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USE OF ALBUMIN IN THE COMPOSITION OF WOOD PELLETS IN ORDER TO IMPROVE THEIR QUALITY

Chemical treatment of wood albumin in the technology of pellets is considered from the point of view of the possible directions of chemical reactions in the interaction of its reactivity with components of wood – lignin and polysaccharides (cellulose and hemicellulose). It has been shown that at high temperature and pressure parameters for the compression step – primary to obtain pellets technology, carbonyl, carboxyl, amine and amide functional groups of albumin may enter into an esterification reaction involving the hydroxyl groups of the reactive lignin and also a reaction of formation of new hydrogen bonds between two electronegative atoms which, together as oxygen and nitrogen acts.

Using albumin as a glue with its variation rate of from 0.1 to 0.5% to a. d. a wood composite pellets composed of different kinds of wood resulting in improved performance pellets complex values characterizing their mechanical strength. Pellets obtained with the introduction of albumin in their composition, meet all the requirements for the materials of the fuel use.

Key words: chemical treatment of wood, technology of pellet, albumin, mechanical strength, ester bonds, hydrogen bonds.

Introduction. Currently, wood pellets being ecological, high-energy and relatively cheap fuel are widely used not only in the home market, but also abroad – mainly for domestic purposes [1]. This requires better quality of pellets for export, which should be up to quality of European standard EN 14961-2 “Solid biofuels. Technical characteristics and fuel-classes. Part 2. Wood pellets for non-industrial non-industrial use” (referred to EN 14961-2).

The main feature of the European standard EN 14961-2 is the requirement for mechanical strength – indicator of the content of indestructible pellets in the production process. This indicator is particularly important as it is when the values that satisfy the requirements of the said standard, provides high dimensional stability of pellet shape while packaging and transportation.

Investigations being previously carried out to determine the mechanical strength of the pellets in terms of indestructible pellets content during their production revealed that its value for the samples of pellets, derived from pine, alder, birch and mixed in the native structure, doesn't meet the requirements of the European standard EN 14961-2 (not less than 97.5%) makes up only 95.0–97.0%.

Therefore, in order to obtain more strong pellets chemical processing of timber by further introducing of chemical reagent composition into the raw-nucleus spring was used, a method capable of enhancing the reaction of its components, such as lignin and polysaccharides (cellulose and hemicellulose).

Main part. In the laboratory of the department of the chemical processing of wood pellet samples were obtained from individual species of timber of pine, alder and birch, as well as for their combined composition at mass fraction of pine – 35%, alder – 45%, birch – 20 %, which is optimized as it was established earlier [2].

Albumin as a reagent of natural origin was used as chemical reagent because it is available, relatively cheap having high reactivity toward lignin and timber polysaccharides, including lignin-carbohydrate bound in the complex [3]. In addition, albumin is non-toxic and did not change ash of pellets when they are burnt because of its organic nature.

Albumin is known to be used as a hardening additive in technology of wet process hardboard manufacture, its dosing volume of 1% of the fiber increases the strength of the plates 20–30% [4].

According to the European standard EN 14961-2, the contents of any chemical additives should not exceed 2% in the pellets. The results of the pre-investigations to establish the influence of albumin withdrawal (as adhesive) on the complex of indicators characterizing the strength of pellets, revealed that the change of pellet strength when increased, occurs at a rate of this additive from 0.1%, and therefore in this research the range variation of albumin withdrawal into the pellet composition was from 0.1 to 0.6% (relative to the masses).

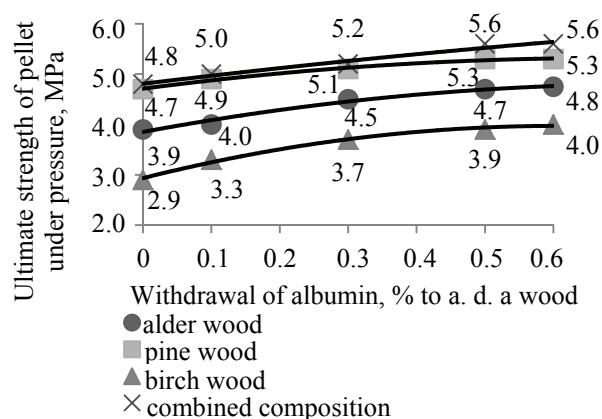


Fig. 1. Influence of albumin withdrawal on ultimate strength of pellet under pressure

