



# Lignin cationization with glycidyltrimethylammonium chloride aiming at water purification applications



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## ABSTRACT

Hardwood organosolv lignin (OSL) and enzymatic hydrolysis lignin (EHL) from softwood were cationized by glycidyltrimethylammonium chloride (GTAC) as new lignin starting materials for the reaction. The products were in detail characterized by  $^{31}\text{P}$ -NMR to elucidate the reactivity of different lignin functionalities in cationization with GTAC. For OSL, a high cationization level (degree of substitution 0.74) was reached leading to a water-soluble product. For EHL, low solubility and lower reactivity were observed, likely due to the high saccharide content. Further, lower reactivity of the guaiacyl type lignin present in softwood, compared to syringyl type lignin in hardwoods, which was shown to react efficiently during the derivatization of OSL, probably played a role. In parallel to cationization, an increase of carboxylic acids (from 0.03 up to 0.55 mmol/g) in the lignin was observed as an unexpected side reaction, possibly as a result of alkaline oxygen oxidation. The applicability of the cationized lignins was tested for water purification applications in three model systems which have only sparingly been studied with cationized lignins. GTAC-OSL and GTAC-EHL were found promising for sulfate removal, with sulfate sorption capacities of up to 54 mg/g. GTAC-OSL was also found suitable for promoting kaolin settling and to some extent for humic acid coagulation.

## 1. Introduction

Lignin is, after cellulose, the second most abundant biopolymer in the World and constitutes approximately 25% of the terrestrial plant biomass (Rastogi and Dwivedi, 2008). The pulping industry produces significant amounts of sulfite and kraft lignin, of which only a small part is sold as technical lignin whereas the majority is incinerated for energy. Future biorefineries will bring new lignin products, such as organosolv (OSL) and enzymatic hydrolysis lignins (EHL) on the market. Especially EHL, a by-product of the emerging cellulosic bioethanol industry, is expected to be produced in enormous quantities. OSLs are characterized by high purity, solubility in alkaline solutions and thus high reactivity and transformability (Rösch and Mülhaupt, 1994). EHL is fundamentally different from OSL, as it often contains high amounts of bound residual polysaccharides (mostly insoluble cellulose) after the enzymatic hydrolysis (Vármai et al., 2010), which decreases its purity, solubility and general reactivity. Apart from incineration, few industrial applications have so far been developed for EHL.

Chemical lignin charge modifications by cationization (Kong et al., 2015; Matsushita and Yasuda, 2003), anionization (Cerrutti et al., 2012; Kalliola et al., 2015) or amination (Du et al., 2014; Matsushita

and Yasuda, 2003) have been reported in the literature. Many lignin derivatizations are nucleophilic substitution reactions performed in alkaline solution, in which the lignin is both soluble and activated as the phenolic groups become nucleophilic phenolates (Kong et al., 2015). Lignin derivatization is of particular interest as a means of tuning lignin solubility. Accordingly, introduction of charged groups onto lignin has been shown to increase its water solubility (Kong et al., 2015). Lignin cationization for water purification applications has been achieved via two alternative routes: amination or direct derivatization of the lignin with a quaternary ammonium group. Amination of lignin with dimethylamine via the Mannich reaction has been reported to produce a highly cationic lignin coagulant (Fang et al., 2010). The charge and coagulation efficiency of the aminated lignin are directly dependent on pH, as low pH leads to protonation of the amine groups. Cationization with e.g. glycidyltrimethylammonium chloride (GTAC) introduces quaternary ammonium groups to the lignin, which are charged irrespective of the pH. These have been reported to be useful as anion exchange resins (Matsushita and Yasuda, 2003) or flocculants for dye removal in waste waters (Kong et al., 2015).

Coagulation/flocculation followed by solid/liquid separation, such as sedimentation, filtration or flotation, is one of the most common ways to remove suspended or dissolved solids, colloids, and organic

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matter present in water (Lee et al., 2014; Yang et al., 2016). Coagulants neutralize repulsive charges between particles and colloids and allow bigger aggregates to be settled. The most widely used flocculants are synthetic water soluble polymers based on polyacrylamide and its derivatives, but the use of synthetic flocculants suffers from relatively high production costs and environmental contamination caused by residual unreacted monomers, which typically are toxic and non-biodegradable (Ahmed et al., 2016; Lee et al., 2014; Yang et al., 2016). Thus, there are activities to develop natural coagulants and flocculants based on renewable biopolymers with widespread availability, low price, non-toxicity and biodegradability. Cationic GTAC derivatives of chitin, starch, nanocrystalline cellulose and hemicelluloses have been studied as flocculants, as reviewed by Kong et al. (2015). Good results have been obtained in dye removal from aqueous solutions using quaternary ammonium salts of lignin in a number of studies (Fang et al., 2003; Kong et al., 2015; Yang et al., 2008). The flocculation efficiency of quaternary ammonium salts of lignin has further been increased by crosslinking it to water-soluble sodium alginate (Zhang et al., 2013).

So far most studies on the use of cationized lignin in water purification applications have been concentrated on removing anionic dyes, the removal of which is easy to follow by common UV–vis spectrometry, but few other water purification applications have been reported with these materials. In this article we describe the synthesis of GTAC-derivatized OSL and EHL and chemical characterization of both the starting materials and products. The aim of the study was to produce GTAC-lignins with different solubility and cationization degree and pinpoint how the different solubility and reactivity characteristics of OSL and EHL could be used for optimizing GTAC-lignin performance in different water purification applications. The cationized lignins were screened for applicability in three different model water purification applications, i.e. sulfate removal, humic acid removal, and kaolin settling.

