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Different Solvents for Organosolv Pulping

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Abstract

Organosolv pulping is a two-stage process involving hydrolysis (decomposition of wood by use of a catalyst) and removal of lignin with an organic solvent (usually a mixture of alcohol and water). The main disadvantage of using an alcohol is its low boiling point, which requires operating at a high pressure and hence using special equipment that is expensive to purchase and operate. One solution to this problem is using alternative organic solvents that afford operation at pressure levels similar to those of classic pulping processes (e.g., the Kraft process). This chapter provides a comprehensive literature review on the organosolv-based production of cellulose pulp by using alternative solvents such as glycols, phenols, esters, organic acids, acetone and amines.

Keywords: organosolv, glycols, phenols, ester, organic acids, acetone, amines, pulp, paper

1. Introduction

The increasing environmental awareness of developed societies has boosted the demand for more sustainable production processes for commodities such as paper and cardboard. Traditional chemical and semi-chemical pulping processes produce large amounts of waste called “black liquor” that is highly polluting (especially when sulfur compounds are used). In response to this problem, the industrial and scientific sectors are increasingly aiming at using new raw materials to replace traditional choices such as annual plants or agricultural and forestry residues, and also at developing new pulping processes based on less polluting, more easily recovered reagents such as organic solvents. Such processes are generically called

“organosolv processes” and afford the production of high-quality pulp and paper with modest industrial investments and low production costs, as well as the efficient, integral use of raw materials to obtain pulp in high yields in addition to by-products and added value.

Since alcohols are the most widely used solvents for organosolv pulping, this chapter reviews the comparatively scant research conducted so far on the use of alternative solvents such as glycols, phenols, ester, organic acids, acetone, ammonia and amines for this purpose.

2. Background

The earliest scientific reference to delignification with organic solvents dates from 1893, when Kason used ethanol and hydrochloric acid for this purpose. This was followed by the work of Aronovsky and Grotner, and Kleinert and Tayenthal, in the 1930s; Brounstein in the 1950s and Kleinert in the 1970s [1, 2]. In those days, organosolv processes had not yet challenged the prevalence of traditional chemical pulping processes. During the 1970s, however, the scientific community began to devise solutions to the many drawbacks of the classical processes including unpleasant odors, low yields, high pollution, difficult brightening of pulp, large investments, and massive consumption of energy, water, raw materials and reagents. Initially, attempts focused on modifying the pulping process; then, new processes using no sulfur as reagent were developed. However, these attempts met new problems such as the difficulty of recovering reagents and the polluting nature of the waste [3].

In the 1980s, new processes using organic solvents started to emerge. Their greatest advantage was that they afforded full use of the raw materials. Some were used to obtain hydrolysable cellulose, phenolic polymers of lignin and sugars [4–6].

Although the Kraft process still prevailed in the 1990s, the environmental problems it caused, and the high investments involved led to the conclusion that alternative pulp production processes should be developed.

The most commonly pulping process used in industry is the Kraft or sulfate process [7]. The most common raw material for this process is wood, especially softwood for unbleached pulp, and hardwoods for bleached pulp, with a much higher consumption than alternative or non-wood vegetables, whose main disadvantage is that some of them have high ash content, which causes serious problems in the recovery circuits of black liquors.

In this process, the reagent replaced is sodium sulfate, although the real agent that acts during the delignification reaction is the sulfur that is generated. The process can be divided into two parts: the first is the production of the pulp and the second is the recovery of the chemicals used [8].

In Kraft pulping, some of the black liquor can be recirculated to be used as a pulping solution. In some cases, 40–60% of pulping solution may be black liquor without affecting the pulping yield or the characteristics of the pulps obtained. By this way, part of the reagents is reused without costly evaporation stage, the reagents' penetration into the chips is encouraged, and the heat energy of the black liquor is used.

Several authors propose modifications to the Kraft process. Wang et al. [9] propose the addition of anthraquinone to green liquor, achieving yield increases of 2% and substantial savings in reagents (23–26%) and energy. The use of polysulfides in the pre-treatment improves the pulp yield by 1.5–3.5% according to the data obtained by Luthe et al. [10]. Gustafsson et al. [11] propose a pre-treatment with polysulfide in an alkaline medium (0–2.5 molar sodium hydroxide), achieving significant improvements in the viscosity of the pulps with a low Kappa number. Brannvall et al. [12] describe hyperalkaline pulping with polysulfide, in which pre-treatment consists of two stages: the first one is an acid neutralization and the second one is a high concentration of alkali and polysulfide.