Fig. 1 shows that an increase in withdrawal of albumin in the given range causes regular improvement of rates of ultimate strength for pellets. However, even for the individual deciduous species of wood of alder and birch, reached values of pellet strength were comparable with the strength of items from wood pine (without chemical processing). The highest values of ultimate strength of pellets under pressure are reached at compression of albumin 0.5%; they range from 3.9 (for birch wood) to 5.6 MPa (for combined species composition, showing the best results).

For ultimate strength at bending, a similar nature of positive influence of albumin on the strength of pellets of various composite structure is observed (Fig. 2).

When albumin withdrawal is 0.5% strength values of pellets at bending reach about 3.9 MPa for the birch wood, 4.4 MPa for alder wood, 5.1 MPa for pine wood and up to 5.3 MPa for the combined species composition.

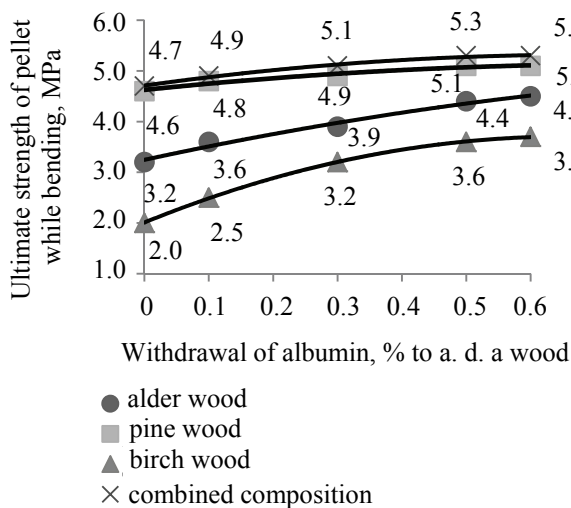


Fig. 2. Influence of albumin withdrawal on ultimate strength of pellet while bending

Due to the fact that the highest values of pellet strength according to two commonly known indicators were obtained when albumin withdrawal was 0.5%. Data defining standardized indicators such as wood-pellet dust abrasion and maintenance of indestructible pellets during the preparation of wood from alder, birch, and their combined species composition are presented at such withdrawal of additive. Investigation results are shown in Fig. 3 and 4.

Fig. 3 shows that the values of the mechanical strength of pellets in terms of content of indestructible pellets in the process of their preparation, with the addition of 0.5% albumin to a. d. wood increased by an amount of 1.0% for pine wood, 1.3% for alder wood, 2.0% for birch wood and 2.0% for the combined composition. Thus, the value of the indicators of pellet strength were not only

corresponded to the requirements of European standard EN 14961-2, but even exceeded them for the combined species composition.

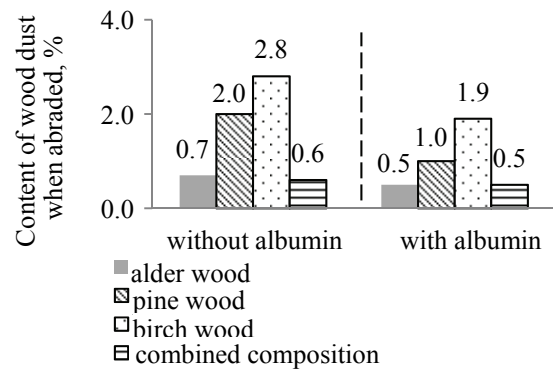


Fig. 3. Effect of albumin on the mechanical pellet strength in terms of content indestructible pellets in the process of obtaining

