SURFACTANT PROPERTIES OF ALKENYL SUCCINATES DERIVED OF LIGNINS

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Abstract

After cellulose, lignin is the second most abundant biopolymer in the vegetable world. Lignin is founded in the cell walls of plants and represents 15-40% by dry weight of plant biomass. Since lignin is a natural phenolic polymer, it is used in various fields and there are a variety of potential products obtainable by chemical modification, including surfactants. In this regard, the technical or commercial lignins are of great interest because they represent a byproduct in the production of pulp industries for papermaking, which usually is burned to generate power and recover the reagents used in the process; however, this byproduct can be harnessed for obtaining aromatic derivatives of industrial interest.

To enhance surfactant properties of lignin is necessary to change existing functional groups in order to change its hydrophilic-lipophilic balance (HLB). Therefore, the microwave assisted chemical modification of lignin was performed by an esterification reaction with alkenylsuccinic anhydrides (C_9, C_{12} and C_{16}). The characterization was carried out by Fourier Transform Infrared Spectroscopy (FTIR). In the FTIR spectra of lignin derivatives it was observed decreased band corresponding to the characteristic hydroxyl groups of the biopolymer (where the reaction occurs), and the appearance of the band associated with the carbonyl groups of carboxylic acid and ester incorporated into structure by ring opening of the anhydride. On the other hand, the evaluation of surfactant properties showed that all the derivatives decreased surface tension of water a greater proportion than the starting lignin. The surfactant character of the derivatives obtained increases with the number of carbon atoms in the chain alkenyl anhydride incorporated due to the hydrophobic effect that makes the derivative migrate to the surface instead of remaining within the solution.

Introduction

Lignin is the most abundant of renewable polymers next to cellulose with a global annual production of 50 million tons largely produced from pulping and second generation biofuel industries. It is found as a cell wall component in all vascular plants. The lignin content in woody stems varies between 15 and 40%. Lignin has a complex chemical structure that is derived from phenylpropanoid monomers joined to form a large amorphous net-work polymer. It specific structure is highly variable and depends on the specific plant source as well as the extraction method. Major differences occur between lignins derived from different pulping processes (1). Based on the first full lignin structure proposed by Adler in 1977 (2), lignin is recognized as a highly branched polymer with a variety of functional groups: aliphatic and phenolic hydroxyls, carboxylic, carbonyl and methoxyl groups.

The limited supply and increasing cost of surfactants for oil recovery have led to the study of renewable resources as sources of oil recovery from the raw material readily available and economical, seeking to reduce the environmental impact caused by the pulp and paper industries. In this regard, technical or commercial lignins are of great interest because they represent a byproduct for pulp and paper industries, which usually is burned to generate energy, and recover the reagents used in the process (3).

A variety of potential products can be obtained by chemical modification of lignin, including surfactants (4). The available hydroxyl groups on the lignin molecule are reactive, plentiful, and local centers of high-polarity susceptible to various chemical reactions. Among all of the reactions involving hydroxyl groups of lignin, esterification is probably the easiest to carry out considering the reaction parameters and reactants used. Three reagents are used: acidic compounds, acid anhydrides and chloride acids. The latter two are the most reactive (5).

The structural modification of lignin depends on the specific application. For its potential use as a surfactant, it is necessary to change the existing functional groups in order to change the HLB. In this work, kraft lignin was modified with alkenylsuccinic anhydrides having various chain lengths to enhance surface activity. Surface activity was measured as the depression of surface tension of water, and the effect of chemical structures of lignin derivatives on the surface activity is discussed.

Experimental

Pine kraft lignin (LA) was used as precursors to obtain alkenyl succinates of lignin. In general, the hydroxyl groups react with nonenylsuccinic anhydride (NSA, Merck), dodecenylsuccinic anhydride (DSA, Aldrich) or hexadecenylsuccinic anhydride (HSA, TCI America) to form the lignin derivatives (**Figure 1**). N,N–Dimethylformamide (DMF, Merck) was used as solvent-catalyst. Reactions were assisted by microwave irradiation in a Milestone ETHOS ONE microwave.
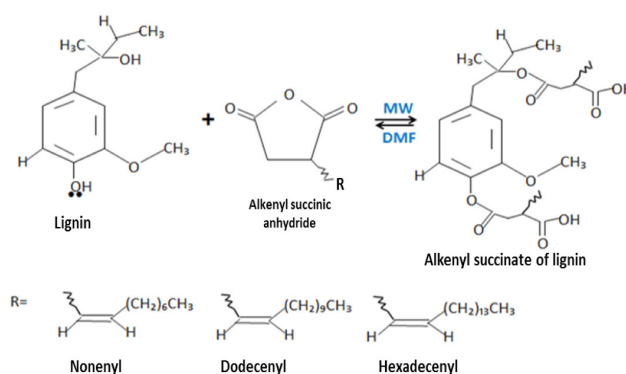

Figure 1. Reaction of esterification of lignin with alkenyl succinic anhydrides

Table 1 shows the reaction conditions for the modification of lignin with each anhydride to obtain the esterified derivatives of lignin: lignol nonenylsuccinate acid (NNSAL), lignol dodecenylsuccinate acid (DDSAL) and lignol hexadecenylsuccinate acid (HDSAL). Once the reaction was completed, the mixture was washed with distilled water, filtered in a Büchner funnel and 0.1 N HCl solution was poured into the filtered solution for precipitation. The obtained dispersion was centrifuged and washed with 0.1 N HCl. Finally, the residue was collected and dried in a freeze dryer (Labconco, LYPH.LOCK 6) for 24 hours.

