DIAGNOSTICS OF POLISACCHARIDE EPR PYROLYSIS

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Abstract

The electron paramagnetic resonance(EPR) method is successfully used for diagnostics of the material properties and of the processes involving unpaired electrons. The paper presents an analysis of new potentialities in the development of the EPR method, as applied to the pyrolytic decomposition processes of carbon-containing materials, and of peculiarities in the paramagnetic properties formation of a pyrolysis product.

A considerable widening of the scope of EPR spectroscopy both in research and in the applied problems solving has been observed since the development of compact specialized EPR analyzers, characterized by high metrological potentialities due to the abandoned functional redundancy of the conventional multi-purpose EPR spectrometers and owing to the use of modern microwave elements, microwave engineering as a whole, and a new structure of the basic analyzer units.

Key words:-method EPR,carbon,Pyrolysis, spectroscopy methods, carbon-containing materials, microwave.

الخلاصة

استخدام أسلوب الرنين الكهروالبارامغناطيسي تم بنجاح لتشخيص خصائص المواد والعمليات التي تنطوي على مزواج الإلكترونات. وتقدم هذه الورقة تحليلا لإمكانات جديدة في تطوير الأسلوب الرنين الكهروالبارامغناطيسي ، على النحو المطبق في عمليات التحلل الحراري من المواد التي تحتوي على الكربون،ومن خصوصيه مميزه لتكوين متوازي المغناطيسية لمنتج الانحلال الحراري.

وقد لوحظ اتساع كبير في نطاق التحليل الطيفي للرنين الكهروالبارامغناطيسي في البحوث وفي حل المشاكل التطبيقية على حد سواء، وقد لوحظ منذ وضع المميزات المتخصصة للمحللات الرنين الكهروالبارامغناطيسي، وتتميز بإمكانات القياس عالية بسبب التكرار الوظيفي لمطيافات الرنين الكهروالبارامغناطيسي متعددة الأغراض التقليدية ويرجع ذلك إلى استخدام العناصر الحديثة تعمل بالموجات الدقيقة، وهندسة الموجات الدقيقة ككل، والبناء الجديد للوحدات الأساسية للمحلل.

ملاحظة :- تم اجراء القياسات في مختبرات جامعة مينسك .

1-Introduction

Na**t**ural coal, formed in the process of natural metamorphism, manifested in a large variety of options Physico-chemical structures, useful properties which are still not used to the fullest. Pyrolysis of polysaccharides used in obtaining high-performance carbon-based sorbents to a certain extent is analogous to prirodnog metamorphism and is receiving increasing attention as a way of biodiesel and other products, valuable for the chemical-based industries(1). The analogy between the processes of natural metamorphosed and pyrolysis of carbonaceous materials, in principle, allows you to create a scientific basis for decision akttualnyh problems of establishing mechanisms for the extraction of coals of various degrees of metamorphism, as well as improve technology promyshoennogo decomposition of carbon-containing raw materials for metallurgy, chemical industry, environment and energy(2).

n order to solve scientific and practical problems of the method of electron spin resonance (ESR) is very effective, because the carbon and hydrocarbon structures characterized by the presence of high concentrations of unpaired electrons localized at the carbon center and having a generally optimal for recording the EPR signals the spin-lattice relaxation(3) .

Supplement EPR techniques based on so-called "oxygen effect" and the ways zaimetvovannymi of pyrolysis technology, further extends the capabilities of the EPR - diagnosis to determine the properties and types of hydrocarbon structures. With EPR, the report analyzes the changing characteristics of paramagnetic and sorption properties of coal a low degree of metamorphism of the deposit Nariyp-Suhayt with pyrolytic degradation of hydrocarbon structure(4).

2-Results

Additional possibilities for the successful use of EPR spectroscopy methods in diagnostics of pyrolysis products are offered: in the process of EPR signal recording and analysis in carbonaceous and carbon-containing materials the features of the intensity variation, spectral position, and signal form are used in combination, and the signals are recorded in the presence or in the absence of molecular oxygen, with changes of the microwave power in a measuring resonator at different pyrolysis stages. The possibilities to control a degree of the pyrolytic decomposition of carbon-containing starting materials and of the sorption activity of a solid carbonaceous product by the EPR measuring results for the pyrolysis products are also studied(5).

