FOLIA FORESTALIA POLONICA
Seria B, zeszyt 23, 1992

INVESTIGATIONS OF THE INFLUENCE OF LOW FREQUENCY ULTRASONIC IRRADIATION ON THE CHANGES OF LIGNIN-CARBOHYDRATE COMPLEX

Adam Wójciak

Institute of Chemical Wood Technology
Academy of Agriculture in Poznań

The investigations of the influence of the ultrasonic treatment in acid and alkaline media on lignin and carbohydrate content in wood were carried out. In both studied media lignin was the wood component the most susceptible to the degradation. Cellulose was resistible to the insonation and noncellulosic polysaccharides showed only partial degradation.

INTRODUCTION

Delignification and carbohydrate hydrolysis differ both with regard to the effected wood structural changes and the products utilization. Many researches have investigated the effects of the application of ultrasonic energy for stimulation of these different processes [15, 16, 17, 25]. That proves the deficiency of the synthetic elaboration concerning chemical changes in sonicated wood. That elaboration joining the elements of the fundamental research with technological aspects should take into consideration not only chemical degradation of the structural componentes of wood but also defibration phenomena.

Also technical questions are important. Prądzyński and Ulrici [16, 25] carried out the study with piezoelectric generator emitting high frequency ultrasonic waves (above 100 kHz). The acoustic waves were passed through transformer oil to the reactor that caused unprofitable reflections and refractions. The application of the high frequency waves didn't allowe utilization of the cavitation effects — the essential reason for the physical and chemical ultrasound action. The changes caused by insonation were of the mechanical and thermic character.

The significant fact is discovery of the cavitation also in the acoustic field of (10 - 200 Hz) that creates prospects for the industrial application [13].

In this work were investigated some chemical changes produced in lignin-carbohydrate complex by the action of low frequency ultrasonic waves, at media favourable to delignification or carbohydrate hydrolysis.

EXPERIMENTAL

The debarked pinewood (*Pinus silvestris* L.) — fraction 0,5 : 1,2 mm — was preliminary extracted with ethanol : benzene (1 : 2) [18]. Weighed portion of the sawdust (near 2 g; 5,2% humidity) were sonicated using the ultrasonic generator (Model UDM-10 from IPPT PAN "Techpan", Warszawa, Poland). The generator was connected to magnetostriction transducer having a nominal frequency 21 kHz. The diameter of the tip of the transformer was 1,8 cm. At 21 kHz the ratio of diameter to wavelength of sound in water was — 0,25. For such a value, the shape of the ultrasonic field should be approximately hemispherical, which would provide a relatively uniform distribution of energy over the cross-section of the treatment vessel (volume — 75 cm^3). The sonications were carried out at the thermostating ($20 \pm 1°C$) glass vessel (diameter — 3,5 cm; height — 9 cm) in the following media: 1% aqueous H_2SO_4, 8% aqueous NaOH and water (reference). The concentration of the acid solution was close to that used in different variants of the wood hydrolysis with diluted acids. The concentration of the alkaline solution was close to percentage alkalinity of the liquor in alkaline pulping.

Table 1

Variable factores of the experience
Parametry ekspozycji ultradźwiękowej

Medium Środowisko	Time (h) Czas (godz)	Amplitude (μm) Amplituda
H_2O	1	40
H_2SO_4	1	40
NaOH	2	48

The ultrasonic treatment was carried out using earlier established parameters (tab. 1) [28].

After sonication the solutions with sawdust were centrifuged (4500 r.p.m.; 1 h). The chemical analyses of the sawdust and decanted solutions were performed.

The sawdust was transfered on the drains and than washed to the

neutral reaction. After air drying and humidity measurement the sawdust was subjected to the following analysis. The solutions were centrifuged again, than decanted to the beakers and subjected to chemical analysis. The same procedure was used to the unsonicated wood (reference). The unsonicated and unsoaked wood is hitherto called — untreated wood. In the sawdust the following parameters determined: Tappi lignin T-13 m [18], Seifert's cellulose [18] and the composition of the carbohydrate fraction with GLC method (chromatography — JEOL 1100 TFP, Takeda Riken TR 2115A integrator). For the chromatographic analysis the two-stage hydrolysis of sawdust with 72% and 3% H_2SO_4 was applied [19, 20]. For separation of trimethylsilil derivatives of sugars [24] a glass column (length — 2 m; I.D. — 3 mm) coated with SE-30/Gas Chrom Q was prepared. The column oven was temperature programed 2 deg/min from 403 K up to 473 K. Helium carrier gas was used Chromatographic parameters have been established for separation of the following sugars: *L*-arabinose, *D*-xylose, *D*-mannose, *D*-galactose and *D*-glucose — anomers α mixed with β after isomerization in water: methanol (1 : 1).

