ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 5, pp. 947–954. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © N.G. Bazarnova, V.I. Markin, I.B. Katrakov, P.V. Kolosov, E.V. Kalyuta, M.Yu. Cheprasova, 2011, published in Rossiiskii Khimicheskii Zhurnal, 2011, Vol. 55, No. 1, pp. 4–9.

Methods of Obtaining Lignin-Carbohydrate Compounds from Chemically Modified Plant Raw Materials

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Received November 1, 2010

Abstract—Chemical modification of plant raw materials aimed at obtaining new valuable products and materials is described. Methods of preliminary treatment and modification of biopolymers (cavitation, microwave irradiation, and application of cross-linking and delignification reagents) making it possible to reduce decomposition of all major components are considered. Modified products can be used as sorbents of heavy metal salts, additives to drilling fluids in drilling of oil and gas wells, in the construction industry etc.

DOI: 10.1134/S1070363212050271

INTRODUCTION

Wood, wood-processing waste, and non-food biomass of annual crops (cereal straw etc.) are valuable raw materials for obtainment of many products for industrial use.

Traditional processing of wood and wood waste is aimed at extraction of cellulose from these materials. In this process other structural components of plant raw materials, i.e. lignin and hemicelluloses, are subject to degradation; therefore, a possibility of their practical application is eliminated.

In recent years there has been an increase of interest to complex chemical modification of plant raw materials resulting in obtainment of a wide range of valuable products and materials. In order to improve the performance properties of wood modifications of its surface are performed. Another way to modify plant raw materials is to transform them into polymer compounds with prescribed properties using chemical methods without preliminary separation of the materials into structure-forming components (lignin, cellulose, and hemicelluloses). This method ensures a more efficient use of plant raw materials as compared to traditional chemical processing. Scientific interest to the problem of complex modification of raw materials has not ceased for more than 50 years; however, it is only now that some processes become technologically implementable and commercially attractive.

Chemical modification of plant raw materials involves treatment of the materials with chemical reagents interacting with reactive functional groups of the biomass major components and forming new covalent bonds. Usually reactions at hydroxyl groups of the structural components of plant raw materials are carried out [1–4]. The most well-studied processes are acylation reactions aimed at obtaining esters [1–3] and reactions resulting in the formation of ethers (first of all, carboxymethylation reaction) [4].

Methods of Wood Carboxymethylation

First of all, it should be noted that the process of carboxymethylation of cellulose is sufficiently well-studied [5–7].

For the last 20 years specialists of the Organic Chemistry Department, Altai State University, have carried out active research on carboxymethylation of plant raw materials without separating them into structural components. Methods of suspension (in a medium of organic solvents) [8–10] and solid-phase (without solvents) carboxymethylation of wood and annual crops biomass without preliminary separation of biomass into individual components were developed [11–14]. Investigations based on chemical and physicochemical research methods demonstrated that all the major structural components of plant raw materials (cellulose, lignin, and hemicelluloses) are subject to carboxymethylation at accessible OH-groups.

Carboxymethylated derivatives of the components of wood raw materials were tested as reagents for preparation of drilling fluids used in drilling of oil and gas wells [15, 16]. Low viscosity of aqueous and aqueous-alkaline solutions is common for all obtained products. In order to increase the performance properties of carboxymethylated products and to expand the range of their application new methods for carboxymethylation of plant raw materials were developed. These techniques make it possible not only to achieve a high content of carboxymethyl groups but also to preserve all high-molecular components of wood in the least degraded form, thus ensuring increased viscosity of solutions of the obtained products.

The limiting stage in carboxymethylation of plant raw materials is diffusion of the reagent to the reaction centers of biomass. In order to increase accessibility of the reaction groups preliminary treatment of plant raw materials is performed. However, in such a case there is a possibility of major decomposition of both the intercomponent bonds and the biomass components themselves [10, 17, 18]. Therefore, researchers face quite a difficult task, on the one hand, to perform such preliminary treatment of plant raw materials that will ensure maximum accessibility of the reaction functional groups of biomass for the chemical reagent and, on the other hand, to minimize the degradation processes.

Carboxymethylation of Wood Preliminary Treated with $CH_3COOH–H_2O_2–H_2SO_4–H_2O$ Mixture

One of the possible ways to reduce degradation of high-molecular components of plant raw materials is preliminary treatment of these materials with a mixture of $CH_3COOH–H_2O_2–H_2O–H_2SO_4$.

