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Lignin from Hydrolyzed Wood By-Product as an Eco-Friendly Emulsion Stabilizer

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Abstract. Aspen sulfur-free soda lignin was obtained as a result of alkaline delignification of hydrolyzed sawdust, a by-product of wood mechanical processing. The pre-hydrolysis of aspen sawdust was performed for enhancing the yield of lignin from the wood residue as well as to decrease the energy consumption of its milling for obtaining a filler for composites. The obtained lignin was characterized by a chemical composition, particle sizes and zeta potential values as well as by the surface-active properties at the air-water and oil-water interfaces. The surface tension of the lignin solutions at the air-water interface decreases with dropping pH values and increasing lignin concentration due to hydrophobization of the lignin macromolecules, which is strengthened in the presence of a low molecular salt. The study of the obtained lignin as an emulsion stabilizer has shown that the O/W emulsion stabilized with alkaline lignin solutions with a concentration less than 0.1% demonstrates the highest stability with the formed smallest emulsion particles, having the highest negative charge, but the stabilization proceeds via the electrostatic mechanism. With decreasing pH values and increasing lignin concentration in the emulsion, the stabilization mechanism is more complicated with a growing role of steric factors.

Keywords: aspen soda lignin**,** O/W emulsion stabilization, surface-active properties.

Conference topic: Environmental protection.

Introduction

In recent years, the increasing demand for energy, limited fossil fuel supplies, as well as environmental pollution and the global climate change lead to a growing interest in renewable resources. In this connection, much attention is given to the rational utilization of biomass for the production of bioenergy and bioproducts with the added value as well as for the replacement of the existing hazardous products with bio-based ones for environmental protection. One of the representatives of wood biomass is lignin that accounts for 15−30% of the total biomass. Lignin represents a major polymeric component of plant cell walls and is the second most widespread renewable bioresource on earth. It has an amorphous polyphenolic nature arising from the enzyme-mediated dehydrogenative polymerization of three phenylpropanoid monomers − coniferyl, sinapyl and p-coumaryl alcohols in wood and grass. Lignin content generally varies from 24 to 33% in softwood, from 19 to 28% in hardwoods and from 11 to 27% in nonwoody lignocellulosic fibers (Forss, Fremer 2003; Fengel, Wegener 1984). Technical lignins are obtained as by-products on a large scale during the cellulose pulping at plants, and utilized mainly for energy consumption coverage. At the same time, the peculiarities of the structure of lignin, combined with its renewability, low cost, biocompatibility and biodegradability, make the design of new added value lignin-based products a challenge for fundamental and applied researches. According to the analysis of the patenting activity of the last years and the occupied application areas, the utilization of lignins for obtaining surface active agents (SAAs) (stabilizers, emulsifiers, detergents and dispersants for treatment of asphalt, latex, soap, cement, clay, etc.) takes the first place in comparison with their usage in resins, composites, concrete as well as for obtaining chemicals (Shulga *et al.* 2008; Aguie-Beghin *et al.* 2002; Baumberger *et al.* 1997). Due to the features of the chemical structure and low molecular masses, technical lignins successfully replace hazardous synthetic SAAs that pollute the aquatic flora and fauna. For example, lignosulfonates are widely used as an effective stabilizer during the extraction process of oil (Chilingarian, Voravutr 1981).

In this work, sulfur-free soda lignin obtained from the hydrolyzed wood by-product was evaluated as a stabilizer of the oil-in-water emulsion.

Materials and methods

Materials

Lignin was obtained as a result of alkaline delignification of hydrolyzed sawdust, a by-product of a Latvian company, which deals with aspen wood mechanical processing. The pre-hydrolysis of aspen sawdust was performed under laboratory conditions with the purpose to enhance the yield of lignin from wood during the cooking as well as to decrease the energy consumption of sawdust milling for obtaining microparticles as a filler (Shulga *et al.* 2016). The hydrolysis parameters of the sawdust were the following: 0.1% HCl at 60°C during 3 h. The delignification of the hydrolyzed sawdust was carried out with a 4.0% NaOH solution at 165°C during 1.5 h at the hydromodulus 1:7 (sawdust/water). Alkaline lignin was precipitated from the black liquor with a 20% sulfuric acid, with the following filtration, washing with distilled water and drying.

