

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

NACARID DELGADO^{1,2,*}, FREDY YSAMBERTT³, RAÚL OCHOA², GERSON CHÁVEZ², BÉLGICA BRAVO², JORGE SANTOS¹ AND DANNY E. GARCÍA^{4,5,6}

¹Área de Bioproductos, Unidad de Desarrollo Tecnológico (UDT), Universidad de Concepción, Coronel, Biobío, Chile

²Laboratorio de Petroquímica y Surfactantes (LPS), Departamento de Química, Facultad Experimental de Ciencias, Universidad del Zulia, Maracaibo, Venezuela

³Laboratorio de Instrumentación Analítica (LIA), Departamento de Química, Facultad Experimental de Ciencias, Universidad del Zulia, Maracaibo, Venezuela

⁴Laboratorio de Fitoquímica, Departamento de Química Ambiental, Facultad de Ciencias, Universidad Católica de la Santísima Concepción (UCSC), Biobío, Chile

⁵Centro de Investigación en Biodiversidad y Ambientes Sustentables (CIBAS), UCSC, Biobío, Chile

⁶Investigador Asociado Área de Bioproductos, UDT, UdeC, Concepción, Biobío, Chile

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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

*E-mail: nacariddelgado@gmail.com
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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):

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

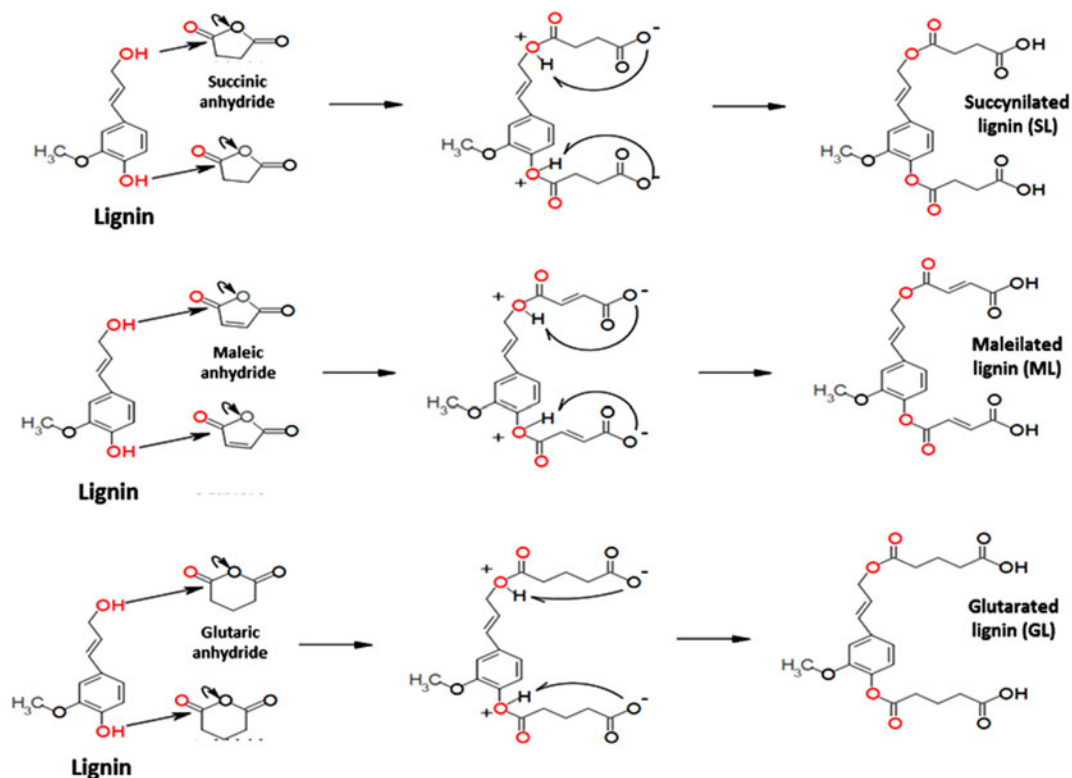


FIG. 1. Mechanism of lignin esterification with cyclic anhydrides.

where m_0 is the initial weight of dried lignin sample (g) and m_1 is the weight of lignin after the esterification reaction (g).