Specialists of the Siberian State Technological University and the Institute of Chemistry and Chemical Technology, Siberian Branch, Russian Academy of Sciences, developed a number of methods to obtain fibrous cellulosic materials from sawdust and wood shavings of aspen, birch, fir, and larch. The selection of conditions for catalytic delignification of samples of the above-listed wood species ensures sufficiently high yield (44–48 wt %) of fibrous products with a low content of residual lignin. Chemically pure and minimally degraded cellulose is obtained under the following delignification conditions: initial concentration of H_2O_2 in the solution of 4.2–6.4 (wt %), concentration of acetic acid of 21.8–28%, hydromodule (ratio of the liquid phase volume to the solid phase weight, ml g^{-1}) of 10–15, concentration of H_2SO_4 (catalyst) of 2 (wt %), process duration of 2–3 h, and temperature of 120–130°C [19].

In order to facilitate the course of diffusion processes and reduce degradation during carboxymethylation it was proposed to perform carboxymethylation of plant raw materials after their preliminary treatment with a mixture of $CH_3COOH–H_2O_2–H_2SO_4–H_2O$ of the optimized composition: concentration of acetic acid of 24.5%, concentration of hydrogen peroxide of 6.4%, and concentration of sulfuric acid of 2% at 100°C [20, 21]. At the same time, there was no task to extract cellulose and completely remove lignin. The objective of such treatment was the decomposition of lignin-carbohydrate bonds and partial oxidation of lignin, which made it possible to carry out the subsequent chemical modification more efficiently due to greater accessibility of OH-groups of the major structural components of plant raw materials. The subsequent process of carboxymethylation was per-formed using the traditional suspension method in 2-propanol medium in the following two stages: alkaline treatment and interaction with sodium monochloro-acetate. The yield of solid carboxymethylated product and its properties depend on the value of hydromodule, the duration of the reaction, and the temperature of the process (Figs. 1, 2). Maximum values, including the yield of carboxymethylation products, the content of carboxymethyl groups, and water solubility, are achieved at the value of hydromodule equal to five. Further increases in hydromodule have no significant impact on the product quality.

The degree of polymerization of wood carboxymethylation products is decreased with increasing duration and growing temperature of the reaction. This fact indicates that more high-viscosity products are obtained from preliminary treated samples.

It should be noted that with regard to carboxymethylated wood the generally accepted concept of polymerization degree makes no sense as carboxymethylated wood is a polymer compound, which con-

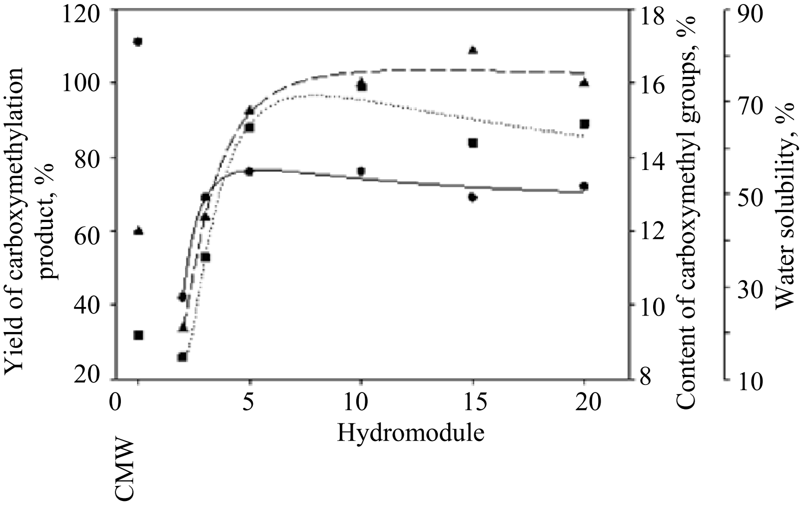

Fig. 1. Dependence of yield and properties of aspen wood carboxymethylation product preliminary treated with $CH_3COOH–H_2O_2–H_2SO_4–H_2O$ mixture on hydromodule. (●) Yield of product, (■) content of carboxymethyl groups, and (▲) solubility of carboxymethylated wood (CMW). (*) CMW sample without preliminary treatment.

tains carboxymethylated lignin and hemicelluloses alongside with carboxymethylated cellulose. A term "conventional degree of polymerization" was introduced in order to make comparisons with values of the polymerization degree of carboxymethylated cellulose standard samples. The conventional degree of polymerization is determined based on the assumption that the entire obtained product, soluble in cadoxene (triethylene–diamine cadmium hydroxide), is represented by carboxymethyl cellulose. (Products of wood carboxymethylation are 98–100% soluble in cadoxene solution.)

