to the conformable cooking liquors, and transfer of a portion of carbonate from sulfite recovery to the kraft cycle for maintaining correct sodium balance. [3]

The figure below presents a flow sheet for unbleached pulp and cooking liquors. The kraft liquor is collected by counter current drum washers (four). Next stage is evaporation and concentration to 60-62% solids which is then burnt together with sulfite liquor. The green liquor portion is passed through a conventional causticizing unit for regeneration of kraft white liquor. The weak liquor from lime mud washing is used to dissolve the furnace smelt. [3]

The spent sulfite liquor is recovered by in-digester displacement with filter-water from the two pressurized sulfite pulp washers operating at 96-97% efficiency. After this SSL is evaporated to 68% solids. [3]

Concentrated liquors from two pulping processes are mixed in a tank and burnt in the Tampella recovery furnace boiler. [3]

The balance  $\text{SO}_2$  and  $\text{H}_2\text{S}$  in the liquor combustion depends generally on the green liquor sulfidity. The flue gas scrubber forms sulfur recovery. The used scrubbing solution containing carbonate and some sulfite is returned to the absorption tower of

the liquor-making plant where it is sulfited with  $\text{SO}_2$  obtained from burning the  $\text{H}_2\text{S}$  and make-up sulfur. [3]

At the final stage, the furnace smelt enters the dissolving tank and forms the common green liquor. [3] In the Figure 10 are presented Tampella recovery system.

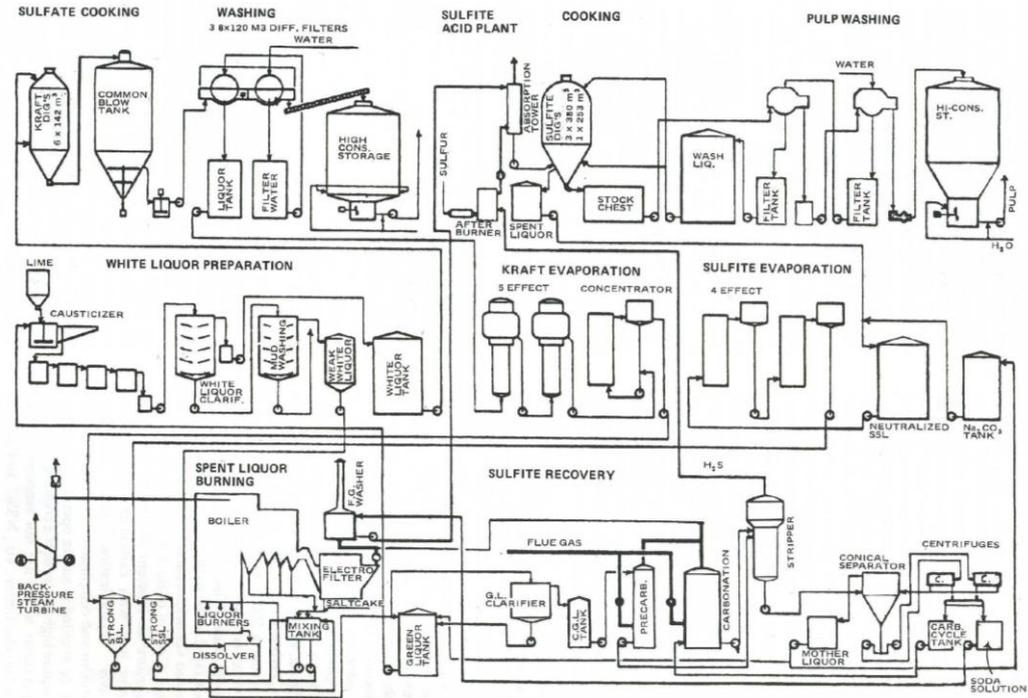


Figure 10. Flow sheet for UPM- Valkeakoski integrated Kraft-sulfite recovery [33]

## **8 Selection of profitable cellulose**

Three kinds of cellulose can be obtained from wood for different purposes. They are cellulose for cardboard production, paper and tissue production and dissolving pulp. The purpose of this work is to find the better parameters for acidic biorefinery. But cellulose should be demanded at the market.

### **8.1 Cardboard (yield 60-80-%)**

The cardboard production is not suitable for biorefinery purpose, because packaging material should have strong mechanical properties. The best type for this is semichemical pulp. Spent sulfite liquor has a small amount of hemicelluloses in the composition by the cooking process in this case. Then it will not be profitable to produce ethanol from SSL. Therefore cardboard is produced from secondary raw materials (waste paper).

### **8.2 Paper and tissue (yield 50-65%)**

As mentioned earlier, Kraft pulp has stronger mechanical properties than sulfite pulp. Also, very important parameter is beating time. In Table II it is represented that Kraft pulp requires a less time than sulfite. [1] It means that kraft paper has better mechanical properties and requires a smaller amount of energy which will lower initial costs. Based on these data it can be concluded that sulfite paper is not demanded at the paper market. But, maybe, it can be used for tissue production.

### **8.3 Dissolving pulp (yield 38-50%)**

The dissolving pulp is pure cellulose; it means that the biggest amount of hemicelluloses is going into the spent sulfite liquor. This aspect is important in ethanol production. End-use application of dissolving pulp is presented in Table IX.

Table IX Dissolving pulp end-use application [3]

<b>Cellulose</b>	<b>End-Use application</b>
Viscose rayon : Tire cord	Tire and belting reinforcement
High Wet Modulus Staple	Apparel, furnishing
Regular Staple, Continuous Filament	Apparel
Cellophane	Packaging
Miscellaneous	Sponger, sausage casing
<b>ESTERS:</b> Acetate:	Membrane production, Apparel, furnishing
Filament	Filter cigarettes
Tow	Film, sheet, extruded articles
Plastics	sheet, extruded articles
<b>Nitrates:</b>	Lacquers, Film, Explosives
<b>Esthers:</b> Carboxymethyl Cellulose	Detergents, cosmetics, food textile and paper sizes, well drilling muds
Hydroxyethyl Cellulose	Latex paints, emulsion polymerization, oil well drilling muds
Methyl Cellulose	Food, paints, pharmaceutical
Ethyl Cellulose	Coating and inks
Hydroxypropil Cellulose	Food and pharmaceutical
Carboxymethyl, Hydroxyethyl Cellulose	Liquid detergents

In my opinion the products will have a big demand at the market.

Cellophane. In present time packaging waste is about 30% by weight. The bigger parts of packaging material are very difficult for recycling. People would like to develop environmentally-conscious ways of packaging consumer goods which are more degradable materials. Cellophane packaging is an example of natural, easily recyclable material, which can be broken down by micro-organisms in the soil just as leaves and plants are. [40]

Acetate cellulose. From acetate cellulose, acetate membrane is produced. We can use these membranes for the ultrafiltration of lignosulfonates at pulp mills also. This product is current and a lot of studies exist in this field. There is a big demand for this product. Moreover, furniture and apparel also have a demand at market.

Acetate filament. At all times people are smoking. I think that such products as cigarette filters will have a demand at market always. But a small amount of this component is required for production of big amount of cigarettes.

Nitrates, Mixed esters and Esthers have a wide field for application also.