Fig. 1 demonstrates: 1 – EPR spectrum for S600 sample of the pyrolysis-treated wood sawdust (T=600°C, t=120 min) measured in the air; 2 – spectrum of an empty resonator with a standard specimen of ruby. The spectrum exhibits both a sharp and a very broad absorption lines. A halfwidth of the broad component comes to 1000-2000 Oe and that of the sharp component is ΔH=6 Oe. Maximum absorption of the broad component is associated with the magnetic field value $H \approx$2600 Oe, that in the measuring conditions used is corresponding to the *g*-фактору $g \approx 2.5$. And maximum absorption of the sharp component is associated with the *g*-factor value $g = 2.003$. A broad absorption line is caused by technological impurities in the sample, possibly Fe and Mn sometimes observed in the wood sawdust used here as a starting material(6).

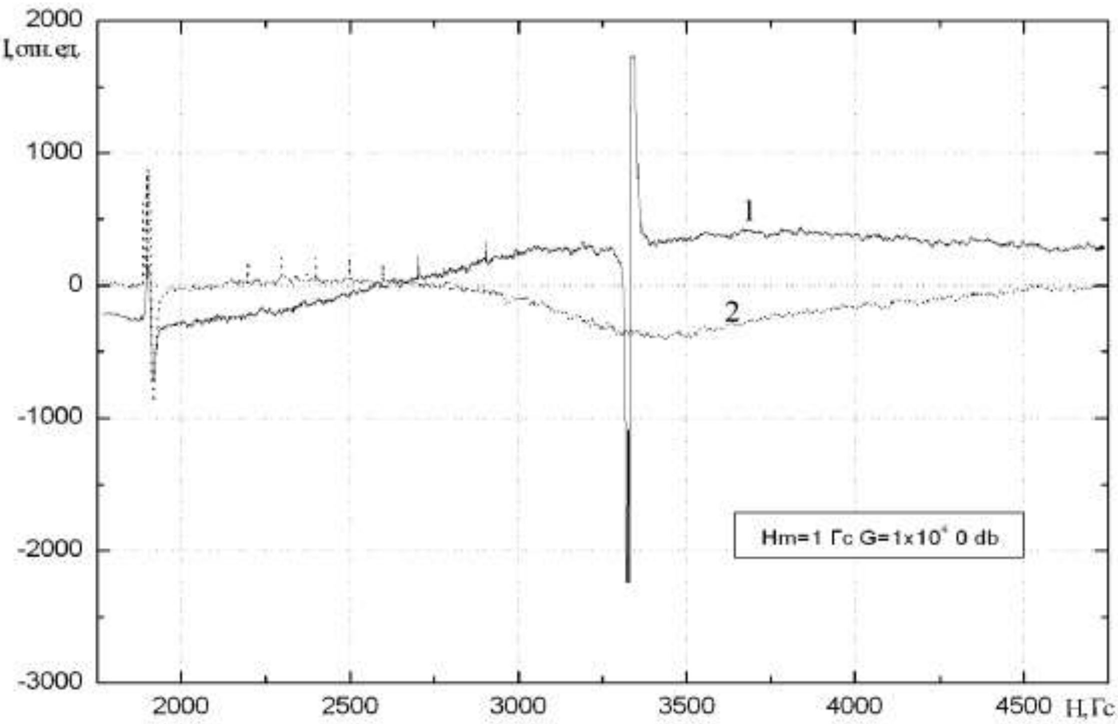

Figure 1 - EPR spectra for S600 sample of the pyrolysis-treated wood sawdust at T=600°C, t=120 min
1 – measured in the air; *2* – spectrum of an empty resonator with the standard ruby specimen

