

ALCOHOL DELIGNIFICATION OF PREHYDROLYZED WOOD

Wood delignification is an industrial process which has one of the highest negative impacts on the environment. There is continuous and ongoing global research for incremental improvements and solutions to this problem. One of the means to improve this process in the cellulose industry could be the alcohol delignification of wood, since it excludes the need for a cation and alcohol regeneration is easily achieved. If prehydrolysis of the wood precedes the delignification process, it is possible to decrease the overload of waste water by extracting the hemicelluloses before the main process, and the resultant hemicelluloses can be used as raw materials for many other useful products. A series of alcohol delignification experiments with prehydrolysis were performed on beech wood. Variations of the process parameters, including the presence or absence of sulfur dioxide, provided an insight into the possibility of obtaining bleached cellulose with the aforementioned benefits of reducing environmental pollution.

Numerous technological processes, in spite of their permanent improvement, present a serious danger to the environment because their wastes pollute air, water and soil. Legal limitations on waste removal make production more expensive, which induces scientists to solve this problem by all possible means.

One of the biggest pollutants of the environment is the cellulose industry. The production of pulp by wood delignification is carried out to the greatest extent by an acidic or alkaline process with some cation (Na, Ca, Mg). The main problem of these processes lies in the huge amount of waste waters with organic materials and salts of the used cations. Investigations to solve this problem are aimed in two directions: one of them consists of equipment and chemical modifications used in conventional processes and the other is searching for completely new options [1].

Among the numerous possibilities there is major interest in so called **organosolv-processes**, which use different organic solvents in the delignification process. The recovery of these chemicals is simple, equipment is cheaper and low quantities of waste waters and other waste make these processes very advisable, especially regarding ecological problems.

There are many organic compounds, which could be used as delignification agents such as simple alcohols, ethylene glycol, glycerol, phenol, sulpholan, various aldehydes and ketones and other species cited in the literature [2].

According to the achieved effects, alcohols give the best results among organic compounds in organosolv-processes, i.e. methanol and ethanol, and they have been investigated more than other solvents.

The first systematic studies of alcohol delignification with explanations of the reaction mechanisms were performed by Kleinert [3–6]. An alcohol delignification process, known as ALCEL, started in the eighties in Canada [7].

Some Russian authors have suggested that a combination of alcohol and sulfite agents, namely sulfur dioxide, could act synergistically and yield good results in a short time and at relatively low temperatures (120–150°C) [8–11]. This is an example of an acidically-catalyzed organosolv-process, while an alkali-catalyzed alcoholic process also exists [12,13]. If no catalyst were initially supplied in the system, the acetic acid formed by the evolution of methoxyl groups from lignin, would take over the role of an acidic catalyst. There are many proposals for alcohol delignification in combination with acetic acid [14–17].

According to Sarkanen [18], lignin dissolves in the organosolv-process because of the acidically catalyzed cracking of ether bonds, such as the α -aryl and aryl-glycerol- β -arylether bonds in the lignin macromolecule. The presence of methanol in alkaline medium does not affect the lignin affinity to reactions with alkalis and, in that case, the alcohol positively influences lignin dissolution or can reduce its tendency to condensation. Kleinert believed [3,4] that lignin depolymerisation proceeds by a free radical process and that its dissolution depends on the pH, temperature and solvent concentration.

Besides ecological problems, the cellulose industry also has serious economic problems. Pulp production can use only half of the wood mass as a final product; the second part, i.e. lignin and hemicelluloses, move into the liquid phase during delignification and only a small part can be recovered and used. The dissolution of cellulose requires very severe process conditions to remove hemicelluloses completely, because they, especially pentosans, make difficulties in

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the acetylation and xantogenation of cellulose [19]. Conventional alkali pulp production processes solve this problem by acidic or aqueous prehydrolysis. The organosolv-process with prehydrolysis has been successfully applied to some one-year plants [20,21].