On condition that the maximum yield of carboxymethylation products (hydromodule of 5), the optimal temperature (60°C), and duration of the process (60 min) are achieved, solutions of the obtained products have high viscosity characteristics and, correspond-dingly, high polymerization degree values. It should be noted that preliminary treatment of the material with $CH_3COOH–H_2O_2–H_2SO_4–H_2O$ system almost under any conditions of the subsequent carboxymethylation results in a significant increase in the degree of polymerization (1500–2100) as compared to

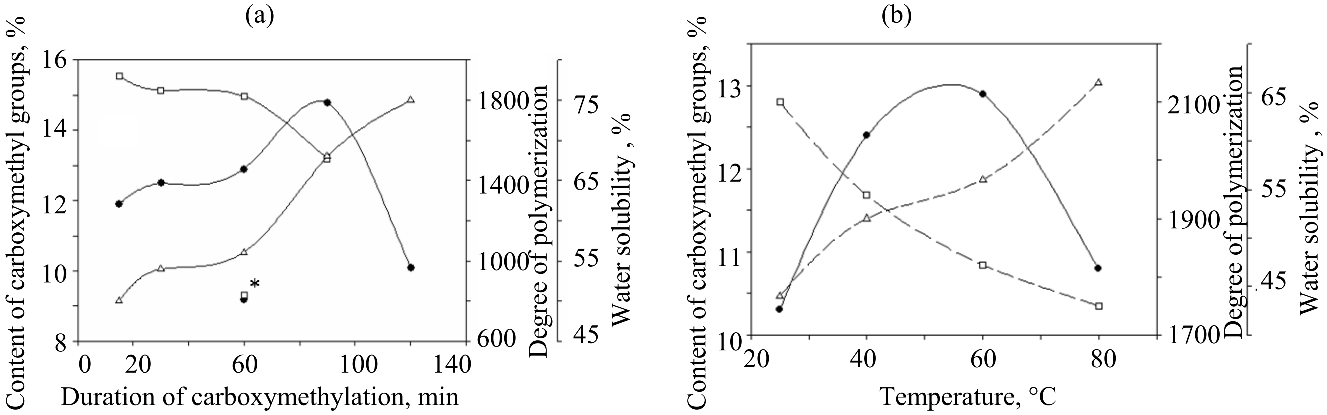

Fig. 2. Dependence of properties of aspen wood carboxymethyl derivatives after preliminary treatment of wood with $CH_3COOH–H_2O_2–H_2SO_4–H_2O$ mixture on (a) carboxymethylation duration and (b) Temperature. (●) Content of carboxymethyl froups, %, (□) degree of polymerization, (Δ) solubility, %. Preliminary treatment: duration of 60 min, temperature of 100°C, and hydromodule of 5; alkaline treatment: duration of 2 h and temperature of 60°C; carboxymethylation: temperature of 60°C. (*) Sample without preliminary treatment.

samples of carboxymethylated wood obtained without such treatment (830).

It is evident that preliminary treatment of plant raw materials with $CH_3COOH–H_2O_2–H_2SO_4–H_2O$ mixture results in partial decomposition of lignin-carbohydrate bonds, oxidation of lignin, degradation of hemicelluloses, and removal of these easily soluble products from the system. The residue subject to carboxymethylation is a cellulose-rich substrate. Moreover, as demonstrated by the values of the polymerization degree of carboxymethyl cellulose extracted from the obtained products, preliminary treatment of the material with the delignifying mixture does not cause major decomposition of cellulose.

As for homogeneity of the carboxymethylated wood composition, this parameter also greatly depends on the value of hydromodule and the duration of preliminary treatment of the source wood with the delignifying mixture preceding carboxymethylation. The most homogeneous carboxymethylated wood in terms of molecular-weight distribution is obtained at hydromodule equal to five. The duration of delignification, the temperature, and the duration of carboxymethylation have almost no impact on the molecular-weight distribution of carboxymethylated products [22].