Research then focused on processes using organic solvents in order to extract not only cellulose fiber, but also other useful products from the raw materials. That is how the concept called “wood refinery” by analogy with the fractionation of crude oil was born [13].

In this way, much research into the delignification of traditional and alternative raw materials with organic solvents to obtain not only pulp, but also lignin, sugars and various other products was conducted [4, 5, 14–24].

The main advantages of organosolv process regarding Kraft process are as follows:

1. More economical than the kraft process for SME.
2. It achieves a good degree of brightness for the pulps, competitive with those obtained for conventional chemical pulps.
3. Less polluting than conventional processes, without bad smells and with less effluents and pollutants.
4. By-products are obtained in greater quantity and quality than in conventional processes.
5. Better use of the raw material due to its higher yields.
6. It requires less water than the Kraft process.

However, this process also has its drawbacks:

1. It cannot be applied to softwoods.
2. Higher production cost, due to the high cost of some solvents as ethanol.
3. Higher cost of recovery of by-products.
4. Requires more external energy than the Kraft process.

3. Organosolv solvents and catalysts

Organosolv processes use a broad range of organic solvents including methanol, ethanol, propanol, butanol, isobutyl alcohol, benzyl alcohol, glycerol, glycol, ethylene glycol, triethylene glycol, phenol, acetone, formic acid, acetic acid, propionic acid, diethyl ether, amines, ethers, esters,

formaldehyde and chloroethanol, among others, either in pure form or in aqueous solutions to which a catalyst (an acid, base or salt) may be added. Solvents with a low boiling point (e.g., methanol, ethanol, acetone and ethyl acetate) can easily be recovered by distillation; on the other hand, those with a high boiling point (e.g., triethylene glycol and ethylene glycol) afford operation at low pressures but are difficult to recover [1, 2, 4, 5, 14–17, 25–64]. In any case, all allow softwood and hardwood to be efficiently delignified without damaging cellulose in the raw material [65].

Alcohols are the most widely used solvents in organosolv processes, and ethanol is one of the most effective for this purpose as it combines a high speed of delignification under favorable operating conditions with easy recovery [5, 66]. Primary alcohols provide more selective delignification than do secondary and tertiary alcohols. Also, methanol causes less marked losses of hemicelluloses than does butanol. Only poplar and aspen wood can be efficiently delignified in the absence of a catalyst [65]. However, the catalysts used for this purpose include mineral acids (sulfuric, hydrochloric and hydrobromic), organic acids (formic, acetic, propionic, oxalic, malic, salicylic, succinic, nicotinic, benzoic, citric and phthalic), salts (chlorides, chlorosulfonates, boric fluoride, chlorides, sulfates and nitrates of calcium and magnesium, sulfites and sulfides) and other compounds such as alkalis, ammonia or anthraquinone [14, 40, 42, 43, 55, 61, 65, 67, 68].

Organic acids are more efficient than mineral acids in delignifying softwood [87–89, 123, 124]. However, sulfuric acid at a concentration below 0.01 M, but particularly 0.01 or 0.02 M, allows the processing temperature of alcohol-based pulping of cottonwood to be lowered from 200 to 170°C [4, 69–73]. Lower sulfuric concentrations cause the acid to be neutralized by ash and other alkaline components, whereas higher concentrations can result in condensation with free lignin, hydrolysis of hemicelluloses, degradation of cellulose and formation of insoluble condensation products in the pulping liquor. Lignin condensing in fibers can only be removed after a large enough amount of hemicelluloses has been dissolved; therefore, the presence of pores facilitates the process but also degrades cellulose and detracts from pulp viscosity as a result. Condensed lignin is insoluble in alcohol-water mixtures and requires another solvent such as acetone, tetrahydrofuran, dimethyl sulfoxide or a 3–5% o.d.m. soda solution [5, 40, 65].

Sulfur dioxide dissolved in the pulping liquor acts as a weak acid; by reaction with lignin, however, it forms sulfonic acids that can be as strong as mineral acids [2, 40].

Adding an alkaline earth salt as a catalyst to the alcohol-water mixture is the only way of completely releasing fibers from some vegetable species and obtaining yields as high as 60% of high-viscosity pulp [65].

Base-catalyzed organosolv processes are highly effective with conifer wood and outperform some sulfite and Kraft processes in pulp yield and properties [40, 65].