### *8.3.1 More about dissolving pulp for apparel purpose.*

The production of viscose fiber is complex multioperation process. The main disadvantage, which determines the reduction in manufacture of viscose fiber in the world, is environmental smearable technology. It is based on usage of carbon disulphide and toxic gas - hydrogen sulphide segregate. The production of viscose fiber requires a large amount of energy and chemical material (more 1,5 kg on 1 kg viscose fibers). [41]. Nowadays, there is another technological process for receiving viscose fibers from wood. These fibers are called – “liocell”.

The conclusion was made from the following data that it is not good way for Finnish pulp and paper industry to produce viscous fiber from dissolving pulp. The basic points of determination are as follows:

Table X The main disadvantages of viscose fibers product from cellulose [41]

<b>Disadvantages</b>	<b>Consequences</b>
It is complex multistage process	Necessary to install new equipment
The addititious time is needed for dissolution of cellulose	Produce-cycle of product, possible some trouble in the process, the big territory is needed
Discharge toxic gas is hydrogen sulphide, using carbon bisulphide	High environmental taxes, new equipment and technology for protect environmental and people
<b>Disadvantages</b>	<b>Consequences</b>
A large expenditure of energy and chemicals	Economically unprofitable, high cost of energy and some chemicals.
Exists different methods for the production of these fibers and also exists materials with better physical-mechanical properties (polyester technical fibers)	Possible non-realization situation

## **9 Calculation of biorefinery cases**

### **9.1 Biorefinery models**

The four different pulp mills are considered in this chapter. Firstly and secondly there are Kraft and sulfite mills with final product is paper or package from both types of cellulose. Thirdly is observed a pure sulfite mill with final product of dissolving pulp. And finally pure Kraft mill with prehydrolysis is studied. The combined recovery process of spent liquors is used in the all cases and spruce is used as a raw material in sulfite process and pine in Kraft process.

Calculation of the biorefinery contains three different cases with different pulp mills. In the first case it is 100 Adt/day of sulfite pulp and 900 Adt/day Kraft pulp for printing paper production. In the second case it is 250 Adt/day of sulfite pulp and 750 Adt/day of Kraft pulp for packaging purposes. And in the last case it is 1000 Adt/day of pure sulfite dissolving pulp. The fourth case shows Kraft mill with prehydrolysis process. The results for the respected process were obtained from literature. [44]

The initial data for the calculation was obtained from literature and assumption data.

The initial data for cooking process was chosen according to the properties of pulp, as it should be pulp for printing and packaging purposes. The batch cooking process was calculated. Therefore the parameters of cooking process are presented in the Table XI:

The cooking process, sulphur regeneration process, preparation liquor to biochemical process, value of possible products was calculated in current work. Also combined regeneration systems for kraft and sulfite spent liquors were assumed and calculated.

#### **9.1.1 Cooking process**

The mass balance calculation of chemical sulfite cooking process was done. By these data approximately composition of spent sulfite liquor was determined and also parameters for further calculation were obtained.

Table XI. Parameters of chemical sulfite cooking process

Volume of digester	320.0	m <sup>3</sup>
Yield of cellulose	49.0	%
Acid compounds		
all SO <sub>2</sub>	8.0	%
Na <sub>2</sub> O	0.9	%
Volumetric level of filling boiler	0.4	
Moisture of chips	40.0	%
Density of spruce	430.0	kg/m <sup>3</sup>
the density of spruce is 389 kg/m <sup>3</sup> when the moisture 40%	389.0	kg/m <sup>3</sup>
Consequently absolutely dry wood's chips input into the 1m <sup>3</sup> of digester is	163.4	kg
Yield of absolutely dry cellulose from 1m <sup>3</sup> of digester is	80.1	kg
air-dry weight	91.0	kg
	29111.3	kg
Yield of air-dry weight cellulose from 1 cooking	29.1	t

The vapor charge on cooking process was calculated for determination energy consumption of process. The results are presented in the Table XII.

Presented data is for cooking process for cellulose for paper production. The presented result is shows normal heat consumption for chemical cooking process.

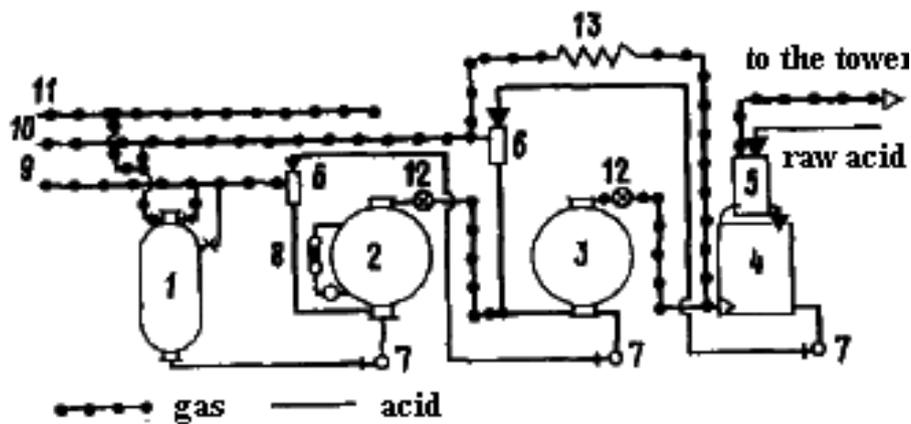
The material and heat balance of sulphur recovery system was made. The aim of the hot sulphur-recovery system is that heat of relief gasses is used for heating of cooking acid in regeneration system. It helps to decrease steam consumption for chemical cooking process.

The scheme of hot regeneration system present in the Figure 11.

In general, the used heat from relief gasses allows increasing temperature of cooking acid by 25-30 °C during normal conditions in comparison with temperature in other regeneration system. Consequently it is allows to decrease steam consumption for chemical cooking process by 15-20%.

Table XII. Vapor charge on the sulfite cooking process

Charge	Heat charge. GJ/Adt			%of all amount of steam charge
	on heating-up	on cooking	total	
1. Heating of chips and organic components	0.09	0.08	0.16	4.85
Heating of moisture in chips	0.15	0.15	0.30	9.08
Condensate	0.02	0.02	0.04	1.14
Acid	1.71	0.76	2.47	74.46
isolation/ insulation	0.00	0.00	0.00	0.10
digester jacket	0.05	0.05	0.09	2.84
Heat losses with heat emission with relief gasses	0.02	0.02	0.04	1.22
	0.02	0.19	0.21	6.30
<b>Total</b>	<b>2.05</b>	<b>1.27</b>	<b>3.32</b>	<b>100.00</b>



1 – digester, 2- high pressure cistern, 3- low pressure cistern, 4- stripping vessel, 5- column, 6-eductor, 7 – pumps, 8 – heater, 9 - relief gasses high pressure, 10 - relief gasses low pressure, 11 - withdrawal gasses to acid tower, 12 - pressure control, 13 – cooler

Figure 11. Typical scheme of hot regeneration system with three-stage absorption [2]

The obtained composition of acid is presented in the Table XII and XIII.

Table XII. Composition of acid

Containers	Composition of acid		T, °C
	SO <sub>2</sub>	Na <sub>2</sub> O	
Stripping tank	3.84	1.17	10
Low pressure tank	5.35	1.12	25
High pressure tank	9.37	1.11	40

Table XIII Composition of acid for summer time

Containers	Composition of acid		T, °C
	SO <sub>2</sub>	Na <sub>2</sub> O	
Stripping tank	3.84	1.17	25
Low pressure tank	5.35	1.12	40
High pressure tank	9.37	1.11	55

As can be seen from the tables in the summer time the temperature of acid is higher, so that less energy is needed to supply for the process. That is good economical benefit.

