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ORIGINAL

Desulfurization of kraft lignin

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Abstract Kraft lignin is a product of the sulfate pulping process. It usually contains 2–3% total sulfur. Sulfur content acts as deterrent to lignin use in some areas. Sulfur-free lignins are more versatile and can be heat-treated without the release of foul-smelling sulfur compounds. These lignins are used to produce various low- and high-molecular products, as well as fuel. The existing soft desulfurization methods of kraft lignin allow reducing the total sulfur content, for example, fivefold by a method combining extraction of elemental sulfur, oxidation and reduction in sulfur compounds. Deeper desulfurization has earlier been achieved by catalytic hydrogenation, which is accompanied by depolymerization of lignin. In this paper, it was established that sequential treatment of sulfate lignin with benzene, silver in dimethylformamide, aqueous sodium sulfite solution and perchloric acid + acetic anhydride mixture can reduce the total sulfur content a hundredfold.

Introduction

Lignins are one of the most common polymers present in the cell walls of almost all terrestrial plants; in their distribution they occupy second place among all natural polymers after cellulose and other carbohydrates and have an important role in the natural carbon cycle (Glasser et al. 1999; Calvo-Flores et al. 2015). The conversion of lignin into valuable products is one way to unleash lignin's potential. Technical lignins can be considered as a potentially interesting raw material,

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since they are produced in processes dealing with the treatment of lignocellulosic materials, and many technical lignins are readily available in large amounts (kraft lignin, lignosulphonates and soda lignin) (Vishtal and Kraslawski 2011). Annually, around 63×10^4 tons of kraft lignin (sulfate lignin or thiolignin) are produced in the sulfate (kraft) pulp cooking process (Chakar and Ragauskas 2004; Vishtal and Kraslawski 2011). Two trademarks of pine kraft lignin are known: BioChoice lignin and Indulin AT, and many names of industrial processes for kraft lignin separation (Hu et al. 2016; Fang and Smith 2016). Thus, LignoBoost and LignoForce were designed based on the acidification concept to isolate kraft lignin from black liquor on the commercial scale, both of which produce pure lignin (Tomani et al. 2011; Kouisni et al. 2016; Fang and Smith 2016). Kraft lignin can easily be separated from black liquor. The use of sulfuric acid as acidification agent for black liquor increases the sulfur content of lignin (Vishtal and Kraslawski 2011), and hence, usage of such lignins should be avoided in sulfur-sensitive applications (Loutfi et al. 1991). So, the presence of sulfur in sulfate lignin is a deterrent to its use.

In the kraft pulping, 20–50% of the amount of sodium sulfide used is wasted. This loss of sulfur is mainly accounted for by “residual sulfur” in sulfate lignin (Sarkanen and Ludwig 1971). Depending on the conditions of delignification, sulfur content in lignin varies from 1.5 to 8%, but usually 2–3% (Field et al. 1958; Bogomolov et al. 1989; Vishtal and Kraslawski 2011; Tomani et al. 2011). The question of the localization of this sulfur in lignin (without taking into account the impurities of hydrogen sulfide, sulfide, hydrosulfide, sulfate, bisulfate, mercaptide ions, methyl mercaptan, dimethyl sulfide and dimethyl disulfide) has been controversial until recently. For example, information on the existence of elemental sulfur (S or S_8) “encrusted” in sulfate lignin (Zhigalov and Tishchenko 1962) has been criticized by Sarkanen and Ludwig (1971). Zhigalov and Tishchenko (1962) used potassium cyanide and sodium sulfite for “binding” an elemental sulfur “encrusted” in the sulfate lignin in the thiocyanate and thiosulfate forms. It has been suggested (Ekman 1966; Kawakami and Takata 1977) that up to 4% of the sulfur in kraft lignin is mainly in such an adsorbed elemental form. Ekman (1966) and Kawakami and Takata (1977) extracted elemental sulfur from kraft lignin by diethyl ether and mixed organic solvents. More than 60 years ago, the existence of the kraft lignin with elemental sulfur (Zhigalov and Tishchenko 1962; Ekman 1966), and sulfur-containing structures as well as the presence of sulfide, disulfide and dithiane groups (Gierer and Alfredsson 1957; Gorbunova 1969; Komshilov et al. 1969; Sarkanen and Ludwig 1971) have caused a dispute. But it was later proved that in the sulfate delignification process various sulfur-containing lignin derivatives are formed (Gierer 1980, 1985) (Fig. 1). In the initial stages of cooking, the kraft lignin is formed containing about 5% of sulfur. At temperatures above 150 °C alkaline hydrolysis occurs with dissolution of a sulfur-containing lignin. The content of organic sulfur in lignin which goes into solution and lignin remaining in the pulp is about the same and amounts to 2–3%. In addition to thiol and episulfide (thiirane) groups, arylmethyl sulfide (Ar–S–Me) lignin structures are formed during the pulping process (Niemelä et al. 2010). Sarkanen and Ludwig (1971) presented a structure of kraft pine lignin with one sulfur atom only (Fig. 1).

