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ИСПОЛЬЗОВАНИЕ ПЕНТОЗАНСОДЕРЖАЩЕЙ ФРАКЦИИ НЕЙТРАЛЬНЫХ ЛИГНОСУЛЬФОНАТОВ ДЛЯ ПОЛУЧЕНИЯ ПРОИЗВОДНЫХ ФУРАНА

И.А. Четвертнева, О.Х. Каримов, Г.А. Тептерева, Э.Р. Бабаев, Н.С. Тивас, Э.М. Мовсумзаде

Ирина Амировна Четвертнева

ООО «Сервисный Центр СБМ», Университетский просп., 12, Москва, Российская Федерация, 119330
E-mail: chetvertneva@ufa.scsbm.ru

Олег Хасанович Каримов

Кафедра физической химии МИРЭА - Российский технологический университет, пр. Вернадского, 86, Москва, Российская Федерация, 119571
E-mail: karimov.oleg@gmail.com

Галина Алексеевна Тептерева*, Наталия Сергеевна Тивас, Эльдар Мирсамедович Мовсумзаде

Кафедра общей, аналитической и прикладной химии, Уфимский государственный нефтяной технический университет, ул.Космонавтов, 1, Уфа, Российская Федерация, 450062
E-mail: teptereva.tga@yandex.ru*, tivas.n.s@gmail.com, eldarmm@yahoo.com

Бабаев Эльбей Расимович

Институт химии присадок им. Ак. А.М. Кулиева НАН Азербайджана, Баку, Беюкшорское шоссе, 2062-й квартал, Баку, Азербайджанская Республика, AZ1029
E-mail: elbeibabaev@yahoo.de

В статье описана технологическая возможность и дана условная схема получения на основе углеводной части нейтрального лигносульфоната таких полезных продуктов, как фурфурол, фуран, тетрагидрофуран, свойства которых имеют ряд существенных физико-химических отличий от свойств лигносульфоната, получаемого в результате сульфитных варок. В статье рассматриваются особенности ароматической и углеводной составляющих нейтральных лигносульфонатов, мономерные звенья ароматической части, структура полисахаридных компонентов углеводной части, а также лигноуглеводной матрицы, характеризующей их сочетание в макромолекуле лигносульфоната. На этом основании изучена и экспериментально реализована возможность использования нейтральных ЛСТ в качестве пентозансодержащего сырья. В экспериментальной части статьи предложена методика фракционирования лигносульфонатов, в нашем случае лигносульфонатов нейтрально-сульфитного способа делигнификации древесного сырья. Пробы нейтрального лигносульфоната, который являлся объектом исследования, подвергали щелочному гидролизу, после чего проводили фракционирование методом эксклюзивной хроматографии или гель-фильтрации на Сефадексе марки 100. В качестве элюента использовалась вода. Фракции отбирались по объему, состав фракций, как ароматической, так и углеводной определяли методом УФ-спектроскопии. Критерием состава фракции являлось наличие или отсутствие пиков на спектрограмме в области длин волн, характерных для гидроксильных фенольных групп ароматической части нейтральных лигносульфонатов и моносахаридов класса пентоз. Объединенные полисахаридные фракции, представленные, в основном, ксиланами (пентозаны), подвергались экстракции в органический растворитель с последующей разгонкой и отбором по температурам кипения фурансодержащих соединений. Составлен материальный баланс процесса получения производных фурана на основе пентозансодержащей составляющей нейтральных лигносульфонатов.

Ключевые слова: лигносульфонат, лигноуглеводная матрица, гель-фильтрация, пентозаны, фуранпроизводные

USE OF PENTOSAN-CONTAINING FRACTION OF NEUTRAL LIGNOSULFONATES FOR OBTAINING FURANE DERIVATIVES

I.A. Chetverneva, O.Kh. Karimov, G.A. Teptereva, E.R. Babaev, N.S. Tivas, E.M. Movsumzade

Irina A. Chetverneva

Service Center SBM LLC, Universitetskiy ave., 12, Moscow, 119330, Russia
E-mail: chetvertneva@ufa.scsbm.ru

Oleg Kh. Karimov

Department of Physical Chemistry, MIREA – Russian Technological University, Vernadsky Avenue, 86, Moscow, 119571, Russia
E-mail: karimov.oleg@gmail.com