The energy consumption regeneration system present in the Table XIV. Calculation was based on amount of coming heat from cooking process and heat losses during processes.

By the Table XIV it is visible that the blowing vapor and absorb gases introduce the bigger amount of heat in the regeneration system. Thereby, acid mixing with by-way fluid is increasing acids temperature almost 20 °C.

Table XIV. Energy consumption of regeneration system

Heat coming	Heat, GJ/Adt	%
1 With blowing/relief fluid	0.18	18.41
2 With blowing vapor	0.38	38.38
3 With raw acid	0.22	22.13
4 With absorb gases	0.20	20.33
5 With non condensated gases and volatile components	0.01	0.76
<b>Total</b>	<b>0.98</b>	<b>100.00</b>

### 9.1.2 Liquor preparation

As explained in the section 5.3.1 the spent sulfite liquor after cooking should be converted to the wort. The scheme of process preparations is presented in the section 5.3.1 also. The amount of liquor that is added to the process after cooking is 6 500 l/Adt (6,5 m<sup>3</sup>/Adt). The material balance stages for liquor preparation are presented in the Table XV.

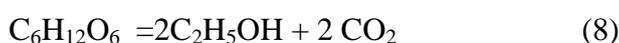
Table XV. Material balance of liquor preparation stage

<b>input</b>		dry	dissolv	<b>charge</b>		dry	dissolv
	m <sup>3</sup>	compo-	compo-		m <sup>3</sup>	comp.	compo-
		nents	nents				nents
	<b>Reception of liquor:</b>						
liquor form cooking	6.50	1.19	0.27	liquor to column	6.47	1.18	0.27
			0.27	Mechanical losses	0.03	0.01	0.00
<i>Total</i>	<i>6.50</i>	<i>1.19</i>		<i>Total</i>	<i>6.50</i>	<i>1.19</i>	<i>0.27</i>
	<b>Liquor blowing through with steam in the column</b>						
				Blowed liquor	6.60	1.17	0.27
liquor	6.47	1.19	0.27	Condensate	0.13		0.00
Steam	255.00			Mech.losses	0.03	0.01	0.00
<i>Total</i>	<i>261.47</i>	<i>1.19</i>	<i>0.27</i>	<i>Total</i>	<i>6.76</i>	<i>1.18</i>	<i>0.27</i>
	<b>Liquor oxydize by air</b>						
Liquor from column	6.60	1.17	0.27	Oxydized liquor	6.60	1.17	0.27
				Moisture vaporized	0.03		
				Mec. losses	0.03	0.01	0.00
<i>Total</i>	<i>6.60</i>	<i>1.17</i>	<i>0.27</i>	<i>Total</i>	<i>6.66</i>	<i>1.17</i>	<i>0.27</i>
	<b>The first stage of neutralization.</b>						
Oxidized liquor	6.53	1.17	0.27	Neitralizate after clarifier	6.50	1.16	0.26
Lime	0.005	0.00		Mech.losses	0.03	0.01	0.00
Gypsum	0.006	0.00					
<i>Total</i>	<i>6.54</i>	<i>1.17</i>	<i>0.27</i>	<i>Total</i>	<i>6.53</i>	<i>1.17</i>	<i>0.27</i>
	<b>Clarifying of neitralizade of 1st stage in the clarifier</b>						
Neitralizate	6.53	1.17	0.27	Claryfied liquor	6.43	0.00	0.26
				Sluge	0.06	1.16	0.00
<i>Total</i>	<i>6.53</i>	<i>1.17</i>	<i>0.27</i>	<i>Total</i>	<i>6.50</i>	<i>1.16</i>	<i>0.26</i>
	<b>The second stage of neutralization</b>						
Clarified liquor	6.43	0.00	0.26	Neitralized and cooling liquor	6.44	0.00	0.26
NH <sub>3</sub> 25%	0.006						
<i>Total</i>	<i>6.44</i>	<i>0.00</i>	<i>0.26</i>	<i>Total</i>	<i>6.44</i>	<i>0.00</i>	<i>0.26</i>

### 9.1.3 Products

The value of products was calculated according to the data about spent sulfite liquor (SSL) after preparation stage. The calculation about amount of product was done based on the Sharkov data. [11] The result was presented as amount of product per one tone air dry cellulose.

By formula which was mentioned in the section 6.1, the amount of ethanol was calculated. However, only hexoses sugars was taken in consideration.



$$180,1566 = 2 \cdot 46,0687 + 2 \cdot 43,9988 \quad (9)$$

The 260 kg of dissolved components situated in the SSL. The hexoses are about 62-67% of total amount of dissolved components. Consequently, SSL consist 164 kg hexoses.

From this amount of hexoses the 84 kg of ethanol can be obtained theoretically. However, the loss is 10 % ethanol so that real yield can be 75 kg. In recalculation in liters it will – 69 l (by density absolute spirit is 0, 79245 g/sm<sup>3</sup> (15°C). The scheme of fermentation process of ethanol is presented in the Figure 12. The obtained spirit contains methanol and other fraction. By the distillation column the components will be separated. The obtained methanol constitutes about 10 % from total amount of spirit. This is also market product also, but in smaller amounts.

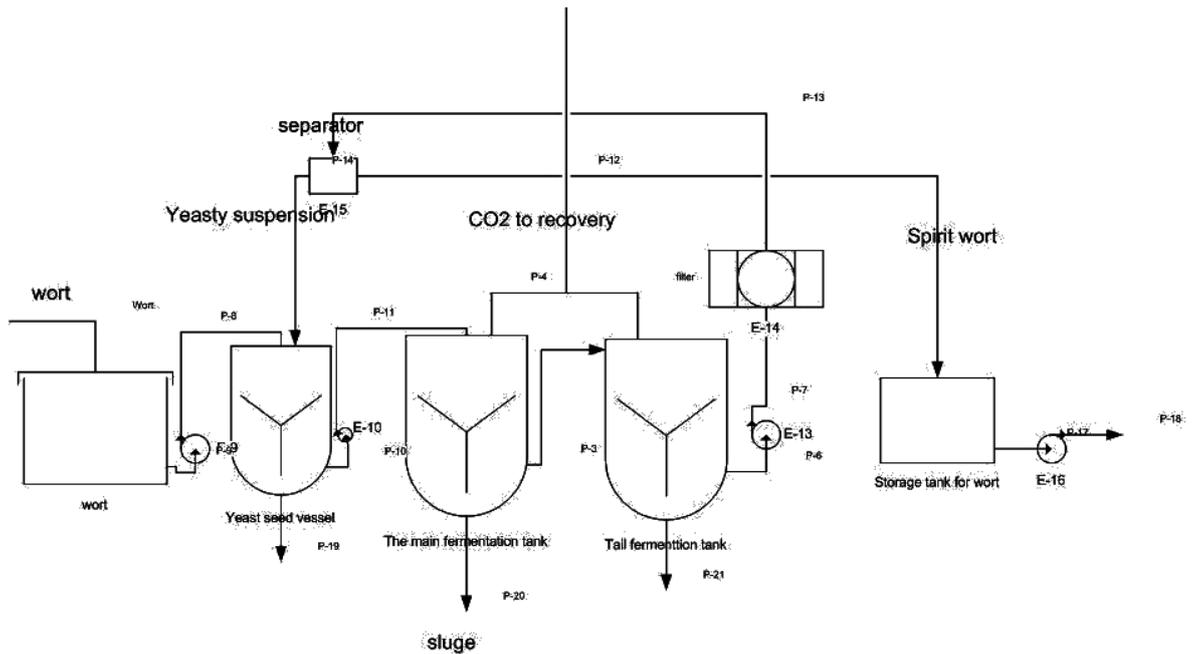


Figure 12. Ethanol fermentation process

The carbon dioxide also obtained from this process. By the ethanol fermentation process 489 kg of CO<sub>2</sub> will produce from 1000 kg hexoses. [11] Then, amount of theoretical yield and practical yield of carbonic dioxide from liquor in this case will be 80,1 kg and 72 kg of acids respectively, because about 10% of product will be lost.