Methods

The chemical composition of lignin was studied by the determination of elements (Elementar Analysensysteme GmbH, Germany) and functional groups' content (methoxyl groups, hydroxyl groups, carbonyl groups, phenolic hydroxyl groups, carboxyl groups) using the Fibok–Shvappakh method, acetylation, interaction with hydroxylamine hydrochloride, and potentiometric and conductometric titration (InoLab level 3), according to Zakis (Zakis 1994). The weight and number average molecular weights of lignin were studied by SEC-MALS20 (Malvern, United Kingdom) in DMSO with lithium bromide as an eluent at 60°C. The surface tension (σ) at the air-water was measured by the Wilhelmy method, respectively, using a tensiometer K 100M (KRUSS, Germany). The oil-in-water (40/60 v/v) emulsions were prepared with a Disperser T10 (IKA) (γ = 9500 rpm) for mixing of 1 min. The stabilizing effect of the lignin was evaluated according to the final volume (H) of the separation of the emulsion after its centrifugation with a centrifuge Hettich EBA 20 at 6000 rpm for 30 min. Surface pressure-area isotherms were obtained at 25°C using a KSV NIMA Langmuir through double-barrier device (KSV Chemicals, Finland) with a barrier speed of 10 mm/min. The size and zeta-potential (Z) of lignin particles and oil droplets were determined with a ZETASIZER NANO ZS Malvern Instrument (Malvern, United Kingdom), at 25°C. The images of the droplets of the emulsions were obtained with an optical microscope Optika Microscopes Serie B -500 (Italy) and a camera „Canon" PowerShot A640.

Results and discussion

The obtained results showed that the yield of the lignin from the hydrolyzed aspen sawdust achieved 18.2% that was higher than its yield from the non-hydrolyzed residue by 3.9%. The obtained lignin was characterized by the following elemental and functional composition: 62.3% C, 6.5% H, 0.15% N, 0.25% S, 30.8% O, 19.3% OCH$_3$, 5.6% total OH, 3.6% phenolic OH, 2.1% COOH, 3.9% CO. The low content of non-lignin substances was testified by the high values of the Klason (91%) and acid-soluble lignin (5.2%) content [4]. The weight molecular and number average molecular weights of the lignin were equal to 10800 Da and 4330 Da, respectively, with a polydispersity index close to 2.5. The particle sizes and charge of the soda lignin in aqueous medium were determined by dynamic light scattering. Fig. 1 shows size distribution graphs of lignin particles in a 0.005% water solution at pH 10.7 and 5.6.