## 2. Materials and methods

### 2.1. Materials

Hardwood organosolv lignin (OSL) from an ethanol-based organosolv process was obtained from Fraunhofer Center for Chemical-Biotechnological Processes CBP (Leuna, Germany) and spruce enzymatic hydrolysis lignin (EHL) after steam explosion pretreatment from SP Technical Research Institute of Sweden (Skellefteå, Sweden) as kind gifts. The EHL was freeze-dried and milled with a Thomas Scientific 2279-K38 Variable Speed Digital ED-5 Wiley mill equipped with a 1 mm sieve.

### 2.2. Chemical characterization

Elemental analysis (carbon, hydrogen, oxygen, nitrogen and sulfur measured) was done with a Thermo Scientific Flash 2000 Organic Elemental Analyser (Rockford, IL, USA). Composition analysis was performed according to the NREL procedure (Sluiter et al., 2008) with the carbohydrates analyzed from the acid hydrolysate by HPLC as described by Tenkanen and Siika-aho (2000).

Zeta potential was measured with a Zetasizer nano ZS (Malvern Instruments, Malvern, UK) in either milli-Q water or 0.1 M NaOH solution. The instrument measures the electrophoretic mobility of particles, which is converted into zeta potential values using the Smoluchowski model.

The amount (mmol/g) of aliphatic –OH, carboxylic –OH and phenolic –OH (*para*-OH phenyl, condensed and syringyl –OH, guaiacyl –OH and catechol –OH groups) was quantified by <sup>31</sup>P-NMR after phosphorylation as previously described (Granata and Argyropoulos, 1995). Conductivity measurements were performed with a Hach (Loveland, CO, USA) HQ14d conductivity meter.

The charge of untreated and cationized lignins was determined by polyelectrolyte titration (SCAN-W 12:04) combined with streaming current detection (Mütek™ PCD-04 and titrator T3, BTG Instruments GmbH, Herrsching, Germany). A lignin solution of about 1 wt-% was prepared using 0.01 M sodium citrate buffer (pH 6). The solution was titrated using cationic and anionic polymers, diallyldimethylammonium chloride (polyDADMAC) or polyethene sodiumsulfonate (PESNa) as titrants. Lignin charge (meq/g) was computed based on the amount of polymer consumed at the equivalence point of the titration i.e. at the point where the measured potential passes zero. All the lignin solutions were titrated at pH 7.4–8.6.

### 2.3. Synthesis of lignin glycidyltrimethylammonium chloride (GTAC) derivatives

OSL or EHL was mixed in 0.5 M NaOH solution at 10 wt-% consistency until dissolved (OSL) or finely dispersed (EHL) and glycidyltrimethylammonium chloride (GTAC) was added to the mixture. The GTAC dosage was calculated as mol-% of the analyzed total amount of phenolic groups. In the case of EHL the phenolic groups could not be analyzed by <sup>31</sup>P-NMR due to solubility issues and EHL was thus for GTAC dosage calculations assumed to contain as many phenolic groups as analyzed in OSL per weight unit. The synthesis was performed at 60 °C under gentle magnetic agitation for 20 h. The reaction completed, the mixture was cooled to room temperature and then poured into cellulose ester dialysis membranes (Spectra/Por™ cellulose ester dialysis membranes, Spectrum Laboratories, CA, USA) with a molecular weight cutoff of 500–1000 g/mol. The reaction mixture was dialyzed against ion-exchanged water until the conductivity and pH value of the permeate did not change after exchanging washing water. Finally, the lignin solution was freeze-dried to yield the product as a dark-brown fleecy solid.

### 2.4. Water purification testing

The synthesized GTAC-lignins were tested for sulfate removal and kaolin settling, and as a coagulant for humic acid. Kaolin was chosen as a model inorganic suspended solid and humic acid as a natural organic matter present in natural waters and wastewaters.

#### 2.4.1. Sulfate removal

The untreated lignins (OSL, EHL) and selected cationized lignins (GTAC-OSL produced with 100 and 200 mol-%, and GTAC-EHL produced with estimated 200 mol-% GTAC dosage) were tested for their capability to remove SO<sub>4</sub><sup>2-</sup> anions in aqueous solution at pH 3, 6, and 9 at room temperature. The experimental solutions of sulfate (100 mg/L) were prepared by dissolving analytical grade Na<sub>2</sub>SO<sub>4</sub> in ion-exchanged water. Solution pH was adjusted using 0.1 M HCl (pH 3) or 0.1 M NaOH (pH 9). The solution was stirred and GTAC-lignin was added at a dosage of 100 mg/10 mg SO<sub>4</sub><sup>2-</sup>. Sampling was done at 10, 30, and 60 min after the lignin addition. For sulfate analysis, the sample solution was filtered through a 0.2 μm membrane (Whatman FP 30/0,2 CA-S, GE Healthcare, Little Chalfont, UK) to separate the lignin material, i.e. the adsorbent. OSL, EHL, and cationized EHL could be separated by the membrane. Cationized OSLs (200 mol-% GTAC and partly 100 mol-% GTAC depending on pH) were soluble and passed the membrane, which was seen as brown color in the filtrate. In a parallel protocol, a 60 min sample was withdrawn and frozen to –18 °C. Freezing caused aggregation and sedimentation of the lignin material, which was separated by decanting from the supernatant after melting the solution.

All the solutions were measured for residual sulfate anions by using a P/ACE MDQ capillary electrophoresis (CE) instrument equipped with a photodiode array UV–vis detector working via indirect detection at 230 nm (Beckman-Coulter Inc., Brea, CA, USA) and quantified based on sulfate standards. Electrolyte solutions were commercial from Analis (Ceofix Anions 5, Ordior/Analis, part number: 10-0004650). A bare

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