The yeast that is supplied the ethanol fermentation process a market product also. After ethanol fermentation process the 352 kg of yeast can be obtained from wort. It is necessary add some components in the wort for yeast production. The amount and components are following: 31,68 kg of nitrogen or 158,4 kg of sulfate nitrogen, 16,9 kg phosphor (P<sub>2</sub>O<sub>5</sub>) or 93,6 kg superphosphate, 9,5 kg of potassium or 17,6 of potassium chloride.

Form all these data it is visible that a big amount of product, especially ethanol can be obtain from acid cooking process. For clearer situation the obtained result are presented in the Table XVI for each case that is considered in current work.

Because the calculation of cooking process and determination of black liquor components was done only for printing paper composition of liquors from dissolving pulp was obtained from literature. [4]

Table XVI. Amount of product in different cases

Type of product	Case 1	Case2	Case 3	Case 4 (kraft)
Ethanol. t/day	7.5	19	114	40
Methanol. t/day	0.001	0.002	1	0
Carbonic dioxide. t/day	7	18	96	38
Yeast. t/day	0.04	0.09	0.22	0

It is understandable from Table XVI that from sulfite cooking process the bigger amount of product, especially ethanol can be obtain. There are three different cases presented in the Table XVII. As it was mentioned in the section 9 the final product depends on market needs, but the biggest amount of ethanol can be obtained from mill that produce dissolving pulp. The mechanical properties of sulfite pulp worse than kraft, therefore the current proportion was chosen. The properties of final product (packaging or printing paper) will not change in the mentioned proportion.

#### 9.1.4 Chemical Recovery

The very important condition of current work is combination of recovery spent liquors from Kraft and sulfite mills. It is vice important, because in other case it will require high investment and running cost. The recovery system one is the most important part of mill, because a chemical regeneration and one is the biggest energy consumption situated here. The purpose of this section is to determine how the combined regeneration will influence melt composition and energy consumption.

The objective of the combined is that liquors should be evaporated separately in order to avoid the precipitation of lignin. The separate evaporation is advantageous to build up, although the more energy is needed in this case.

The evaporation plant was taken in consideration with following work parameters:

The weak liquor joins the 4<sup>th</sup> column, after this – 5-6 and when liquor will join to the 3<sup>d</sup> column temperature will increase. The 3<sup>d</sup> column has the biggest corrosion damage from of all evaporation plant.

By the obtained result from calculation result and also literature data the composition of mix sulfite and Kraft liquors was made. The result is presented in the Table XVII.

The composition of mix spent sulfite and kraft liquor is presented. In the case with 25% of sulfite pulp the bigger amount of mineral components is situated in the liquors, because a lot of mineral components added in the preparation stage. By these data the heat consumption for the recovery will be calculated and approximate parameters of caustization process were determined.

The results obtained from heat consumption calculation shown that in the case when mix contains 25% heat consumption is less than in other case. It is connected with initial composition liquors that present in the Table XVII.

In the Tables XVII and XVIII the heat balances of sodoregeneration boiler in calculation per 1 t of cellulose. These results show how much energy is necessary for combine regeneration of liquors.

The possible composition of melt was determined base on calculation chemical reaction components of mix spent liquors. In the Table XX, XXI, XXII are presented the melt composition for three different cases that studied in this work.

Table XVII. Composition of liquors mix

Components	Mix of liquor10%		Mix of liquor25%	
	%	Kg/Adt	%	Kg/Adt
Organical part:				
Carbon C	43.71	540.68	47.12	587.87
Hydrogen H	5.05	62.42	5.41	67.49
Oxygen O	22.92	283.53	26.06	325.065
Organical sulphur	1.84	22.79	1.91	23.765
Total org.components:	73.52	909.42	80.50	1004.19
Mineral part				
Free NaOH	1.19	14.76	1.18	14.76
Organically associated NaOH	23.67	292.74	23.47	292.74
Mineral components (salt for biochemical purpose)	1.05	13	2.61	32.5
Na <sub>2</sub> S	0.20	2.46	0.20	2.46
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	1.59	19.68	1.58	19.68
Na <sub>2</sub> CO <sub>3</sub>	3.58	44.28	3.55	44.28
Na <sub>2</sub> SO <sub>3</sub>	0.47	5.85	1.17	14.625
NaHCO <sub>3</sub>	1.48	18.33	3.67	45.825
Na <sub>2</sub> SO <sub>4</sub>	1.00	12.31	1.28	16.015
Organically associated Na <sub>2</sub> SO <sub>3</sub> .	0.42	5.2	1.04	13
NaHSO <sub>3</sub>	1.78	21.97	4.40	54.925
Total mineral components	36.43	450.58	44.15	550.81
Total:	109.94	1237.00	124.65	1247.50
Total Na <sub>2</sub> O		292.35004		320.04
Total S		42.99131		57.47

Table XVIII. Heat balance of sodoregeneration boiler in calculation per 1 t of cellulose (25 % sulfite and 75% of kraft cellulose)

Incoming heat			Charge of heat		
	GJ	%		GJ	%
Physical heat of solid residual of mix liquors	0.20	0.96	Heat consumption on melting of salt	0.15	0.72
Moisture of liquor	0.42	2.02	Regeneration of sulfite	0.54	2.60
Reheat dry air	1.08	5.23	Regeneration of sulphate	0.72	3.47
Heat of mix liquor burning	18.96	91.79	Physical heat coming out with melt	0.60	2.91
	20.65	100	Heat losses to environmental	0.31	1.5
			Losses of heat	0.36	1.74
			Heat consumption on expulsion of water and overheating water vapor	4.25	20.56
			Total amount of heat that exited with gases	0.69	3.33
			Absorbed heat by screen. steam boiler and economizer	13.04	63.16
			Total	20.65	100

Table XIX Heat balance of sodoregeneration boiler in calculation per 1 t of cellulose (10 % sulfite and 90 % of kraft cellulose)

Incoming heat			Charge of heat		
	GJ	%		GJ	%
Physical heat of solid residual of mix liquors	0.20	0.91	Heat consumption on melting of salt	0.15	0.67
Moisture of liquor	0.40	1.84	Regeneration of sulfite	0.21	1.00
Reheat dry air	1.01	4.70	Regeneration of sulphate	0.74	3.44
Heat of mix liquor burning	19.96	92.55	Physical heat coming out with melt	0.57	2.63
Total	21.57	100	Heat losses to environmental	0.32	1.50
			Losses of heat	0.33	1.55
			Heat consumption on expulsion of water and overheating water vapor	4.25	19.69
			Total amount of heat that exited with gases	0.69	3.20
			Absorbed heat by screen. steam boiler and economizer	14.30	66.32
			Total	21.57	100

