Rheological Behavior of Lignin Based Dispersions Intended for Composite Fuel Production

T. Savitskaya[1], I. Reznikov[1]*, D. Grinshpan[1]

[1]Belarusian State University, Faculty of Chemistry, 4 Nezavisimosti Av., 220030 Minsk, Belarus

*Corresponding author: ivanreznikov@gmail.com

Abstract:

Dispersions of acid hydrophobized hydrolysis lignin in light crude oil, industrial oil, and diesel fuel were found to demonstrate the transition from Newtonian to non-Newtonian behavior with shear-thinning and thixotropy within the increase in lignin concentration. Lignin-in-diesel fuel dispersions were shown to have the smallest apparent viscosity while lignin-in-industrial oil dispersions have the highest one and the sharpest drop of viscosity with shear rate increasing. At the same time, relative viscosity demonstrates the inverse dependence: It is highest for lignin-in-diesel fuel suspensions. Calculation of parameters based on microrheological model of elastic flocs with generalized Casson equation allowed determining of the parameters k and A that describe hydrodynamic interaction between separated particles and their aggregates under flow, parameter F_A, characterizing the force impeding the break of aggregates and numbers of particles in the floc for different systems as the dependence of shear stress. The explanation based on a higher affinity of diesel fuel to lignin unlike industrial oil and light crude oil as dispersing medium has been given.

Key words:

Lignin, dispersion, rheological properties, floc, oil products, fuel

1 INTRODUCTION

Lignin is the second most abundant organic material in nature. It is the component of wood along with cellulose and hemicelluloses. There is about $3 \cdot 10^{11}$ metric tons of lignin in the biosphere and biosynthesis rate is estimated as $2 \cdot 10^{10}$ metric tons annually. Natural lignins, namely softwood, hardwood and grass, differ in chemical composition and structure from technical lignins that are isolated from biofeedstocks. One of the lignin isolation way is the conversion of biomass to ethyl alcohol. This kind of technical lignin is called "acid hydrolysis lignin" in the case of its separation in solid form by the percolation acid hydrolysis with dilute acids, for example H_2SO_4. From the chemical point of view, lignin is a largely amorphous material of complex structure and is currently pictured as a cross-linked network macromolecule based on three structural units, i. e. monolignol monomers methoxylated to various degree: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol [1]. Despite much research done the world over, the use of hydrolysis lignin and other technical lignins (kraft, soda, organosolv, lignosulphonates) also remains relatively low. There are a lot of proposals for applications: filler for concrete, asphalt, production of carbon fiber, activated charcoal, nanotubes,

free radical scavenger, antioxidants, dispersants, but a very small part, namely hydrolysis lignin is used for the production of value-added products. Because of rather high combustion heat, lignin is used in the sector of energy directly for the production of fuel briquettes, pellets, pyrolysis bio-oil, and fuel gas [2, 3].

There is the following situation with energy and lignin in Belarus: Fossil fuels constitute no more than 15 % of the needs. Belarus imports 20 – 30 % of the electric energy. Three million tons of hydrolysis lignin are in the dumps and create environmental hazards. Hydrolysis lignin has many condensed structures, produced by dehydration reactions between the benzylic carbon atoms and the reactive sites of the aromatic rings. According to the aromatic structure it is not surprising that the biodegradability of lignin appears to be quite low [4] and the only palisade wood-destroying fungi causing the white rot (*Coriolusversicolor, Fomesfomentarius*) and some nesting basidiomycetes (*Collybria, Marasmius, Mycena*) activate the degradation of lignin [5].