Galina A. Teptereva*, Natalia S. Tivas, Eldar M. Movsumzade

Department of General, Analytical and Applied Chemistry, Ufa State Petroleum Technical University, Cosmonavtov st., 1, Ufa, 450062, Russia
E-mail: teptereva.tga@yandex.ru*, tivas.n.s@gmail.com, eldarmm@yahoo.com

Elbay R. Babayev

Academician A.M. Guliyev Institute of Chemistry of Additives NAS of Azerbaijan, Beyukshor Highway,
Block 2062, Baku, AZ 1029, Republic of Azerbaijan
E-mail: elbeibabaev@yahoo.de

The article describes the technological possibility and gives a conditional scheme of obtaining, based on the carbohydrate part of neutral lignosulfonate, useful products such as furfurol, furan, tetrahydrofuran, properties which have a number of significant physicochemical differences from the properties of lignosulfonate obtained as a result of sulphite brews. The article discusses features of aromatic and carbohydrate constituents of neutral lignosulfonates, monomeric units of aromatic part, structure of polysaccharide components of carbohydrate part, as well as lignocarboxylic matrix characterizing their combination in macromolecule of lignosulfonate. On this basis, the possibility of using neutral LSTs as pentose-containing raw materials was studied and experimentally realized. The experimental part of the article proposes a method of fractionation of lignosulfonates, in our case lignosulfonates of the neutral-sulfite method of delignification of wood raw materials. Samples of the neutral lignosulfonate that was the subject of the study were subjected to alkaline hydrolysis, after which fractionation was carried out by exclusive chromatography or gel filtration on Sephadex grade 100. Water was used as eluent. Fractions were taken by volume, the composition of fractions, both aromatic and carbohydrate, was determined by UV spectroscopy. The criterion for the composition of the fraction was the presence or absence of peaks on the spectrogram in the wavelength region characteristic of the hydroxyl phenolic groups of the aromatic part of neutral lignosulfonates and monosaccharides of the pentose class. The combined polysaccharide fractions represented mainly by xylanes (pentosans) were extracted into an organic solvent, followed by distillation and boiling of the furan-containing compounds. Material balance of the process of producing furan derivatives based on pentose-containing component of neutral lignosulfonates is drawn up.

Key words: lignosulfonate, lignocarboxylic matrix, gel filtration, pentosanes, furan derivatives

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It is known that LST is the lignin derivative. LST is a by-product of wood pulping (delignification) and the main substance of sulfite liquor. The composition of sulfite liquor is complex and quite diverse, moreover, it highly depends on the method for delignification of wood.

The lignin macromolecule is a symbiosis of aromatic and carbohydrate components connected by various bonds and it can be represented as a product of polymerization of *p*-hydroxycinnamic alcohols – *p*-Coumaryl (**I**), Coniferyl (**II**) and Sinapyl (**III**), which are primary structural units of lignin [1-4].

The formation of the lignin macromolecules in a plant (lignification) is a system of complex biological, biochemical and chemical processes. The carbohydrate part of the macromolecule is cellulose and hemicellulose [4, 6, 8].

In chemical terms, the following substances can be considered as analogs of these components: for lignin – phenol, vanillin, guaiacol; for cellulose – glucose; for hemicellulose – arabinose and xylose (pentose), galactose and mannose (hexose), which is reflected by the structure diagram of the ligno-carbohydrate matrix [5, 6, 8].

It is seen that the structure of the ligno-carbohydrate matrix is due to the presence of hydrogen, carbon-carbon, ether chemical bonds of aromatic and carbohydrate components. Since cellulose and lignin are thermodynamically incompatible substances, they form microheterogeneous zones surrounded by hemicellulose gel [6, 8, 9, 11]. It is known that if two components are incompatible, then when a third which is compatible with each of the two separately, is added, the incompatible components become compatible.

Among the wood components, hemicelluloses seem to be the third component that contributes to the compatibility of incompatible biopolymers – cellulose and lignin.

In this case, hemicelluloses play the role of compatibilizers due to the formation of a transition layer on the surface of elementary cellulose fibrils and its limited thermodynamic compatibility with lignin [6, 8, 9].