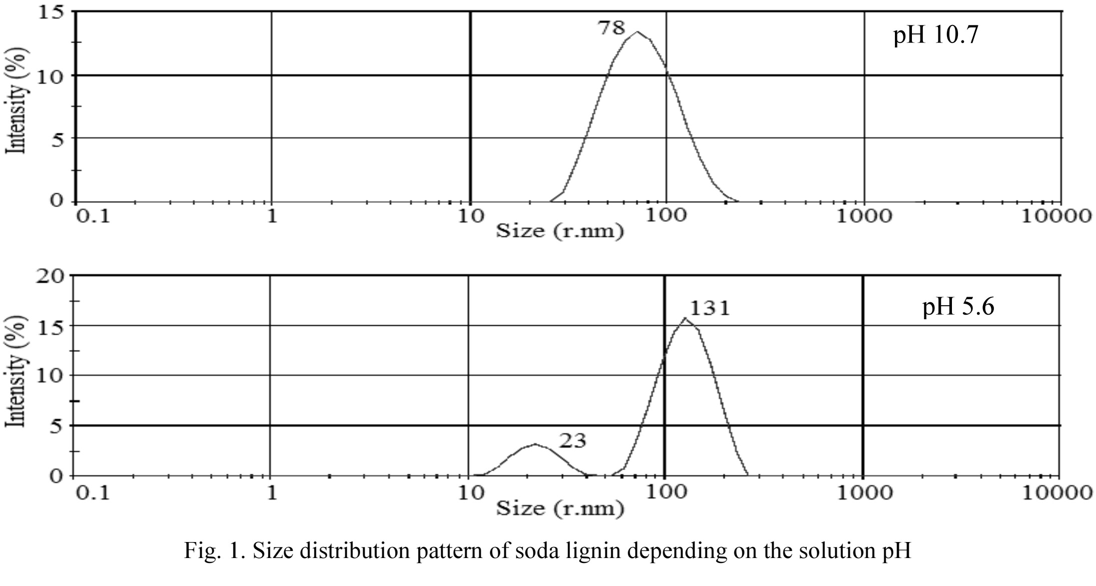


Fig. 1. Size distribution pattern of soda lignin depending on the solution pH

It can be seen that the distribution of lignin particles in alkaline medium has a monomodal character with average hydrodynamic radii of 78 nm. Literature data show that the species with hydrodynamic radii less than 3.0 nm are close in sizes to the individual macromolecules of lignin (Norgren, Lindstrom 2000; Garver, Callaghan 1991). Hence, the observed particles are associates, consisting of individual macromolecules of aspen lignin. The presence of the associates testifies that the lignin alkaline solution is a structured one. With changing pH of the lignin solution, the mode of the distribution of its particles changes. For weak acidic (pH 5.6) media, this distribution has a bimodal nature. Table 1 lists average particle sizes of the lignin, with their values of the intensity area and polydispersity index (PDI) as well as the average zeta potentials of the lignin particles in a 0.006% lignin solution depending on its pH values.

Table 1. Soda lignin particles' characteristics

pH	Size, nm / Intensity, %		Polydispersity index	Zeta potential, mV
	peak 1	peak 2		
11.7	78 / 100	–	0.218	−43
5.0	131 / 86	23 / 14	0.356	−19

According to the obtained data, with decreasing solution pH, the particle sizes of the aspen lignin increase, but its charge falls dramatically in acidic medium. This may indicate the strengthening of the association of lignin macromolecules at pH 5.6, leading to the formation of lignin particles with lesser charge and larger sizes than those in the alkaline solution.

Due to the increasing requirements for environmental protection, obtaining of "green" surfactants from natural feedstock represents both scientific and practical interest. The effect of the obtained sample of aspen lignin on the surface tension at the water-air interface in the pH range of 5.0−12.8 is shown in Fig. 2.

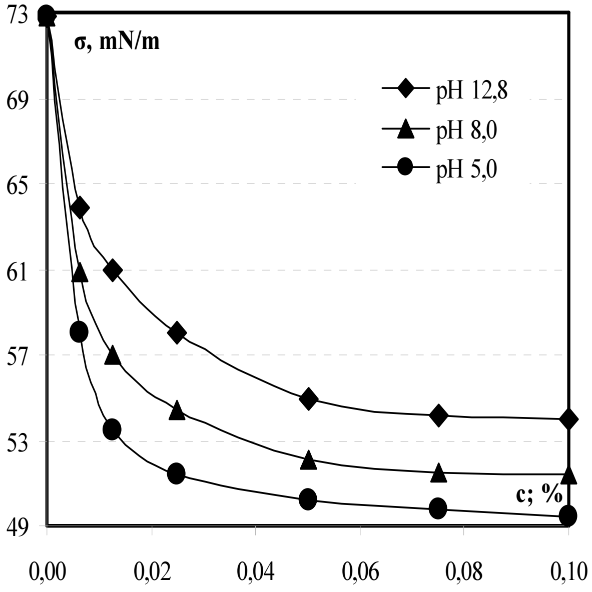


Fig. 2. Isotherms of the surface tension at the air-water interface of soda lignin solutions depending on their concentration at different pH values

It can be seen that the surface tension (σ) of the lignin solutions decreases with dropping pH values to its maximum magnitude of 49.4 mN/m at pH 5.0 and a lignin concentration of 0.1%. The presence of sodium chloride had a positive effect on the surface-active properties of the lignin at the air-water interface. In alkaline medium (Fig. 3), the surface tension of a 0.1% lignin solution drops from 54 mN/m to 40 mN/m with increasing ionic strength due to the presence of 1 M NaCl. This may be governed by the growing hydrophobicity of the lignin particles due to the protonization of their ionic acidic groups as a result of decreasing pH (Fig. 2) and the screening of the surface charge of the lignin particles due to the presence of the low molecular salt (Fig. 3).