Acidic prehydrolysis has greater active acidity than aqueous prehydrolysis, thus a large amount of hemicelluloses is transferred into solution and their hydrolysis to monoses proceeds faster. Such process conditions should not damage the cellulose molecules and there are data that the rate of cellulose hydrolysis under those hydrolytic conditions is about 1 500 times lower than that of pentosans [22].

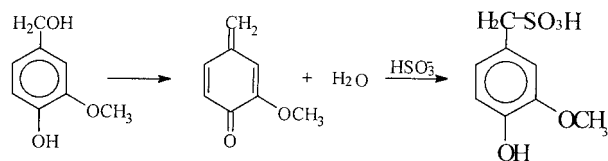
Wood prehydrolysis yields hemicelluloses which are transferred to the liquid phase before pulp processing and they can be profitably used as raw materials for various products [23]. In that way a large amount of organic wastes do not come to stream waters, as usually occurs in common pulp production.

Some authors [24] have claimed that SO_2 has priority as a prehydrolysis agent over sulfuric and hydrochloric acids because its presence in the early phases of the process could prevent undesired lignin condensation in the subsequent phase, by sulfonation.

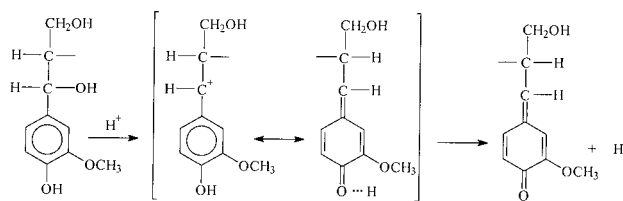
Reactions between sulfur dioxide and the wood material could be considered as delignification without a cation. Such a process should be carried out very carefully especially with higher SO_2 concentrations because of undesired lignin condensation, as succeeded by Nikitin et al. [25]. But prehydrolysis is a process with only the aim of dissolving hemicelluloses, not lignin, so mild conditions would be sufficient.

The mechanism of the sulfonation reaction is based on the increasing reaction capability of benzyl alcohol and benzyl ether groups in highly acidic medium and this reaction has the character of a nucleophilic aliphatic substitution of a bimolecular reaction because of the phenolic hydroxyl on the aromatic ring.

The reaction of lignin sulfonation is considered as a two-step process: in the first step α -oxy-p-alkylphenol is transformed to chinonmethide and in the second, sulfurous acid and its salts are bound forming sulfo-compounds [26,27]. The following reaction scheme may present a general form of this reaction mechanism:



In these reactions a carbonium ion and the extremely active chinonmethide species appear as intermediates:



Sulfurous acid and its salts reduce the chinonmethide form of lignin and a four-valent sulfur transforms to the six-valent form. That means that the sulfonation reaction of lignin has a redox character.

According to Nepešin's investigations [28], previous lignin sulfonation (more than 3%S) can eliminate the conditions for lignin condensation, the more so as the sulfonation level is higher. Sulfonated lignin can swell considerably, so its reacting groups are physically separated. These statements support our idea to try a two-step process with SO_2 -prehydrolysis in the first step and after that alcohol delignification as the second step of the process. In that way cation presence in these processes is not necessary, which is very important because of cheaper agent regeneration and the lower pollution of waste waters.

Delignification with prehydrolysis of beech wood has been investigated at the Faculty of Technology in Banja Luka for a long time [29-31]. Sulfur dioxide was used as the most suitable agent for prehydrolysis because it is cheap, easily removed and it can serve as a conservation substance for sugar hydrolyzates.

Experiments of alcohol delignification were carried out using previous experience on sulfite delignification with prehydrolysis, so similar process parameters were varied and some combinations gave very good results encouraging further research in that direction.

EXPERIMENTAL

Three series of alcohol delignification of beech wood prepared for delignification in a cellulose factory were performed. Two of them used processed prehydrolyzed wood, while raw wooden material was used in the third group of experiments. Prehydrolysis was performed at 120°C for 45 minutes with 3% SO_2 with respect to a.d. wood and a hydromodulus of 1:5.