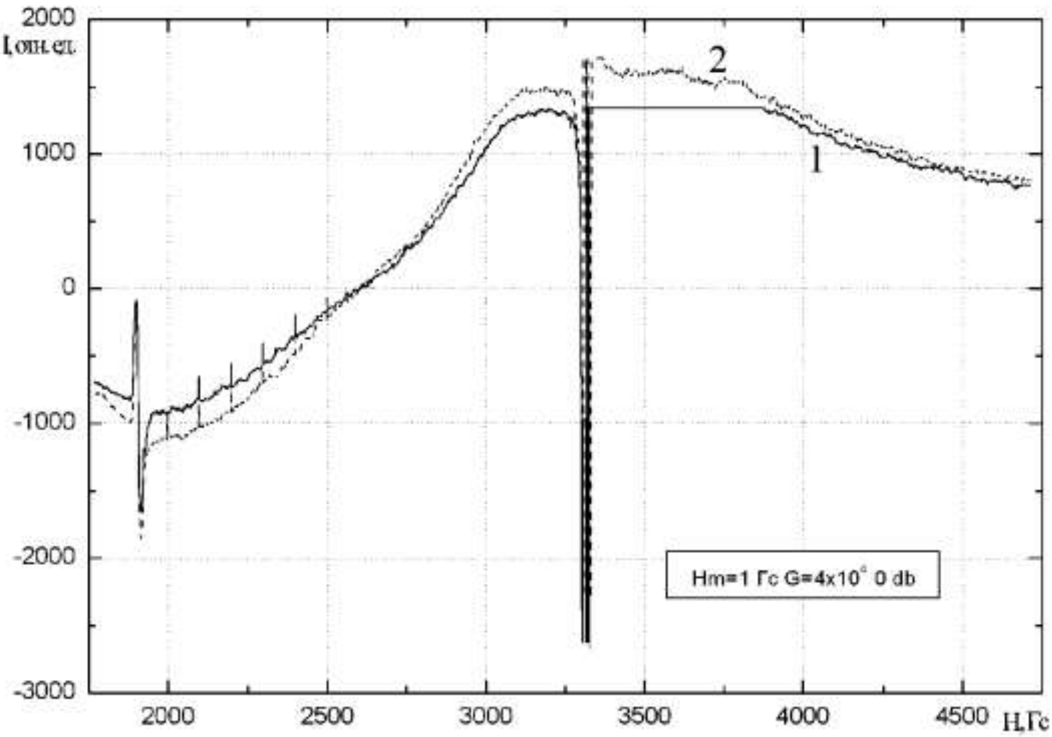

Figure 2 – EPR spectra for S600 sample of the pyrolysis-treated wood sawdust at T=600°C, t=120min
1 – measured in the air; *2* – on evacuation

Fig. 2 reveals the absorption signal behavior for S600 sample in the air and on evacuation. In the spectrum some manifestations of the oxygen effect may be observed, leading to an increase in the intensity of the broad line when the ampoule is evacuated.

Even though the intensity is low, a tremendous line width of 2300 Oe points to a large number of the inhomogeneously broadened centers which, *inter alia*, represent a source of the material sorption properties.

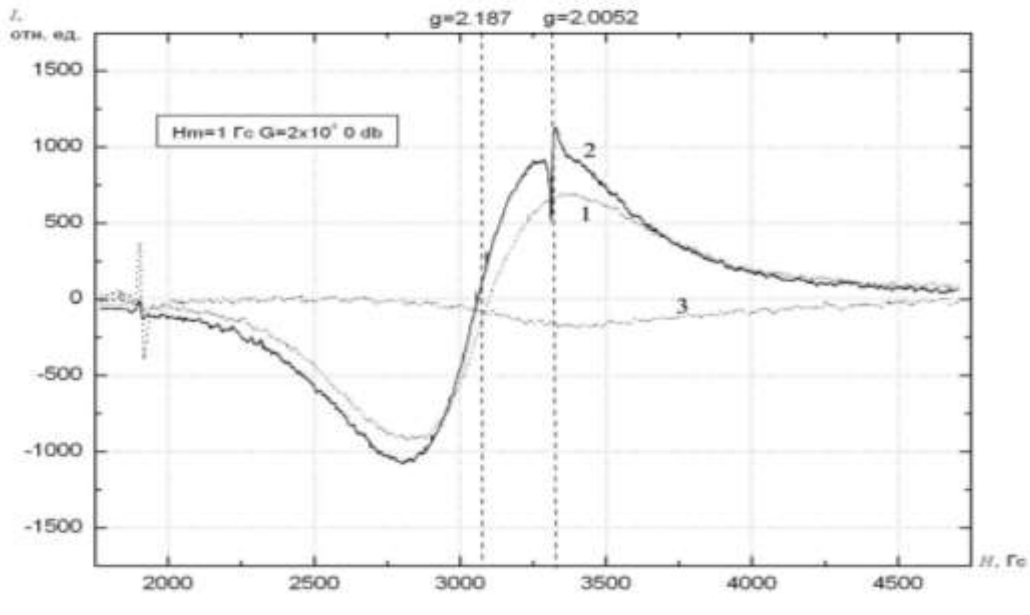

Figure 3 – EPR spectra for S700 sample of the pyrolysis-treated wood sawdust at T=700°C, t=100 min with the use of Ni catalyst
1 – measured in the air; *2* – on evacuation;
3 –spectrum of an empty resonator with the standard ruby specimen