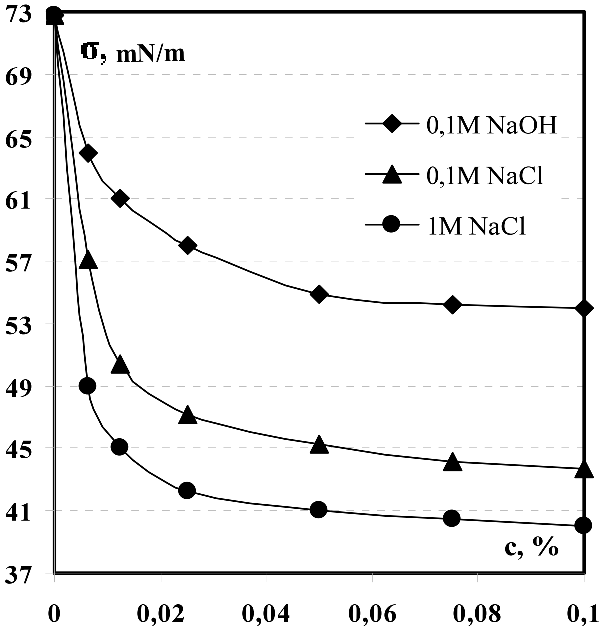
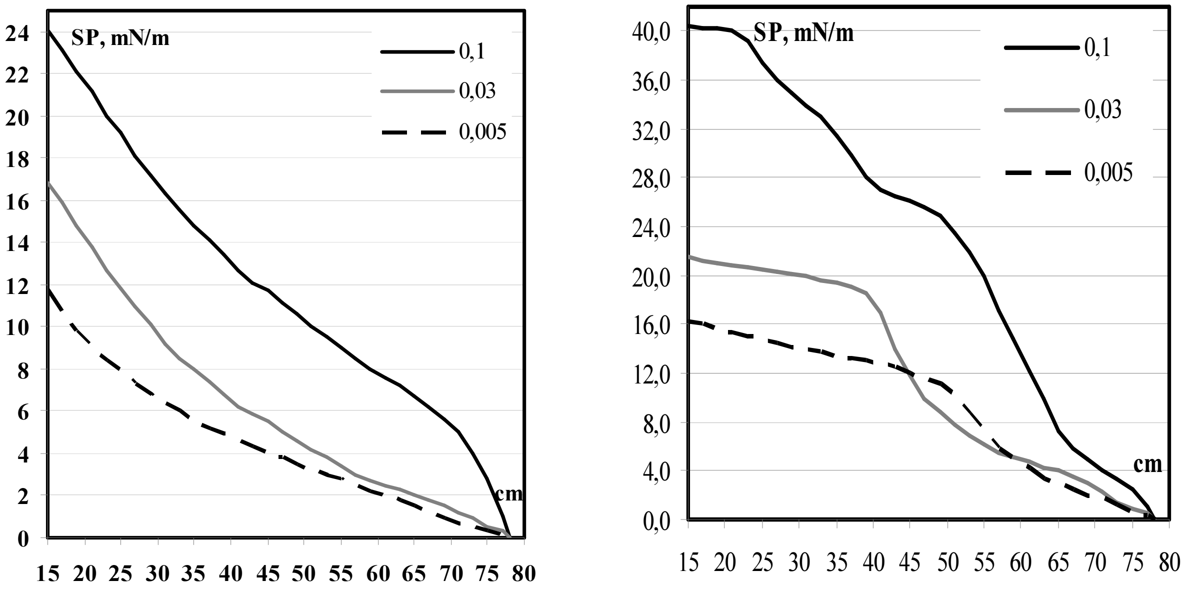


Fig. 3. Isotherms of surface tension at the air-water interface for soda lignin solutions in the presence of low molecular salt depending on its concentration at pH 12.8

The hydrophobization of the lignin structure as a result of the protonization of the phenolic hydroxyl and carboxyl groups promoted the association of the lignin macromolecules. In a 0.1% lignin acidic solution, with increasing NaCl concentration from 0 to 1 M, the increase in the size of the lignin particles was more pronounced and varied from 217 nm to 614 nm, but the decrease in the negative values of zeta-potential was from −22.5 mv to −10.6 mv.