In fact, this is a polymer composition, the mechanical strength of which is imparted by the interlocking of segments of lignin and hemicellulose macromolecules both with each other and with cellulose.

Thus, in general, according to K. Freudenberg, the lignin formula, which takes into account the presence of both aromatic and carbohydrate components [4, 11].

During sulfonation in the process of delignification, the sulfogroup HSO_3- occupies the α, β or γ position in the propane chain of lignin (PPU) [1-4, 11].

The objective of the research is the practical separation of the carbohydrate component of LST (lignin sulfoderivative) from the aromatic part by gel-filtration method. The production of lignin sulfoderivatives – LSTs from wood raw materials can be represented by the following block diagram (Fig. 1):

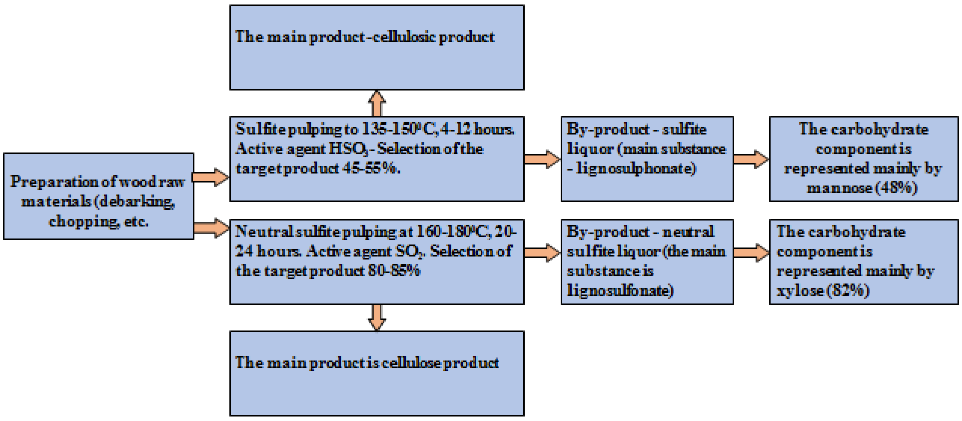
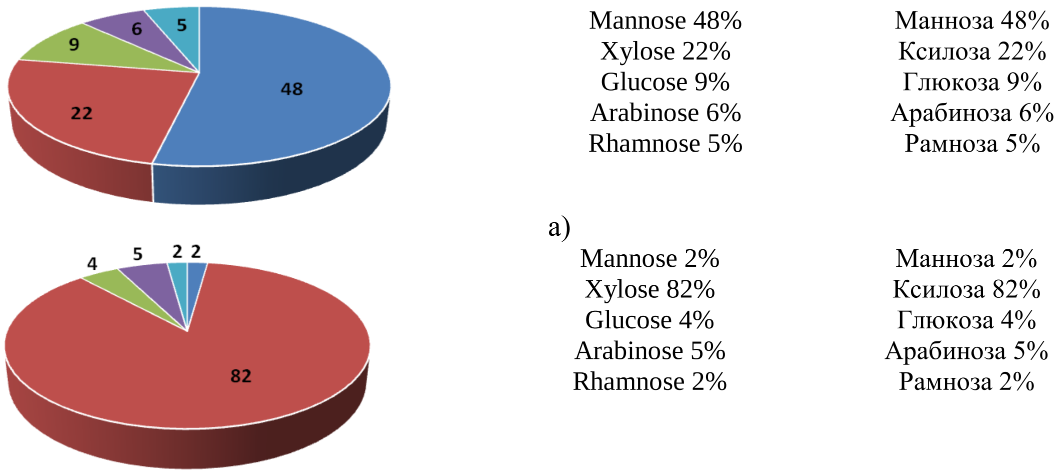


Fig. 1. Distinctive features of the carbohydrate part of LSTs obtained by various methods of delignification of wood raw materials
Рис. 1. Отличительные особенности углеводной части лигносульфонатов, полученных различными способами делигнификацией древесного сырья

During sulfite pulping wood hemicelluloses almost completely turn into the composition of the target product in the form of monosaccharides [5, 10, 16-20]. During neutral sulfite pulping, hemicelluloses almost completely remain in the composition of sulfite liquor as polysaccharides. This is a significant difference between the carbohydrate part of the LSTs obtained by the sulfite and neutral sulfite methods of wood raw materials pulping [1, 2, 10, 11, 16, 17].