Fig. 3 shows EPR spectra of the sample subjected to the pyrolysis procedure at T=700°C, t=100 min with the use of the Ni catalytic impurity enabling one to reduce the pyrolysis time. Spectrum 1 is characteristic for measurements in the air; spectrum 2 – on evacuation. The solid carbonaceous residual resultant from pyrolysis and the standard adsorbent both have qualitatively similar EPR signals.

A broad line is associated with the technological iron impurities (Fe_2O_3), while a sharp line is caused by the unpaired electrons of carbon atoms. Amount of the oxygen effect is indicative of the fact that oxygen molecules are within reach of unpaired electrons demonstrating porosity of the material under study. Because of this, the carbonaceous material is characterized by the sorption properties. In this manner the EPR method makes it possible to control the samples produced by pyrolysis and the impurities in them(7).

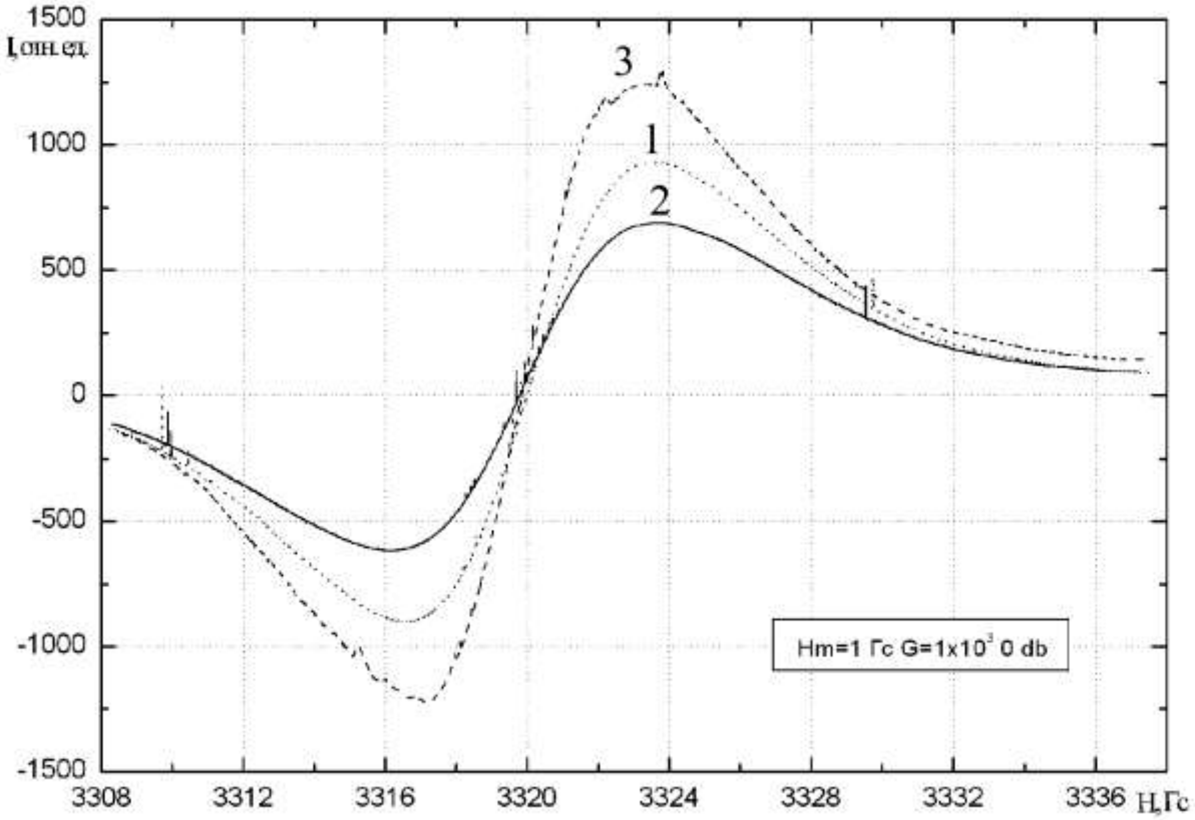

Figure 4 – EPR spectra for S600 sample of the pyrolysis-treated wood sawdust at T=600°C, t=120 min
1 – measured in the air; *2* – on evacuation;
3 – on the air inflow