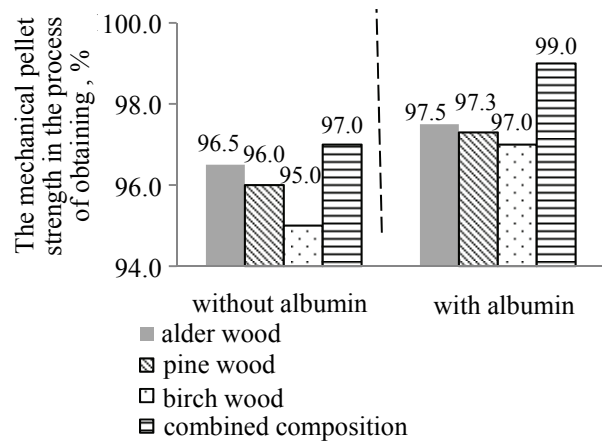


Fig. 4. Effect of albumin on the mechanical pellet strength in terms of content of wood dust when abraded

The data in Fig. 4 show that the introduction of albumin in the pellet composition, obtained from the individual wood species as well as from combined species composition, as it was expected, reduces the formation of dust fractions when abraded. This chemical treatment of alder wood resulted in a reduction of dust from pellets up to the value of strength, comparable with those obtained from pine wood; at the same time pellets from birch wood considerably conceded to them in strength – almost by 2 times. However, in the presence of birch wood in the combined species composition of pellets with the use of albumin was reached the lowest value of the resulting wood dust abraded – 0.5%, which significantly exceeded the standards of the domestic STB 2027 and foreign EN 14961-2.

In our opinion, the effectiveness of the strengthening action of albumin in getting pellets is primarily due to its chemical nature and interaction with components of lignocarbhydrate matrix in the course

of their formation. It is known [5], that albumin is high-molecular-compound consisting of α -amino acid residues such as leucine (isoleucine), cystine, glutamic acid, lysine, etc., connected to each other by peptide bonds forming long polypeptide chains.

The polypeptide chain side groups on albumin-comprise such amino acid residues as glutamine acid, as well as asparagine, leucine, isoleucine, and others. They contain such functional groups as hydroxyl ($-\text{OH}$), carboxyl ($-\text{COOH}$), amino groups ($-\text{NH}_2$), which may react with components of wood –lignin and polysaccharides [6, 7], comprising its lignocarbhydrate matrix.

The lignin also has a large number of functional groups, including methoxyl, hydroxyl, – aliphatic and phenolic, carbonyl – ketone and aldehyde, carboxyl [6]. A variety of types of relationships between phenylpropane items (the EPF) of lignin, its functional groups make lignin reactive material. At this time, the reactivity of the individual positions of the benzene ring and side chain EPF-lignin to a considerable degree is determined by the pH of the medium of chemical reactions [8].

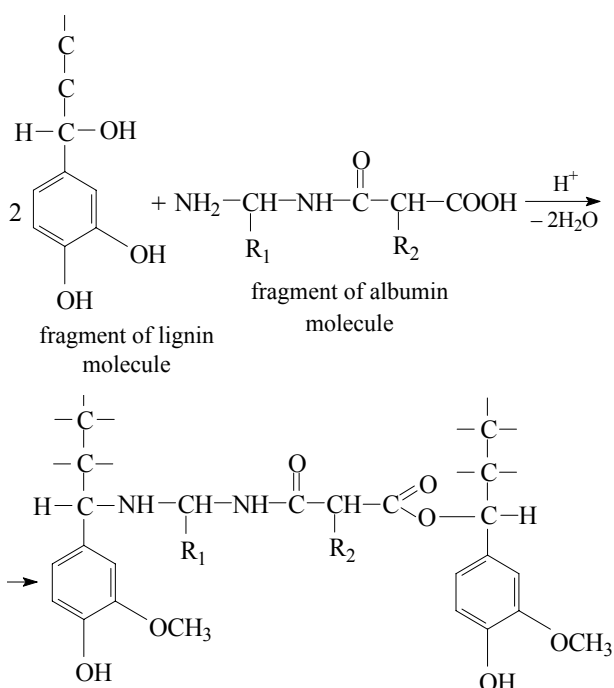


Fig. 5. Scheme of feasible direction of the reaction lignin with albumin:

R_1, R_2 – α -amino acid residues, which comprises albumin

Investigations previously carried out by us have shown that aqueous solution of albumin with concentration of 10% is slightly acidic in nature ($\text{pH} = 4.7$). Therefore from a lot of reactions, which albumin is capable of interacting with components of wood known from sources [9], we chose the most specific for conditions of weak-acid and elevated temperature environment. Fig. 5 shows a possible direction of the reactions of al-

bumin with lignin – stitching, contributing to the strengthening of the formed pellets.

