

Modification of Hydrolysis Lignin by Hydrogen Peroxide to Obtain an Effective Adsorbent of Highly Toxic Rocket Fuel

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Abstract

Lignin, a large scale by-product of papermaking and bioethanol production, is applied now in various fields. One of the main areas of use is in the development of different adsorbents, including those intended for detoxification of the spills of 1,1-dimethylhydrazine-based rocket fuel. The present work has shown the possibility of oxidative modification of hydrolytic lignin by hydrogen peroxide to improve the efficiency of the adsorbent. The change in functional composition of the modified adsorbent was studied by IR and NMR spectroscopy. It was shown that the oxidative treatment led to an increase in the content of carbonyl and carboxyl groups, which act as the active adsorption centres for hydrazine molecules. The optimum oxidation conditions were found. An increase in treatment duration from 15 to 120 min and in concentration of hydrogen peroxide from 6 to 30% did not have a significant effect on the functional composition and adsorption properties of lignin.

1. Introduction

Space rocket activities (SRA) have a significant impact on the environment. Chemical effects on natural environments that appear as a result of emissions and spills of liquid rocket fuel components are considered to be particularly significant. One of the most dangerous components of rocket fuel is unsymmetrical dimethylhydrazine (UDMH, 1,1-dimethylhydrazine). It results in many negative environmental consequences associated with its high volatility, almost unlimited solubility in water and ability for migration and accumulation [1–4].

UDMH is a substance of Hazard Class 1 and during its decomposition highly toxic and carcinogenic products such as hydrazine, methylhydrazine, nitrosodimethylamine (NDMA), tetramethyltetrazene, formaldehyde, etc. are formed [5–7].

In view of this, in addition to the assessment of environmental impacts and SRA monitoring, in the present day the problem of development of methods for rapid elimination of accident consequences related to rocket fuel spills has acquired a particular relevance. One such method involves

the use of inexpensive, readily available and effective adsorbents of 1,1-dimethylhydrazine capable of binding it into inactive forms. Technical lignins, large-tonnage by-products from pulp-and-paper and bioethanol production industries, can be used as such UDMH adsorbents.

Previously, we have investigated the possibility of using hydrolytic lignin as an adsorbent of hydrazine based rocket fuel [8]. The conditions of UDMH adsorption from solution aimed at achieving a residual concentration not exceeding the maximum permissible concentration level accepted by the Russian Federation (MPC = 0.02 mg/L) were determined. As a result, a patented adsorbent based on hydrolytic lignin with high moisture content for decontamination of rocket fuel spills was developed [9]. It was found that such adsorbent could also be used to prevent air pollution by 1,1-dimethylhydrazine.

However, the adsorption capacity of hydrolytic lignin in relation to UDMH in comparison with other known adsorbents, such as activated charcoal or zeolites, is relatively low due to lower values of surface characteristics (specific surface

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area, porosity, etc.) [8, 10]. On the other hand, the main adsorption mechanism in this case is chemical adsorption, due to interaction of UDMH with carbonyl and carboxyl groups of lignin. This confers an advantage because an organic adsorbent with UDMH strongly chemically bound could be disposed of by incineration at relatively low temperatures, in contrast to the disposal of mineral adsorbents, which requires a higher temperature to prevent UDMH, desorption into the gas phase due to weak physical adsorption.

As a result of the above, it would be advisable to conduct modifications of hydrolytic lignin in order to improve its adsorption capacity by increasing the number of active sorption centres and/or surface characteristics.

Today many methods for detoxification of UDMH using modified adsorbents are known [11–13].

Peat, activated carbon and carbon-mineral shungite rocks are often used as active matrices. Orthophosphoric and sulfuric acids, salts of transition metals (as catalysts), superheated water steam are used as modifying additives.

An increase of carbonyl and carboxyl groups capable of binding hydrazines in the sorbent, by means of oxidation with various reagents, is a perspective for modification. The most available reagent is hydrogen peroxide. This is one of the most common, safe, non-toxic and available oxidants used in various industries (pulp and paper, textiles, food, as an oxidizer for liquid rocket fuels, etc.) [14–16].

The purpose of this research is to study possible modifications of hydrolytic lignin by hydrogen peroxide to obtain an effective adsorbent of highly toxic rocket fuel.