Fig. 4 gives the spectra for the studied sample in the region of a sharp line. The measurements were performed in the air, on evacuation, and on the air inflow. Positions of the absorption spectral lines in different conditions point to the so-called “abnormal” oxygen effect. As distinct from the spectrum in Fig. 2, the signal intensity on evacuation in Fig. 4 is decreased rather than growing. The “abnormal” oxygen effect seems to be associated not with the physical effect of oxygen but with the spectrometer recording mode effect for centers of this type(8).

Figs. 5 and 6 demonstrate EPR spectra for S600 sample at different powers of electromagnetic waves: Fig. 5 – spectrum measured in the air, Fig. 6 – on evacuation.

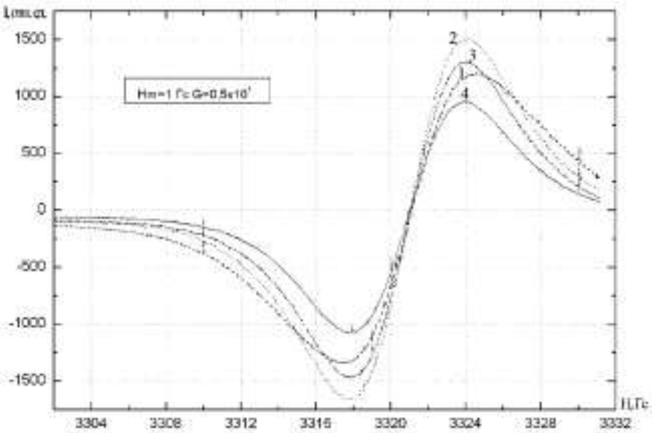

Figure 5 – EPR spectra family for S600 sample of the pyrolysis-treated wood sawdust at T=600°C, t=120 min for different attenuations in the air:
1 – 0 db; *2* – 10 db; *3* – 15 db;
4 – 20 db

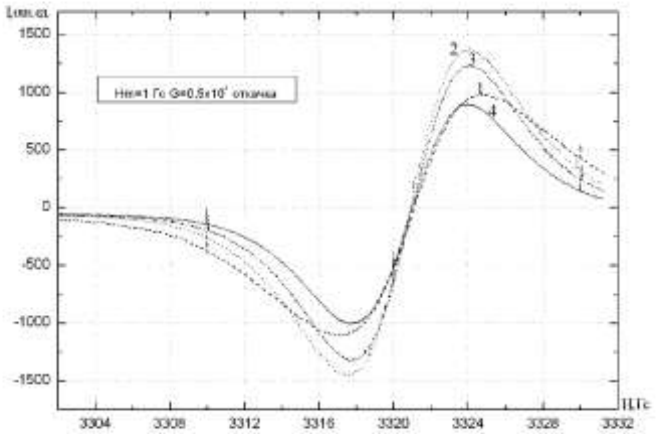

Figure 6 – EPR spectra family for S600 sample of the pyrolysis-treated wood sawdust at T=600°C, t=120 min for different attenuations on evacuation:
1 – 0 db; *2* – 10 db; *3* – 15 db;
4 – 20 db

For more convenient demonstration of the spectra as a function of the power, the saturation curves have been plotted (see Fig. 7). On the abscissa of this graph the magnetic component power is plotted (in arbitrary units), and on the ordinate – absorption signal amplitude.