Earlier it was found that carbohydrate part in the composition of LSTs obtained by the neutral method was represented mainly by xylans (pentosans). The quantitative content of xylans in LSTs of sulfite and neutral sulfite pulping is shown in Fig. 2.



a)

b)

Fig. 2. Composition of monosaccharides of a carbohydrate part of the lignosulphonates received by cookings: a) sulphitic and b) neutrally sulphitic

Рис. 2. Состав моносахаридов углеводной части лигносульфонатов, полученных варками: а) сульфитной и b) нейтрально сульфитной

This confirms the presence of a significant amount of monosaccharides of the pentosan class – xylose ($C_5H_{10}O_5$), in the carbohydrate part of neutral LSTs, which suggest that neutral LSTs is a promising pentosan-containing raw materials containing the polysaccharide xylan. One of a number of known practical components here is the possibility of obtaining, as a result of the hydrogenation of hemicellulose hydrolysates of pentosan-containing raw materials, xylite – $CH_2OH(CHOH)_3CH_2OH$ – a polyhydric alcohol (pentanpentanol), widely known and used for many decades in pharmaceuticals and medicine as a sugar substitute [12].

With the aim of practical use of the pentosan-containing fraction of neutral LSTs isolated as a result of fractionation by the gel filtration method, the preparation of furan derivatives has been successfully tested in laboratory conditions [13, 14]. The separation of aromatic and carbohydrate components was carried out on Sephadex 75, 100, 150. It was taken into account that each brand of Sephadex fractionated high-molecular substances in a certain limit of molecular weights. So, large-porous gels G-25, G-50 mainly fractionate in the low-molecular-weight region. Fine-porous ones G-100, G-200, having a wider range of fractionation, mainly separate the high-molecular part, therefore it is recommended to use a mixture of Sephadex 75, 100, 200 in a ratio of 25:25:50. Fractionation by the gel filtration method is based on the fact that fractions of LST with a lower molecular weight are successively washed out (eluted) with solvents from the swollen Sephadex gel [13, 14].

When a prepared LST sample is eluted through Sephadex (alkaline hydrolysis, pH 8.0-8.5), water is used as a solvent.

The separation technique by gel filtration method is as follows:

1. 3 ml of 1% LST solution is added to a column of 500 mm length and 16-20 mm diameter, filled with Sephadex pre-swollen in a water bath or Sephadex mixture.

2. The sample is placed on the surface of the wet gel and immediately after its penetration into the gel is poured with a solvent and elution continues until all the colored solution leaves the column.

3. Fraction samples are taken by an automatic collector, which rotates after a certain time, substituting the next test tube. The selection of fractions begins immediately after applying the LST sample to the gel.

4. After the end of the fractionation, the volume of each fraction is measured with a 5 ml measuring cylinder and its optical density is measured on a spectrophotometer in 1 ml layer thickness ditch.

5. A curve representing the molecular weight distribution of a given LST sample is plotted. The values of the optical density Dj of each fraction are plotted on the ordinate, and, the number of milliliters corresponding to the volume of the elute taken from the beginning of the experiment to the j fraction (ΣVj), half the volume of the j fraction (0.5 Vj) on the abscissa.

The ratio of fractions obtained by gel filtration method is 48-55% for the first fraction (aromatic alcohols), 25-30% for the second (pentosans). The separation of the carbohydrate part was controlled on SPECS-700 device at a wavelength of 280 nm, characteristic for the aromatic part (phenolic hydroxyl groups of coniferyl alcohol – LST PPU) [2, 13, 14].

