

Esterified lignins from *Pinus caribaea* as bentonite-dispersing agents

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ABSTRACT: Chemical modification of kraft lignin from *Pinus caribaea* (Sénécl.) W.H.G. was performed with cyclic anhydrides (succinic, maleic and glutaric) assisted by microwave radiation. Esterification of the lignin was proven by the mass increase and Fourier Transform Infrared (FTIR) spectroscopy. Aqueous suspensions of bentonite were prepared using unmodified lignin and the corresponding derivatives as dispersants. Suspensions were evaluated in term of stability, viscosity and dispersibility. The esterified derivatives showed better dispersing properties than the neat lignin because the derivatives-based suspensions were less viscous. The dispersing properties of lignin and the esterified derivatives were compared with those of a high-molecular-weight lignin fraction obtained by ultrafiltration. In addition, two commercial lignosulfonate dispersants commonly used for drilling muds were used as references. The high-molecular-weight esterified derivatives proved to be better dispersants than their unfractionated counterparts. In general, the esterified derivatives showed similar properties to those obtained with the commercial dispersants. Modified lignin based on succinic-, maleic- and glutaric-anhydride is expected to play a key role in the design of novel bio-based dispersants for drilling-mud applications.

KEYWORDS: lignin, esterification, dispersant, bentonite.

Lignin is the second most abundant polymer in nature (15–30 wt.% of lignocellulosic biomass) and is obtained as a byproduct of the kraft process during the production of pulp and paper. The process allows

extraction of >90% of the lignin from wood. The amount of lignin extracted from pulp-manufacturing operations worldwide is estimated to exceed 70 million tonnes per year. However, <2% is recovered for use as a renewable chemical (Chakar & Ragauskas, 2004; Lora, 2008).

Kraft lignin chemistry has been a subject of great interest because of the interesting properties of lignin

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derivatives. In fact, it is expected that lignin will play an important role as an alternative in petroleum-based chemistry. One of the potential applications of lignin is as a natural surfactant. Polar groups from the aromatic moieties confer on lignin the dual affinity typical in surfactants (Selyanina & Selivanova, 2007; Rojas *et al.*, 2007; Selyanina *et al.*, 2007). However, the surface activity of lignin must be modified for the applications envisaged (Laurichesse & Avérous, 2014). The grafting of polar or non-polar functional groups may vary the hydrophilic-lipophilic balance (HLB) for the design of lignin-based surfactants (Homma *et al.*, 2008, 2010; Cerrutti *et al.*, 2012; Gan *et al.*, 2013; Chen *et al.*, 2014; Li *et al.*, 2014; Lin *et al.*, 2014; Zhou *et al.*, 2015; Konduri *et al.*, 2015; Chen *et al.*, 2016).

On the other hand, cyclic anhydrides are commonly used for lignin derivatization, as the bifunctional ester-carboxylic acid moieties confer significant change on physicochemical properties (Xiao *et al.*, 2001; Thielemans & Wool, 2005).

The best known commercial lignin-based surfactants are lignosulfonates. Sulfonated lignin has been evaluated as a dispersing agent for gypsum particles (Matsushita & Yasuda, 2005; Matsushita *et al.*, 2009), coal (Zhou *et al.*, 2007) and cement (Ouyang *et al.*, 2009). Previous works (Zhou *et al.*, 2007; Yang *et al.*, 2007) indicated that sulfonated lignin fractions of high molecular weight showed greater dispersing capacity and lower viscosity.

The main objective of this work was to evaluate the bentonite dispersant properties of kraft lignin derivatives esterified with cyclic anhydrides (succinic, maleic and glutaric), by using microwave radiation (Delgado *et al.*, 2012, 2015). The dispersing properties of lignin and lignin derivatives were compared with those of a high molecular weight (MW) fraction of lignin and the corresponding derivatives. In addition, two commercial lignosulfonate dispersants commonly used in the formulation of drilling sludge were used in order to compare the results.

MATERIALS AND METHODS

Pine (*Pinus caribaea*) kraft lignin (KL) was used. The KL was isolated from the black liquor of Smurfit Mocarpe Carton de Venezuela Company by acid precipitation (pH=3). The high molecular weight fraction (HKL) was obtained by ultrafiltration using a 15 KDa ceramic membrane according to a method previously reported (Delgado *et al.*, 2012). Both lignins were esterified with succinic

(SA, Riedel-de-Haën, 99%), maleic (MA, Riedel-de-Haën, 99.9%) and glutaric (GA, TCI America, 99.9%) anhydride. Acetonitrile (Burdick & Jackson, 99.9%), ethanol (Merck, 99.9%), hydrochloric acid (Sigma Aldrich, 37%), sodium hydroxide (Merck, 99.9%) and potassium bromide (Sigma Aldrich, ≥ 99.0%) were used. Bentonite was provided by Baker Hughes Company (USA). Two commercial dispersants were used (ammonium lignosulfonate (DP875-LS) provided by M&P Supply & Services, C.A., Italy, and sodium lignosulfonate (CF-LS) provided by Borregard Lignotech, Norway).

Lignin esterification

The proposed mechanism for lignin esterification is shown in Fig. 1. Two fundamental steps occur: (1) a nucleophilic attack by the hydroxyl groups (both phenolic and aliphatic), causing ring opening of the cyclic anhydride, and (2) the deprotonation of the hydroxyl groups for the formation of the novel carboxylic acid functional groups.

The esterification reactions were carried out in a microwave oven (Panasonic, 1200 W). The reaction conditions are summarized in Table 1. Succinylated lignin (SL), maleilated lignin (ML), glutarated lignin (GL), high MW succinylated lignin (HSL), high MW maleilated lignin (HML) and high MW glutarated lignin (HGL) were obtained. In order to synthesize SL and HSL, the lignin and succinic anhydride were mixed in a glass reactor with 5 mL of an acetonitrile/ethanol (ACN/EtOH ratio, 4:1). The mixture was placed in an ultrasonic bath (Branson, CPX) for 5 min and then the reactants were subjected to microwave irradiation (60–80 s); 5 mL of 5% HCl solution (wt./v) was then added to precipitate the products, which were centrifuged (IEC, Centra CL2) for 15 min at 5000 rpm. The product was washed twice with distilled water to remove excess anhydride, centrifuged and finally dried in a vacuum oven (Cole-Parmer, EW-05053-10) at 50°C for 12 h (Delgado *et al.*, 2015). In order to synthesize ML and HML as well as GL and HGL products the same procedure was followed, except for the fact that both reactions were carried out in solid phase (Delgado *et al.*, 2012).

After the chemical modification the lignin products were weighed to determine the increase in weight (WI %) according to the following equation (Gordobil *et al.*, 2016):

$$\text{WI (\%)} = \left[\frac{m_1 - m_0}{m_0} \right] \times 100 \quad (1)$$