Table XX. Composition of melt (1/4 sulfite/kraft pulp)

Melt composition	kg	%
Na <sub>2</sub> CO <sub>3</sub>	432	77.5
Na <sub>2</sub> S	114	20.4
Na <sub>2</sub> SO <sub>4</sub>	12	2.1
Total	557	100.0
Na <sub>2</sub> O	348	
S	49	

Table XXI. Composition of melt (1/10 sulfite/kraft pulp)

Melt composition	kg	%
Na <sub>2</sub> CO <sub>3</sub>	431	82.2
Na <sub>2</sub> S	80	15.3
Na <sub>2</sub> SO <sub>4</sub>	13	2.5
Total	525	100
Na <sub>2</sub> O	322	
S	36	

Table XXII. Composition of melt (1/1 sulfite/kraft pulp)

Melt composition	kg	%
Na <sub>2</sub> CO <sub>3</sub>	434	60.5
Na <sub>2</sub> S	2799	38.8
Na <sub>2</sub> SO <sub>4</sub>	5	0.7
Total	718	100.0
Na <sub>2</sub> O	478	
S	115	

From the Tables it is visible that there is not so much different between melt composition by different liquors mix composition. Therefore, if the separate evaporation system for liquors is used at a mill then no problems with regeneration liquors will be. But in the spent sulfite liquors big amounts of mineral components exists. This has influence on the energy consumption.

The heat consumption on caustization process present in the Table XXIII

Table XXIII. The heat consumption on caustization process

Heat consumption	GJ/t
Heat of green liquor	0.50
Heat of lime slurry	0.03
Water evaporation from liquor by slaking of lime and causticization	0.16
Heat coming at the expense of slaking of lime	-0.24
Heat losses by heat emission through wall of damper-classificator and causticizator	0.05
Total heat consumption with subject to heat emission	0.49

## **10 Results and discussion**

The approximate heat and mass balances were presented in the chapter 9. The three cases are then summarized briefly in section 10.4. The effects of the integration of the bioethanol process on the pulp mill operation are discussed in section 10.5. Profitability assessment of the integration is then presented in section 10.6.

### **10.1 Case 1.**

In this case 10% of sulfite pulp and 90% of Kraft pulp were mixed together in order to produce printing paper. The amount of sulfite pulp was determined as 10%, because in this proportion paper will maintain the same properties as if it was produced from pure Kraft. Then for production of 1000 Adt of mixed pulp, it is necessary to use 100 t of sulfite pulp that can be obtained from 180 t of debarked spruce. The bark and logging residue are directed to the bark boilers.

Ethanol production is also a target. In such proportion the 7, 57 t/Adt of ethanol can be produced. The additional investment in this case is required for preparation stage of liquor for biochemical treatment and fermentation stage, also for special tank and equipment for product and yeast storage. Amount of other products was presented in the section 9.1.3.

The heat balance is presented in the section 9.1.4. In comparison with another case (25% of sulfite pulp) it is visible that there is no big difference between heat and mass balances.

### **10.2 Case 2**

In this case the 25% of sulfite pulp and 75% of Kraft pulp were mixed together in order to produce package. For production of 1000 Adt of mixed pulp, it is necessary to use 250 t of sulfite pulp that can be obtained from 450 t of debarked spruce. The bark and logging residue are directed to the bark boilers.

Ethanol production is also target. In such proportion the 18, 92 t/Adt of ethanol can be produced. But this amount is achieved, because bigger amount of pulp is required. The target of wood cooking for packaging production is cellulose with good mechanical properties. During this process the extractions of hemicelluloses are not carried out so well, therefore less amount of source for ethanol production is left in the liquor. However, if Kraft and sulfite pulp are compared, the first one provides better mechanical properties, but another one provides better optical properties. In the proportion 25% to 75% it allows to economize on bleaching stage.

### **10.3 Case 3**

In the third case the pure sulfite cellulose production was considered as dissolving pulp assumption. The biggest amount of ethanol can be obtained from this mill, but the bigger amount of energy should be applied to the process. Because it is the longest process during which the hemicelluloses are transferred to the spent sulfite liquor, complete selection cellulose from hemicelluloses is the aim of this process.

The possible application for dissolving pulp was presented in the section 9. If there is a demand for this product on the market, then it is most suitable example of ethanol production purpose. About 113, 5 t/Adt of ethanol can be obtained from 1000 t of cellulose. It is really a huge amount of side product.

### **10.4 Case 4**

As case number four, the biorefinery model Kraft process with water prehydrolysis was observed. The data was obtained from other project [44]. In this case 1000 t of Kraft pulp for printing purpose and 40 t/Adt of ethanol can be produce from 2700 Odt/day pine raw wood. Bark and logging residue in this case are directed to the bark boiler. [44]

## 10.5 Comparison of cases

The biggest amount of ethanol can be obtained during dissolving pulp production, the second place takes biorefinery case of Kraft cooking with water prehydrolysis. It is equivalent mills. The less amount of ethanol will be produced in the cases with mixed of pulp, but it happens because yield of Kraft mill is much bigger than that of sulfite mill.

For ethanol production it is necessary to add some components in fermentation process, but they are cheap enough and a small amount of them is needed.

The energy consumption is difficult to evaluate, because for sulfite process only some stages were calculated.

By the way ethanol production from acidic process looks enough attractive by this data for pulp and paper industry. A big amount of ethanol can be produced, methanol as biofuel produced in a small amount, and also another products that should be profitable at the market. But a big problem is the investment cost of this process, because at the mill a second line for sulfite pulp production should be installed. Also the separate evaporation plant requires a huge amount of energy. On the assumption of this point the profits that can be achieved from ethanol and additional products can be equal cost or slightly higher. In any case first time it will unprofitable process, because to cover big investment costs a long repayment period is necessary.

In the Table XXIV the comparison of different methods are shown. By these data profitability of mill can be estimate.

Table XXIV. Comparison of biorefinery cases

Type of product	Case 1	Case 2	Case 3	Case 4 (kraft)
Raw material				
Spruce as raw material, Odt/day	181	417	2564	-
Pine, as raw material, Odt/day	2430	2025	-	2700
Lime, t/day	0.0006	0.0015	0.006	-
Gypsum, t/day	0.9	2.25	9	-
NH <sub>3</sub> 25% solution t/day	0.55	1.38	5.5	-
Products				
Pulp, Adt/day	100	250	1000	1000
Ethanol, t/day	7.5	19	113	40
Methanol, t/day	0.001	0.002	1.13	0
Carbonic dioxide, t/day	4.5	11.4	67.8	38
Yeast, t/day	0.035	0.088	0.22	0

## 10.6 Effects of operations on pulp mill

Integrating the bioethanol process to a pulp mill affects the operation of the mill. In this section 10.5, the effects on the fiberline and chemical recovery of the pulp mill will be discussed. The effects are reviewed as an upgrade from the conventional pulp mill the bioethanol producing biorefineries and comparison with the kraft biorefinery case.