FTIR spectra were collected between 4000 and 400 cm^{-1} . A resolution of 4 cm^{-1} and 25 scans were used during spectra collection.

Characterization of lignin and esterified lignin

Lignin and esterified derivatives were characterized by Fourier Transform Infrared Spectroscopy (FTIR, Shimadzu; 8400S) with IR Solution software. The

Preparation of bentonite suspensions

Aqueous bentonite suspensions were prepared by mixing either 50 mL of (1) a solution of lignin or (2) a solution of the corresponding derivatives

TABLE 1. Reaction conditions for lignin esterification using microwave irradiation.

Derivative	Lignin (mg)	Anhydride (mg)	Solvent	Time (s)	Power (w)
SL/HSL	100	200	ACN/EtOH 5 mL (4:1)	80	1200
ML/HML	100	500	None	60	1200
GL/HGL	100	200	None	60	1200

SL: succinylated lignin; HSL: High MW succinylated lignin; ML: maleilated lignin; HML: high MW maleilated lignin; GL: glutarated lignin; HGL: high MW glutarated lignin; ACN: acetonitrile; EtOH: ethanol.

(0–5000 mg/L) in 0.1 M NaOH with bentonite (2% wt/v). Bentonite was added gradually under constant stirring using a blender mixer (IKA-WERKE; Eurostar) at 150 rpm.

After bentonite addition, the suspensions were stirred at 500 rpm (10 min) for homogenization. In order to compare the dispersant properties of the synthesized derivatives, the commercial dispersants, as well as the high molecular weight lignin derivative solutions, were prepared. A dispersant concentration of 5000 mg/L, and a bentonite content of 7% (wt/v) were used. These conditions were defined by considering the concentration of components commonly used for drilling mud (Caenn *et al.*, 2011).

Stability of bentonite suspensions

The stability of the suspensions was determined under static conditions by the volumetric separation method. The suspensions were taken to graduated tubes, which were maintained at 25°C. The volume of separated water was monitored every 24 hours over a period of 30 days. The experiments were carried out in triplicate and the average value was reported.

Viscosity and rheological behaviour of bentonite suspensions

A rheometer (Brookfield; LVDV-III+) was used. The relationship between the shear stress and the shear rate was evaluated. Viscosity was estimated using the consistency index described in the equation of the Power Law model (2), determined with the *Rheocalc32* software.

$$\log \tau = \log K + n \log \gamma \quad (2)$$

where τ = shear stress, γ = shear rate, K = consistency index and n = flow index.

The experiments were carried out in triplicate and the average value was reported.

Dispersibility of bentonite suspensions

Dispersibility of lignin and lignin derivatives for bentonite suspensions was measured with modifications according to previous reports (Homma *et al.*, 2010). The bentonite suspension (10 mL) was poured into a plastic cylinder (25 mm diameter, 25 mm height), the bottom of which was placed on a glass plate. After 60 s, the cylinder was removed to give the bentonite suspension spread on the glass. The final diameter of the bentonite suspension was measured.

The experiment was repeated at least three times. The average value was used to calculate the flow value (3) (Nadif *et al.*, 2002; Homma *et al.*, 2010):

$$\text{Flow value (\%)} = \frac{\Phi_{\text{final}} - \Phi_{\text{initial}}}{\Phi_{\text{initial}}} \times 100 \quad (3)$$

where Φ_{final} is the final diameter of bentonite suspension and Φ_{initial} is the initial diameter (25 mm).

RESULTS AND DISCUSSION

Lignin esterification evidence

The yield of the lignin esterification reaction was evaluated using the weight increase (WI%) value, as an indication of the degree of conversion to esters of several macromolecules (Liu *et al.*, 2008; Maldhure *et al.*, 2011; Ratanakamnuana *et al.*, 2012; Gordobil *et al.*, 2016). The WI values which are shown in Fig. 2 are in accord with those reported in previous works (Delgado *et al.*, 2012, 2014, 2015).