Table 1. Reaction conditions to obtain lignin derivatives NNSAL, HDSAL and DDSAL under microwave heating.

Reaction conditions				
Derivative	T (°C)	t (s)	P (W)	C (mmol)
NNSAL	100	180	600	0,715
DDSAL	80	180	800	0,590
HDSAL	80	90	600	0,370

T= temperature; t= time; P= power; C= anhydride mass by 100 mg of lignin

The esterification reaction was confirmed by FTIR. Analysis was performed using a Perkin Elmer Frontier instrument in transmission mode. Surface tension measurements were performed using a Du Nouy ring tensiometer. A given amount of lignin derivative was dispersed in a 45% DMF in distilled water solution over 24 h equilibration time at room temperature (6).

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Results and discussion

Infrared spectra of the modified lignin samples were compared to spectra of unmodified lignin to stablish the extent of esterification reactions **(Figure 2)**, and the peaks were assigned according to published data (7).
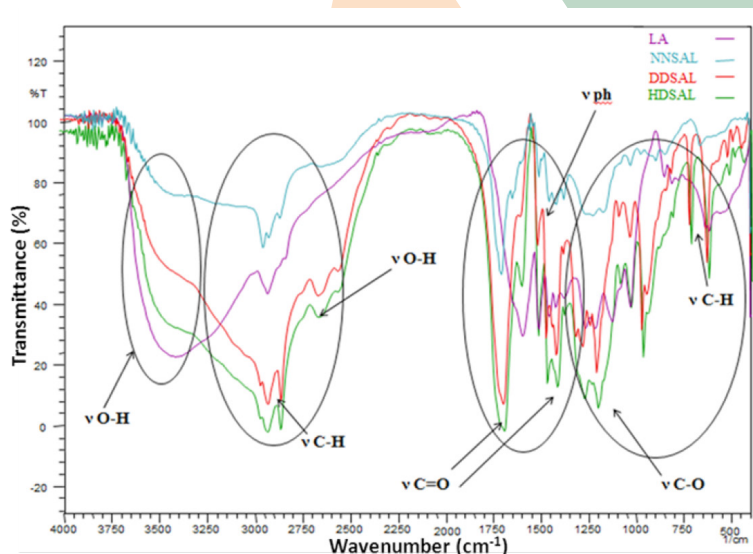

Figure 2. FTIR spectra of unmodified (LA) and esterified lignins (NNSAL, DDSAL and HDSAL)

The unmodified lignin (LA) exhibited a strong broad band at 3424 cm^{-1}, which is attributed to the OH stretching in phenolic and aliphatic structures. Esterification reactions with NSA, DSA y HSA resulted in a decrease in the hydroxyl groups of lignin, along with the appearance of major absorption bands around 1713 cm^{-1} (C=O stretch) assigned to carbonyl stretching of ester and carboxylic groups in lignin.

The bands at 2941 and 2846 cm^{-1}, predominantly attributed to C–H vibration in methyl and methylene groups of side chains and aromatic methoxyl groups in lignin, increased after DSA and HSA modification, whereas no significant increase was observed when treated with NSA modification. The bands at 1595, 1510 and 1427 cm^{-1} are related to the aromatic skeletal vibrations in lignin and NNSAL, DDSAL and HDSAL. There was also a significant increase in intensity of ether vibration band at 1130 cm^{-1} after esterification.

According to **Figure 3**, the surface tension at the air–water interface of starting lignin and NNSAL, HDSAL and DDSAL derivatives aqueous solutions decreases with the grown in the concentration.

Figure 3 also shows that the isotherms of the surface tension of esterified lignins are curves typical of polymer-surfactants interactions. There is a break in the surface tension at a concentration below the normal critic micellar concentration (CMC), associated with the critical aggregation concentration (CAC), which corresponds to the onset of micelle formation on the polymer. As more surfactant is added the polymer becomes saturated with surfactant micelles, this causes the surface tension to drop below the plateau region in the figure until the surfactant concentration is high enough for it to form free micelles (8).