In the solutions were determined: lignins, furfural derivatives and composition of carbohydrate fraction.

The diluted lignin content was measured by UV spectrophotometric method [14]; as a standard the lignin prepared after the modified Bjorkman method was used [2, 23]; the lignin preparation was dissolved in dioxane and dilluted with water, 1% aqueous H_2SO_4 and 8% NaOH (1 : 7); the absorption measurements (near 258 nm) allowed to estimate the analytical curve formulae: $y=0{,}0156x+0{,}0052$ — for the neutral medium, $y=0{,}0159x+0{,}0013$ — for the acid medium and $y=0{,}0149x+0{,}0509$ for the alkaline one; in order to eliminate influence of the carbohydrates and their derivatives the method of reduction with $NaBH_4$ was used; the reduction was performed on the standard and sonicated solutions. The measurements were performed with C. Zeiss (Jena) SPECORD M-40.

The furfural derivatives content was measured by UV spectrophotometric method [14]; as a standard the Merck's furfural p.f.a. was used; furfural was dissolved in water and 1% aqueous H_2SO_4; the absorption measurements (277,6 nm) allowed to estimate the analitycal curve formulae: $y=0{,}2546x+0{,}0236$ for the neutral medium and $y=0{,}3255x-0{,}0499$ for the acid medium; the sonicated solutions were centrifuged and then analysed at 277 nm; the absorbance difference (before and after $NaBH_4$ reduction) was used in the furfural derivatives calculation.

The composition of the carbohydrate fraction was measured by GLC method; the acid and alkaline sonicated solutions were neutralized and then treated after earlier described S w e e l y' s method [24].

The mean results (5 samples) are presented in the tab. 2 - 5.

RESULTS AND DISCUSSION

Wood defibration facilitates chemical processing therefore the study of changes in sonicated lignin-carbohydrate complex was performed with earlier established parametres (time, amplitude) assuring the biggest dynamics of the defibration [28].

The data from tab. 2 show the results of lignin and cellulose determinations. The preliminary study was performed for the unsonicated sawdust. At room temperature, water didn't cause significant changes in wood. In the same conditions dilluted acid didn't attack lignin and cellulose. Dilluted alkaline solvents can affect not only the hemicellulose but also cause partial dissolving of the lignin.

Table 2

The effect of the ultrasonic treatment on the changes of lignin and cellulose content
Wpływ obróbki ultradźwiękowej na zmiany zawartości ligniny i celulozy w drewnie

	Lignin and cellulose content i % dry mass of wood Zawartość ligniny i celulozy w % masy b.s. drewna						
	sonicated				unsonicated		
	untreated wood	H_2O	H_2SO_4	NaOH	H_2O	H_2SO_4	NaOH
Lignin Lignina	29.60	29.03	28.94	28.33	26.60	23.59	21.15
Cellulose Celuloza	43.29	43.27	43.01	43.06	43.14	41.90	42.26

Note: In tables 2, 3, 5 the following words should be exchanged: "sonicated" → "unsonicated" and "unsonicated" → "sonicated"

In the interpretation of the lignin dissolving it is helpful to use the spectrophotometric method (fig. 1). In the neutral medium the distinct absorbtion bands characteristic for lignins weren't observed. On the contrary, the acid and alkaline spectrums are similar to these of the lignin standard. This confirms the assumption that milled wood lignin macromolecule contains the weakly bounded part of the lignin [5, 6, 7]. The MWL's spectrum differs the widest band at 205 nm and more distinct at 230 nm. The essential difference is the highest absorption ranging from 300 up to 350 nm. This absorption characteristic for the dioxane lignin is caused by the presence of the conjugated α — carbonyl groups in the side chains [1, 7].

The contents of the dissolved lignin (tab. 3) reflects the observations from gravimetric analysis. Traces of lignin were measured in water, more in acid (0,16%) and alkaine media (0,71%). It is worthwhile noticing that the total results of the gravimetric and spectral measurements include the parts of lignin dissolved in acid but not seized in the results of conventional gravimetric determinations.