There is a great interest in finding additional applications for this plentiful but underused resource. The production of composite fuel based on hydrophobized hydrolysis lignin and waste oil products was chosen to be investigated. There are different sources of oil prod-
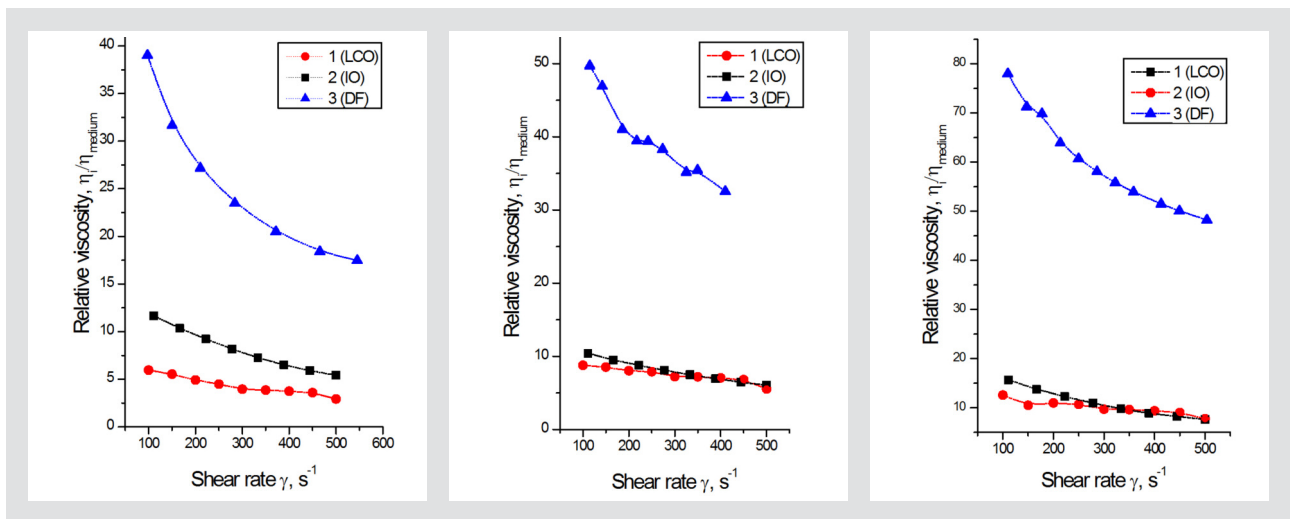
Figure 5: Relative viscosity versus shear rate for AHL suspensions with AHL content 40 % (a), 42 % (b), and 44 % (c) in LCO (1), IO (2), and DF (3).
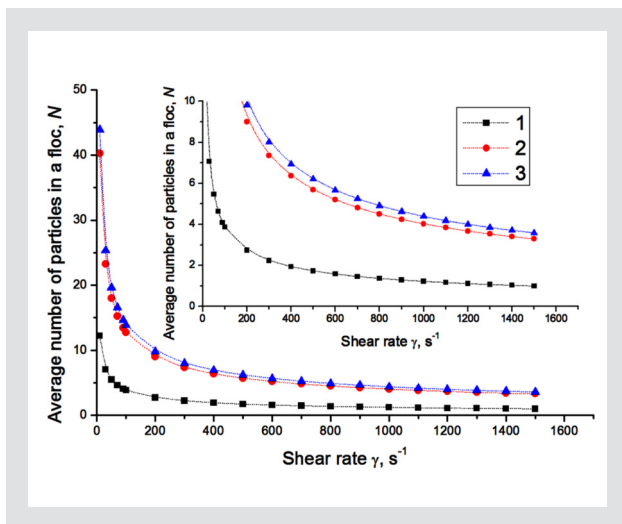