4. Delignification mechanisms

Delignification with organic solvents is believed to be resulted from hydrolysis of α -aryl-ether and lignin-hemicellulose links with a pseudo-first order kinetics [65] and from dissolution of lignin by cleavage of α -aryl and aryl-glycerol- β -aryl-ether links [40, 74–77].

The rate of delignification in acid-catalyzed organosolv pulping processes is governed by the hydrolysis of α -ether links in lignin [98–102]. The process also involves other complex reactions such as condensation, partial hydrolysis of β -aryl links, release of formaldehyde and recombination of free radicals [40, 78–81].

In acid media, the delignification of lignin is preceded by cleavage of α -aryl-ether and β -aryl-ether bonds by H^+ ions. The concentration of hydrogen ions increases with increasing ethanol concentration and liquid/solid ratio but decreases with increasing processing time [82]. Although the cleavage of α -aryl-ether linkages is a primary factor, the cleavage of β -aryl-ether links is also influential (especially with hardwood). The hydrolysis of β -aryl-ether units in addition to α -aryl-ether links was found to have a direct impact on the initial rate of delignification of aspen wood with methanol; also, the extent of delignification was additionally affected by condensation reactions with lignin [83].

The reactions involved in the soda-methanol process are possibly similar to those of the soda process except that lignin is dissolved by the alcohol and formation of condensation products which is more limited [40]. In alkaline processes, the cleavage of β -aryl-ether bonds is more important than that of α -aryl-ether bonds [84].

Phenol as solvent reacts with lignin and facilitates its dissolution; subsequently, it causes some degradation of carbohydrates and lignin through mild acid hydrolysis [85]. With butanediol, lignin-carbohydrate complexes react with benzyl ethers, especially in the presence of acetic acid [86]. The kinetics of delignification of bagasse is first order with butanol but second order with soda [87].

Removal of lignin in the pulping of eucalyptus with acetic and hydrochloric acids results from the hydrolysis of α -aryl-ether links, which occurs in two parallel first-order reactions involving the hydrolysis of hemicellulose (the faster) and cellulose (the slower) [85]. The latter reaction does not occur at low temperatures and concentrations of hydrochloric acid [88–90]. The acetosolv pulping of pinewood also involves two parallel first-order hydrolysis reactions the first of which is faster than the second [91–93].

The pulping of spruce exhibits two distinct stages of delignification, both with first-order kinetics. In the first (the faster), 70% of the lignin is rapidly removed, the remainder being eliminated more slowly. Complete release of fibers is achieved when the yield drops to 57% and the kappa number is 72 (10% lignin). Delignification at these stages occurs largely in outer cell walls and the middle lamella, and is still relatively scarce in secondary walls. Although all lignin in the middle lamella is removed with a yield of 60%, some residual lignin remains in outer and secondary walls. As confirmed by various techniques, the ease of delignification of the middle lamella decreases in the following sequence: catalyzed organic solvents > acid chlorite > neutral sulfite > acid sulfite > Kraft. On the other hand, the sequence for the secondary wall is Kraft > acid sulfite > catalyzed organic solvents > neutral sulfite > acid chlorite. Delignification of the secondary wall is governed by diffusion (specifically, by physical and chemical differences between lignin in various morphological regions of plant tissues) [94].

Overall, hardwood is easier to delignify than softwood by virtue of its lower content in lignin, higher concentration of α -aryl-ether links—which make it easier to hydrolyze, lower tendency to lignin condensation and higher reactivity of β -aryl-ether links [82].

Brogdon and Dimmel have conducted interesting research into various types of reactions involved in quinone-based pulping processes [95–99].

5. Pulping with different organic solvents

5.1. Glycols

The earliest use of ethylene glycol to obtain cellulose pulp was reported in 1941 by Nakanun and Takanti, who applied it to spruce [15]. In the late 1970s, Unger [4] confirmed that propylene glycol, butylene glycol and other higher glycols were useful for pulping, especially if the raw materials were previously impregnated with sulfuric acid. In the 1980s, Gast et al. [100–102] found the efficiency of ethylene glycol to be improved by using aluminum sulfate or chloride as a catalyst; also they studied the kinetics of pulping of birch with the glycol. In the 1990s, Thring et al. conducted research into the by-products of lignin recovery in the pulping with ethylene glycol, and also the fractionation of poplar in a two-step process yielding cellulose in one and hemicellulose and lignin in the other [4].