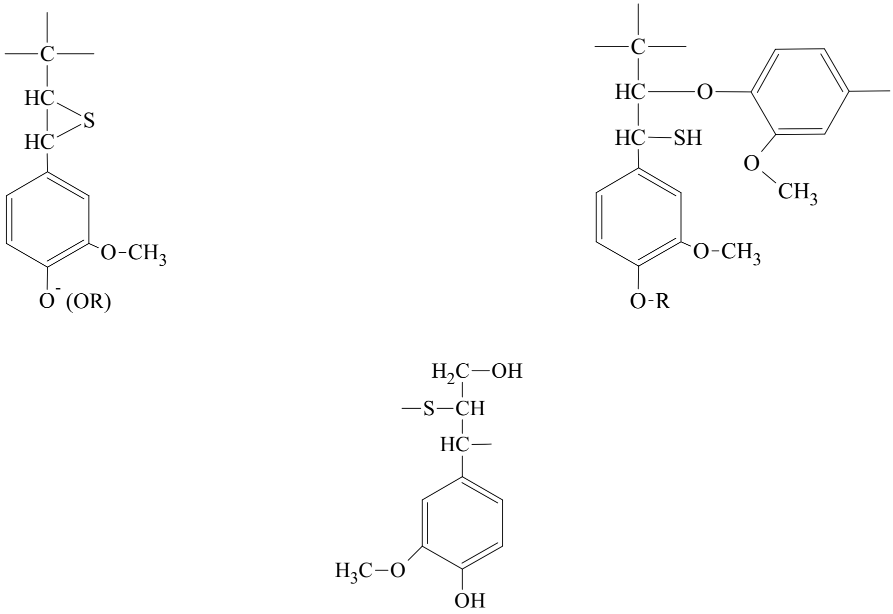


Fig. 1 Sulfur-containing lignin structures

Some authors suggested that in sulfate lignin, there are at least five types of sulfur bonds. Among these, thiol, thiirane and sulfide groups have been found (Field et al. 1958; Gorbunova 1969; Komshilov et al. 1969; Sarkanen and Ludwig 1971; Sjöström 1993), but there are apparently no organic disulfide, polysulfide, thiocarbonyl and dialkyl sulfide groups (Field et al. 1958; Sarkanen and Ludwig 1971). However, it is noted that lignin mercaptans can be oxidized under the conditions of kraft pulping and separation of lignin from black liquor to form disulfides and sulfonic acids. Svensson (2008) supposed that the sulfur in the kraft lignin is believed to be present as inorganic sulfur; mainly as sulfate ion (SO_4^{2-}), as elemental sulfur (S_0), as adsorbed polysulfide (S_nS^{2-}) and as organically bound sulfur; thiol (-SH), sulfide (–S–) and disulfide bonds (–S–S–). Some authors (Field et al. 1958; Gorbunova 1969; Sarkanen and Ludwig 1971) assumed the presence of sulfone and sulfoxide groups in the kraft lignin.

The methods for reducing the total sulfur content in black liquor soap, tall oil and its fractions had earlier been proposed based on adsorption; isolation of sulfur-containing lignin by sodium hydroxide treatment; the oxidation of thiols and sulfides to sulfoxides and sulfones with subsequent extraction with polar organic solvents (or extraction by organic solvents without oxidation); recovering organic sulfur compounds by P(III)-based systems as well as elemental sulfur recovery with heavy metals and sodium sulfite; and neutralization of acidic and basic sulfur compounds to form respective salts (Oliver and Palmer 1943; Sanderson 1972; Pollock et al. 2012; Kurzin et al. 2014; Trifonova 2015; Evdokimov et al. 2014, 2017a, b). Methods are known for desulfurization of lignin including an extraction of elemental sulfur by some organic solvents; oxidation of some sulfur-organic groups by O_2; reduction by Raney nickel, metal hydrogenation catalysts, sodium borohydride or lithium aluminum hydride; and treatment with sodium sulfite (Field et al. 1958; Gorbunova 1969; Komshilov et al. 1969; Bogomolov and Gorbunova 1974; Kawakami and Takata 1977; Svensson 2008; Radoykova et al. 2013; Huang 2014; Tymchyshyn 2015; Molinari et al. 2016; Kouisni et al. 2016). Some of these desulfurization methods based on deep depolymerization of kraft lignin are very effective and give zero ppm total sulfur content. Svensson (2008) used for desulfurization the combination of extraction, oxidation and reduction in sulfurous compounds of kraft lignin separated from black liquor by treatment of CO_2. As a result, the total sulfur content was reduced from 2.6 to 0.54%. This work is a continuation of investigations on desulfurization of kraft pulping by-products (exclude crude sulfate turpentine)—black liquor soap, crude and distilled tall oils, tall oil fatty and rosin acids and pitch (Kurzin et al. 2014; Trifonova 2015; Evdokimov et al. 2014, 2017a, b).