2. Experimental

2.1. Subject of research

The subject of this research is hydrolytic lignin (HL), modified by hydrogen peroxide in various conditions according to the scheme that follows. Initial samples of lignin were collected from open dumps at the Onega Hydrolysis Plant (Arkhangelsk region, Russia) in 2013 from the depth 50–60 cm according to the method of “envelope” from five points with the subsequent averaging. The age of lignin was at least 15 years. Table 1 presents its characteristics in terms of moisture content, ash content, content of Klason lignin [17] and functional composition [18].

Table 1

Characteristics of initial sample of hydrolytic lignin

Moisture, %		4.2±0.1
Ash, %		2.7±0.2
Klason lignin, %		77±2.0
Functional composition, %	COOH	1.42±0.02
	COOH+OH	5.65±0.12
	CO	3.77±0.05

2.2. Modification of hydrolytic lignin

Treatment with hydrogen peroxide was carried out by varying the following parameters: treatment time of 15, 30, 45, 60, 120 min and concentration of H₂O₂ of 6, 10, 15, 20, 25 and 30%. In all experiments, the treatment was carried out at a ratio of sorbent mass to solution volume of 1:50.

Modification of HL by hydrogen peroxide with variation of treatment time was carried out according to the following scheme: 5 g of lignin was placed in a 500 mL conical flask with a ground stopper, to which 250 mL of hydrogen peroxide solution of concentration 30% was then added and kept for the required time in the shaker (IKA KS 260 basic, Germany). The lignin was separated from the solution in a ROTINA 380 centrifuge (Hettich Zentrifugen, Germany), washed with distilled water to pH 7 and dried in Petri dishes to air-dry condition.

Modification of HL by hydrogen peroxide with variation of concentrations of modifying agent was performed in a similar way by changing the concentration of H₂O₂ in the specified range at a constant treatment time of 2 h.

2.3. Characteristics of the functional composition of lignins by IR spectroscopy.

IR spectra of lignin samples has been recorded in the range from 4000 to 400 cm⁻¹ using a Vertex-70IR spectrometer (Bruker, Germany) with a Glad-iATR (Pike tech., USA) attenuated total reflection attachment with diamond prism. As a result of analysis of the IR spectra, relative optical densities of the main absorption bands typical for the different functional groups of lignins were calculated. As an internal standard, the absorption band at 1512 cm⁻¹ was selected, which corresponds to skeletal vibrations of the aromatic ring. Values of the relative optical densities (ROD, %) of the other bands were calculated in relation to that band, according to equation:

$$ROD = \frac{D_i}{D_{1512}},$$

where D_i – value of optical density at the i -th wave number and D_{1512} – value of optical density at 1512 cm^{-1} .

2.4. Characteristics of functional composition of lignins by NMR spectroscopy

In order to investigate the functional composition of the lignin samples ^{13}C NMR spectra were recorded on a Fourier-NMR spectrometer with superconducting magnet AVANCEIII 600 MHz (Bruker, Germany). A solid state sensor was used to record spectra, as hydrolytic lignin and modified samples of lignin are not soluble in solvents used in NMR spectroscopy. During the analysis a method of polarisation transfer of hydrogen atoms was used, which facilitated assignment of signals in the spectra to the structural groups CH, CH_2 or CH_3 [19, 23].

The spectra has been recorded with the following parameters: spectrum width 301 mD; spectrum registration time 0.023 sec; delay between the impulses 5 sec; contact time 2 msec; proton impulse duration 2.25 μsec ; number of accumulations 4096; frequency of magic-angle spinning 10 kHz .

By analysis of NMR spectra, relative signal intensities were calculated corresponding to different functional groups of lignin.

2.5. Characterization of surface of the sorbent

Analysis of the porosity composition was performed on surface area and porosity analyser ASAP 2020 mp (Micromeritics, USA). The samples were first degassed in the degas port of the device at 100 $^\circ\text{C}$ to a residual pressure of 5 $\mu\text{m Hg}$ with storage time under specified conditions for 2 h, the sample weight was 300–600 mg.