The separation process by gel filtration method can be represented by the following block-diagram (Fig. 3):

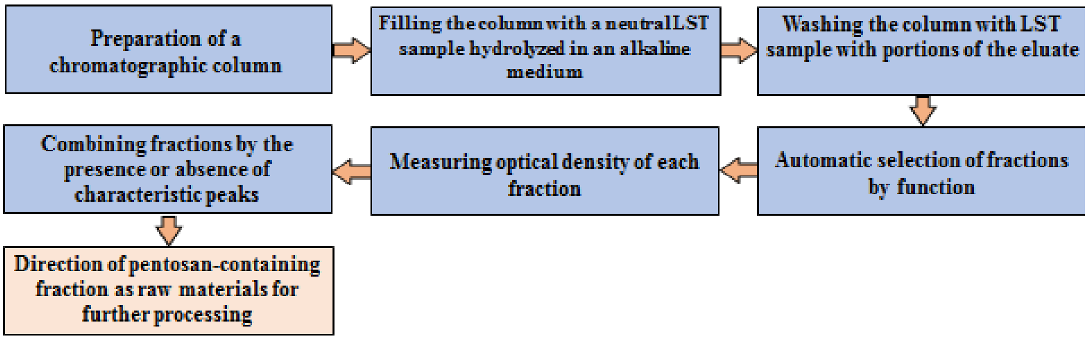


Fig. 3. Basic technological scheme of the separation of neutral LST with the isolation of the pentosan-containing fraction
Рис. 3. Принципиальная технологическая схема разделения нейтральных ЛСТ с выделением пентозансодержащей фракции

The process of obtaining furan and its derivatives from LST obtained by neutral method, carried out by us in laboratory conditions, boils down to several main stages:

1. preparation of raw materials:

stirring neutral LST sample, quartering a sample weighing at least 500-600 g;

2. fractionation of raw materials:

neutral LST sample weighing 100 g was treated with a weak alkali solution (5% NaOH solution) to pH 8.0 and fed into a pre-prepared glass column of 2 cm diameter, filled to 2/3 of its volume with Sephadex-100 granules for fractionation. The essence of the gel filtration process consisted in the priority passing aromatic alcohol molecules between the Sephadex granules – fraction 1 was selected. Xylose molecules penetrated into the Sephadex granules and, after washing with hot water (40 °C), formed the following fractions. The selection of fractions was carried out according to the volume of the outflowing liquid (no more than 15-20 ml) into replaceable receivers. After analyzing all the selected fractions by the UV method at a wavelength of 280 nm, we combined those fractions where there were no peaks characteristic for aromatic alcohols in the spectra. In percentage terms, this volume was about 30-32%;

3. preparation of a pentosan sample:

the obtained fractions of pentosans were mixed, quartered, there was taken a sample weighed 5 g (accurate to 0.01 g) and dissolved in 250 ml of water at room temperature in a 500 ml heat-resistant conical flask (flask 1);

4. hydrolysis of pentosans to pentoses (xylose) was carried out in flask 1 with heating to 200 °C for 1.5 h to a volume of 150 ml;

5. stage of separation and dehydration:

the hydrolysis product was placed into 500 ml separating funnel, in the case of the appearance of a phase boundary, the lower layer, after settling, was removed; the upper layer was poured into a 500 ml heat-resistant conical flask 2, and then xylose was dehydrated with 15 ml sulfuric acid on iron III chloride catalyst for 7-10 minutes at room temperature until the smell of rye bread characteristic of furfural appeared [12, 15];

6. extraction stage:

the formed furfural was extracted into the organic layer in flask 2 by adding 100 ml of toluene. Two layers were obtained: organic and aqueous, where there furfural was too. The aqueous layer was returned to stage 3 (recycling), preliminary qualitative reactions for furfural were carried out [17-20];

7. stage of separation of furfural:

the volume of the organic layer was measured and transferred to a round-bottom flask 3 and distillation was carried out at boiling points with the selection of fractions of furfural and related products, taking into account that the boiling points are, respectively: furan – 31.4 °C, tetrahydrofuran – 66 °C, toluene – 110 °C. Furfural, the boiling point of which is 161 °C remained in the residue in flask 3.

Thus, the basic block diagram of the isolation of furan derivatives from the pentosan-containing fraction of neutral LSTs is (Fig. 4).