The growth of the hydrophobicity of the soda lignin particles causes the increase of the surface pressure at the air-water interface and the formation of a more rigid lignin's film at the interface (Fig. 4 a, b). Due to the strengthening of the hydrophobic interaction between the lignin particles, with increasing concentration of lignin in water solution from 0.006% to 0.1% and decreasing pH values of the solution from 12.8 to 6.0, the surface film pressure at the air-water interface increases 1.2−1.6 times, achieving 41 mN/m for the highest lignin content at pH 6.



a) b)

Fig. 4. Isotherms of surface pressure of soda lignin solutions depending on their concentration and pH: 12.8 (a), 6.0 (b)

It is known that lignins are used as stabilizers of different emulsions and dispersions (Li *et al.* 2016; Shulga *et al.* 2011). Fig. 5 shows the values of the separation volume of the rapeseed oil-in-water (O/W) emulsion depending on the pH of the aqueous phase, containing lignin with a concentration of 0.006%–0.1%. It can be seen that the O/W emulsions stabilized with the alkaline lignin solutions demonstrate the highest stability. At the same time, with increasing content of lignin in the alkaline solution, the stability of the emulsion slightly decreases. At the same time, the O/W emulsions prepared with the help of the lignin solutions with pH 8.0 and 5.0, respectively, are characterized by a lower stability, which improves with growing lignin content in the O/W emulsion. Different mechanisms of the stabilization of emulsions with lignin at the liquid-liquid interface are suggested, and the main of them are electrostatic and steric ones. The findings indicate that the stabilization of the "rapeseed oil-in-water" emulsion with alkaline lignin solutions proceeds via the electrostatic stabilization mechanism, while in neutral and acidic medium, with increasing lignin concentration, the stabilization mechanism is more complicated with the growing role of the steric factors.

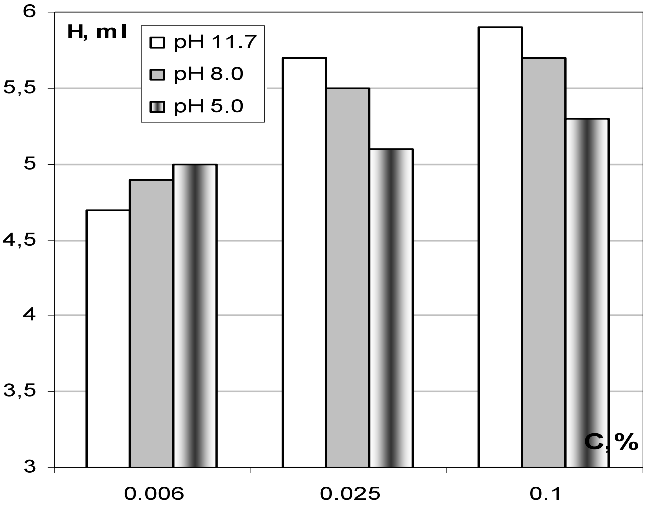


Fig. 5. Separation volume of the O/W emulsion depending on the lignin solution concentration at different pH values

The quality of the O/W emulsion stabilization is reflected by the size and zeta-potential value of the formed oil droplets. Fig. 6 shows that, with increasing lignin concentration in alkaline medium from 0.006% to 0.1%, the size of the emulsion droplets grows from 398 nm to 1260 nm, but the separation volume of the emulsion increases from 4.7 ml to 5.0 ml.

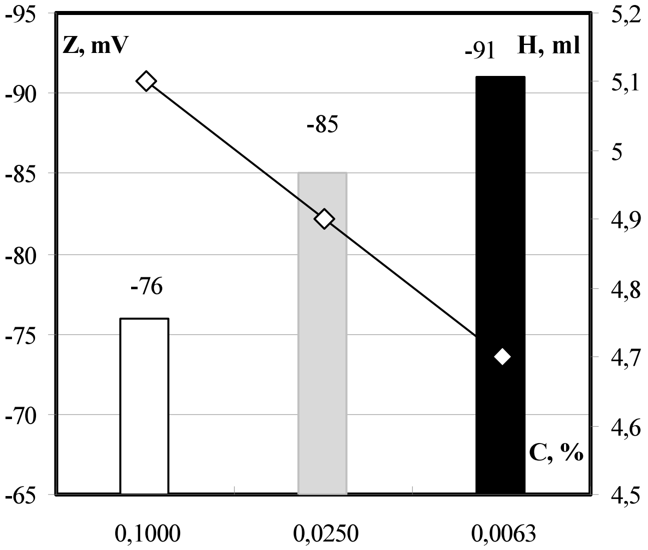


Fig. 6. Zeta potential of emulsion droplets and separation volume (H) of the emulsion depending on the applied concentration of alkaline lignin solution (pH 11.7)

