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Sorption Properties of Technical-Grade Lignins with Respect to 1,1-Dimethylhydrazine

M. P. SEMUSHINA¹, K. G. BOGOLITSYN^{1,2}, A. YU. KOZHEVNIKOV^{1,2} and D. S. KOSYAKOV^{1,2}¹Lomonosov Northern (Arctic) Federal University,
Naberezhnaya Severnoy Dviny 17, Arkhangelsk 163002 (Russia)

E-mail: m-semushina@mail.ru

²Institute of Ecological Problems in the North, Ural Branch of the Russian Academy of Sciences,
Naberezhnaya Severnoy Dviny 23, Arkhangelsk 163061 (Russia)

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Abstract

The sorption properties of technical-grade lignins were studied with respect to 1,1-dimethylhydrazine. It has been found that the lignin obtained by means of hydrolysis exhibits a high sorption capacity with respect to 1,1-dimethylhydrazine owing to a greater number of active sorption centers. Dynamics has been studied for binding unsymmetrical dimethylhydrazine by the hydrolytic lignin.

Key words: sorption, propellant, 1,1-dimethylhydrazine, UDMH, lignin

INTRODUCTION

In the course of operation in the field of rocketry and refueling on the launch pads in launching carrier rockets, accidental spills of highly toxic propellants containing 1,1-dimethylhydrazine (unsymmetrical dimethyl hydrazine, UDMH) are quite possible. The latter is able to quickly evaporate from the surface and to contaminate atmospheric air [1]. When released into the environment the UDMH is accumulated in ecosystems and decomposes to form highly toxic products [2, 3]. In accordance with the State Standard GOST 12.1.006–76, the UDMH according to the mid-lethal concentration thereof and the coefficient of possible inhalation poisoning belongs to the substances of the first hazard class [4], so the propellant spills must be immediately removed. In this regard, cheap, available and efficient propellant sorbents capable of binding hydrazine species into low-mobility forms those further could be utilized disposed of under the action of high temperature.

At the present time, several UDMH sorbents are developed. The authors of [5] revealed that a high capacity is exhibited by the sorbents based on the DAU grade activated charcoal, on the naturally occurring peat and peat modified with sulphuric acid, as well as on the sorbent obtained *via* treating the peat and charcoal by superheated steam. The authors of [6] in order to retain and neutralize UDMH spills used a sorbent based on modified peat containing transition metal salts. There is a known method for air purification from UDMH with the use of a ligand-exchange sorbent selective with respect to ammonia and amines [7]. The authors of [8] proposed a composition for neutralizing the soil from spills of toxic organic substances including propellants those contain UDMH. This composition is a mixture of alkali or alkaline earth metal peroxides with a carbonaceous adsorbent-catalyst.

As a sorbent of UDMH in our work we have chosen one of wood components such as lignin having active reaction centers (carbonyl and

carboxyl groups) [9]. The presence of the reaction centers in the lignin in determines a mechanism of UDMH binding [10].

Earlier we investigated the sorption properties of peat with respect to UDMH [11, 12]. The authors of [12] revealed the determining role of the lignin and humic components of peat soil in the chemical transformations of the UDMH. It has been demonstrated that the lignin exhibits a maximal retention of UDMH derivatives as compared to the peat and humic acids.

Thus, searching for the most efficient sorbents of UDMH among technical-grade lignins is relevant, both from the standpoint of the environmental support of space-rocket hardware activities, and from the standpoint of waste disposal from the hydrolysis and pulp-and-paper industries.

The purpose of this work consisted in studying the sorption properties of technical-grade lignins with respect to UDMH. To achieve this objective it is necessary to solve several problems: to investigate the functional nature of technical-grade lignins, to determine the sorption capacity of the samples of technical-grade lignins under investigation with respect to UDMH, to reveal the optimal conditions of the sorption process for the sample of technical-grade lignin, having the maximum sorption level with respect to UDMH.

EXPERIMENTAL

As the sorbents of the UDMH we used sulphate lignin isolated from black liquor taken from sulphate softwood cellulose production at the Arkhangelsk Pulp and Paper Mill (APPM) and hydrolytic lignin from the dumps of hydrolytic manufacture at Arkhangelsk and Onega Hydrolysis Plants.