Fig. 5 shows that the interaction reactive functional groups (carboxylic, amino groups) of albumin can proceed by carbonyl and hydroxyl groups of lignin propane chains. As a result of the dehydration additional ester linkages are formed, which may reinforce pellets. So passing of condensation processes is possible at least a rare cross-linking with the 5th and 6th position of the benzene ring of the lignin.

It should be noted the possibility of proceeding reactions of lignin woodself-condensation, characteristic of acidic environment, which are aimed primarily at partial splitting of lignocarbhydrate bonds followed by the formation of new ether and even carbon-carbon bonds to form compounds with higher molecular weight [10].

As a result of interaction of albumin wood with such polysaccharides as cellulose and hemicellulose, the formation of hydrogen bonds between electronegative atoms not only oxygen, but also nitrogen is of high-probability. Fig. 6 shows the scheme of the possible directions of forming hydrogen bonds between the polysaccharides with albumin on the example of cellulose.

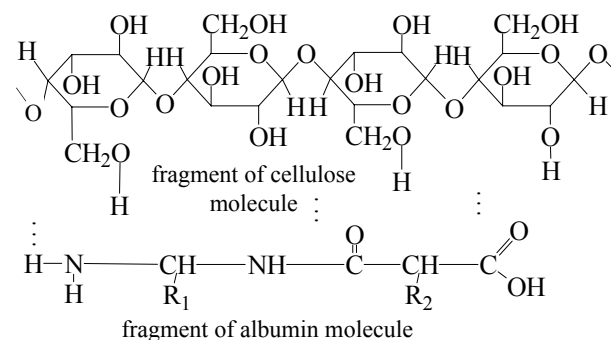


Fig. 6. Scheme of feasible direction of forming hydrogen bonds with albumin on the example of cellulose:

R_1, R_2 – α -amino acids residues, which comprises albumin

To justify the proposed directions of reactions of albumin with the components of the lignocarbhydrate matrix of wood were further involved the results of IR spectroscopic analysis, which reflects the structural changes occurring in the pellet samples derived from the pine, alder and birch wood, and their combined species composition. Increased intensity of IR absorption at $1,610\text{--}1,660\text{ cm}^{-1}$ maximum at $1,655\text{ cm}^{-1}$ in samples of pellets containing albumin, as compared with similar, but without this additive, shows its binding in wood complexes due to the imposition of bending vibrations of nitrogen-containing groups; significant reduce of integral intensity of the absorption in the frequency range $3,000\text{--}3,700\text{ cm}^{-1}$ may be a result of the entry of the hydroxyl groups of lignin and polysaccharides in interaction with the formation of ether and hydrogen bonds.

Physical and mechanical indicators of quality of pellet samples prepared with albumin

Name indicator	Requirements STB 2027 (group 1)	Requirements EN 14961-2 (class A1)	Pellet samples, prepared from various wood species			Optimized species composition of pellets composed of wood pine (35%), birch (23%), alder (42%)
			pine	alder	birch	
Moisture, %	not more than 10	not more than 10	7.9	7.5	6.8	6.3
Ash content, %	not more than 0.70	not more than 0.70	0.50	0.52	0.54	0.51
Mechanical strength (content of wood dust by abrasion of pellets), %	not more than 0.8	not more than 1.0	0.8	1.0	1.9	0.5
Mechanical strength (indestructible content of pellets in the process of obtaining), %	not standarted	not less than 97.5	97.5	97.3	97.0	99.0
The lowest combustion value (thermal value), MJ/kg	not less than 17.5	16.0–19.0	17.5	17.5	17.6	17.8

The confirmation of this opinion about the chemical nature of the reinforcing effect of albumin on the pellets are the results to determine the physical and mechanical indicators of the quality of pellet samples obtained from three woods and their mixtures treated with albumin at a rate of 0.5% (Table).