Compared with the lowest applied lignin concentration, the droplets' size increased from 1.8 to 3.2 times for the emulsion stabilized with a 0.1% lignin alkaline solution. It is obvious that the higher the formed emulsion particle size, the faster the separation and the loss of the stability of the O/W emulsion. According to Fig. 7, the emulsion droplets stabilized with the lignin solution with the lowest concentration have an enhanced stability and are characterized by the highest average charge of – 91 mv, which testifies the electrostatic mechanism of the stabilization of the O/W emulsion.

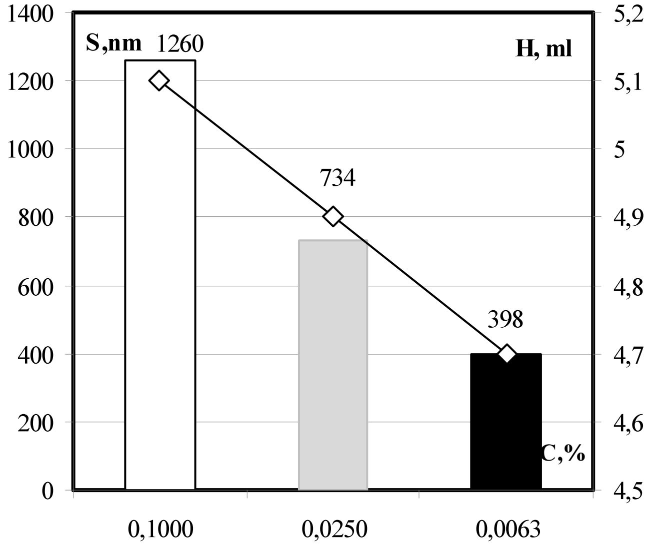


Fig. 7. Size of emulsion droplets and separation volume (H) of the emulsion depending on the applied concentration of the alkaline lignin solution (pH 11.7)

The images of the emulsions after 10 min of their preparation were made using an optical microscope with a magnification of 160 times. The images show (Fig. 8) that the droplets of the emulsion stabilized with the lowest concentration of the alkaline lignin solution have a more uniform size and are much smaller than the particles of the non-stabilized emulsion.

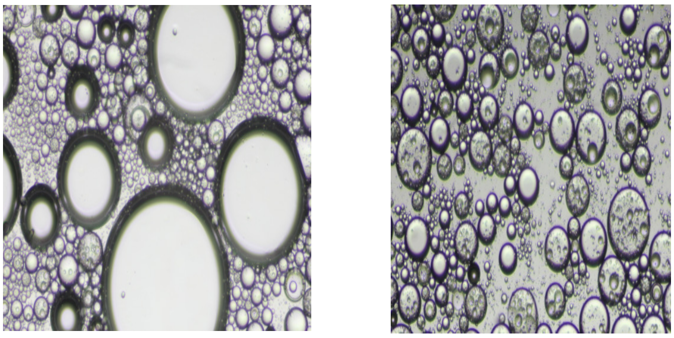


Fig. 8. Optical images of emulsion droplets in the non-stabilized O/W emulsion (to the left) and that stabilized with soda lignin solution with pH 11.7 (to the right)

Conclusions

Thus, the conducted experiments show that the alkaline pretreatment of the aspen wood residue allows an increase in the yield of the soda aspen lignin by 3.9%. The obtained lignin has pronounced surface active properties of both the air-water and oil-water interfaces. The surface tension of the lignin solutions at the air-water interface decreases with dropping pH values and increasing lignin concentration due to the hydrophobization of the lignin macromolecules, which is strengthened in the presence of a low molecular salt. The study of the obtained lignin as an emulsion stabilizer has shown that the O/W emulsion stabilized with the alkaline lignin solutions with a concentration less than 0.1% demonstrates the highest stability with the formed smallest emulsion particles, having the highest negative charge, but the stabilization proceeds via the electrostatic mechanism. With decreasing pH values and increasing lignin concentration in the emulsion, the stabilization mechanism is more complicated with a growing role of the steric factors. For improving the surface-active properties, the soda lignin should be modified.

Acknowledgements

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