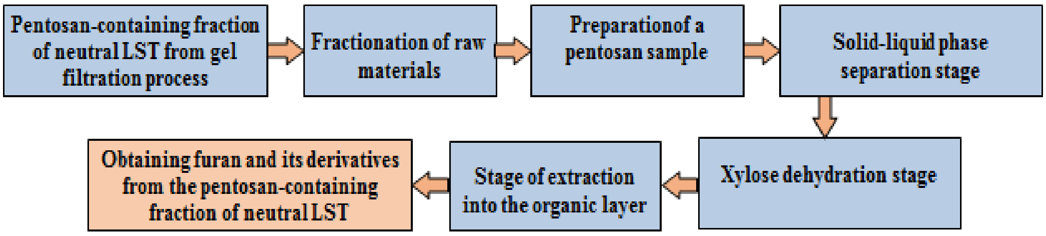


Fig. 4. Basic technological scheme for obtaining neutral LST from the pentosan-containing fraction
Рис. 4. Принципиальная технологическая схема получения из пентозансодержащей фракции нейтральных ЛСТ

Table

Material balance of the dehydration process of pentosan-containing fraction in the composition of neutral LST

***Таблица.* Материальный баланс процесса дегидратациип пентозансодержащей фракции в составе нейтральных лигносульфонатов**

Input	m, г	w, % mass	Output	m, г	w, % mass
Stage 2. Fractionation of raw material by gel-filtration method					
1.Neutral sodium LST	100	100			
2. Fraction 1 Aromatic				50	50
3.Fraction 2 polysaccharide (pentosan-containing)				30	30
			4.Loss	20	20
Total	**100**	100	Total	**100**	100
Stage 4. Pentosan-containing fraction hydrolysis					
Pentosan (xylan)	5	2			
Water	250	98	1.Xylose	150	65,4
			3.Loss (evaporation)	105	34,6
Total	**255**	100	Total	**255**	100
Stage 5. Separation and dehydration					
1.Hydrolized product (xylose)	150	91	1.Solid phase	10	6
2.Sulfuric acid	15	9	Liquid phase	150	91
			3.Loss	5	3
Total	**165**	100	Total	**165**	100
Stage 6. Extraction of furfural by toluene					
1.Liquid phase after separation	155	60,8			
2. Toluene	100	39,2	1.Organic layer	155	60,8
			2.Aqua layer (recycling)	100	39,2
			3.Loss	0	0
Total	**255**	100	Total	**255**	100
Stage7. Extraction of furfural and intermediate products by the method of distillation by boiling temperature					
Organic Layer	140	100	1.Fraction 1 Furan (31 °C)	15	10,7
			2.Fraction THF (66 °C)	15	10,7
			3.Fraction 3 Toluene (110 °C)	50	35,7
			4.Fraction 4 Furfural (161 °C)	50	35,7
			5.Loss	10	7,2
Total	**140**	100	Total	**140**	100
In all	**915**	**100**	**In all**	**915**	**100**

Based on the experiments, the material balance of the process was compiled (Table).

Thus, totally 80 g of useful products – furan, THF and furfural have been isolated from 155 g of xylose solution, it makes 57% of the products in relation to the raw material. Despite such poor results, we believe that this allows us to successfully solve the problem of increasing the level of demand and the use of neutral LSTs, which today have become a low-demand stockpiled waste of the pulp and paper industry. This result can be considered quite acceptable and it transforms neutral LSTs into the resource base of the domestic pentosan-containing raw material component for obtaining useful products.

However, in our opinion, the effect of terpenes (wood extractives), which reduce the quality of furan derivatives is promising, but not taken into account in this study.

Thus, we have considered the possibility of obtaining furan from the carbohydrate fraction of neutral LST. This can expand the scope of application of LSTs and reduce environmental risks resulting from the low demand for inactive neutral LST, which, as shown above, is a valuable domestic pentosan-containing raw materials.

CONCLUSIONS

It has been shown that the content of xylose in neutral LSTs reaches 80% or more, which is almost four times more than their content in sulfite LST, which gives reason to consider neutral LSTs pentosan-containing raw materials.

By the method of gel filtration fractionation of neutral LSTs with a ratio of aromatic and carbohydrate components of 48:30, respectively, has been implemented, the loss (mixture of fractions) is about 25-27%. There is observed increase in aromatic content and decrease in carbohydrate content of sulfite LSTs.

By the method of laboratory experiment the possibility of isolating furan derivatives from the pentosan-containing (xylose) fraction of neutral LSTs with a yield of 57% has been established.

The laboratory-technological cycle has been carried out and the working conditions for obtaining furan and its derivatives have been selected.

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