For integration sulfite mill into sulfite biorefinery mill, it is necessary to add special stages and equipments for spent liquor regeneration. And also in the case first and second (co-production Kraft and sulfite pulp) the additional line for production of sulfite pulp is necessary.

In the cases different amount of chips is fed to the digester, because the different cooking process is used. The bigger amount of wood should be for dissolving pulp production (with yield 38%). This influences the amount of obtained ethanol from process. Then less yield of cellulose, it means that the pure cellulose produced, than bigger amount of ethanol can be fermented, because the bigger amount of hemicelluloses is transferred to the spent liquor from chips.

For ethanol production and other product it is necessary to install new stage for liquor preparation for biochemical treatment, fermentation, separation stage, and carbon dioxide recovery and yeast fermentation stage. Also the distillation columns should be implemented in the mill for cleaning of ethanol form other ingredient (methanol and etc).

The steam consumption will be higher in the biorefinery pulp mill case than in usual pulp mill. The schemes of stage are presented in the section 5.2. The bigger heat consumption in added stage will be in the liquor preparation process (liquor blowing for SO<sub>2</sub> removed) and distillation of ethanol. In comparison with biorefinery case at the Kraft pulp mill, it is possible to assume that heat consumption in the both cases will be approximately the same by following point:

- In the sulfite biorefinery mill additional energy is necessary for liquor preparation process
- In the Kraft biorefinery case additional energy is necessary for prehydrolysis process
- Fermentation process in both cases will take approximately the same amount of energy
- The amount of energy for prehydrolysis process, assumed a slightly higher than for liquor preparation process
- The distillation of ethanol should be in the both cases
- In the sulfite case additional energy is necessary for production yeast and carbon dioxide also, as by-products from ethanol fermentation process
- In the Kraft case energy is used for carbon dioxide also, but not for yeast.

These points present that approximately the same amount of energy is necessary in the both biorefinery cases for the same amount of pulp.

If equipments are taken into consideration, then in the sulfite biorefinery case a bigger amount of new equipments should be installed for ethanol and other product production and also new line for sulfite pulp production should be at the pulp mill, because the sulfite process is assumed as additional line to Kraft process.

The chemical recovery in the all biorefinery cases is the same. When the sulfite biorefinery used the liquors will regenerated together, but the liquors should be evaporated separately. This difference will be in the equipment and energy consumption between these cases. But it is important that the bigger amount of ethanol can be obtained from sulfite mill, therefore these enclosures should compensate the amount of products. But investment cost in this case enough high, that can influence on cover of expenditure of the project.

## 10.7 Profitability assessment

The profitability of the biorefinery was appraised by setting a required internal rate of return IRR for the bioethanol integration project and then calculating the acceptable investment costs to get a positive net present value NPV. The NPV equation is presented below in the equation (10).

$$NPV = \sum_{t=1}^T \frac{CF_t}{(1 + IRR)^t} - C_0 \quad (10)$$

The required IRR for the upgrade project was set to 18 %, which according to Diesen and literature [44] is the minimum IRR requirement for a large modernization project. The time horizon of the project T was assumed to be 20 years, as in the case with Kraft biorefinery for more exactly comparison. The plant was assumed to be in operation one year after start-up and salvage value of the equipment was assumed to be 0, the same as in the kraft with prehydrolysis project. [44]

The annual cashflows CF<sub>t</sub> assumed as the additional cashflow from raw materials and product generated in the biorefinery cases. Only these parameters were taken in consideration, other parameters were assumed not to change.

The raw material and product prices were estimated using current market prices. The price for spruce was taken from TimberConsulting site [45]. The price on spruce logs is 19 €/ m<sup>3</sup> in the April 2010. The price was converted to the 42,2 €/t by the density of dry spruce 450 m<sup>3</sup>/kg [46]. The ethanol price was obtained from “Ethanol Market”, where price on 15.05.2010 is 1,8403 \$/ gallon [47] . This parameter was converted to 327 €/t with a EUR-USD exchange rate of 1.2375 of 15th May 2010. The price of ethanol was estimated the same price as for ethanol 327 €/t. Gypsum and lime prices was obtained from [48]. The gypsum price is 21.75\$/t and it is recalculated as 26,9 €/t on 15.05.2010, the lime price is 16,00 \$/t it is recalculated as 19,8 €/t. For comparison kraft and sulfite biorefinery price on wood was assumed. In the Tables XXV, XXVI, XXVII the results for each case are presented.

As it is visible from the Tables XXVI, XXVII and XXVIII the case number 1 is the most profitable. But in this case dissolving pulp is produced for the marketing demand that is not so well-known as paper or packaging, therefore there is some risk in this case.

The second case – it is case 2 with production paper for packaging purpose, but this case won the case 1 only because the bigger amount of pulp and consequently spent liquor produce at the mill.

With a required hurdle rate of 18 %, the maximum investment costs C<sub>0</sub> to get a positive net present value are approximately 73 million euros in the third case, 12,15 million Euros in the second case and 4,76 million Euros in the upgrade to second case. In the case of kraft biorefinery with prehydrolysis these number higher (it is 100 and 50 million Euros in the different cases).

Table XXV. The additional annual cashflows is in the case 1.

	Case 1	Price, €/t	Additional cashflow, €/a
<b>Raw material</b>			
Spruce, Odt/day	181		
Pine, Odt/day	2493		
Lime (10% solution), t/day	0.0006	19.8 (100%)	-0.043
Gypsum (10% solution), t/day	0.9	26.9 (100%)	-88.37
NH3 25% solution t/day	0.55		
<b>Products</b>			
Pulp, Adt/day	1000		
Ethanol, t/day	7.5	327	895162,5
Methanol, t/day	0.001	327	119.36
Yeast	0.035		
<b>Net annual additional cashflow</b>			<b>0.89*10<sup>6</sup></b>

Table XXVI. The additional annual cashflows is in the case 2.

	Case 2	Price, €/t	Additional cashflow, €/a
Raw material			
Spruce, Odt/day	417		
Pine, Odt/day	2025		
Lime (10% solution), t/day	0.0015	19.8 (100%)	-0.11
Gypsum (10% solution), t/day	2.25	26.9 (100%)	-220.9
NH3 25% solution t/day	1.38		
Products			
Pulp, Adt/day	1000		
Ethanol, t/day	19	327	2267745
Methanol, t/day	0.002	327	238.71
Yeast	0.088		
<b>Net annual additional cashflow</b>			<b>2.27*10<sup>6</sup></b>

Table XXVII. The additional annual cashflows is in the case 3.

	Case3	Price, €/t	Additional cashflow, €/a
Raw material			
Spruce as raw material, Odt/day	2564		
Lime (10% solution), t/day	0.006	19,8 (100%)	- 4.3
Gypsum (10% solution), t/day	9	26,9	- 883
NH3 25% solution t/day	5.5		
Products			
Pulp, Adt/day	1000		
Ethanol, t/day	113	327	13.49*10 <sup>6</sup>
Methanol, t/day	1.13	327	0.13*10 <sup>6</sup>
Yeast	0.22		
<b>Net annual additional cashflow</b>			<b>13.62*10<sup>6</sup></b>

Also the energy consumption has a big role in the profitable calculation. By the data that was obtained in this work and data from Kraft biorefinery case it is possible assume that the energy balance will approximately the same or in the sulfite case will slightly higher.

