The effect of pH on the ability of different lignins to stabilize the oil-in-water emulsion

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Abstract. The ability of aspen soda and wheat straw soda lignin to stabilize the “rapeseed oil-in-water” (O/W) emulsion, depending on the pH value and concentration of the applied water solutions as well as on the lignin chemical composition and molecular mass, and the sizes and zeta potential of lignin particles was studied. It was shown that the O/W emulsion stabilized with the alkaline water solutions of wheat straw lignin demonstrated the highest stability in alkaline medium, while the ability of aspen soda lignin to prevent the coalescence of oil droplets manifested itself in a whole range of the studied pH values. With decreasing pH values of the wheat straw lignin water solution, the drop in the separation volume of the O/W emulsion was insignificant with the exception for the lignin enhanced concentrations in acidic medium. The aggregative stability of the O/W emulsion, which was stabilized with aspen soda lignin, increased with decreasing pH values and increasing lignin content in the emulsion. The findings indicated that the stabilization of the O/W emulsion with the alkaline lignin solutions proceeded via the electrostatic stabilization mechanism, while in the neutral and acidic medium, this mechanism was more complicated, with a growing role of the ability of lignin to form interfacial polymeric films at the liquid/liquid interface. The comparison of the stability of the O/W emulsion showed that aspen soda lignin was a better stabilizer of the O/W emulsion than wheat straw lignin.

1. Introduction

The need for efficient surface active agents, including detergents, surfactants and dispersants, grows annually and has led to ongoing researches to develop the surface active agents not only with an enhanced surface activity, but also with a pronounced biodegradability. In this connection, much attention is given to the rational utilization of biomass for the replacement of the existing non-eco-friendly products with bio-based ones. One of the representatives of biomass is wood lignin that accounts for 15-30% of the total biomass. 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 fibres [1, 2]. The peculiarities of the structure and chemical composition of lignin, combined with its renewability, low cost, biocompatibility and biodegradability, make the design of new value added lignin-based products a challenge for fundamental and applied research. The chemical properties of lignin are highly dependent on the wood or grass species, and the pulping and recovery process. These
factors affect the chemical composition, reactivity and properties of lignin. According to the literature analysis, the application of technical lignins for obtaining surface active agents such as stabilizers, emulsifiers, detergents and dispersants for treatment of asphalt, latex, soap, cement, clay, etc. is a very promising field [3-9], which takes the first place in comparison with lignin application in other areas, namely, for obtaining resins, biocomposites, concrete and chemicals.

In this work, aspen soda and wheat straw soda lignin were comparatively evaluated as a potential stabilizer of the oil-in-water emulsion.

2. Experimental

Hardwood lignin was obtained by soda delignification of pre-hydrolyzed aspen sawdust. The pre-hydrolysis was performed under laboratory conditions with the purpose to enhance the yield of lignin during wood delignification as well as to decrease the energy consumption of aspen sawdust in the process of its milling for obtaining microparticles used as a filler for wood-polymer composites [10]. The hydrolysis parameters of the sawdust were 0.1% HCl at 60°C for 3 h. The delignification was carried out with a 4.0% NaOH solution at 165°C at the hydromodulus 1:7 (sawdust/water) for 1.5 h using a laboratory autoclave at a pressure 0.45 MPa. Soda lignin was precipitated from the black liquor with a 20% sulphuric acid, with the following filtration, washing with distilled water and drying. Wheat straw soda lignin was a commercial product of the biorefinery process (GreenValue SA, Switzerland).

The chemical composition of lignin was studied by elements (Elementar Analysensysteme GmbH, Germany) and functional groups (methoxyl and aliphatic hydroxyl groups (OH_{al}), carbonyl groups, phenolic hydroxyl groups (OH_{ph}), carboxyl groups) analysis using the Fikob-Shvappakh method, acetylation, interaction with hydroxylamine hydrochloride, and potentiometric and conductometric titration (InoLab level 3), according to Zakis [11]. The average molecular weights of lignins (M_w, M_n) were studied by SEC-MALS20 (Malvern, United Kingdom) in DMSO with lithium bromide as an eluent at 60°C. The average molecular mass (M_w) of aspen and straw lignin was 10.8 kDa and 15.7 kDa, respectively. The oil-in-water (40/60 v/v) emulsions (O/W) were prepared with a Disperser T10 (IKA) (γ = 9500 rpm) for mixing of 1 min. A commercial rapeseed oil (saturated fat acids – 61%, polyunsaturated fat acids – 32%, saturated fat acids – 7%) was used as the oil phase. The water phase of the emulsion was adjusted to various pH values by adding 0.1 M NaOH or 0.1 M HCl. The stabilizing effect of lignin was evaluated according to the final volume of the separation (H) of the emulsion after its centrifugation with a centrifuge Hettich EBA 20 at 6000 rpm for 30 min. The velocity of separation was evaluated on the basis of the volume of the released water phase during the first ten minutes after the preparation of the emulsion. Due to the good comparability of the obtained results, a number of the repeated measurements of the final separation volumes of the emulsion samples and their separation velocities, obtained by the centrifugation for each sample, was equal to three, and the final results represented the arithmetic mean values.