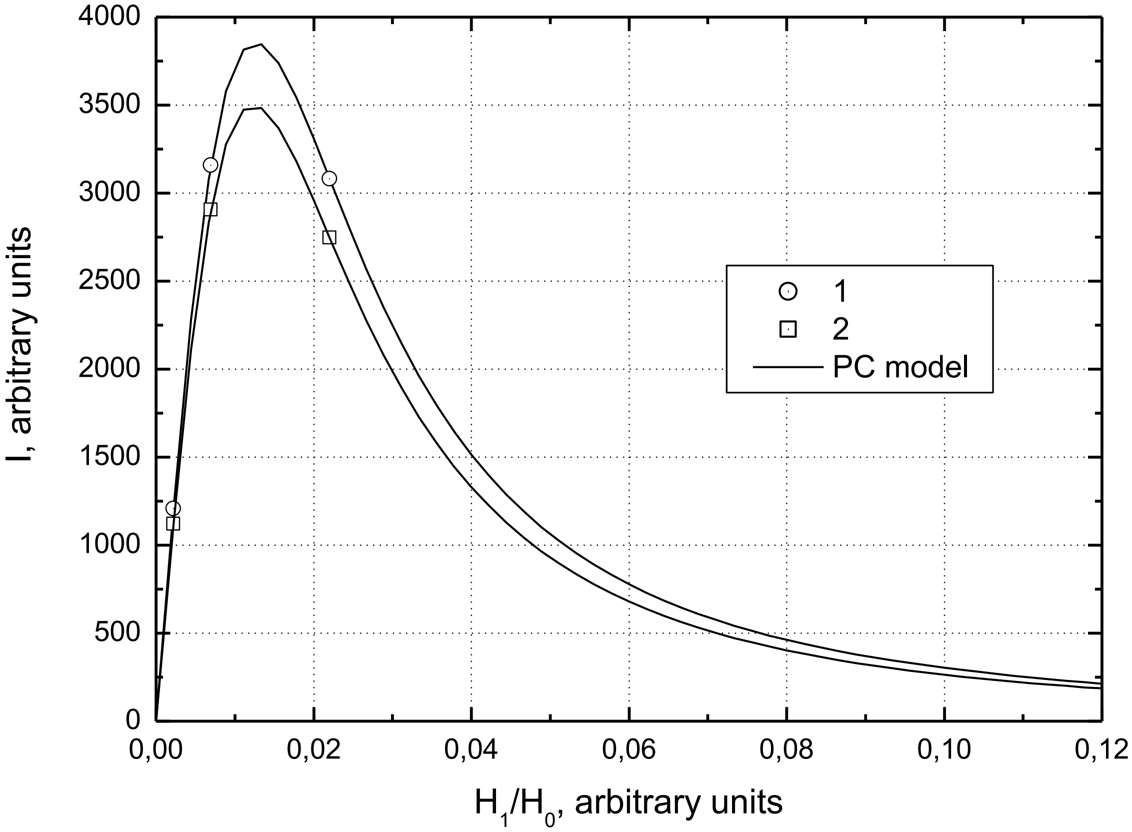

Figure 7 – Absorption curves for the absorption signals of EPR spectra for S600 sample of the pyrolysis-treated wood sawdust at T=600°C,
t=120 min
1 – measured in the air; *2* – on evacuation

The EPR method may be used for the quality diagnostics of a sorbent. Changes of the sorption properties of a standard sorbent – absorbent (activated) carbon used as a water filter – are quite characteristics.

Fig. 8 shows EPR spectra for the activated carbon specimen. Spectrum 1 is associated with measurements in the air; 2 – on evacuation; 3 – heating of the sample for 10 minutes at T=150°C on evacuation; 4 – spectrum of an empty resonator with the standard ruby specimen.