As shown in Table 2 the ultrasonic treatment caused real losses of

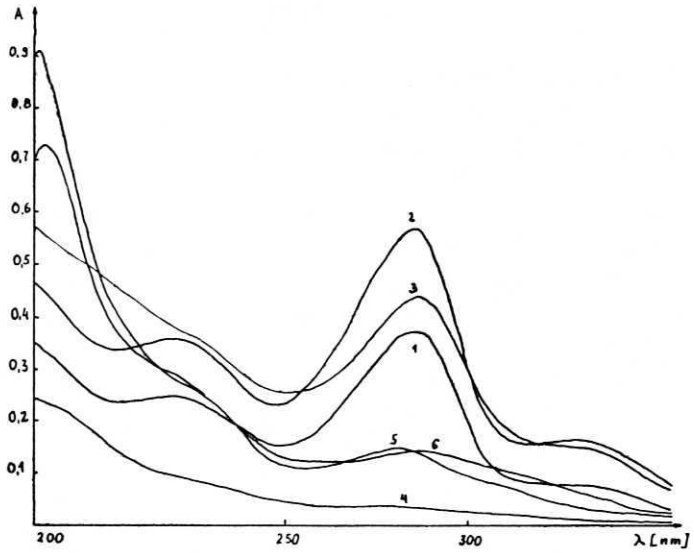

Fig. 1. Ultraviolet absorption of lignin standards and the solutions from unsonicated experiences (reference)

1 — lignin (neutral medium), *2* — lignin (acid medium), *3* — lignin (alkaline medium), *4* — neutral solution, *5* — acid solution, *6* — alkaline solution

Rys. 1. Absorpcja w nadfiolecie preparatu wzorcowego ligniny oraz roztworów z prób nienadźwiękawianych

1 — lignina (środowisko obojętne), *2* — lignina (środowisko kwaśne), *3* — lignina (środowisko zasadowe), *4* — roztwór obojętny, *5* — roztwór kwaśny, *6* — roztwór zasadowy

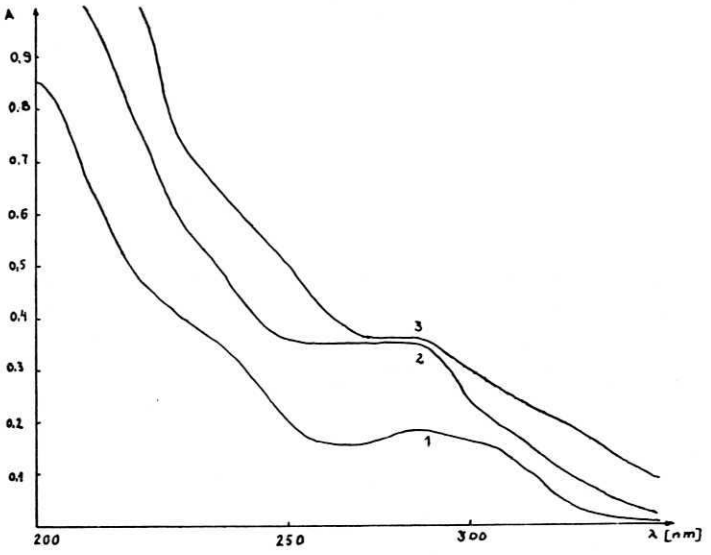

Fig. 2. Ultraviolet absorption of the solutions after insonation

1 — neutral solution, *2* — acid solution, *3* — alkaline solution

Rys. 2. Spektrofotometryczne krzywe absorpcji roztworów z prób nadźwiękawianych

1 — roztwór obojętny, *2* — roztwór kwaśny, *3* — roztwór zasadowy

lignin in all the tested media. After sonication at 8% aqueous NaOH were measured above 27% less of lignin than in the untreated wood. After sonication at acid solutions the lignin content lowered by about 19% and at water by about 8,5% (in comparison to untreated wood). It is necessary to observe that it is impossible to separate Klason lignin from the products of polysacchardies degradation. During the determination occurs also the decrease of lignin dissolving in hot hydrolytic solution. In case of coniferous wood these decreases are smaller and don't exceed 0,5% [3, 23].

The mentioned inaccuracies can be partialy compensated with the aid of the UV spectrophotometry. As shown at the fig. 2 the insonation caused intensification of the wood decomposition. The real changes in the absorption maximum position weren't yet observed. Only for the neutral solution the extension of the band ranged from 280 up to 310 nm was noticed that can be caused by interaction of the side chains carbonyl group in α-position f.ex: $-CO-CHOH-CH_3$ [1]. The alkalization didn't bring about shift that indicates the weak character of these interactions, not influenced by quantitative determinations.