Figure 6: Number of particles in a floc for AHL suspensions in DF (1), IO (2), and LCO (3) versus share rate.
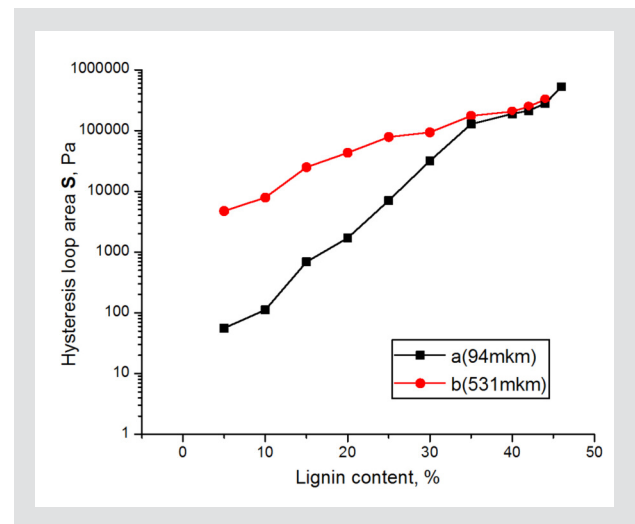

Figure 7: Plots of hysteresis loops square versus AHL content for two fractions of AHL particles with $D_x 50 = 94$ mkm (a) and 531 mkm (b) for AHL-in-IO suspensions at 1000 s^{-1} shear stress.

ered to assume the loss of energy from moving of liquid around the aggregates and between particles inside the aggregate as the main impact of energy dissipation under flow. As it is seen from Table 4 while parameters k_1 and A_1 that describe the hydrodynamic interaction between separated particles under flow have the highest values for suspensions of AHL-in-DF. Parameter F_A characterizing the force impeding the break of aggregates have minimal values for this system (Table 5). The value of $\tau_{oc}^{1/2}$ that characterizes the strength of suspension structure is also minimal for this system.

Medium	$\tau_0 c^{1/2}$	F_A
DF	0.23	4.46±0.22
LCO	0.99	109.55±5.48
IO	7.65	314.62±15.73

Table 5: Calculated parameters on microrheological model of elastic flocs for AHL dispersions in various media.

Calculated numbers of the particles in the floc for different systems as the dependence of shear stress are presented in Figure 6. The smallest size of the flocs, i.e. aggregates of particles including liquid inside and having hydrodynamic volume, takes place in AHL-in-DF suspension. The smaller the floc size, the larger the density (number of network points) of the volume-filling network in the suspension. This is in a general agreement with higher affinity of DF to AHL. The data of thermal analysis of solid concentrated dispersion of AHL-in-DF (composition is 1:1 by mass) in the comparison with AHL-in-IO can be considered as an indirect evidence. In particular, the experimental value of maximum thermal decomposition velocity in the comparison with calculated additive value is higher in the case of AHL-in-DF system and lower in the case of AHL-in-IO, correspondingly 312 to 291 ℃ and 305 to 338 ℃. The influence of AHL particles size for rheological behavior parameters was estimated for the suspensions of three fraction
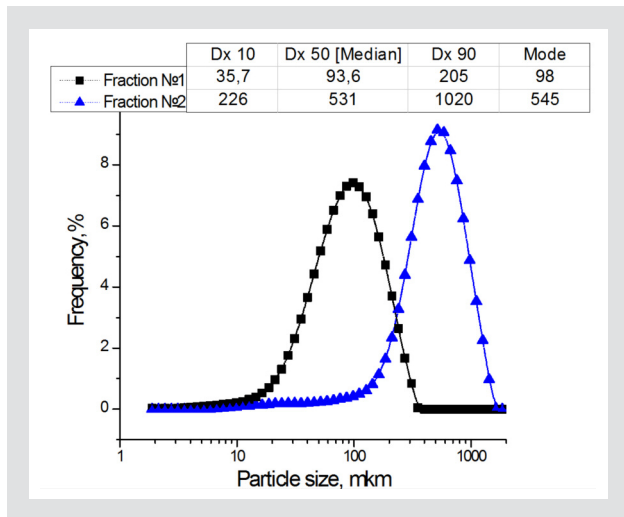
Figure 8: Particles size distribution for the fractions of hydro-phobized hydrolysis lignin sample.