The esterification of KL was confirmed by FTIR spectroscopy (Fig. 3). The FTIR spectra of the neat KL, and the KL derivatives show the typical signals described in similar studies (Nada *et al.*, 1998; Rana *et al.*, 2010; Toledano *et al.*, 2013). A broad band at $\sim 3400 \text{ cm}^{-1}$ (hydroxyl groups stretching), as well as the bands appearing at 2941 and 2846 cm^{-1} (C-H stretching in methyl and methylene groups), were observed. In addition, the bands at 1595, 1510 and 1427 cm^{-1} are attributed to the vibrations of the aromatic skeleton, and the bands between 1000 and 1250 cm^{-1} are assigned to the C–O stretching of methoxyl groups and of alcohols.

The KL also shows a typical band (1700 cm^{-1}) attributed to carbonyl groups, commonly associated

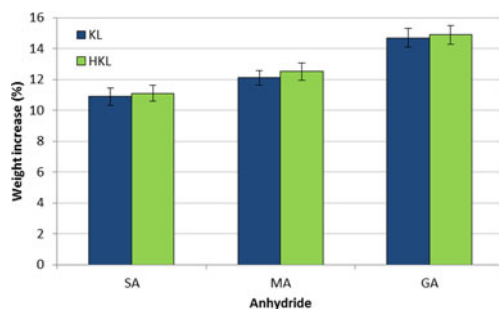


FIG. 2. Weight increase (WI %) of KL and HKL upon esterification (SA: succinic anhydride, MA: maleic anhydride, GA: glutaric anhydride).

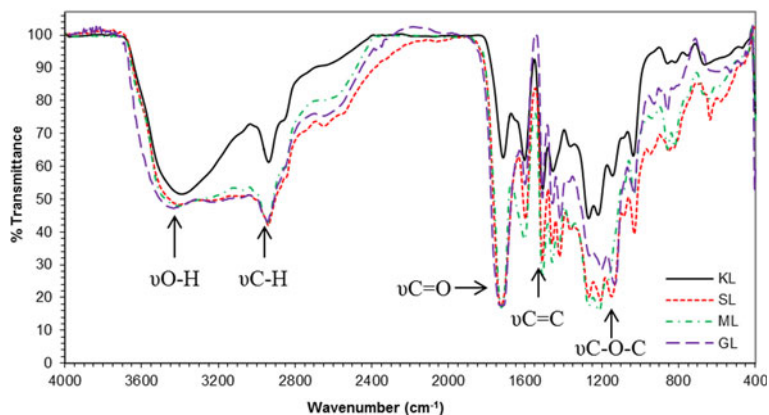


FIG. 3. FTIR spectra of KL and KL derivatives (SL: succinated lignin, ML: maleilated lignin, GL: glutarated lignin).

with the acid precipitation process used for the isolation of the lignin from the black liquor. Such apparent degradation of lignin has been also reported by Boeriu *et al.* (2004) as a consequence of the oxidation.

The spectra of the esterified KL-based products (SL, ML and GL) show a sharp band at $\sim 1725\text{ cm}^{-1}$, corresponding to carbonyl groups. The signals of the ester groups (1750 cm^{-1}), and carboxylic acids (1712 cm^{-1}) overlap. The intensity of the aforementioned band is greater than that of the KL. Such spectral differences confirm that esterification was successful (Xiao *et al.*, 2001; Thielemans & Wool, 2005; Maldhure *et al.*, 2011). The increase in absorption at $\sim 1250\text{--}1100\text{ cm}^{-1}$ (stretching of the C–O bond of esters and carboxylic acids), as well as a slight change in the aliphatic CH tension signal intensity ($2950\text{--}2870\text{ cm}^{-1}$), and the flexural C–H vibration (1460 cm^{-1}) are additional insights into the lignin esterification.

The results are in accord with Xiao *et al.* (2001), who performed the chemical modification of lignin with SA using conventional heating (1–12 h), and with Maldhure *et al.* (2011), who achieved the esterification of lignin with MA using microwaves in short reaction times (20 min). The modified products showed similar structural features as shown by FTIR. However, the use of microwaves allowed the preparation of esters from lignin in a single step in very short reaction times (60–80 s).

Dispersing properties of lignin and esterified lignin

The stability, dispersibility and rheological properties of aqueous bentonite (2 wt. %/v) were evaluated by

varying the concentration of the dispersants (lignin and esterified lignin) between 0 and 5000 mg L^{-1} .