In order to investigate the molecular-topological structure of carboxymethylated wood and carboxymethylated cellulose extracted from such wood the solution-free method of thermomechanical spectroscopy developed by the Institute of Problems of Chemical Physics, Russian Academy of Sciences (town of Chernogolovka, Moscow oblast) was applied [23–25]. The characteristic property of this method is work with solid samples, while traditionally solution-based methods are used to study the molecular-weight distribution of cellulose esters.

Therefore, preliminary treatment of wood with $CH_3COOH–H_2O_2–H_2SO_4–H_2O$ mixture with the subsequent carboxymethylation results in the formation of highly-substituted polymer compounds of methyl ethers of cellulose, lignin, and hemicelluloses, forming more viscous solutions than in case of carboxymethylation without preliminary treatment. Preliminary treatment of wood makes it possible to reduce the duration of the subsequent carboxymethylation to 15 min and to lower the process temperature to 25°C.

Treatment of Wood with Formaldehyde

It is known that treatment of cellulose with formaldehyde results in the formation of high-molecular compounds with a three-dimensional network structure. Moreover, such treatment can also be performed in order to obtain cellulose ethers, including methyl ethers [26, 27].

Treatment of wood with formaldehyde using both individual compounds and different formaldehyde-containing resins is widely used on an industrial scale, in particular, in chipboard production. Methods of the wood surface modification using formaldehyde are also well-known.

Treatment of wood with formaldehyde solution serves two tasks. Firstly, molecules of formaldehyde penetrate between the fibers, destroy their supramolecular structure, and, correspondingly, increase accessibility of the reaction centers of biomass. Secondly, formaldehyde can enter into chemical reactions with hydroxyl groups of the structural components of wood, forming hemiacetals and acetals. Interaction of formaldehyde with two hydroxyl groups of the neighboring macromolecules results in an increase in the biopolymer molecular weight due to formation of cross-links and bridges between the components [2, 28].

Patent [29] describes a method of carboxymethylation of lignin-carbohydrate materials, which uses cereal straw (oat, rye, and wheat straw) as a feedstock for the process. The method involves treatment of raw materials with formaldehyde in the presence of an alkaline catalyst. The content of carboxyl groups is increased 2.2-fold on average. The cross-linking results in a significant increase in resistance of the samples to aqueous and non-aqueous media.

The influence of the conditions of wood treatment with formaldehyde solution on properties of wood carboxymethylation products was studied [21]. Pine and aspen wood was subject to carboxymethylation with sodium monochloroacetate in an alkaline medium both with preliminary treatment of raw materials with formaldehyde in an acidic medium and with the subsequent treatment of carboxymethylation products with formaldehyde under different conditions.

Preliminary treatment of wood with formaldehyde, contributing to increased reactivity of hydroxyl groups of the wood major components, ensures the content of carboxymethyl groups in wood carboxymethylation products within a range of 20–28%, while without wood treatment with formaldehyde the content of carboxymethyl groups amounts to 10.2% only. Solution viscosity of products obtained using preliminary treatment is also increased [30, 31].

In case wood is treated with formaldehyde in an acidic medium, the effect of the carboxymethylation reagent is mainly directed at cellulose, and in an alkaline medium, at the aromatic rings of lignin [32, 33].

The most optimal wood carboxymethylation products with regard to the complex of their properties are achieved when wood is preliminary treated with formaldehyde solution in acidic or alkaline media at a molar ratio for formaldehyde to OH-group of 1:1.

The effect of formaldehyde on wood in an acidic medium causes more intensive degradation of the wood components. Thus, the polymerization degree of carboxymethyl cellulose extracted from carboxymethylated wood is much lower (380) than in case of carboxymethylation without preliminary treatment of raw materials with formaldehyde (800). The content of carboxymethyl groups is comparable. In case of preliminary treatment of wood with formaldehyde in an alkaline medium, the situation is different, i.e. the polymerization degree of carboxymethyl cellulose is much higher (1170–2700).

Thus, preliminary treatment of wood with aqueous solutions of formaldehyde in an alkaline medium contributes to the obtainment of high-molecular compounds with a high content of carboxymethyl groups and, correspondingly, low solubility in the course of the subsequent carboxymethylation [21].