Several authors have explored the pulping of aspen, birch, beech and pine wood, vine shoots, olive tree prunings, forest residues and bagasse with ethylene glycol [45, 46, 49, 64, 103–108]; rice straw with diethylene glycol-ethylene glycol and diethylene glycol-ethylene glycol-soda mixtures [109]; and cellulose linters, wood sawdust, *Miscanthus sinensis* and *Eucalyptus globulus* with glycols [110]. Using glycol-acetic-water systems with aspen and pinewood proved an effective modification of the glycol delignification method with substantial savings in energy (temperature and time) [106, 111]. A study investigated the origin of the losses of ethylene glycol during pulping [112].

Glycerols have also been used in pulp production [49, 113–115]. Thus, treating *Ailanthus altissima* and *Spruce orientalis* wood with glycerol provided optimal delignification results in the presence of an alkali, which, however, led to increased cellulose losses.

Butanediol and propylene glycol have also been used for pulping [56, 64, 115], and so have mixtures of ethanol and ethylene glycol [46, 116].

5.2. Phenols

The Battelle-Genoa process uses phenol as solvent. This is the best-known pulping process using a high-boiling point solvent in combination with HCl as a catalyst. The process is especially efficient with hardwood, spruce and herbaceous plants. With softwood, however, it usually takes a long time and yields pulp with inferior properties relative to the Kraft process. The advantages of the Battelle-Genoa process include a low cost of the industrial plant and the production of small volumes of black liquor; on the other hand, its disadvantages include problems arising from washing of the pulp, recovery of the reagents and detoxification of the effluents, which usually contain small amounts of phenols and cresols [2, 39].

The phenol-ethanol process is also well known [14] and has been successfully used to delignify wood [85, 117, 118], wheat straw [119] and *Ulex europaeus* [120]. Phenols have also been used for pulp production by Schweers et al. [53, 54].

Finally, cresols have been used as reagents for spruce pulping [121]; the raw material, at 70% consistency, was delignified at 180°C for 2 h in the presence of acetic acid.

5.3. Esters

The ester pulping process, patented by Young and Baiertl, uses a mixture of water, acetic acid (catalyst) and ethyl acetate (solvent) to dissolve fragmented (hydrolyzed) lignin. This process is suitable for poplar, but not for other types of hardwood (e.g., red oak, eucalyptus) and softwood species (e.g., pine, white spruce); nor is suitable when the aim is to obtain pulp for subsequent bleaching. The properties of poplar pulp obtained with this process are in between those of sulfite pulp and Kraft pulp [39]. According to some authors, however, this process efficiently delignifies both hardwood and softwood and provides pulp with good mechanical properties [14].

5.4. Organic acids

The acetocell process uses acetic acid and, usually, hydrochloric or sulfuric acid as a catalyst. The process has been used with various raw materials including bagasse [120], birch and hardwood [121, 122], *Pinus pinaster* [123, 124], *Eucalyptus globulus* [61, 125–128] and *Eucalyptus grandis* [42]. Also, it has been applied to softwood and annuals, using a high temperature but no catalyst. With Norwegian spruce, the acetocell process provides pulp with high yield and a Kappa number of 16–20 that is easily bleached with ozone and hydrogen peroxide, and largely retains its mechanical properties [129].

A study examined the kinetics of delignification of wood and correlated kinetic parameters with the catalyst concentration [126, 130]. With acetic-hydrochloric acid mixtures, the selectivity of the process was independent of the concentration of HCl and temperature, and yields were as high as 50% [131]. Another study explored the delignification of red spruce with acetic acid-water, acetic acid-carbon dioxide and acetic acid-water-carbon dioxide mixtures under supercritical conditions; also, it examined the effects of the concentration of acetic acid, pressure, temperature and time on the extent of delignification. The best results were obtained with acetic acid-water mixtures [132]. Acetic acid has also been used in the pulping of birch with provision for the influence of pre-hydrolysis, hydrogen peroxide and some other variables [133], and also in the pulping of rice straw at atmospheric pressure [134]. More recently, a study examined the pulping of beech with acetic acid in the presence of hydrochloric acid as a catalyst [135].