The parameters of porosity composition were calculated according to obtained isotherms using the device software. The total pore volume, specific surface area and average pore size were determined according to the Brunauer–Emmett–Teller (BET) method, the micropore volume according to a t-method, the mesopore volume according to the Barrett–Joyner–Halenda (BJH) method, and Horvath–Kawazoe method was used to calculate the average micropore width [20–23].

2.6. Sorption of UDMH by original and modified hydrolytic lignin

Sorption experiments were performed in static conditions according to the following general scheme: a lignin sample weighing 200 mg was placed into 100 mL conical flasks with a ground stopper, and 50 mL of UDMH aqueous solution of concentration 500 mg/L was added and kept under continuous stirring on a magnetic stirrer (IKA KS 260 Basic, Germany) for 2 h. On completing the sorption, the solution was filtered through a membrane filter with a pore diameter of 0.2 μm . The UDMH concentration in the filtrate, as well as in the initial solution before sorption, was determined by ion chromatography using a “Stayer” (Akvilon, Russia) HPLC system with an amperometric detector (Khimavtomatika, Russia) [24]. Experimental results were expressed as an UDMH sorption value determined by equation:

$$C_E = \frac{(C_o - C_p) \cdot V}{g},$$

where C_E – amount of adsorbed UDMH (mg/g); C_o , C_p – initial and equilibrium concentration of UDMH in solution, respectively (mg/L); V – solution volume (L); g – sorbent mass (g).

3. Results and discussion

3.1. Modification of the functional composition of lignin samples

Comparisons of the relative optical densities of the main absorption bands in IR spectra (Fig. 1) corresponding to the vibrations of the respective functional groups in the lignin samples are presented in Tables 2 and 3.

As a result of comparison of the relative optical densities of the main absorption bands it was found that the content of carbonyl groups (1704 cm^{-1}), C–O valence bonds (1080 cm^{-1}) and C–O in carboxyl groups (1220 cm^{-1}) had increased, indicating the oxidation of HL. Thus, IR spectroscopy showed the increase in the content of carboxyl and carbonyl groups in the modified lignin, which could perform as active sorption centers in relation to UDMH. Moreover, oxidation of HL had already occurred during treatment by hydrogen peroxide of concentration 6%. Further increase of concentration of modifying agent did not significantly increase the number of sorption centres.

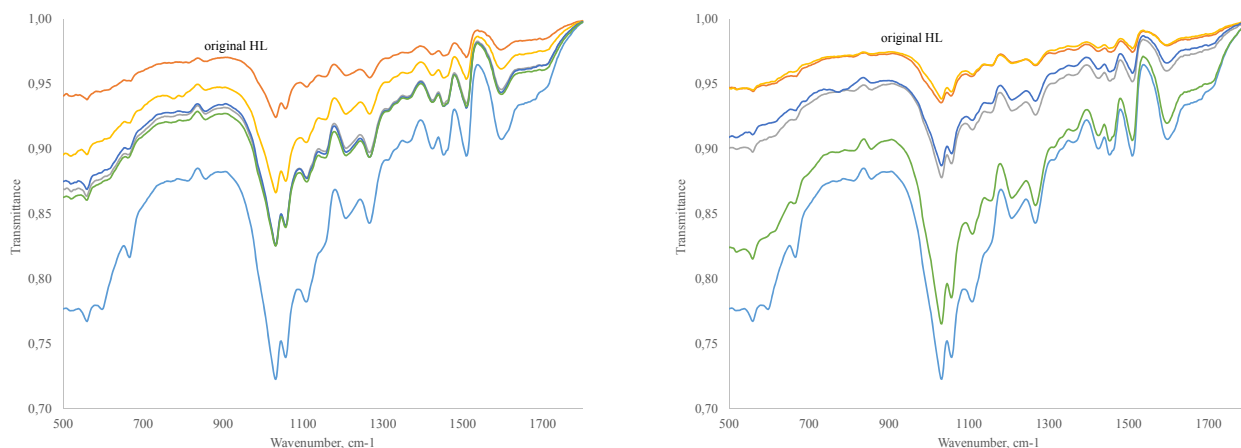


Fig. 1. IR spectra of lignins: (a) original HL and treated with 30% hydrogen peroxide solution for different times; (b) original HL and treated with hydrogen peroxide solution of various concentrations (treatment time 2 h).