Table 3

Dissolved lignin content before and after ultrasonic treatment
Zawartość ligniny w roztworach przed i po obróbce ultradźwiękowej

Lignin content in % dry mass of wood Zawartość ligniny w % masy b.s. drewna					
sonicated			unsonicated		
H_2O	H_2SO_4	NaOH	H_2O	H_2SO_4	NaOH
0.07	0.16	0.71	1.80	3.61	5.45

As shown on the Table 3, more lignins were measured at alkaline medium (5,45%) than at acid (3,61%) and least at water (1,80%). The total results of the gravimetric and spectrophotometric determinations (H_2O — 28,4%; H_2SO_4 — 27,2%; NaOH — 26,6%) are in every case less than in untreated sawdust — 29,06%. Take into consideration the data from the similar comparison for unsonicated samples allowed to suppose that part of degraded after insonation lignins, were dissolved in acid during determination with the Tappi method.

The investigations of influence of ultrasonic irradiation on carbohydrates were begun with analysis of cellulose changes. As shown in the Table 2 the sonication in water didn't cause the cellulose degradation. Ther's no difference when the results of the experiences in acid and alkaline media are compared. The real differences were observed between the results of sonication in acid and acid reference. Although

the small degradation of cellulose, particularly in disorder areas is possible, however the observed differences — 1% — between the results can be caused by hydrolysis of the residual pentosanes that in Seifert's cellulose don't exceed 2% [11]. More informations about carbohydrates transformations was provided by GLC study. For both experiments (reference and sonicated) the predominant tendency is decrease of the hemicellulosic carbohydrates proportions to the glucose. The insonation accelerates the hemicellulose degradation. That is cleary visible in alkaline medium. The relative amount of the hemicelluloses in alkalii lowered by about 10% and in acid by about 10%. The ultrasonic treatment didn't cause the total hydrolysis of none of the determined components of polysaccharides. Detailed analysis indicates some regularity. The α-arabinose portion in neutral and acid media is less than in alkaline one. That sugar — component of 4-0-methylglucuronoarabinoxylan and also arabinogalactan easy hydrolyses in acids particularly in α [1 - 3] glycosidic bonds with *D*-xylose [12]. Xylans are resisted to alkalines that confirms the stability of *D*-xylose portion in results of the study performed in 8% NaOH. The glucomannans show the sensitivity to alkaline degradation. Lowering of α-mannose portions was observed in the result of unsonicated and sonicated experimences.

Table 4

The effect of ultrasonic treatment on wood carbohydrates chances
Wpływ obróbki ultradźwiękowej na zmiany składu frakcji węglowodanowej

Samples / Material badawczy / Mono-saccharides	Percent share of wood carbohydrates / Skład procentowy frakcji węglowodanowej						
	untreated wood	unsonicated			sonicated		
		H_2O	H_2SO_4	NaOH	H_2O	H_2SO_4	NaOH
Arabinose	1.63	1.05	1.47	2.13	1.17	1.37	1.78
Xylose	4.37	5.90	4.26	6.78	6.07	6.53	6.18
α-Mannose	21.40	18.93	18.37	14.50	16.06	14.43	13.05
α-Galactose	0.80	0.60	0.80	0.80	1.60	0.93	0.93
α-Mannose β-Galactose	9.60	7.38	7.27	8.78	6.07	7.50	6.20
Glucose	62.20	66.15	66.20	67.03	68.47	69.27	72.05

Although the presented results proved that ultrasounds caused acceleration of the hemicellulose decomposition, subsequently performed analysis of the sonicated solutions indicates only traces of the sugars. In the neutral and acid media were revealed *D*-xylose, α-mannose and *D*-glucose traces. It is possible that in low frequency ultrasonic field occured a phenomenon of cavitation causing degradation of dissolved sugars. Although the monosaccharides decomposition proceeds in alkaline medium without action of additional agents but insonation can these processes intensify.

The comparison of results of lignin and carbohydrate determination (tab. 2 - 4) proved that independently of the used media the ultrasounds are the predominant agent of wood degradation. The wood components most susceptible to the degradation was lignin. That is the result of its disordered chemical structure particularly physically bounded low molecular fractions. In case of acid media ultrasounds can intensify the cleavage of α-ethers already occuring in mild conditions of acid lignin hydrolysis. In alkalies insonation stimulates not only solvolytic ether cleavage between phenylpropane units but also cleavage of C-C bond and condensation processes.