Stability

The stability was evaluated taking into account the time for separating 40% of the total volume of the suspension ($t_{40\%}$). Variation in $t_{40\%}$ as a function of KL concentration and of the esterified derivative is shown in Fig. 4. The esterified derivatives-based suspension took longer to separate than those in which KL was used, indicating that derivatives have better dispersing properties of bentonite than the unmodified lignin. The result is in accord with previous works where greater surface activity of esterified lignins was reported (Delgado *et al.*, 2012, 2014).

Stable suspensions were prepared with ML as a dispersant, apparently due to the unsaturated chain.

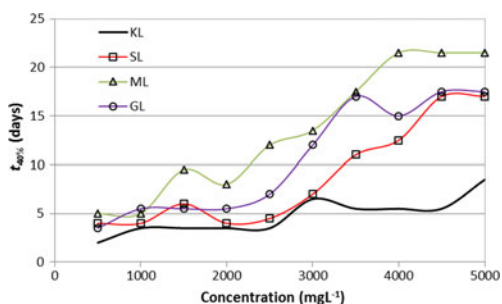


FIG. 4. Stability of aqueous suspensions of bentonite as a function of the concentration of KL and esterified derivatives (2 wt. %/v bentonite; $T = 25^\circ\text{C}$) $t_{40\%}$: time for separating 40% of the total volume of the suspension.

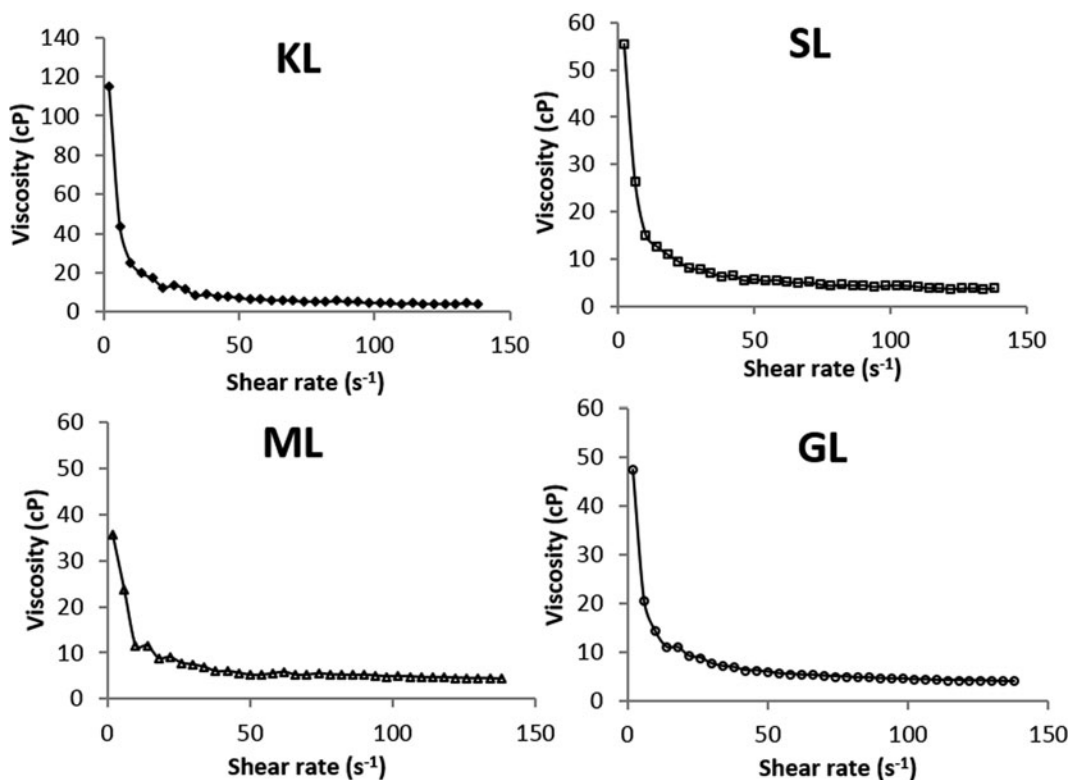


FIG. 5. Variation of viscosity for aqueous bentonite formulated with KL and esterified derivatives (2 wt. %/v of bentonite; 5000 mg L⁻¹ of KL or KL-based derivatives; $T = 25^{\circ}\text{C}$).