The product of wood carboxymethylation with preliminary treatment of wood with formaldehyde can be used as a sorbent of heavy metals [21, 34], in particular, for decontamination of wastewater from compounds of iron(III). Such a product can absorb 6 times as much iron(III) as carboxymethylated wood obtained without preliminary treatment.

Carboxymethylation of Wood Using Microwave Irradiation

A possibility to use microwave irradiation for modification of wood is not sufficiently studied yet. On an industrial scale it is proposed to perform vacuum drying of wood using microwave irradiation [35–37]. There is a number of works dedicated to acylation of wood biomass [38–40] and carboxymethylation of cellulose [41–43] under conditions of microwave irradiation; however, these works are few in number.

The use of microwave irradiation for obtainment of carboxymethylated products on the basis of plant raw material is undoubtedly a matter of practical interest [44, 45]. Under such conditions optimization of the process can be achieved, i.e. the reaction duration can be significantly reduced. Moreover, it is possible to obtain more homogeneous products due to uniform heating of wood, which ensures uniform distribution of carboxymethyl groups in the wood stock.

During the corresponding experiments alkaline treatment of wood raw materials and the subsequent reaction of wood carboxymethylation were carried out under the influence of microwave irradiation with the frequency of 2450 MHz and the capacity ranging from 210 to 800 W. The achieved results demonstrated that microwave irradiation of raw materials significantly reduced the duration of both the first stage of alkaline treatment and the following stage of carboxymethylation. The total period of microwave irradiation does not exceed 2 min (duration of the process based on thermal heating within the framework of the traditional suspension method amounting to 1–4 h). The content of carboxymethyl groups in the product is 10–27%, which is comparable to the content of these groups in case the traditional method of carboxymethylation is applied. An increase in the quantity of the reagent (sodium monochloroacetate) results in an increase in the content of carboxymethyl groups in the wood components, although the maximum possible content cannot be achieved. It is evident that not all OH-groups are accessible for the reagent and the reaction rate is limited with diffusion of the reagent to the reaction centers of biomass. Water solubility of carboxymethylated derivatives of wood is twice lower as compared to products obtained using thermal heating. It is evident that under the influence of microwave irradiation the processes of degradation of the wood high-molecular components are less active.

Cavitation Pretreatment of Wood

More and more attention is given to studies of the effect of cavitation on plant raw materials [46–50]. It is determined that in the course of cavitation treatment of pine, fir, and aspen wood sawdust, as well as of annual crops waste (wheat, buckwheat, and rye straw) in acidic, alkaline, and neutral media for 15–120 min at 20–100°C at hydromodule of 10 the greatest impact is made on the vegetative part of annual crops, followed by soft wood, while hard wood is less affected by the treatment.

Cavitation treatment makes an influence on the major components of wood. At the initial stage (15–30 min) polysaccharides are decomposed, while a longer impact time (more than 60 min) results in degradation of lignin and cellulose. The greatest influence of cavitation processes is observed in alkaline media [46].

The content of cellulose extracted from aspen wood after cavitation treatment is 4.4% lower (reduced from 41.4 to 37.0%), as its easily hydrolysable amorphous part passes into solution. The average degree of polymerization of cellulose under the influence of cavitation is decreased 1.8-fold (from 580 to 320), which is related to the hydrolytic processes.

The content of easily hydrolysable polysaccharides in the samples is gradually decreased after cavitation treatment by 3.5%, while after 30 min of treatment it remains almost the same. The content of hardly hydrolysable polysaccharides in the samples is drastically reduced already after 10 min of treatment, later remaining almost unchanged (8.0%), which is probably related to the almost completed process of hydrolysis. Depending on the duration of cavitation treatment, the quantity of lignin in the samples changes non-monotonically and in general increases by 3.6%.

Investigations of the process of cavitation treatment of aspen wood demonstrated that the content of carboxyl groups in the extracted dioxane lignin increased by a factor of 3.4 [51]. It was suggested that [52] during cavitation in an aqueous medium hydrogen peroxide was formed; in the presence of iron (material of the tank, in which cavitation treatment was performed) hydrogen peroxide decomposed generating active particles – hydroxide and peroxide radicals. As a result the network structure of lignin decomposed with the formation of carboxyl groups.