Delignification was carried out with water-methanol and water-ethanol solutions, 1:1, with and without SO_2 (3% SO_2 with respect to a.d. wood), at 140 and 160°C . Two cooking orders were applied, with or without a one-hour pause at 110°C . All the prehydrolysis and delignification experiments were performed in a rotating laboratory autoclave on 200 gram wood samples.

According to the cited parameter combinations, 24 experiments of alcohol delignification were performed. After each delignification process all the samples were defibred, washed and sorted and subsequently each

one was bleached the by multi-stage CEH-bleaching process. The chlorination phase was performed with 60% of the required chlorine, with 3% mass consistency, at 20°C for 30 minutes. Afterwards, alkaline extraction was performed in 12% mass consistency, with 3% NaOH according to the pulp mass, at 90°C, for two hours. The pulp bleaching was finished with NaOCl solution at pH=9, with a pulp consistency of 7%, at 40°C for two hours.

Standard analysis of the bleached cellulose samples, such as the α -cellulose quantity, copper number and brightness, was performed. The α -cellulose quantity was determined according to the sample solubility in 17.5% NaOH solution at 20°C under standard conditions. The copper number was analysed according to the Schwalbe-Haglund method. The samples brightness was measured on an ELREPHO-device, with MgO as the standard for brightness.

RESULTS AND DISCUSSION

All the designated parameter combinations did not give satisfactory results. As can be seen in Table 1, there are some squares with a negative sign ("-"). That means that those parameter combinations produced either insufficiently cooked wood or overcooked wood. Temperature and the presence or absence of SO₂ had the biggest influence on the results. The type of applied

Table 1. Experiment success rate of alcohol delignification

agent		methanol		ethanol	
temperature, °C		140	160	140	160
prehydrolysis, cooking without pause	with SO ₂		-		-
	without SO ₂	-	-	-	-
prehydrolysis, cooking with pause	with SO ₂		-		-
	without SO ₂	-	-	-	-
without prehydrolysis, cooking with pause	with SO ₂		-		-
	without SO ₂	-	-	-	-

Table 2. Main characteristics of cellulose samples produced by alcohol delignification

	α -cellulose, %		Cu-number		brightness, °Elrepho	
	methanol	ethanol	methanol	ethanol	methanol	ethanol
140°C, with SO ₂						
prehydrolysis, cooking without pause	89.19	88.73	1.09	1.29	88.60	90.00
prehydrolysis, cooking with pause	89.32	90.27	1.18	1.51	71.80	77.40
without prehydrolysis, cooking with pause	85.90	84.74	1.07	1.17	90.05	92.40
160°C						
prehydrolysis, cooking with pause, without SO ₂		82.59		1.56		83.80
without prehydrolysis, cooking with pause, with SO ₂		67.10		2.04		84.80

alcohol had a minor influence, as well as prehydrolysis, except in one case.

The final effects of different parameter combinations in the alcohol delignification process of beech wood are shown in Table 2, as the major properties of the bleached cellulose samples.

Temperature effect

Temperature is one of the most important parameters of delignification, but its action is related to other process conditions. As can be seen in Table 1 delignification at 140°C was carried out with both types of alcohols. A 20°C increase caused the destruction of the wood mass, so the cellulose component was saved in only two of twelve experiments at 160°C. Even these two cellulose samples had bad properties.

SO₂ effect

Sulfur dioxide had a large influence on the success of the alcohol delignification of beech wood under the applied conditions in the performed experiments. That is obvious in experiments at 140°C which were successful, if SO₂ was present. Without SO₂ the obtained mass was hard, uncooked, without the possibility of bleaching.

Prehydrolysis effect

The prehydrolysis process positively affects the wood mass preparation for further delignification [24], but the bleaching possibilities of those samples were slightly lower than for samples obtained without prehydrolysis. That was particularly expressed in delignification processes with a temperature pause. But the amount of α -cellulose in those samples was higher (about 90%) than in samples without prehydrolysis (about 86%). If one takes into consideration that the processes with prehydrolysis give separated hemicelluloses, which could be a raw material for many useful products [23], then the alcohol delignification process with prehydrolysis can be recommended.