The α,β -unsaturated carboxylate group confers a rigid constraint in comparison to the rest of the derivatives. Some evidence suggests that structural constraints of surface-level arrangements stabilize or destabilize the dispersing system. Similar results were obtained by Zürcher & Graule (2005) who compared the dispersing properties of palmitic acid, stearic acid and oleic acid. Dispersions with oleic acid showed lower viscosity compared to the other two fatty acids listed. This difference, despite the similarity in the chain length, is probably due to the presence of the double bond in the oleic acid chain, which increases the polarizability of the molecule.

Rheological behaviour

The viscosity of bentonite suspensions decreases with increasing shear rate for KL- and esterified derivatives (Fig. 5), suggesting that the bentonite suspensions behave as non-Newtonian fluids (pseudoplastic type). This is because the derivatives-based

suspensions show lower viscosity than suspensions prepared with unmodified lignin.

The consistency index decreases as the concentration of the dispersants increases, as shown in Fig. 6a. The results suggest that both KL and the esterified derivatives show bentonite-dispersing properties. Also, the viscosity of the derivatives-based suspensions was lowest. In addition, the stability trends confirm that the esterified derivatives are better dispersants than the unmodified lignin.

The surface tension as a function of the concentration is illustrated in Fig. 6a. In order to linearize the trend, the data were transformed by a logarithmic model. The variation of the consistency index is shown in Fig. 6(b-d). The results allow the approximate point at which the viscosity reduction trend tends to be constant (optimum dispersion concentration, ODC) to be determined. Such a value corresponds to: (1) the point at which the surface of the bentonite particles is saturated with the dispersant; and (2) the concentration at which the dispersant shows maximum effectiveness.

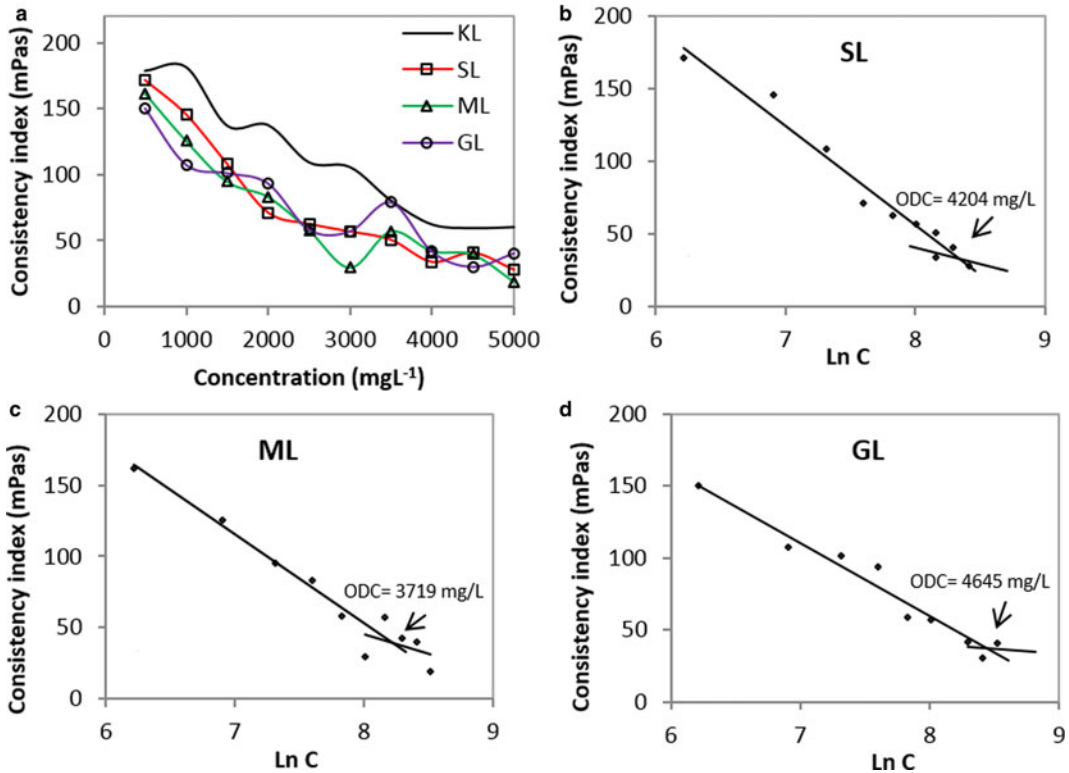


FIG. 6. Consistency index as a function of concentration for: (a) KL and the esterified derivatives; (b) SL; (c) ML; (d) GL (2 wt.%/v of bentonite; $T = 25^{\circ}\text{C}$).