Cavitation treatment of wood raw materials results in the decomposition of the lignin-carbohydrate matrix and obtainment of products suitable for briquetting and molding. In the first place, the most accessible reaction sites, hemicelluloses (easily hydrolysable component of wood), are subject to degradation; lignin-carbohydrate bonds are also decomposed, which results in an increase in functional groups.

It should be noted that the problem of obtaining plate materials on the basis of plant raw materials without using synthetic binders has been attracting researchers' attention for a long time. Plate materials with the average density of 1190–1350 kg m^{-3} and the moisture content of 3–9% were obtained. With regard to their strength (bending strength of 13–22 MPa) and hydrophobic properties (water absorption of 20–40% in 24 h and swelling in thickness of 12–35% in 24 h) plate materials are in full compliance with the requirements of EN-312 and EN-622 European standards. The resulting products are non-toxic and easy to process [53, 54].

A possible mechanism for structure formation of molding materials produced from plant raw materials using cavitation treatment [55] and a method to obtain plate materials using cavitation pretreatment [56] were proposed.

Cavitation treatment of plant raw materials can be used as an efficient method of activation preceding chemical modification. This method contributes to an increase in reactivity of the wood components. Moreover, it is economically effective, environmentally sound, and relatively easy in technological implementation.

CONCLUSIONS

The presented methods to activate reactivity of the components of plant raw materials ensure increased efficiency of their utilization. These methods make it possible to intensify the process of obtainment of lignin-carbohydrate compounds, to control the composition of the target product and, correspondingly, its properties, and to increase the target product yield.

The resulting products can be used as sorbents of heavy metal salts, additives to drilling fluids in drilling of oil and gas wells, in the construction industry etc.

REFERENCES

1. *Chemical Modification of Lignocellulosic Materials*, Hon, D.N.-S., Ed., Marcel Dekker, 1996, p. 370.
2. *Wood Modification: Chemical, Thermal and Other Processes,* Hill, C.A.S., Ed., John Wiley & Sons Ltd, 2006, p. 248.
3. *Handbook of Wood Chemistry and Wood Composites*, Rowell, R.M., Ed., CRC Press, 2005, p. 473.
4. Bazarnova, N.G., Katrakov, I.B., and Markin, V.I., *Ross. Khim. Zh. (Zh. Ros. Khim. Obshchestva im. D.I. Mendeleeva)*, 2004, vol. 48, no. 3, pp. 108–115.
5. Kishi, H. and Shiraishi, N., *Mokuzai Gakkaishi*, 1986, vol. 32, p. 520.