Although ultrasounds make easier penetration of the reagents into cell walls, the strong chemical bonds and accessible with difficulty, fibrous structure cause than cellulose does not undergo considerable degradation. Minor resistance of hemicellulose to insonation results from smaller DP and its ordered state.

Table 5

The effect of ultrasonic treatment on changes of content of monosaccharidic degradation products

Wpływ obróbki ultradźwiękowej na zmiany zawatrości produktów degradacji monosacharydów

Monosaccharidic degradation products Produkty degradacji monosacharydów (mg/dm³)			
sonicated		unsonicated	
H_2O	H_2SO_4	H_2O	H_2SO_4
0.20	0.22	2.72	7.05

The data in the table 5 show the results of the determinations of carbohydrate degradation products. It is known that in low frequency ultrasonic fields, in water occur different thermic phenomena (phase boundary absorption, cavitation). These effects, in acid media can cause dehydration of dissolved monosaccharides and formation of furfural, 5-hydroxymethylfurfural. These reactions can be initiated also during sonication in water, when the pH lowers to about 5,7. In case of the determinations in water the obtained results are not comparable to similar analysis performed even for shortlived hydrothermal treatment of the sawdust at 373 K (14). After sonication in acid medium the amount of furfural derivatives was similar to the results of 1-hour treatment of sawdust in hot water (14). Taking into consideration the relative losses of hemicellulose sugars both in water and in acid solution it is possible that these sugars undergo transformations to the simple acid products.

CONCLUSIONS

1. The influence of low frequency ultrasonic field on wood components depends on structural orientation of wood polymers:

a) indenpendently of the experimental media lignin was most susceptible on ultrasonic degradation,

b) between the polysaccharides — independently of media of experiments — cellulose was resistant to degradative action of ultrasounds and hemicellulose underrent only partial decomposition.

2. The interaction of ultrasounds and chemical reagents didn't cause total hydrolysis in none of the determined saccharidic components. The phenomena occuring during insonation, favourable to sugars transformation limits the possibility of utilization of ultrabiounds in polysaccharides hydrolysis.

Received in January 1992

REFERENCES

1. Aulin-Erdtman G.: Svensk Papperstidn 1953, no 53, p. 287. In Sarkanen K. V., Ludwig C. H.: Lignins-occurence, formations, structure and reactions. Wiley-Interscience, New York. 1971.
2. Bjorkmann A.: Studies on Finaly Divided Wood, Part 1. Extraction of Lignin with Neutral Solvents. Svensk Papperstidn, 1956, no 59, p. 477 - 485.
3. Browning B. L.: Method of Wood Chemistry, Vol. 3, Chapt. 34, Interscience, New York, 1967.
4. Fengel D., Wegener G.: Wood Chemistry-Ultrastructure, Reactions, Walter de Gruyter, New York, 1984.
5. Goldschmid O.: The Effect of Alkali and Strong Acid on the Ultraviolet Spectrophotometry. J. Am. Chem. Soc., 1953, no 75, p. 3780 - 3783.
6. Goldschmid O.: Determination of Phenolic Hydroxyl Content of Lignin Preparations by Ultraviolet Spectrophotometry. Anal. Chem., 1954, no 13, p. 1421 - 1423.
7. Goldschmid O.: Ultraviolet Spectra. (In) Sarkanen K. V., Ludwig C. H.: Lignins-occurence ... Wiley-Intercsience, New York, 1971.
8. Jankowskij B. A.: Wlijanije ultrazwukowo abłuczenija pri wydjelenii lignina neutralnymi rastworitieliami. Chimija Drewiesiny. 1968, no 3, p. 49 - 51.
9. Jankowskij B. A., Pierszina P. A.: O diejstwije ultrazwuka na drewiesinu. Chimija Drewiesiny. 1969, no 3, p. 53 - 55.
10. Kaszyńska J.: Oznaczenie małych ilości ligniny w masach celulozowych metodą spektrofotometryczną. Przegląd Papierniczy 1973, no 7, p. 234 - 239.
11. Kaszyńska J.: Przegląd metod oznaczania celulozy w drewnie. Zeszyty Problemowe Postępu Nauk Rolniczych. 1976, no 185, p. 25 - 32.
12. Kin Z.: Hemicelulozy — chemia i wykorzystanie. PWRiL, Warszawa, 1980.
13. Margulis M. A.: Zwukochimiczeskije reakcii i sonoluminescencja. Chimija, Moskwa 1986.
14. Niechajczuk A. D.: Spektrofotometriczeskije isliedowanije sodierżanija cellułozy i lignina. Riga, 1974, p. 242 - 248.
15. Niepienin J. N., Beigielman A. B.: Wlijanije mechaniczeskowo piere-