Although the surface activity of lignin was very limited and could not determine the CMC, all esterified derivatives did strongly depress surface tension of DMF-water, and showed clear CMC. It can be seen that DDSAL is characterized by the lowest values of surface tension, while the initial lignin has the largest values of the surface tension. When DMF-water surface tensions in 10.000 ppm of lignin or lignin derivative solution were compared, DDSAL showed minimum value **(Table 2)** suggesting the derivatization with DSA was more effective to prepare a surfactant than that with NSA or HSA.
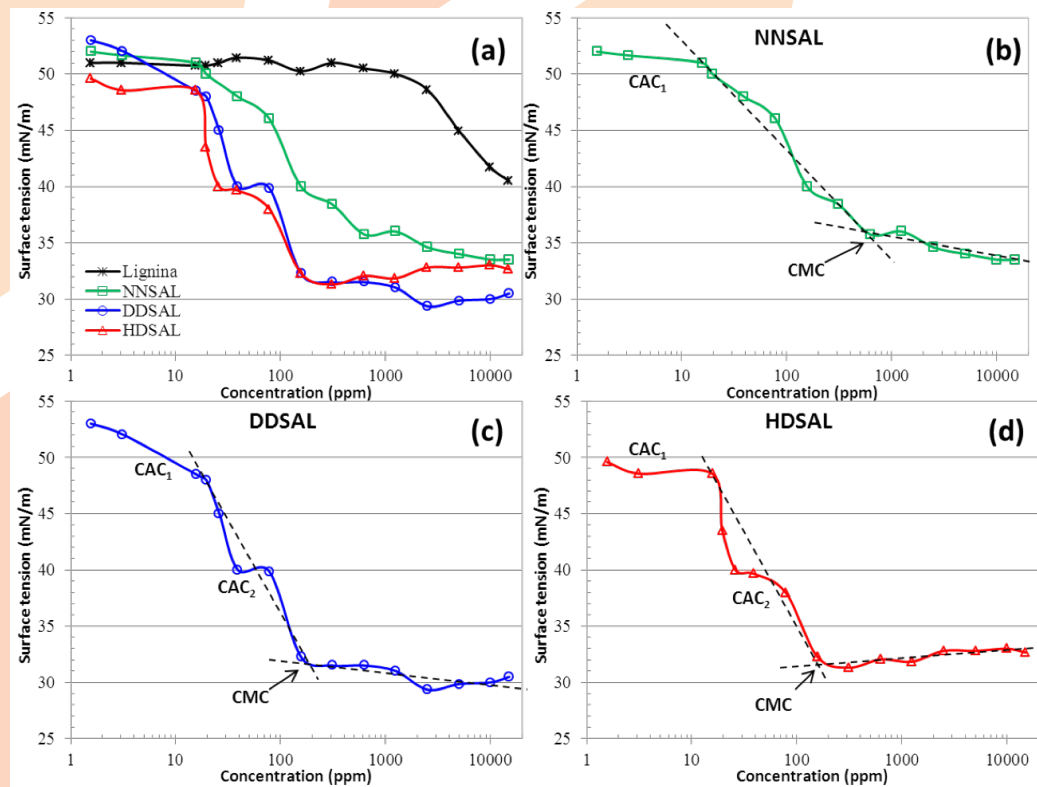
Figure 3. Surface tension-concentration isotherms for (a) Comparison between unmodified lignin and derivatives. (b) NNSAL (c) DDSAL (d) HDSAL

The results suggest that DSA introduction into technical lignins is a very useful and facile derivatization to obtain surfactants (9). As show in **Table 2**, HDSAL exhibited the lowest CMC among all the lignin derivatives prepared in this study, although the surface tension was in the similar level with DDSAL.

Table 2. Surface tension and CMC values of Lignin, NNSAL, DDSAL and HDSAL

	Surface tension (mN/m) at 10.000 ppm	CMC (ppm)	Surface tension (mN/m) at CMC
Lignin	41,7	ND	ND
NNSAL	33,5	625,00	35,8
DDSAL	30,0	195,25	31,7
HDSAL	33,0	156,25	31,7

ND= Not detected

These results indicate that as the anhydride alkenyl chain increases the surface tension decreases. These results are associated with the hydrophobic effect present in the derivatives, which in this case is higher for the HDSAL; this effect is not given by the attraction between non-polar groups, but originates to avoid extremely weak attractive forces between water molecules and the hydrophobic chains of the surfactant molecules compared with the strong intermolecular interactions between the water molecules. As a result, the system tends to reduce its free energy by eliminating the alkyl chains-water contacts, remaining monomers surfactant oriented so that the polar head is in contact with the aqueous medium and the hydrophobic tail is in contact with the air phase (10).

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The simultaneous presence of the pronounced aromatic hydrophobic fragments and hydrophilic ones, containing the enhanced amount of carboxylic group in NNSAL, DDSAL and HDSAL governs the high tendency of the modified lignin to self-aggregation and self-organization at the interface layers, resulting in more dense packing of the lignin macromolecules in them, leading to lowering the surface tension (11).

Conclusions

The results suggest that NSA, DSA and HSA introduction into technical lignins is a very useful and facile derivatization to obtain surfactants, because all esterified derivatives did strongly depress surface tension of DMF-water, and showed clear CMC compared to the starting lignin, under conditions which the measurements were made. The increase in the number of carbon atoms in the anhydride alkenyl chain is an inversely proportional to the surface tension due to the hydrophobic effect.

Acknowledgements

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