Influence of alcohol type

There were no big differences in the cellulose quality between samples obtained with ethanol and methanol. Ethanol enabled the obtaining of higher brightness, but the Cu-number, an indicator of cellulose degradation, was lower, that means better for samples with methanol. However, ethanol enabled the obtaining of bleachable pulp even at 160°C, but not with methanol. That is important information because the higher the temperature, the shorter was the delignification.

These experiments show an interesting connection between prehydrolysis and sulfur dioxide action, because it seems that they can substitute one another. For example, the data in Table 1 show that delignification with ethanol at 160°C was successful in only two cases: without prehydrolysis with SO₂ or with prehydrolysis without SO₂.

Cooking order effect

According to the obtained results cellulose bleachability depends on the temperature regime, i.e. whether there was a one-hour pause at 110°C or not. Prehydrolysis also influences in these cases, so cooking with a pause and prehydrolysis produced dark, hardly bleachable pulp. Extended high temperature action probably causes lignin condensation in the wood mass, which was unprotected after prehydrolysis. Cellulose samples obtained under the same process conditions, but without prehydrolysis, which reached high brightness could be a confirmation of this assumption. This phenomenon was independent of alcohol type.

Alcohol delignification in any case is an advisable process from the ecological aspect, because this agent can easily be recovered from waste liquids. The second advantage of the examined delignification process is cation absence, the regeneration of which would make the whole process more expensive and in spite of its recovery, a significant amount of the cation would go to waste waters. Sulfur dioxide, as an auxiliary means in prehydrolysis and delignification, can be recovered very easily by heating.

Alcohol delignification requires less time (5–6 hours) than common acidic delignification with a cation.

All the listed advantages, such as simple agent regeneration, hemicellulose separation from the hydrolyzate and its useful usage, as well as much shorter processing time, make the alcohol delignification process with SO₂ gas and with prehydrolysis as the first stage a process to be recommended. This process has economical, as well as ecological advantages.

CONCLUSION

1. Bleachable, good quality cellulose can be obtained by the alcohol delignification of beech wood in the presence of sulfur dioxide.

2. Alcohol delignification with SO₂-prehydrolysis at 140°C gave good quality pulp.

3. Delignification processes with ethanol and methanol did not show many differences, except that the success rate of the experiments with ethanol was higher.

4. The possibility of fully recovering the alcohol and sulfur dioxide, as well as hemicelluloses separation in the prehydrolysis process, reduce water pollution, which is important in regard to environmental protection.

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IZVOD

ALKOHOLNA DELIGNIFIKACIJA PREHIDROLIZIRANOG DRVETA

(Naučni rad)

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Delignifikacija drveta spada u procese koji predstavljaju najveće zagađivače životne sredine. To je jedan od glavnih razloga što se stalno traže nova rješenja za ovaj problem. Jedan od načina poboljšanja procesa u celuloznoj industriji mogla bi biti alkoholna delignifikacija drveta, jer isključuje potrebu za katjonom, a i regeneracija alkohola se veoma lako obavlja. Ako predhidroliza drveta prethodi procesu delignifikacije onda se smanjuje opterećenost otpadnih voda i time što će se hemiceluloze izdvojiti prije glavnog procesa, a te hemiceluloze mogu poslužiti kao sirovine za mnoge korisne produkte.

Niz eksperimenata alkoholne delignifikacije bukovog drveta sa predhidrolizom izveden je uz variranje parametara procesa, kao što su: temperatura, vrsta alkohola, kuvanje sa ili bez pauze i kuvanje sa ili bez prisustva sumpordoksida. Uspješni eksperimenti su nastavljeni bijeljenjem dobijenih uzoraka celuloze i njihovim analizama. Rezultati su dali pregled mogućnosti dobijanja bijeljene celuloze alkoholnom delignifikacijom sa predhidrolizom, uz sve navedene prednosti zbog smanjenja ekoloških problema.

Ključne reči: Celuloza • Alkoholna delignifikacija • Predhidroliza drveta •

Key words: Cellulose • Alcohol delignification • Wood prehydrolysis •