Materials and methods

Analytical reagent (AR)-grade sulfuric acid, perchloric acid, dimethylformamide, desulfurized benzene (total sulfur content less 3 ppm), sodium sulfite and acetic anhydride were purchased from the market (Vekton and LenReaktiv, Saint Petersburg). Silver ($\geq$99.99%, in wire, diameter 2.0 mm) was purchased from Sigma-Aldrich. Aqueous solutions of sulfuric and perchloric acids, as well as sodium sulfite solution, were prepared by the weight method. The total sulfur content in the lignin was determined by the standard test method according to ASTM D4294-16e1 (2016) by using 1.5 g for each sample. An Oxford Lab-X 3500 X-ray fluorescence spectrometer was used for analysis. Statistical errors of determination of the total sulfur content were estimated on the basis of the number of measurements. Each measurement was tested four times. The spent black liquor (from hardwood and softwood kraft pulping) was supplied by International Paper (Svetogorsk, Russia). This black liquor was used in the separation process of lignin.

Separation of lignin

Lignin from black liquor was isolated by treatment with 30 and 78% sulfuric acid (Komshilov et al. 1969; Kazakov et al. 2016), as well as 60% perchloric acid. For this purpose, 600 g black liquor (30% based on dry solids) was treated with 500 g solution of H_2SO_4 or $HClO_4$ (Table 1), stirred for 2 h at 80 °C and kept for 4 h at 25 °C. The lignin was further separated by filtration with glass filter funnel and thoroughly washed (20×500 g) with hot water (80 °C) and air-dried.

Method of the lignin desulfurization

The lignin samples (50 g) were heated without access of oxygen in a vacuum at 100 °C for 8 h, and extracted with benzene in a Soxhlet extractor for 10 h. After

Table 1 Total sulfur content in kraft lignin

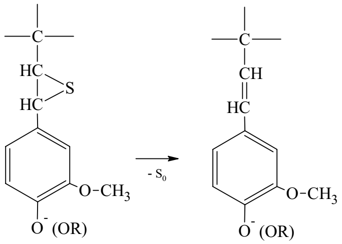
Reagent for lignin separation from black liquor	Total sulfur content (ppm)[a]				
	Before desulfurization	After consistent treatment with			
		Benzene	DMF + silver	Sodium sulfite solution	60% aqueous perchloric acid + acetic anhydride
30% H_2SO_4	27,800 ± 200	17,500 ± 150	14,200 ± 120	2210 ± 30	855 ± 20
78% H_2SO_4	28,400 ± 200	17,800 ± 150	16,100 ± 120	2470 ± 30	394 ± 15
60% $HClO_4$	23,800 ± 150	19,400 ± 150	10,400 ± 100	1730 ± 30	235 ± 10

[a] Repeatability $r = 0.4347 \times X^{0.6446}$, reproducibility $R = 1.9182 \times X^{0.6446}$, where X means the result of four tests