For sulfite biorefinery process capital investment in the equipments for new stages should be needed as well as in the Kraft case. But new equipment for cooking process also should be installed in the case with sulfite chemical cooking because this process assumed as additional process to Kraft mills.

## **11 Conclusion**

This thesis work is directed to analysis feasibility of integration bioethanol production process at sulfite pulp mill. The calculation of three biorefinery cases was done. All cases are inlaying the combined recovery system with chemical regeneration. The calculation was preceded according to literature data and assumption data based on the literature. A more exact model of sulfite biorefinery can be done when laboratory experiment will be available.

The preliminary results suggest that in the first case, in a pulp mill producing 1000 Adt/d of pulp. This pulp is mix of 100 Adt/d sulfite pulp and 900 Adt/day Kraft pulp. This pulp can be used for production printing paper. This proportion was chosen based on the pulp properties such way that paper properties will not decrease. In this case from pulp mill by the spent sulfite liquor fermentation process about 7, 5 t ethanol can be produced, but it is really a less amount for industrial value. Increase of bioethanol amount can be reached by two ways. First – to raise all amount of pulp production at a pulp mill and second – by the laboratory experiment determine the proportion of two pulps that allow produce enough qualitative paper appropriate to the market demand.

The second case was assumed as pulp mix for packaging purpose. The amount of product the same 1000 Adt/day, but another proportion used for this target. The 750 Adt/d of Kraft pulp and 250 Adt/d of sulfite pulp were calculated. The sulfite pulp has better opacity properties than Kraft pulp. These properties can be advantage for sulfite

pulp in the packaging area, because a less charge is necessary for production any package. The mechanical properties of package will better in the combination sulfite pulp with Kraft pulp. The amount of ethanol that can produce in the case 2 is 19 t/day. It is not big amount, but already appreciable. The same way to increase bioethanol amount can be used in this case. It should be a bigger production of mix pulp or other proportion of components. Also, it is possible to produce package from pure sulfite pulp, but it is not so good, because the amount of hemicelluloses that is transferred to the spent sulfite liquor is the smallest of all cases.

The last calculated third case. This case assumes that 1000 Adt/d of pure sulfite pulp produced at the pulp mill. This pulp is dissolving pulp that used for different purpose the application of this product was present in the section 8.3. This case has the best condition for bioethanol production. The biggest amount ethanol can be obtained from this process by cooking condition – it is first, and the biggest amount of sulfite pulp produced at the pulp mill- it is second parameters. In this case 114 t of ethanol can be produced per day. It is besides pulp and other product.

For more accurate data about amount of ethanol that can be fermented from spent sulfite liquors it is necessary to make laboratory experiments. Nowadays there exist types of yeast used in the fermentation process that can ferment both the hexoses and pethoses.

The profitability of all cases was evaluated and it seems positive in long period. It is visible that the ethanol production does not require big running costs, but instead big investment costs. The new equipments for new stage and for pulp cooking line should be installed at the mill, therefore big installation costs and recoupment of capital investment can take long time. But in present time the biofuels is very important and very demanding product that can stimulate development of this project.

In comparison with Kraft mill with water prehydrolysis this project seems profitable from products side. The bigger amount of bioethanol can be produced by the same value of Kraft pulp or from wood amount. Also other products will be formed during this process. These products have also enough demand at the market. But the investment side should be taken in consideration also. From this point of wiew sulfite

process has a weakness, because big investment costs for this project, especially in first and second case (when additional pulp line is necessary).

The first and second cases of acid biorefinery were considered as combined production Kraft and sulfite pulp, therefore combined recovery system was calculated.

Approximately data presented that there were not big difference between compositions of melt by different proportion of pulp. But the main point here was that the evaporation system should be separate for each type of liquor. Consequently there is no problems are with combined recovery at pulp mill.

In this work the energy balance was calculated only for some stages therefore it is possible only assume that the energy consumption will approximately be the same as in the Kraft with water prehydrolysis case. It is connected such way – the big amount of energy consumes on prehydrolysis process and in the acid biorefinery – approximately the same amount of energy consume on preparation and fermentation stage. The slightly bigger demand of energy can be in the sulfite process.

According to all the data from this work it is possible to say that acidic biorefinery concept seems actual in present time. In the comparison with Kraft biorefinery case the acidic biorefinery case have an advantage – the bigger amount of bioethanol can be produced, disadvantage – the new equipments should be installed at the pulp mill and, consequently, the bigger energy consumption will exist. The sulfite cooking biorefinery process required a high investment cost. As it was mentioned in the description of cases, the additional cooking line should be installed. Also the evaporation system should be different because a lot of energy is needed. The recoupment of capital investment will take a lot of time, but in the present situation it can be justified investment in the future.

In present time the biofuels demand is increasing fast. The biofuels from agricultures land have disadvantages; therefore the biofuel production from pulp mill as case of biorefinery can have a strong position and this project can be interesting by these data.