The functional composition of the samples of technical-grade lignins was determined by means of infrared spectroscopy. The IR spectra of the lignin samples under investigation were registered within the wave number range of 400–4000 cm^{-1} using a Vertex70 infrared spectrometer (Bruker, Germany) with a GladiATR attenuated total reflection attachment (Pike, USA). According to IR spectroscopic data, relative optical density (absorbance) values were

calculated for main absorption bands inherent in different functional groups of lignin. As an internal standard we chose an absorption band at 1512 cm^{-1} corresponding to skeleton vibrations in the aromatic nucleus that was used as a denominator in the course of calculating the relative optical density (ROD, %, absorbance) of other bands:

$$\text{ROD} = D_i/D_{1512} \quad (1)$$

where D_i is the absorbance at the i -th wave number; D_{1512} is the absorbance at 1512 cm^{-1} .

Table 1 presents data concerning the ROD of main absorption bands corresponding to the vibrations of different functional groups inherent in the samples of lignins under investigation.

The sorption properties of lignin samples are to a considerable extent caused by a developed specific surface value thereof. Using the nitrogen adsorption method according to the BET theory we determined the specific surface area (S_{sp}) for all the samples of technical-grade lignins under investigation with the help of an Autosorb-iQ-MP analyzer (Quantachrome, USA). The lignin samples were previously degassed to remove distillery vapours and gases adsorbed by the surface of lignin. The maximum temperature of degassing was equal to 160 $^{\circ}\text{C}$; the duration of the process was equal to 150 min. The values of S_{sp} for the sample of the sulphate lignin (APPM), and for hydrolytic lignin samples from the Arkhangelsk and Onega Hydrolysis Plants amounted to 42.0, 5.8 and 14.8 m^2/g , respectively.

Studying the UDMH sorption by technical-grade lignins was performed under static conditions at an optimum value of pH (5.5), which corresponds to the maximum sorption capacity of lignin-humic substances with respect to UDMH [11, 12]. The choice of the pH value as connected with the fact that the peat soil within the areas of the European North of Russia where the separating parts of rockets use to fall are typically characterized by such an acidity (pH 4.5–6.0), wherein there occurs a rapid and sufficiently strong binding of 1,1-dimethylhydrazine. Just this could serve as an explanation of a local character inherent in UDMH contamination [13]. To a 100 mL dry clean conical flask with a sealing plug was placed a weighed sample portion of lignin. The acidity required was provided using a univer-

TABLE 1

Data concerning the relative optical density of the main absorption bands (MAB) in the IR spectra of technical-grade lignins

Wave number, cm ⁻¹	Assignment of vibrations	ROD, %			
		Sulphate lignin		Hydrolytic lignin	
		APPM	Sigma Aldrich	AHP	OHP
3420	OH valence bond	52.75	60.00	73.40	86.44
1695–1784	C=O valence bonds:				
1695	α,β-unsaturated aromatic aldehydes, and carboxylic acids	48.95	43.59	67.69	78.05
1715	unconjugated ketones, <i>para</i> -substituted aryl ketones	47.85	39.41	63.35	75.09
1722	α,β-unsaturated esters	44.66	37.31	58.90	69.86
1730	aliphatic aldehydes	41.03	35.57	54.87	64.46
1742	saturated aliphatic esters	33.66	33.04	47.46	55.92
1760	saturated aliphatic carboxylic acids	24.42	31.12	39.41	46.52
1784	saturated acyclic anhydrides	18.70	29.73	34.96	37.63
1080	C–O valence bonds	104.40	126.96	126.60	218.64
1030	O–C–C bonds in the esters of primary alcohols (stretching vibrations of an “alcoholic” fragment C–O)	127.47	116.52	142.55	240.68

Note. APPM – the Arkhangelsk Pulp and Paper Mill; AHP, OHP – the Arkhangelsk Hydrolysis Plant and Onega Hydrolysis Plant, respectively.

sal buffer solution. For the most complete wetting and swelling of the sorbent, each weighed portion of lignin was flooded with 25 mL of the buffer solution to hold during 24 h, with a periodical stirring. Then, 25 mL of the solution with a preset UDMH concentration (UDMH was dissolved in the universal buffer solution) to kept hold permanent stirring for a certain time, with maintaining a constant temperature value (20 °C).