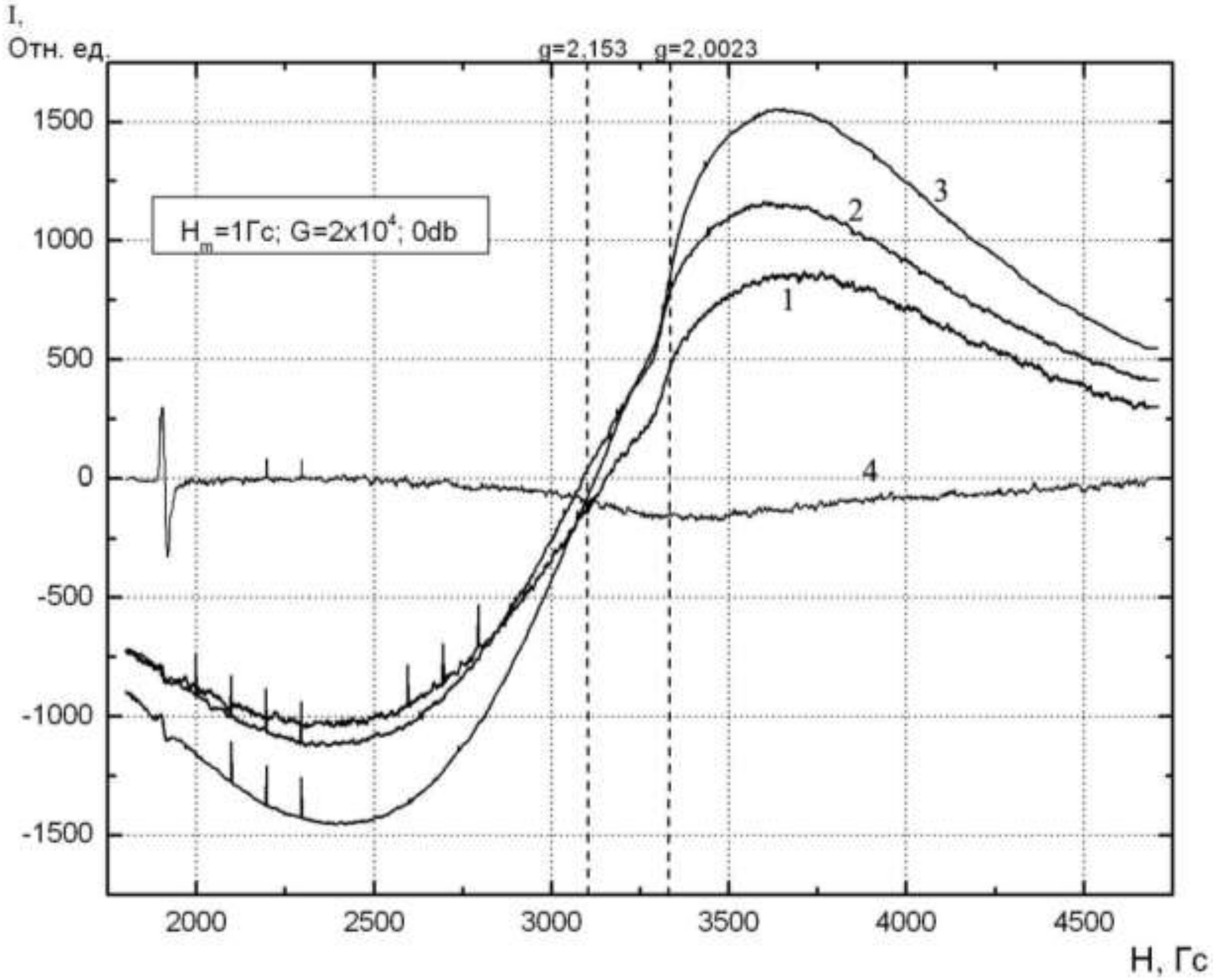

Figure 8 – EPR spectra of activated carbon (standard sorbent)
1 – in the air; *2* – on evacuation; *3* – heating of the sample for 10 min at T=150°C on evacuation; *4* – spectrum of an empty resonator with the standard ruby specimen

It may be noted that the spectrum represents a sufficiently broad absorption line. When the air is evacuated, the intensity is increased, i.e. the oxygen effect is normal. Heating of the sample also contributes to growing of the absorption intensity. In the region of the magnetic field value *H*=3333 Oe, that in the conditions used is corresponding to the *g*-factor *g* =2.003, one can observe some bending of the curve. The measured line halfwidth is *ΔH*=530 Oe(9).