6. Nakano, T., *Holzforschung*, 1993, vol. 47, no. 3, pp. 202–206.
7. Shiraishi, N. and Kishi, H., *J. Appl. Polym. Sci*., 1986, vol. 32, no. 1, pp. 3189–3209.
8. Markin, V.I., Bazarnova, N.G., and Galochkin, A.I., *Khim. Rastit. Syr'ya*, 1997, no. 1, pp. 26–28.
9. Russian Patent no. 2130947, 1999.
10. Markin, V.I., Bazarnova, N.G., Galochkin, A.I., and Zakharova, V.V., *Izv. Vyssh. Ucheb, Zaved., Ser. Khim. i Khim. Tekhnol*., 1998, no. 5, pp. 108–111.
11. Markin, V.I., Galochkin, A.I., et al., *Khimiya v Interesakh Ustoichivogo Razvitiya*, 1997, vol. 5, no. 5, pp. 523–528.
12. Russian Patent no. 2131884, 1999.
13. Russian Patent no. 2135517, 1999.
14. Markin, V.I., Bazarnova, N.G., Galochkin, A.I., and Tokareva, I.V., *Khimiya v Interesakh Ustoichivogo Razvitiya*, 1998, no. 6, p. 223.
15. Russian Patent no. 2127294, 1999.
16. Bazarnova, N.G., Markin, V.I., Mikushina, I.V., Morozov, S.Yu., Nazarova, A.K., and Putintsev, S.A., *Burenie*, 2005, no. 3, p. 16.
17. Markin, V.I., Bazarnova, N.G., and Galochkin, A.I., *Plast. Massy*, 1998, no. 7, pp. 31–34.
18. Bazarnova, N.G., Markin, V.I., Kalyuta, E.V., Mikushina, I.V., and Katrakov, I.B., *Khim. Rastit. Syr'ya*, 2005, no. 3, pp. 75–84.
19. Yatsenkova, O.V., *Cand. Sci. (Chem.) Dissertation*, Krasnoyarsk, 2005.
20. Kolosov, P.V., Markin, V.I., Bazarnova, N.G., Kalyuta, E.V., and Zazdravnykh, L.Yu., *Khim. Rastit. Syr'ya*, 2008, no. 2, pp. 25–30.
21. Kolosov, P.V., *Cand. Sci. (Chem.) Dissertation*, Krasnoyarsk, 2008, p. 22.
22. Kalyuta, E.V., Kolosov, P.V., Bazarnova, N.G., and Markin, V.I., Abstracts of Papers*, Mater. IV Vseros. nauchn. konf. "Novye dostizheniya v khimii i khimicheskoi tekhnologii rastitel'nogo syr'ya* (Proc. IV All-Russian Scientific Conf. "New Achievements in Chemistry and Chemical Technology of Plant Raw Materials"), Barnaul, 2009, pp. 93–95.
23. Bazarnova, N.G., Karpova, E.V., Katrakov, I.B., Markin, V.I., et al., *Metody issledovaniya drevesiny i ee proizvodnykh* (Methods of Studies of Wood and Its Derivatives), Barnaul: Alt. Gos. Univ., 2002, p. 160.
24. Ol'khov, Yu. A. and Baturin, S.M., *Tekhnika Mashinostroeniya*, 1995, no. 4, pp. 20–32.
25. Irzhak, V.I., *Usp. Khim*., 2000, vol. 69, no. 8, pp. 780–788.
26. Katalevskaya, I.V., Tribunskii, V.V., and Prokof'eva, M.V., *Khimiya Drevesiny*, 1987, no. 4, pp. 17–21.
27. Turaev, A.S., Khudaikulov, Yu.Ch., and Nadzhimutinov, Sh., *Khimiya Drevesiny*, 1990, no. 5, pp. 14–18.
28. *Wood and Cellulosic Chemistry*, Hon, D.N.-S. and Shiraishi, N., Eds., 2nd ed., New York: Marcel Drekker, 2000, p. 923.
29. Russian Patent no. 2252941, 2005.
30. Kolosov, P.V., Markin, V.I., Bazarnova, N.G., Ol'khov, Yu.A., and Generalova, E.N., *Khim. Rastit. Syr'ya*, 2008, no. 3, pp. 55–58.
31. Russian Patent no. 2374264, 2009.
32. Klevinskaya, V.Ya., Treimanis, A.P., Alksne, A.Ya., Freiberga, A.K., and Zarinya, M.Yu., *Khimiya Drevesiny*, 1991, no. 1, pp. 57–65.
33. Kononov, G.N., *Khimiya drevesiny i ee osnovnykh komponentov* (Chemistry of Wood and Its Major Components), Moscow: MGUL, 1999, p. 247.
34. Kolosov, P.V., Markin, V.I., Bazarnova, N.G., Yusupov, V.R., and Generalova, E.N., *Khim. Rastit. Syr'ya*, 2009, no. 3, pp. 39–42.
35. Leiker, M. and Adamska, M.A., *Holz Roh-und Werks*., 2004, vol. 62, no. 3, pp. 203–208.
36. Sun, L., Li, Z., and Cao, W., *2009 WRI Global Congress on Intelligent Systems*, GCIS 2009, Xiamen, pp. 447–450.
37. Oloyede, A. and Groombridge, P., *J. Mater. Processing. Technol*., 2000, vol. 100, no. 1, pp. 67–73.
38. Brelid, P.L., Simonson, R., and Risman, P.O., *Holz Roh-und Werks*., 1999, vol. 57, no. 4, pp. 259–263.
39. Brelid, P.L. and Simonson, R., *Ibid*., 1999, vol. 57, no. 5, pp. 383–389.
40. Brelid., P.L., *Ibid*., 2002, vol. 60, no. 2, pp. 92–95.
41. Nadagouda, M.N. and Varma, R.S., *Biomacromolecules*, 2007, vol. 8, no. 9, pp. 2762–2767.
42. Tomanova, V., Pielichowski, K., et al., *Polymer Bull*., 2008, vol. 60, no. 1, pp. 15–25.
43. Tomanova, V., Srokova, I., Malovikova, A., and Ebringerova, A., *Mol. Cryst. and Liquid Cryst*., 2008, vol. 484, pp. 238–249.
44. Positive Decision on Russian Application no. 2008148427, 2008.
45. Cheprasova, M.Yu., Mikhailidi, A.M., et al., Abstracts of Papers, *Mater. IV Vseros. nauchn. konf. "Novye dostizheniya v khimii i khimicheskoi tekhnologii rastitel'nogo syr'ya"* (Proc. IV All-Russian Scientific Conf. "New Achievements in Chemistry and Chemical Technology of Plant Raw Materials"), Barnaul, 2009, pp. 100–101.
46. Katrakov, I.B., Markin, V.I., Petrakov, A.D., Bazarnova, N.G., and Frolova, T.V., Abstracts of Papers, *Trudy IV mezhd. simpoziuma "Stroenie, svoistva i kachestvo drevesiny"* (Proc. IV International Symposium "Structure, Properties, and Quality of Wood"), St. Petersburg, 2004, pp. 241–244.
47. Katrakov, I.B., Markin, V.I., and Bazarnova, N.G., Abstracts of Papers, *III Vseros. konf. "Khimiya i*