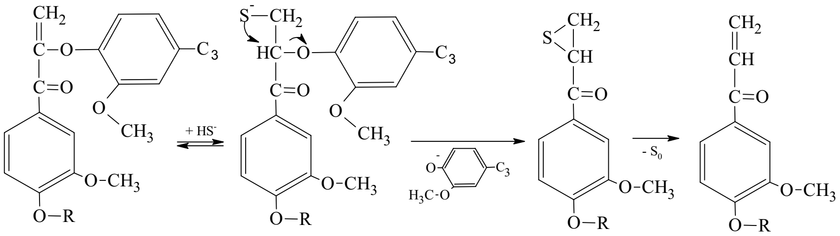
this, residual benzene was removed from the lignin samples by evaporation. Further, the lignin was mixed with 300 g of DMF and silver wire (8 g) and refluxed for 5 h. At the end, the lignin was separated from the silver and the solvent and mixed with 100 g of 5% aqueous sodium sulfite solution and refluxed for 1 h. At the end, the lignin was separated and thoroughly washed first with cold (5 °C) and then hot water (60 °C). The lignin was further separated and dried in vacuo. Furthermore a washing solution consisting of a mixture of 45 g 60% $HClO_4$ aqueous solution and 100 g acetic anhydride was added to 20 g of the lignin. The mixture was stirred for 8 h at 60 °C, cooled to 25 °C and allowed to stand for 2 h at 25 °C, and then the washing solution was removed. The washing was repeated twice. After water treatment (3 × 300 g) at 25 °C the lignin was dried in vacuum.

Results and discussion

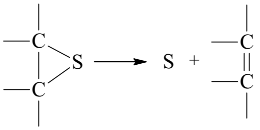
Based on the sulfur-containing lignin structures presented above, the desulfurization of sulfate lignin should be based on the removal and/or binding of thiol, thiirane (episulfide) and sulfide groups, as well as elemental sulfur. However, in the case of desulfurization of sulfate lignin samples obtained by treatment with sulfuric acid, they were initially treated with hot water to remove inorganic sulfur-containing anions (primarily HSO_4^-, SO_4^{2-} and other). It was known that significant portion of sulfur in the form of elemental sulfur splits off from α-episulfide (Gierer 1970, 1980, 1985)



or *β*-episulfide (Azarov et al. 1999) lignin structure by reactions.



The formation of episulfide as an intermediate in delignification reactions in the kraft pulping (Gierer 1970, 1980, 1985) is cited in many literature sources on wood and pulping chemistry (Komshilov et al. 1969; Fengel and Wegener 1984; Nepenin 1990; Sjöström 1993; Azarov et al. 1999; Svensson 2008). The aryl-substituted episulfides are difficult to hydrolyze, but they readily split off elemental sulfur upon heating (Sander 1966) by reaction



which corresponds to the above-mentioned schemes for the formation of elemental sulfur from lignin α- and β-episulfides. Lignin samples were heated without oxygen access in vacuum at 100 °C for 8 h. To remove the elemental sulfur formed in these conditions and the elemental sulfur originally found in samples of sulfate lignin, a two-stage method was used. In the first stage, elemental sulfur was extracted with desulfurized benzene. The known method is extraction of sulfur from sulfate lignin by pentane (Svensson 2008). However, benzene was chosen as an extractant; the solubility of sulfur in benzene is 2.1 g/100 g at 25 °C (Meyer 1976). It has to be noted that the successful extraction of elemental sulfur from black liquor by toluene is also known (Radoykova et al. 2013). The use of silver in DMF also contributes to the removal of elemental sulfur from lignin. The formation of a black surface layer of silver sulfide proves this. It is likely that the use of silver can also catalyze the desulfurization of episulfides and other sulfur-containing organic substances, for example sulfides. In the second stage, the treatment is done with 5% aqueous solution of sodium sulfite, which binds elemental sulfur to form thiosulfate

$$S + Na_2SO_3 \rightarrow Na_2S_2O_3,$$

and also neutralizes acidic sulfur compounds, thiols and, probably, formed sulfonic acids

$$\begin{gathered} RSH + Na_2SO_3 \rightarrow RSNa + NaHSO_3, \\ RSO_3H + Na_2SO_3 \rightarrow RSO_3Na + NaHSO_3. \end{gathered}$$

It is known (Bogomolov and Gorbunova 1974) that treatment with sodium sulfite reduces the content of sulfide and disulfide sulfur in sulfate lignin

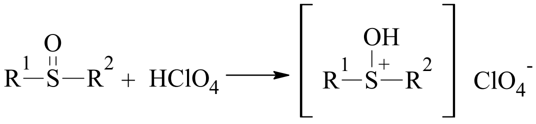
$$\begin{gathered} \text{R-S-R} + Na_2SO_3 + H_2O \rightarrow ROH + RH + Na_2S_2O_3, \\ \text{R-S-S-R} + 2Na_2SO_3 + H_2O \rightarrow ROH + RH + 2Na_2S_2O_3. \end{gathered}$$

However, Enkvist and Rinaman (1963) assumed that in the reaction of sodium sulfite with disulfide structures of lignin, the corresponding sodium thiolate and alkylthiosulfate are formed