R, D$_x$50, mkm	$\tau_{0c}^{1/2}$	F$_A$	F$_S$·10^7	k$_1$	A$_1$
531	9.58	300.33±15.02	5.01	2.72	0.17
134	7.65	314.62±15.73	1.32	2.36	0.67
94	5.34	309.72±15.49	0.93	2.51	1.11

Table 6: Calculated parameters on microrheological model of elastic flocs for AHL dispersions with different particles size in IO.

of AHL in the same dispersing medium. Figure 7 illustrates the influence of particle size on thixotropic behavior of dispersed system on the example of AHL-in-IO suspensions. As follows from Figure 7 data the smaller the size, the larger the hysteresis loops area at high values of shear rate. Particles size distribution for AHL fractions is shown in Figure 8. The data of Table 6 give insight into how the particle size at high shear rate influences on the rheological behavior of dispersed systems in the frame of elastic flocs model. It is evidenced that rheological parameters are slightly depended on the particle size except on adhesion force between particles and thus strength of system structure that increases with particle size increasing.

4 CONCLUSIONS

Dilute dispersions of hydrophobized hydrolysis lignin in LCO, IO and DF were found to be Newtonian fluids while the concentrated dispersions demonstrate non-Newtonian behavior with shear-thinning and thixotropy. The structure of dispersions depends on the viscosity of dispersing medium and its affinity to lignin by nature. AHL-in-DF dispersions were shown to have the smallest apparent viscosity at the interval of shear rate under study, the smallest size of flocs characterizing by the smallest contracting force and the force impeding the break of particles aggregates, the highest density of volume-filling network. These properties are the consequence of the highest affinity of DF to AHL in the comparison with LCO and IO that we assumed on the basis

of the number of particles in a floc for different oil products. For one of the oil product the hydrodynamic interaction between separated particles under flow depends of the particle size: the smaller the particle sizes the higher the interaction. Finely divided lignin powder is preferable for structuring of dispersions and may be recommended for practical objectives.

REFERENCES

[1] Vanholme R, Demedts B, Morreel K, Ralph J, Boerjan,W: Lignin biosynthesis and structure, Plant Physiol. 153 (2010) 895−905.
[2] Stokke D. Wu Q, Han G: Introduction to wood and natural fiber composites, John Wiley & Sons (2013).
[3] Vishtal AG, Kraslawski A: Challenges in industrial applications of technical lignins. BioResources 6 (2011) 3547−3568.
[4] Stevens ES: Green plastics: An introduction to the new science of biodegradable plastics, Princeton University Press (2002).
[5] Schramm G: A practical approach to rheology and rheometry, Haake (1994).
[6] Savitskaya TA, Reznikov IV, Shcheglov VA, Tsygankova NG, Telysheva GM, Grinshpan DD: Rheological properties of disperse systems based on hydrolyzed lignin and oil, J. Eng. Phys. Thermophys. 85 (2012) 662−667.
[7] Technical Brief: Sampling of Powders, http://www.particlesciences.com/docs/technical_briefs/TB_2011_5.pd, (2011).
[8] Sato ACK, Perrechil FA, Cunha RL: Rheological behavior of suspensions dispersed in non-Newtonian matrix, Appl. Rheol. 23 (2013) 45397.
[9] Yang D, Hrymak A: Rheology of aqueous dispersions of hydrogenated castor oil, Appl. Rheol. 23 (2013) 23622.
[10] Casson N: Rheology of disperse systems, CC Mill (1959).
[11] Kirsanov EA, Remizov SV, Novoselova NV, Matveenko VN: Physical meaning of the rheological coefficients in the generalized Casson model, Moscow Univ. Chem. Bull. 62 (2007) 18−21.
[12] Simanzhenkov V, Idem R: Crude oil chemistry, CRC Press (2003).
[13] Speight JG: Petroleum asphaltenes. Part 1: Asphaltenes, resins and the structure of petroleum, Oil Gas Sci. Technol. 59 (2004) 467−477.
[14] Hiemenz PC, Rajagopalan R: Principles of colloid and surface chemistry, revised and expanded, CRC Press (1997).