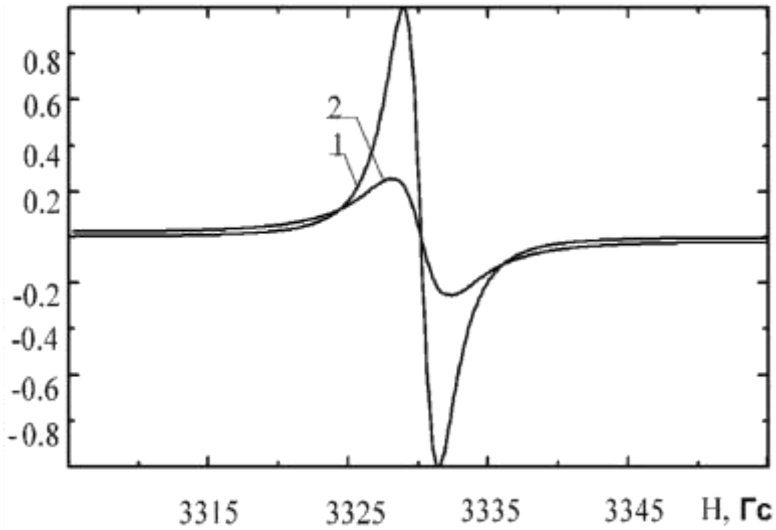

Figure 9 – EPR spectrum of the natural cellulose (triticale straw) when the final temperature of thermal treatment is 750°C
1 – on evacuation, 2 – on the air inflow

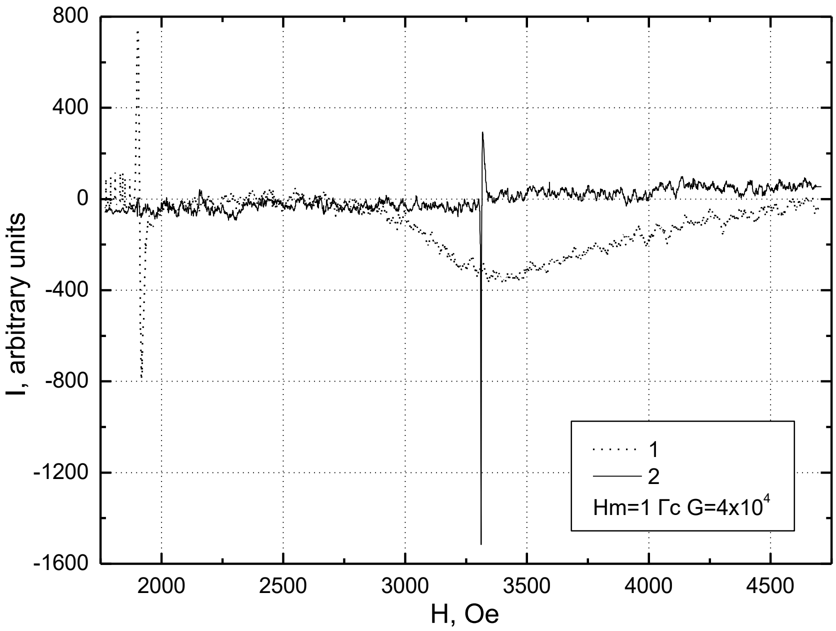

Figure 10 – EPR spectrum for S780-2sample of the pyrolysis-treated straw at T=780°C, t=4.5 h
1 – measured in the air; *2* – on evacuation

Figs. 9-10 reveal high values of the “normal” oxygen effect for the structures of less dense natural polysaccharides (straw and hay) after their pyrolysis. Increased porosity of such samples contributes to greater “accessibility” of the carbonaceous paramagnetic centers for paramagnetic oxygen molecules. This is in the end exhibited by the increased sorption activity of such solid carbonaceous pyrolysis residuals.

CONCLUSIONS

It is demonstrated that additional possibilities for the successful application of the EPR spectroscopy methods in diagnostics of pyrolysis products are offered by the combined use, during recording and analysis of EPR signals in carbonaceous and carbon-containing materials, of the features characteristic for changes in the intensity, spectral position, and form of EPR signals recorded in the presence or in the absence of molecular oxygen, on variations of microwave power in a measuring resonator at different pyrolysis stages. The EPR method enables one to control the technological operations of pyrolysis: e.g., effectiveness of the introduced catalyst, shortened pyrolysis time. The standard adsorbent and the solid carbonaceous residual produced by the pyrolysis method are characterized by qualitatively similar EPR signals.The EPR method proposed makes it possible to control the sorptive properties effectiveness of a carbonaceous pyrolysis product due to changes in the characteristics of paramagnetic absorption when spectra of the samples are measured in the air and in the vacuum.Amount of the oxygen effect for EPR spectra demonstrates the sorption properties of a carbonaceous material enabling the use of solid carbonaceous materials as sorbents.

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