It is shown, that the reduction of wood dust by abrasion of pellets as well as increasing content of indestructible pellets in the process of obtaining, proves their high dimensional stability both in their preparation and in the packaging and transportation. In addition, these pellets meet all requirements of the standards relating to the composite materials for combustion purposes: humidity – no more than 10%; ash – not more than 0.7%, the calorific value – not less than 17.5 MJ/kg.

Conclusion. Scientifically substantiated and experimentally established the effectiveness of the chemical processing of wood by albumin because

of its high reactivity, manifested by interaction with functional groups of the main components of wood in the following areas: reaction of esterification with the hydroxyl groups of lignin; and the reaction of formation of new hydrogen bonds as a result of interaction with wood polysaccharides (cellulose and hemicellulose) due to the participation not only of electronegative oxygen atoms but nitrogen as well. At albumin consumption 0.5% to a.c. of wood in the pellet composition obtained from various species of wood and their combined composition, the values of ultimate strength when compressed, make from 3.9 to 5.6 MPa, ultimate strength at bending – from 3.6 to 5.3 MPa, the content of wood dust at abrasion – from 0.5 to 1.9%, and the content of the indestructible pellets in the process of preparation is from 97.0 to 99.0%. The last two standardized indices of pellet mechanical strength not only meet the requirements of STB 2027 and EN 14961-2, but also exceed them.

References

1. Borovskaya M. E., Kuzina M. V. The efficiency of production of pellets in the Republic of Belarus. *Noveyshie dostizheniya v oblasti importozameshcheniya v khimicheskoy promyshlennosti i proizvodstve stroitel'nykh materialov. Materialy mezhdunarodnoy nauchno-tekhnicheskoy konferentsii* [The latest achievements in the field of import substitution in the chemical industry and the production of construction materials: Materials of the International scientific and technical conference]. Minsk, 2012, part 2, pp. 166–170 (in Russian).
2. Sycheva N. A., Hmyzov I. A., Solov'yova T. V. The impact on the species composition of wood pellets quality indicators. *Materialy, tekhnologii, instrumenty* [Materials, technologies, tools]. Gomel, 2015, vol. 20, no. 2, pp. 70–74 (in Russian).
3. Shugaley I. V., Garabadzhiu A. V., Tselinsky I. V. *Khimiya belka* [Protein chemistry]. St. Petersburg, Prospekt Nauki Publ., 2011. 254 p.
4. Rebrin S. P., Mersov E. D., Evdokimov V. G. *Tekhnologiya drevesnovoloknistykh plit* [Technology fibreboard]. Moscow, Lesnaya promyshlennost' Publ., 1982. 272 p.
5. Preobrazhenskiy N. A., Evstigneeva A. A. *Khimiya biologicheskii aktivnykh prirodnykh soedineniy: v 2 t. T. 1* [Chemistry of biologically active natural compounds: vol. 1]. Moscow, Khimiya Publ., 1970. 456 p.
6. Azarov V. I., Burov A. V., Obolenskaya A. V. *Khimiya drevesiny i sinteticheskikh polimerov* [Wood chemistry and synthetic polymers]. St. Petersburg: Lan' Publ., 2010. 624 p.

7. Shcherbina A. E., Matusevich L. G., Sen'ko I. V. [et al.]. *Organicheskaya khimiya. Reaktsionnaya sposobnost' osnovnykh klassov organicheskikh soedineniy* [Organic chemistry. The reactivity of the main classes of organic compounds]. Minsk, BGTU Publ, 2000. 612 p.

8. Shorygina N. N., Reznikov V. M., Elkin V. V. *Reaktsionnaya sposobnost' lignina* [Reactivity of lignin]. Moscow, Nauka Publ., 1976. 368 p.

9. Reznikov V. M. *Prevrashcheniya lignina v nukleofil'nykh reaktsiyakh: dis. ... d-ra khim. nauk* [Transformation of lignin in nucleophilic reactions. Doct. Dis.] Riga, 1971. 406 p.

10. Domburg G. E., Scripchenko M. N. The formation of the intermediate structures during thermal prerotations lignins. 5. Contribution of the reactions rekombinatsii paramagnetic centers. *Khimiya drevesiny* [Chemical wood], 1982, pp. 781–788 (in Russian).

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