The use of formic acid for delignification dates from 1917, when it was applied to wood and cereal straw. This process has some advantages over others using other organic solvents such as a low cost, and the ability to use low temperatures and pressures [136, 137]. In one study, it was applied to different types of hardwood such as that from *E. globulus* and *E. grandis* [138]. The best operating conditions for the latter species were 92% formic acid, 0.22% hydrochloric acid and 90°C for 90 min, the results being even better with refluxing. The presence of water was found to benefit fibers and yields as a result of its helping remove not only lignin, but also much hemicellulose and little α -cellulose [137].

The Milox process is a variant using peroxyformic acid spontaneously formed upon mixing of formic acid (80%) and hydrogen peroxide [2, 139–141]. This process is highly suitable for

delignifying birch in three stages [142], namely: treatment with the acid at 80°C, application of formic acid at 100°C and bleaching with hydrogen peroxide to obtain pulp with 90% ISO brightness. The mechanical properties of the resulting pulp are on a par with those of Kraft pulp. The results with conifer wood are worse, however, as a consequence of solvent recovery by distillation leading to the formation of an azeotrope of inadequate concentration between formic acid and water (78%) [2]. The Milox process has also been used with spruce [139] and alternative raw materials [140, 141]. Several studies conducted in recent years were used to delignify different materials [57, 59, 143, 144] in addition to spruce [67, 145], eucalyptus [146–148], pine [149], bagasse [147], rice straw [150, 151], rods [152] and banana stems [153].

The formacell process, which uses acetic acid-water-formic acid mixtures, has enabled the production of pulp with small kappa numbers from beech, pine and aspen. With aspen and birch wood, a low temperature and a high concentration of acetic acid are recommended to prevent hemicellulose losses [154, 155]. With wheat straw, the process provides pulp with a small kappa number and a high viscosity [156].

Using acetic acid containing small amounts of sulfuric acid and phenols provided good results with birch [157], and so did the acetic acid-carbon dioxide-water system under supercritical conditions [158].

5.5. Acetone

Jiménez et al. used acetone alone [159–161] and in mixtures with ethanol [162, 163] for delignification. Other authors have used mixtures of formic acid and acetone [149, 164, 165] or acetone alone on previously steamed raw materials [166].

One process using oxygen in aqueous acetone was applied to cotton stalks, eucalyptus and poplar wood. The influence of temperature, time and oxygen partial pressure on the delignification rate was examined, and the transfer of oxygen found to be the parent stage of the delignification process [167, 168]. The process was also applied to spruce and other types of wood [111].

5.6. Ammonia and amines

The processes using ammonia or amino bases provide pulp with a high yield by effect of their preserving hemicelluloses. Thus, 1, 6-hexamethylenediamine (HMDA) gives pulp with a high yield from both hardwood and softwood, but the pulp is difficult to bleach. Ammonia in combination with acetone or methylethyl ketone provides spruce pulp with higher yields and better properties—tear index excepted—than the Kraft process. Using ammonium sulfide with ethanol allows one to operate at lower temperatures than with ammonia to obtain pulp with similarly good properties from hardwood, cereal straw and bagasse, and strong pulp with a high yield and low lignin content relative to softwood. However, the processes using ammonia and amino bases are subject to problems arising from the recovery of reagents, the high boiling point of HMDA, condensation of lignin and formation of polluting sulfur volatiles [2].

Pulping poplar chips with supercritical ammonia-water mixtures revealed that the extents of removal of cellulose, hemicellulose and lignin were a function of time, pressure and, especially, temperature and solvent concentration [169].

The earliest work on pulping with ethanolamines dates from the late 1970s, when Wallis [48] applied them to pine and eucalyptus wood, and monoethanolamine proved more effective than diethanolamine and triethanolamine; yields were 11–16% higher than with the Kraft process and the resulting pulp had similar strength-related properties. Wallis [170] also pulped *Pinus elliottii* with ethanolamine and obtained pulp similarly strong to Kraft pulp but in higher yields (5–10% higher).

Ethanolamines have also been used to pulp spruce [47] and rice straw [63]. Adding ethanolamine to the alkaline cooking liquor was found to increase the rate of lignin degradation [171]. Finally, some authors have also used amines to pulp various raw materials such as beech, spruce, olive tree prunings, jute and cotton [172–179].

5.7. Other solvents

Processing bagasse as raw material with formamide and dimethylformamide provided pulps with a high content in α -cellulose in addition to good physical and mechanical properties [180, 181]. Some authors have pulped eucalyptus with dioxane in the presence of hydrochloric acid (catalyst) [182] or its absence [55, 183–185], and hardwood with the sulfur dioxide-ethanol-water system [186].

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