tekhnologiya rastitel'nykh veshchestv" (III All-Russian Conf. "Chemistry and Technology of Plant Substances"), Saratov, 2004, pp. 313–314.

48. Katrakov, I.B., Karpova, E.V., Markin, V.I., Bazarnova, N.G., and Frolova, T.V., Abstracts of Papers*, III Vseros. konf. "Khimiya i tekhnologiya rastitel'nykh veshchestv"* (III All-Russian Conf. "Chemistry and Technology of Plant Substances"), Saratov, 2004, pp. 315–317.
49. Efanov, M.V. and Galochkin, A.I., *Plast. Massy*, 2007, no. 8, p. 41.
50. Efanov, M.V., Galochkin, A.I., and Petrakov, A.D., *Zh. Prikl. Khim.*, 2008, vol. 81, no. 6, pp. 1019–1022.
51. Katrakov, I.B., Bazarnova, N.G., Markin, V.I., and Stepycheva, T.N., Abstracts of Papers*, Mater. IV Vseros. nauchn. konf. "Novye dostizheniya v khimii i khimicheskoi tekhnologii rastitel'nogo syr'ya* (Proc. IV All-Russian Scientific Conf. "New Achievements in Chemistry and Chemical Technology of Plant Raw Materials"), Barnaul, 2009, p. 155.
52. Volkov, V.I., Bekker, V.N., Kirkolup, E.R., Katrakov, I.B., and Ivanov, M.G., *Izv. Alt. Gos. Univ*., 2007, no. 3, pp. 63–70.
53. Katrakov, I.B., Gaidukov, M.N., Markin, V.I., and Bazarnova, N.G., Abstracts of Papers*, Mater. IV Vseros. nauchn. konf. "Novye dostizheniya v khimii i khimicheskoi tekhnologii rastitel'nogo syr'ya* (Proc. IV All-Russian Scientific Conf. "New Achievements in Chemistry and Chemical Technology of Plant Raw Materials"), Barnaul: Alt. Gos. Univ., 2005, pp. 683–685.
54. Katrakov, I.B., Markin, V.I., and Bazarnova, N.G., Abstracts of Papers*, Mater. III Vseros. nauchn. konf. "Novye dostizheniya v khimii i khimicheskoi tekhnologii rastitel'nogo syr'ya* (Proc. III All-Russian Scientific Conf. "New Achievements in Chemistry and Chemical Technology of Plant Raw Materials"), Barnaul: Alt. Gos. Univ., 2007, pp. 150–151.
55. Ivanov, M.G., Katrakov, I.B., Markin, V.I., and Bazarnova, N.G., Abstracts of Papers*, Mater. IV Vseros. nauchn. konf. "Novye dostizheniya v khimii i khimicheskoi tekhnologii rastitel'nogo syr'ya* (Proc. IV All-Russian Scientific Conf. "New Achievements in Chemistry and Chemical Technology of Plant Raw Materials"), Barnaul, 2009, p. 210.
56. Russian Patent no. 2381244, 2010.