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. Five replicates were made for each measuring, and standard deviation for each index was calculated.

3. Results and Discussion

The chemical composition of aspen soda lignin and wheat straw soda lignin is given in Table 1. According to the obtained data, the lignins differ in the content of the functional groups. Straw lignin contains more carboxyl and carbonyl groups, but less phenolic and aliphatic hydroxyl groups in comparison with aspen lignin. The degree of oxidation calculated as the ratio O/C for straw and aspen lignin was 0.51 and 0.47, respectively. A higher ratio of the degree of oxidation for straw lignin may be associated with the higher content of carboxyl and carbonyl groups. The ability of the lignins to stabilize the rapeseed oil-in-water emulsion was examined as a function of pH and the concentration of the applied lignin solutions. The separation process of the emulsion resulted in a distinct interface between the water and oil phase. The initial emulsion samples had a white colour, but after a few
Table 1. Chemical composition of lignins

| Lignin | C  | H  | O  | N  | S  | OCH₃ | CO  | OH₀₂ | COOH | OH₈₁₂ |
|--------|----|----|----|----|----|------|-----|------|------|-------|
| Aspen  | 63.3 | 6.5 | 29.8 | 0.2 | < 0.3 | 18.30 | 2.12 | 4.49 | 3.15 | 3.31 |
| Straw  | 61.2 | 5.7 | 31.3 | 1.6 | < 0.3 | 12.50 | 2.69 | 3.57 | 5.95 | 1.46 |

minutes, the lower part of the test-glass was coloured with a brown colour. Figure 1 shows the values of the separation volume of the rapeseed oil-in-water (O/W) emulsion depending on the pH of the water phase, containing the lignins with a concentration of 0.006%-0.1%. The O/W emulsion stabilized with the alkaline straw lignin solutions demonstrates a higher stability compared with aspen lignin. With increasing content of straw lignin in the water solution, the stability of the emulsion changes insignificantly. The emulsion prepared with the neutral solutions of straw lignin is characterized by the lowest stability that slightly increases with growing lignin content in the O/W emulsion. In acidic medium, the ability of straw lignin to prevent the separation of the O/W emulsion does not change for its low concentrations in the water solutions but grows for a concentration of 0.05-0.1%.

![Figure 1](image-url)

**Figure 1.** Separation volume (H) of the O/W emulsion depending on the lignin solution concentration at different pH values

In contrast, the highest ability of aspen lignin to stabilize the emulsion appears in neutral and acidic media. With decreasing pH value and increasing content of aspen lignin in a water solution, the stability of the emulsion essentially increases and is characterized by the remarkably lower separation volumes compared with the emulsion stabilized with straw lignin. The effect of the pH value and concentration of the lignins on the velocity of the emulsion separation for the first ten minutes after its preparation is given in Table 2. It can be seen that, for straw lignin, the lowest velocity values of 7.5-
9.5\times 10^{-2} \text{ ml/min} \) are observed in alkaline medium, but the highest separation velocity, reaching 55-59\times 10^{-2} \text{ ml/min}, takes place when the straw lignin neutral and acidic solutions are applied. Aspen lignin is characterized by the lowest velocity of separation of 3.5-7.5\times 10^{-2} \text{ ml/min} in the alkaline and acidic medium, while in the neutral medium it has the moderate values of 17.5-22.5\times 10^{-2} \text{ ml/min}.

It is known that an emulsion can be stabilized via different mechanisms, namely, the introduction of a charge at the O/W interface or the formation of a steric interfacial film at the interface. In our case, the presence of ionic groups such as carboxylic and phenolic hydroxyl groups imparts an essential negative charge for lignin macromolecules in alkaline solution.

| Table 2. Velocity of emulsion separation after the first ten minutes as the emulsion was prepared |
| --- |
| Concentration, 10^{-2}, %/ | Velocity, 10^{-2}, ml/min | Aspen lignin | Straw lignin |
| 0.63 | 9.5 | 22.5 | 19.0 | 10.0 | 59.0 | 55.0 |
| 1.25 | 9.5 | 50.0 | 13.0 | 9.5 | 56.0 | 54.0 |
| 2.50 | 9.0 | 18.0 | 8.0 | 8.0 | 54.5 | 48.0 |
| 5.0 | 8.0 | 18.5 | 5.5 | 7.5 | 27.0 | 30.0 |
| 10.0 | 7.5 | 17.5 | 3.5 | 6.5 | 20.0 | 17.0 |

The lignin macromolecules, being adsorbed at the oil droplets, stabilize the O/W emulsion by forming the inner Helmholtz layer, which leads to the increase of the zeta potential and the aggregative stability of the emulsion due to the repulsion interaction between the negatively charged emulsion droplets.