Table 2

Comparison of ROD of the main absorption bands in the IR spectra for the original HL, and after treatment with 30% hydrogen peroxide solution for various times

Wave number, cm ⁻¹	Assignment of vibrations	ROD, %					
		Treatment time, min					
		0	15	30	45	60	120
1704	C=O valence bonds	28	41	43	42	45	47
1220	C-O in COOH (partially OH)	108	149	152	156	151	158
1080	C-O valence bonds	198	262	251	253	256	259

Table 3

Comparison of ROD of the main absorption bands in the IR spectra for the original HL and treated with hydrogen peroxide solution of various concentrations (treatment time 2 h)

Wave number, cm ⁻¹	Assignment of vibrations	ROD, %						
		Concentration of hydrogen peroxide, %						
		0	6	10	15	20	25	30
1704	C=O valence bonds	28	46	47	49	51	51	47
1220	C-O in COOH (partially OH)	108	161	158	159	160	158	158
1080	C-O valence bonds	198	256	266	270	265	261	259

3.2. Characteristics of the functional composition of lignin samples by NMR spectroscopy

The basic functional groups and lignin fragments are identified by chemical shift value (Table 4) according to Ref. [25].

According to NMR analysis, it was determined that the content of functional groups active in the adsorption of UDMH (-COOH, -COO⁻, -COX) in the sample of hydrolytic lignin modified by hydrogen peroxide increased relative to their content in the original sample. The band corresponding to carbonyl group was not detected in the NMR spectra. Thus, data from nuclear magnetic resonance spec-

troscopy confirm the conclusion about the increase in the number of carboxyl groups.

Table 4

Results of NMR analysis of original and modified lignin

Group	Chemical shift, ppm	Relative intensity	
		HL, original	HL, treated by 6% H ₂ O ₂
-C=O	212	-	-
-COOH -COX -COO ⁻	174	1.0	1.5
-CH=CH-	148	13.2	13.7
-CH=CH ₂	115	10.9	11.2

Table 5
Composition characteristics of modified lignins

#	Average micropore width, nm	Average mesopore width, nm	$V_{\text{micropore}} \cdot 10^3, \text{ cm}^3/\text{g}$				$V_{\text{mesopore}} \cdot 10^2$ (1.7-50 nm)	$V_{\Sigma\text{pore}} \cdot 10^2$	Specific surface	Mesopore specific surface, (1.7-50 nm)	Average adsorption energy
			Horvath-Kawazoe	BET (4V/A)	Horvath-Kawazoe	Dubinin-Radushk	BET	T-plot, Carbon Black STSA	cm^3/g	cm^3/g	m^2/g
	Horvath-Kawazoe	BET (4V/A)	Horvath-Kawazoe	Dubinin-Radushk	BET	T-plot, Carbon Black STSA	BJHdes, Broekhoff-de Boer	BET	BET	BJHdes, Broekhoff-de Boer	Dubinin-Radushk
1	1.474	20.59	4.19	5.69	4.19	0.548	4.01	5.96	11.58	9.91	9.72
2	1.517	20.18	4.45	5.03	4.45	0.306	4.82	6.50	12.88	11.61	10.01

3.2. Surface characteristics and sorption capacity of modified lignins

As a result of the modification of lignin samples, slight increases in the volume of micro- and mesopores, specific surface area and adsorption energy were found (Table 5). When compared with such a common adsorbent as activated carbon [10], the surface area and micropores volume of lignin are two orders of magnitude smaller. This fact indicates the insignificant ability of the obtained adsorbent to the physical sorption. Taking into account the ability of carbon based adsorbents to bind up to 30% (by weight) of 1,1-dimethylhydrazine, one can expect that due to physical factors, hydrolytic lignin can adsorb up to 0.2–0.3% of UDMH from gaseous medium and even much less from aqueous solution.

As a result of sorption capacity measurements the following values of UDMH maximum adsorption were obtained: 15.7 ± 0.1 mg UDMH per 1g HL modified by hydrogen peroxide and 8.3 ± 0.1 mg UDMH per 1 g of untreated hydrolysis lignin.