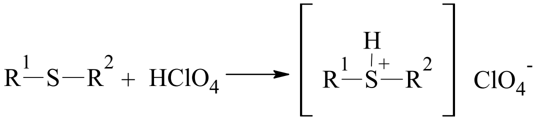
$$\text{R-S-S-R} + Na_2SO_3 \rightarrow RSNa + RSSO_3Na.$$

The use of sodium sulfite to reduce the content of total sulfur in sulfate lignin has a major drawback—the need for washing to remove sulfite and hydrosulfite ions. In addition, when sulfate lignin is treated with sodium thiosulfate, the thiosulfate lignin is formed (Zhigalov and Tishchenko 1962).

The presence of residual total sulfur after desulfurization in lignin samples can be explained by the presence of sulfoxides and sulfones formed during oxidation. To remove sulfoxides in the form of perchlorates of sulfonium salts (Oae 1977) from monomer structures of lignin, a mixture of 60% aqueous perchloric acid + acetic anhydride was used. Note that in this case sulfides of sulfate lignin will also form sulfonium salts.

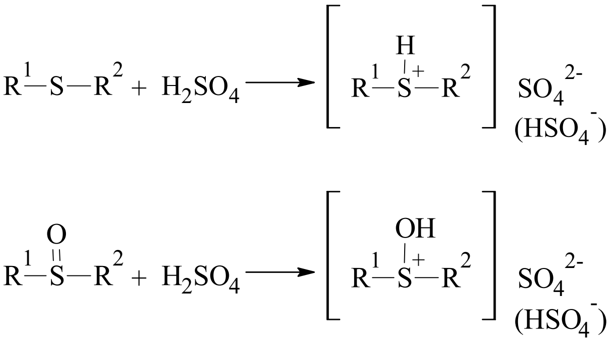


$$R^1{-}\overset{\overset{\large O}{\|}}{S}{-}R^2 + HClO_4 \longrightarrow \left[R^1{-}\overset{\overset{OH}{|}}{S^+}{-}R^2 \right] ClO_4^-$$



$$R^1{-}S{-}R^2 + HClO_4 \longrightarrow \left[R^1{-}\overset{\overset{H}{|}}{S^+}{-}R^2 \right] ClO_4^-$$

As can be seen from Table 1, the proposed method of reducing total sulfur is more effective for a sample of lignin separated by perchloric acid. The smaller total sulfur content in lignin samples isolated by treatment of 78% sulfuric acid can be explained by the fact that in this case (as opposed to using 30% sulfuric acid) the sulfates (or bisulfates) of sulfonium salts are formed (Oae 1977).



$$R^1{-}S{-}R^2 + H_2SO_4 \longrightarrow \left[R^1{-}\overset{H}{\overset{|}{S^{+}}}{-}R^2 \right] SO_4^{2-}\ (HSO_4^{-})$$

$$R^1{-}\overset{O}{\overset{\|}{S}}{-}R^2 + H_2SO_4 \longrightarrow \left[R^1{-}\overset{OH}{\overset{|}{S^{+}}}{-}R^2 \right] SO_4^{2-}\ (HSO_4^{-})$$

This is the main difference between the proposed method of desulfurization of sulfate lignin from the one used by Svensson (2008). The presence of residual sulfur can be explained by the presence of sulfone groups formed due to oxidation. Note that low-reactivity sulfone groups are the most difficult ones to remove. It is known that sulfones are hydrogenated under hard conditions (Oae 1977). In addition, information has been published on failed attempts to completely desulfurize sulfate lignin with strong reducing agents—lithium aluminum hydride (Gorbunova 1969) and Raney nickel (Field et al. 1958; Svensson 2008). Therefore, when desulfurizing sulfate lignin, the use of strong oxidizing agents that promote the formation of sulfones is not recommended. However, the statement is confirmed that oxidants can be used to remove the "sulfurous" smell of sulfate lignin (Kouisni et al. 2016).

Conclusion

A method of reducing the content of total sulfur in samples of sulfate lignin separated from black liquor by sulfuric and perchloric acids is proposed. The method is based on the sequential removal of elemental sulfur, thiol, thiirane, sulfide and sulfoxide groups of lignin by treatment with benzene (after heating at 100 °C in vacuum), silver in DMF, sodium sulfite and a mixture of 60% aqueous perchloric acid + acetic anhydride. The content of total sulfur in the purified samples of sulfate lignin was reduced from 23,800 to 27,800 ppm to 235–855 ppm.

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