After the lapse of the sorption time, the solution was filtered through a nylon membrane filter with a pore diameter of 0.2 μm, then the equilibrium concentration of UDMH was determined in the filtrate by means of ion chromatography using a “Stayer” HPLC system (Akvilon JSC, Russia) with an amperometric detector (Khimavtomatika JSC, Russia) [14]. The separation of hydrazines was carried in cationic form, with the use of a column packed with a sulpho-cation-exchange sorbent (Ecoanalytical Association (EAA) “Ecoanalitika”, Russia). As an elution agent we used a buffer solution with pH 5.4 (EAA “Analitika”, Russia). The measurements were performed at an eluent flow

rate equal to 1 mL/min in a constant current mode at the potential of the glassy carbon working electrode equal to +1.300 V. The experimental results were expressed as the UDMH sorption level (*A*):

$$A = (C_0 - C_p)V/g \quad (2)$$

where *A* is the amount of UDMH sorbed, mg/g; *C*₀, *C*_{eq} are the initial and equilibrium concentrations of UDMH in the solution, respectively, mg/L; *V* is the volume of the solution, L; *g* is the mass of the sorbent in the air-dry state, g.

RESULTS AND DISCUSSION

In order to select the most efficient propellant sorbent among the technical-grade lignins, we investigated the sorption capacity of the samples of technical-grade lignins with respect to UDMH. The experiment was performed at a sorbent/solution ratio equal to 1 : 250 (for the lignin sample portion mass amounting to 0.2 g and the UDMH solution volume equal to 50 mL), UDMH working solution concentration amounting to 500 mg/L, and sorption time

equal to 2 h. The level of UDMH sorption for the sulphate lignin (from APPM) has been revealed to amount to (3.56 ± 0.43) mg/g, whereas that for the samples of hydrolytic lignin from the Arkhangelsk and Onega Hydrolysis Plant (6.71 ± 0.81) and (20.76 ± 2.49) mg/g, respectively. Thus, the hydrolytic lignin from the Onega Hydrolysis Plant is characterized by the maximum level of sorption with respect to UDMH. Therefore, for the further studies concerning the determination of the optimal conditions for the UDMH sorption process, we used this sample.

The increased adsorption properties of the hydrolytic lignin taken from the Onega Hydrolysis Plant could be, to all appearance, caused by a higher content of functional groups those represent active lignin reaction centers, which is confirmed by means of IR spectroscopy.

Low sorption capacity with respect to UDMH inherent in the sulphate lignin could be, to all appearance, connected with a low content of carbonyl groups those act as hydrazine binding centers due to the formation of hydrazones.

In order to determine the time required for maximum level of UDMH sorption, we studied the sorption dynamics of hydrolytic lignin (Fig. 1) within the range of 0.5–4 h at intervals of 30 min at a ratio between the solid and liquid phase amounting to 1 : 250, UDMH concentration 500 mg/L, pH 5.5 and at the temperature of 20 °C. The sorption equilibrium in the system is established at the phase contact time equal to 2 h, whereby the hydrolytic lignin sorption capacity with respect to UDMH amounts to 20 mg/g.

In order to determine the optimum ratio between the volume of the solution and the

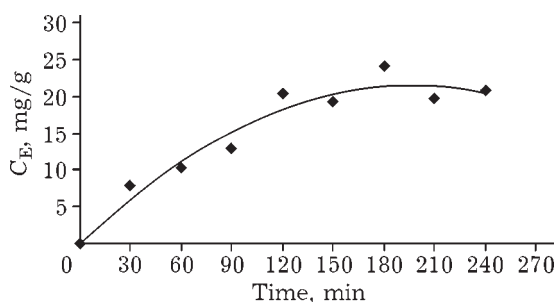


Fig. 1. UDMH sorption dynamics by hydrolytic lignin at the concentration of UDMH equal to 500 mg/L.