The experimental results showed that treatment of hydrolysis lignin with hydrogen peroxide positively affects the sorption capacity in relation to UDMH and leads to its increase by 2 times. The obtained value (1.57%) is an order of magnitude higher than expected for physical sorption, which is additional evidence of the chemical binding of UDMH with carbonyl and carboxyl groups of lignin.

In this situation, the lower value of the sorption capacity compared to adsorbents such as activated charcoal and zeolites cannot be regarded as a drawback of modified hydrolysis lignin. This is due to the strong binding of hydrazines and possible prod-

ucts of their transformation with the adsorbent, which was already noted by us in the introduction. One more important factor is also the cost of the adsorbent, which is absolutely not comparable for lignin and the mentioned above very expensive alternatives.

Characterizing the obtained sorbent, one should also mention such an important factor as the possibility of the formation of toxic products of oxidative transformation of UDMH [26] and their release from the surface of the adsorbent into environment. Unlike mineral adsorbents acting as catalysts for such processes [27], lignin inhibits oxidative transformations of hydrazines due to chemical binding to less reactive hydrazones and salt forms. This effect is well known and is considered as a reason for the prolonged preservation of 1,1-dimethylhydrazine in bound forms at the sites of the fall of carrier rockets with predominance of peat bog soils [28].

In order to achieve the most effective sorption process, studies of the sorption capacity of modified lignins under various treatment conditions were conducted (Fig. 2).

In all cases the increase in sorption capacity of modified lignin compared to original can be observed. Changes in the time of lignin treatment by reagents and their concentration in the ranges covered did not lead to a significant change in the sorption capacity in relation to UDMH.

The increase in sorption of modified lignins in relation to UDMH can be associated with an increase in the number of active functional groups and, to a lesser degree, with an increase in specific surface area and porosity.

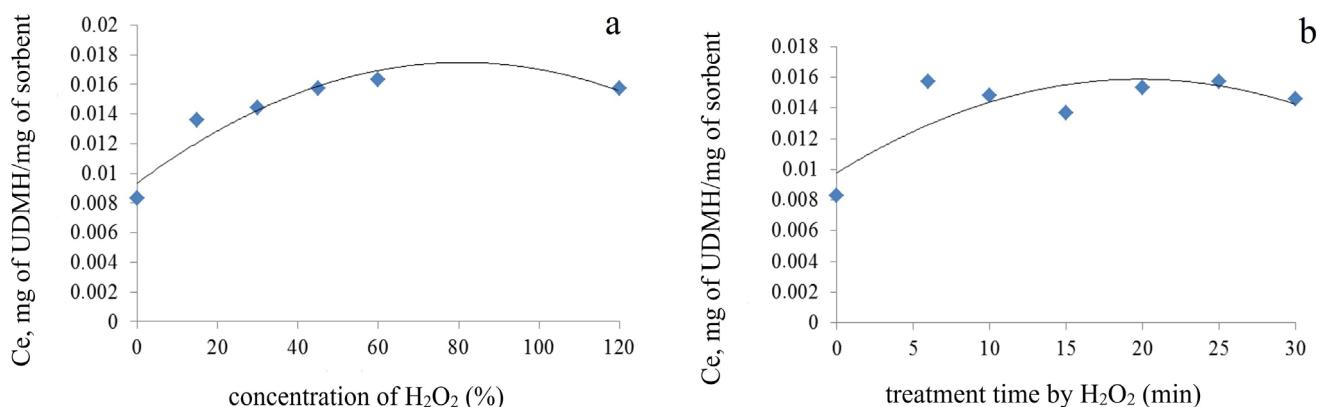


Fig. 2. Effect of concentration of hydrogen peroxide (a) and treatment time (b) of hydrolytic lignin by 6% H₂O₂ on its adsorption capacity in relation to UDMH.

4. Conclusion

A new approach to increase the efficiency of hydrolytic lignin as a sorbent of UDMH was suggested, which consisted in its modification by hydrogen peroxide. Modification of HL increased the efficiency of the sorbent by 2 times. Moreover, the increase in the content of carbonyl and carboxyl groups in the sorbent functioning as active sorption centres takes place.

Increase in treatment duration from 15 to 120 min and in concentration of hydrogen peroxide from 6% to 30% did not make a significant impact on the functional composition of lignin.

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