The ML derivative displays minimum ODC, indicating that a smaller amount of ML dispersant would be necessary to achieve comparable viscosity by decreasing the SL- and GL-based dispersants.

Dispersibility

The variation of the flow value as a function of the concentration is shown in Fig. 7. In addition, the flow value of the referential suspension prepared without any dispersant is provided.

The maximum flow value is close to 4500 mg L^{-1} , 4000 mg L^{-1} and $\sim 4500\text{ mg L}^{-1}$ for SL, ML and GL, respectively, confirming that at the aforementioned concentrations the derivatives show a greater dispersing capacity. Although the ODC was calculated from a mathematical model, the results show a good correlation with the experimentally calculated dispersibility.

The suspensions prepared with the esterified derivatives have better dispersing properties than the

unmodified lignin. The ML derivative induces the most stable and least viscous suspensions, with a greater dispersibility. Both lignin and the esterified derivatives provide bentonite dispersing properties considering the flow value of the referential suspensions.

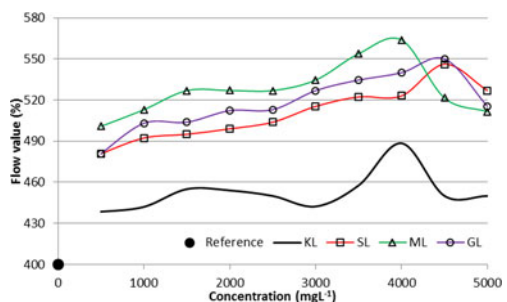


FIG. 7. Dispersibility of aqueous suspensions of bentonite prepared with KL and the corresponding esterified derivatives (2 wt.%/v of bentonite; $T = 25^{\circ}\text{C}$).

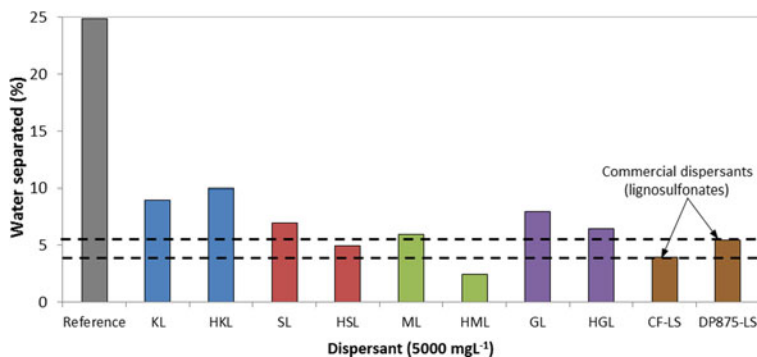


FIG. 8. Percentage of separated aqueous phase in bentonite suspensions prepared with several dispersants (7 wt.%/v of bentonite, $t = 30$ days, $T = 25$ °C) CF-LS: commercial sodium lignosulfonate, DP875-LS: commercial ammonium lignosulfonate.

The double bond from the carboxylic chain of the derivatives appears to have a favourable effect on the dispersing properties, as the ML-based derivatives show a more stabilizing effect of the suspensions (lower ODC).

Comparison of the dispersing properties

It is well known that high-molecular-weight lignin and lignosulfonates show better dispersing properties than their corresponding unfractionated counterparts (Zhou *et al.*, 2007; Yang *et al.*, 2007; Li & Ge, 2011). Therefore, the dispersing results were compared with those obtained using a high-molar-weight lignin fraction (HKL) and the corresponding esterified derivatives.

The HKL-based suspensions were more stable than those obtained using unfractionated derivatives. In addition, only the high-molecular-weight derivatives showed stability results comparable to those obtained

using the commercial dispersants. In fact, the HML-based suspensions were highly stable in comparison to the commercial dispersants (Fig. 8).