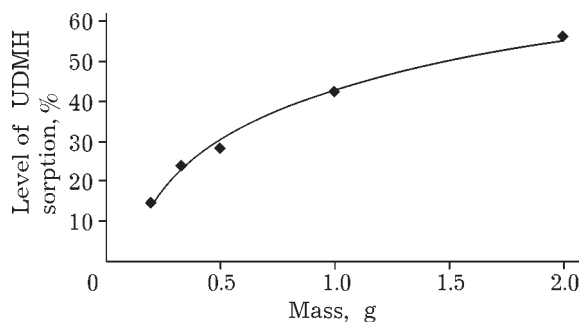


Fig. 2. Level of UDMH sorption depending on the mass hydrolytic lignin.

mass of hydrolytic lignin, we studied an effect of the sorbent mass exerted on the UDMH sorption process (Fig. 2). The experiment was conducted at UDMH concentration amounting to 500 mg/L, sorption time 2 h, pH 5.5 and 20 °C. The masses of the weighed lignin sample portions amounted to 2.0, 1.0, 0.5, 0.33, 0.2 g, the volume of the UDMH solution was equal to 50 mL. The highest level of UDMH sorption was observed at the hydromodulus value equal to 25/1.

In order to determine the conditions for the maximum level of UDMH extraction from the solution, we investigated the process of UDMH sorption within the range of a lower concentration of the initial solution of 1,1-dimethylhydrazine. The level of UDMH extraction depending on the ratio between UDMH content and the mass of lignin is presented in Fig. 3. The concentration of UDMH working solution was varied within the range from 20 to 500 mg/L. The experiment was conducted at the phase contact time equal to 2, hydromodulus amounting to 25/1 and pH 5.5.

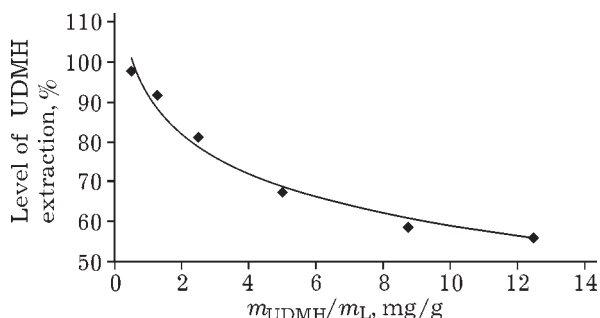


Fig. 3. Level of UDMH extraction depending on the concentration.

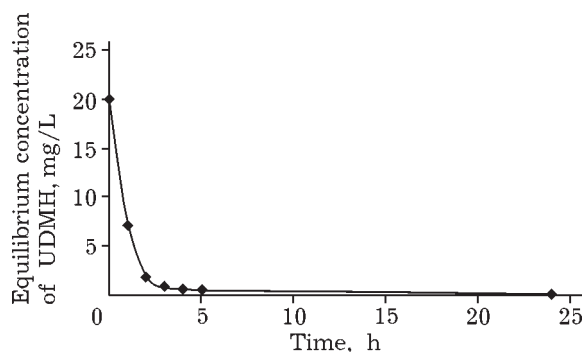


Fig. 4. UDMH sorption dynamics by hydrolytic lignin at the concentration of UDMH equal to 20 mg/L.

It has been found that the maximum level of UDMH extraction can be achieved at the concentration of UDMH solution amounting to 20 mg/L (0.5 mg of UDMH/g of lignin); the value is equal to 97.5 % with respect to the initial UDMH content in the solution. The residual concentration of UDMH is equal to 0.5 mg/L being 25 times higher than the MPC of UDMH in potable water (0.02 mg/L). In this connection, we investigated the dynamics of UDMH sorption by the hydrolytic lignin at the UDMH concentration in the solution equal to 20 mg/L (Fig. 4). The experiment was conducted at the hydromodulus of 25/1 and pH 5.5. After 24 h, the concentration of UDMH in the solution did not exceed the MPC value amounting to 0.016 mg/L, which corresponds to the level of UDMH extraction equal to 99.92 %.

CONCLUSION

The results of the studies performed can lead to the following conclusions:

1. The humified technical-grade lignins (hydrolytic lignin from the Onega Hydrolysis Plant JSC) are characterized by a high content of reaction centers and, as a consequence, by high sorption properties with respect to UDMH as to compare with other technical-grade lignins.

2. The sorption of UDMH by the hydrolytic lignin is caused by the presence of active reaction centers such as carbonyl and carboxyl groups in the structure of the sorbent, as well

as by a developed spatial structure of the sorbent. For the concentration of UDMH in the solution equal to 20 mg/L and the hydromodulus amounting to 25/1, the level of UDMH extraction after 24 h amounts up to 99.92 %, whereas the residual concentration of UDMH does not exceed the MPC value required for potable water.

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