According to Table 3, wheat straw soda and aspen soda lignin have the high values of zeta potential at pH 11.0. In neutral and acidic medium, the electrostatic repulsion plays a second role in the emulsion stability, but the ability of the lignins to form steric semi-rigid polymeric films at the interface comes to fore. Taking into account the values of the degree of oxidation of both the lignins, aspen soda lignin is more hydrophobic than wheat straw lignin that positively affects its surface activity.

| Table 3. Size and zeta potential of the particles of hardwood soda and wheat straw soda lignin |
| --- |
| Lignin | S, nm | Z, mv |
| Aspen | pH 11.0 | pH 5.8 | pH 3.5 | pH 11.0 | pH 5.8 | pH 3.5 |
| Straw | 164 ± 8 | 192 ± 15 | 120 ± 19 | -51 ± 3 | -33 ± 5 | -19 ± 3 |
| 363 ± 10 | 288 ± 21 | 212 ± 28 | -36 ± 5 | -31 ± 4 | -29 ± 4 |

On the other hand, straw soda lignin forms associates of a larger size in the water solutions in the whole range of the studied pH values compared with aspen soda lignin (Table 3) that may be associated with a higher value of its molecular mass compared with aspen lignin. This may hamper the adsorption and orientation of the lignin macromolecules at the oil/water interface and negatively affects the formation of the interface polymeric film. Thus, aspen soda lignin is a better stabilizer for the rapeseed-water emulsion in the studied interval of concentrations and pH values of the applied water solutions.

Another way to determine the effectiveness of the emulsion stabilization is based on the evaluation of the sizes and zeta potential values of the formed droplets in the treated emulsion. Figure 2 shows that, with increasing aspen soda lignin concentration in alkaline medium from 0.006 % to 0.1 %, the size of the emulsion droplets grows from 398 nm to 1260 nm, while the separation volume of the emulsion increases.
Figure 2. Size of emulsion droplets and separation volume (\(\mu\)) of the emulsion depending on the applied concentration of the alkaline aspen lignin solution

Compared with the lowest applied aspen lignin concentration, the droplets’ size increases almost threefold for the emulsion stabilized with the highest concentration of the aspen 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.

Figure 3. Zeta potential of emulsion droplets and the separation volume (\(\mu\)) of the emulsion depending on the applied concentration of the alkaline aspen lignin solution

According to Figure 3, the emulsion droplets characterized by an enhanced stability have the highest negative zeta potential in a range of \(-76 - -91\, \text{mv}\) that testifies the electrostatic mechanism of the enhanced stabilization of the O/W emulsion with lignin in alkaline medium.

4. Conclusions

A strong pH dependency of the surface activity of aspen soda and wheat straw soda lignin at the rapeseed oil-water interface was observed. Different mechanisms of the stabilization of the O/W emulsion with lignin particles are suggested. The findings indicate that the stabilization of the emulsion with alkaline lignin solutions proceeds via the electrostatic mechanism, while in neutral and acidic medium, with increasing lignin concentration, the stabilization mechanism is more complicated, with the growing role of the formation of steric semi-rigid polymeric films. Due to a smaller hydrophobicity and the pronounced ability to form large macromolecule associates in water solutions, which are favoured by the peculiarities of its chemical composition, wheat straw lignin is a weaker stabilizer for the O/W emulsions compared with aspen soda lignin.
5. Acknowledgements
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6. References
[1] Fengel D and Wegener G 1984 Wood - Chemistry, Ultrastructure, Reactions, Walter de Gruyter Berlin and New York
[2] Forss K G and Fremer K E 2003 The Nature and Reactions of Lignin – a New Paradigm, OY Nord Print Ab Helsinki
[3] Chilingarian G and Voravutr P 1981 Drilling and Drilling Fluids Elsevier Scientific Pub. New York
[4] Aguiè-Beghin V, Baumberger S, Monties B and Douillard R 2002 Fr. Langmuir 18 5190
[5] Baumberger S, Aguiè-Beghin V, Douillard R, Lapierre C and Monties B 1997 Industrial Crops and Products 6 259
[6] Gundersen S A, Sæther Ø, Sjöblom J 2001 Colloids and Surfaces A: Physicochem. Eng. Aspects 186 141
[7] Shulga G, Shakels V, Brovkina J, Solodovniks P and Skudra S 2008 Proceedings of the 7th World Surfactants Congress ‘CESIO 2008’ Paris France 98
[8] Shulga G, Skudra S and Shakels V 2011 Proceedings of the 8th International Scientific and Practical Conference - Environment. Technology. Resource, Rezekne Latvia 276
[9] Li S, Willoughby J A and Rojas O J 2016 ChemSusChem 9 2460
[10] Shulga G, Neiberte B, Verovkins A, Vitolina S, Jaunslavietis J and Ozolins J 2016 Materials Science (Medžiagotyra) 22 370
[11] Zakis G F Functional Analysis of Lignins and their Derivatives, Tappi Press, Atlanta, 1994