Suspensions formulated with high-molecular-weight polyphenol-based dispersants were less viscous than those formulated with the unfractionated counterparts (Fig. 9). This is in accordance with the finding about stability. In addition, the viscosity of the HML- and HGL-based systems is lower than that of the DP875-LS reference, and slightly higher than that of the CF-LS counterpart.

All systems formulated with high-molecular-weight lignin fraction are more fluid than their unfractionated counterparts (Fig. 10). The fluidity of the systems formulated with dispersants of high molar weight is comparable to that of the DP875-LS dispersant, but slightly lower than that of the CF-LS dispersant.

In general, the high-molecular-weight esterified derivatives possess better dispersing properties than

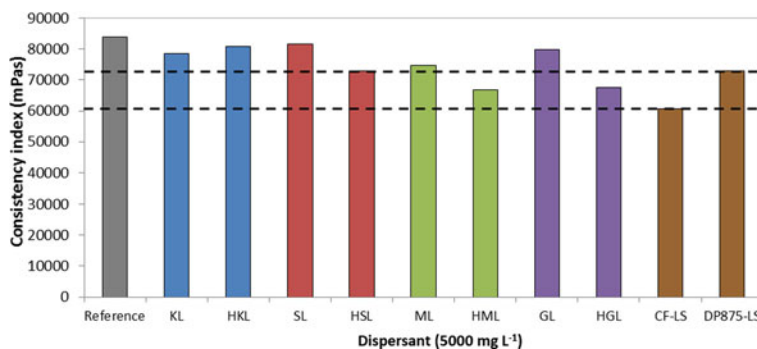


FIG. 9. Consistency index of bentonite suspensions prepared with different dispersants (7 wt.%/v of bentonite; $T = 25$ °C) CF-LS: commercial sodium lignosulfonate, DP875-LS: commercial ammonium lignosulfonate.

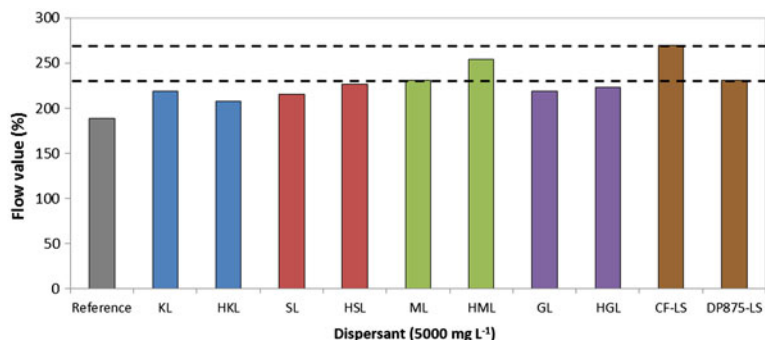


FIG. 10. Dispersibility of bentonite suspensions prepared with several dispersants (7 wt.%/v of bentonite; $T = 25^{\circ}\text{C}$)
 CF-LS: commercial sodium lignosulfonate, DP875-LS: commercial ammonium lignosulfonate.

their unmodified counterparts. This result may be explained by the effect of steric hindrance on the stabilization of the suspensions. In fact, the high-molecular-weight derivatives appear to prevent flocculation/aggregation due to the molecular size.

On the other hand, the HML derivative shows the most stable and least viscous suspensions. Finally, the effectiveness of the high-molecular-weight dispersants was similar to the commercial products (DP875-LS, CF-LS). These results indicate that esterification is a viable alternative to be used in tailoring the dispersing properties of lignin for the formulation of bentonite drilling muds in the oil industry.

CONCLUSIONS

Lignin and high-molecular-weight fractions of lignin were modified with cyclic anhydrides under microwave radiation. The esterification was proven by the increase in mass, as well as by FTIR spectroscopy. The lignin esterified derivatives synthesized show better dispersing properties of bentonite than unmodified lignin. The ML-based derivative exhibited better dispersant properties in terms of the higher stabilizing capacity of suspensions, and the lower ODC. Structural features may be the main reason for this remarkable behaviour.

The high-molecular-weight fractionated lignin derivatives were more efficient dispersants than the non-fractionated lignin derivatives fraction. The high dispersity of such natural polyphenol affects significantly the molecular properties of the resulting bio-based dispersant.

The fractionation and esterification of pine lignin may contribute to the design of bio-based chemicals for drilling-mud technologies.

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