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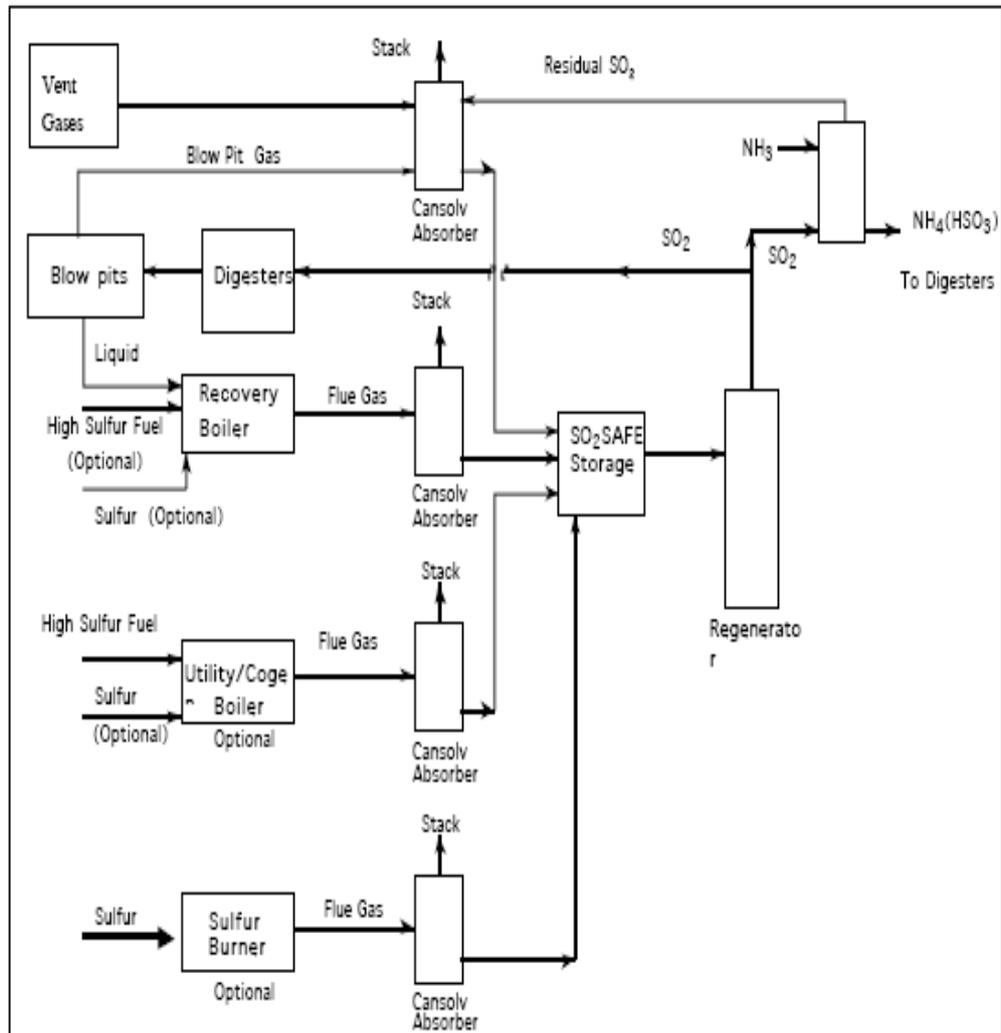
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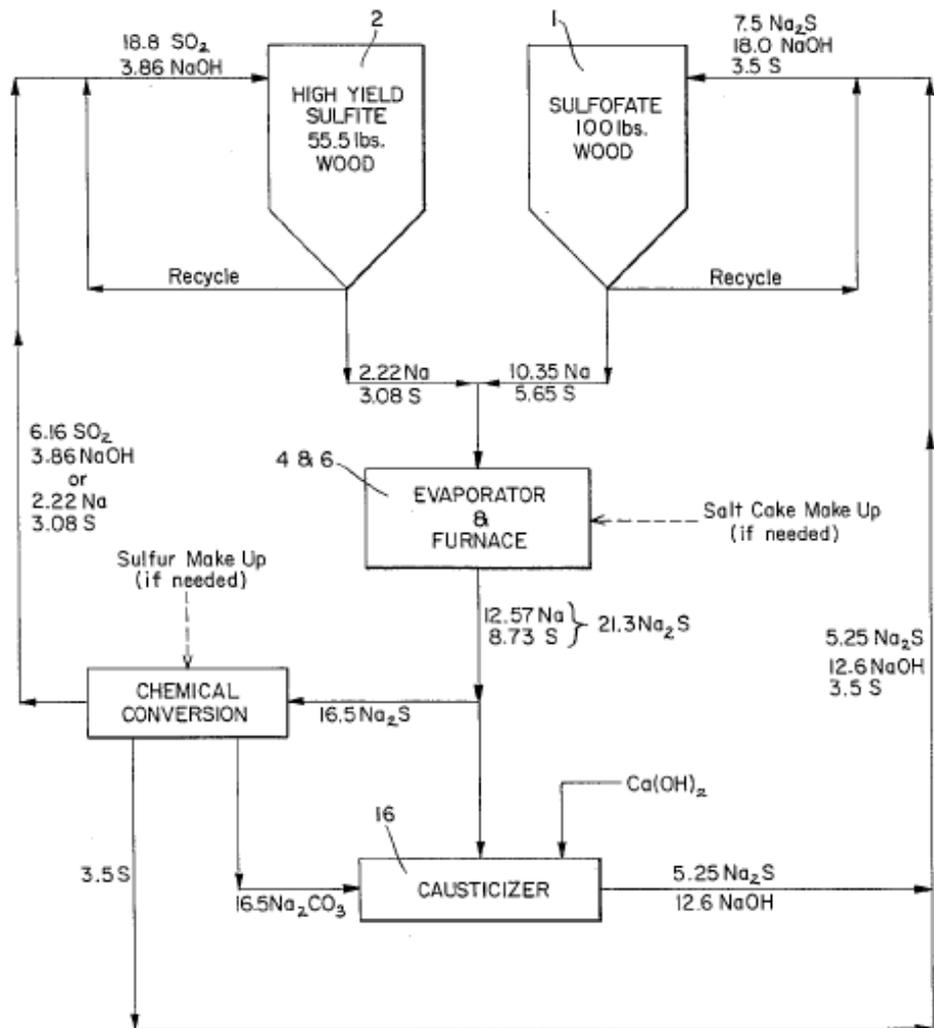
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Combined Acid Sulfite and modified sulfate pulping process with Appendix II recovery cycle



Combined Acid Sulfite and modified sulfate pulping process with Appendix II recovery cycle

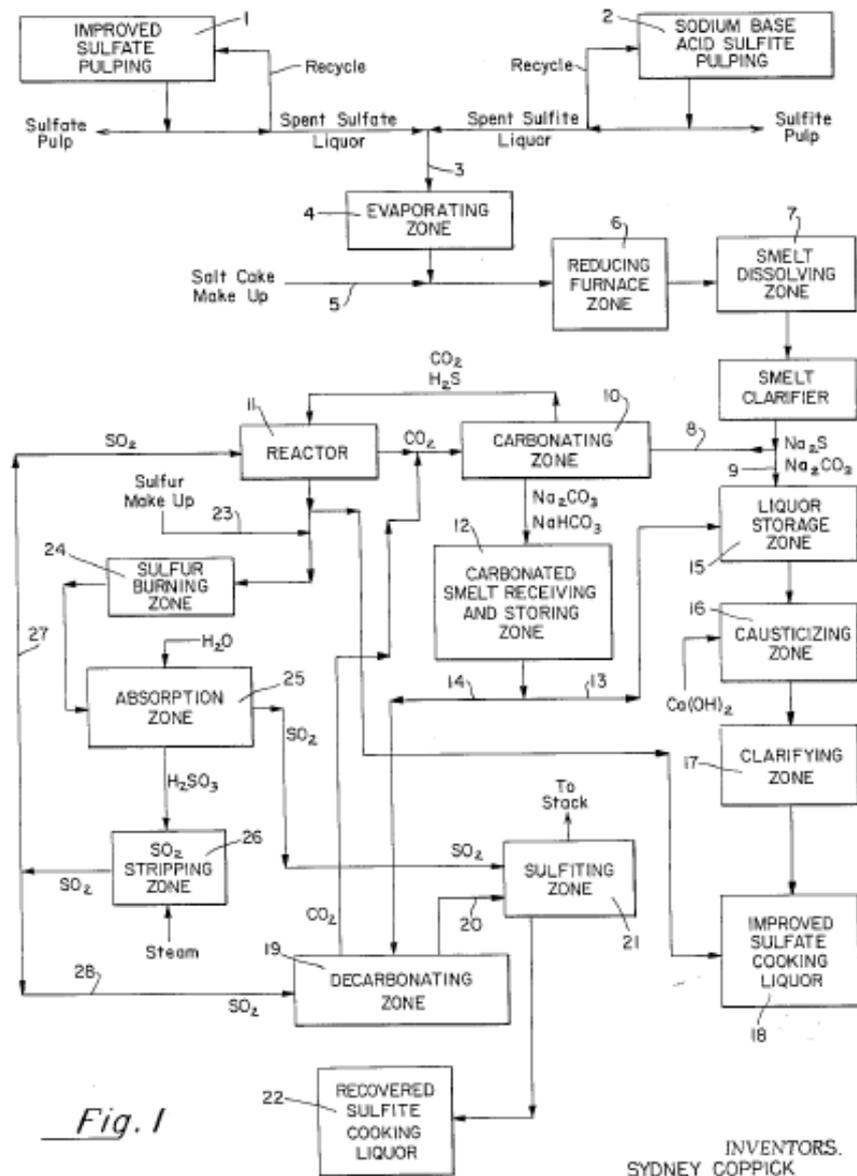


Fig. 1

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