mieszivanija i ultrazwukowych koliebanij na skorost delignifikacji pri szcziołocznoj warkie cellułozy. Chimija cellułozy i lignina. Riga, 1974, p. 302 - 308.
16. Prądzyński W., Gawędzki T.: Wpływ ultradźwięków wysokiej częstotliwości na intensyfikację procesu hydrolizy drewna. Roczn. AR Poznań 1979, no 117, p. 81 - 89.
17. Prądzyński W.: Wpływ oddziaływania ultradźwięków na drewno i zawartość w nim ligniny. Zesz. Nauk. ATR Bydgoszcz 1985, no 115, p. 25 - 35.
18. Prosiński S.: Chemia drewna. PWRiL, Warszawa, 1984.
19. Pszonka B., Stupińska H.: Oznaczenie węglowodanów w surowcach i produktach przemysłu celulozowo-papierniczego metodą chromatografii gatowej. Zeszyty Problemowe Postępu Nauk Rolniczych 1976, no 185, p. 41 - 51.
20. Pszonka B., Stupińska H.: Oznaczanie składu węglowodanów w surowcach i produktach przemysłu celulozowo-papierniczego metodą chromatografii gazowej. Przegląd Papierniczy 1979, no 1, p. 11 - 14.
21. Sajdalimow S. A., Smirnowa L. S., Abduazimow H. A.: Isliedowanije lignina wydielonnowo iz stebliej chłopczatnika s pomoszcziu ultrazwuka. Chimija Drewiesiny 1976, no 2, p. 75 - 77.
22. Salnikow W. W., Riempiel S. J.: Wozdiejstwije ultrazwuka na gidroliznyj lignin. Trudy Uralskowo Liesotechniczieskowo Instituta 1962, no 18, p. 9 - 21.
23. Sarkanen K. V., Ludwig C. H.: Lignins — Occurence, Formation, Structure and Reactions. Wiley-Interscience, New York 1971.
24. Sweely C. C., Bentley R., Makita M., Wells W.: Carbohydrate Method of Determination by Gas Chromatography. J. Am. Chem. Soc. 1963, no 85, p. 2497 - 2501.
25. Ulrici G.: Verfahren zur Behandlung von Zellulosestoffen durch Ultraschallwellen insbesondere zur Herstellung von Papiermasse. Deutsches Patentamt. Patentschrift no 815602.
26. Wegener G., Stoll M.: Eine Schnelle Isolierung von Milled Wood Lignin mit Hilfen von Ultraschall. Cell. Chem. Technol. 1976, no 10, p. 611 - 616.
27. Wegener G., Fengel D.: Rapid Ultrasonic Isolation of Milled Wood Lignin. TAPPI 1975, no 62, p. 97 - 100.
28. Wójciak A.: Badania degradacji drewna sosny (*Pinus silvestris* L.) poprzez oddziaływanie pola ultradźwiękowego niskiej częstotliwości. Praca doktorska. Wydz. Technol. Drewna AR Poznań 1991.

Authors address:
Dr inż. Adam Wójciak
Instytut Chemicznej Technologii Drewna
AR w Poznaniu
ul. Wojska Polskiego 38/42
60-637 Poznań — Poland

Z BADAŃ NAD ZMIANAMI ZACHODZĄCYMI W KOMPLEKSIE LIGNINO-WĘGLOWODANOWYMI DREWNA POD WPŁYWEM ODDZIAŁYWANIA POLA ULTRADŹWIĘKOWEGO NISKIEJ CZĘSTOTLIWOŚCI

Streszczenie

Celem badań było dokonanie oceny zmian zachodzących w układzie lignino-węglowodanowych drewna wywołanych oddziaływaniem fal ultradźwiękowych niskiej częstotliwości w środowiskach chemicznych sprzyjających procesom: delignifikacji i hydrolizy części węglowodanowej drewna.

Nadźwiękawianie trocin sosnowych prowadzono stosując ustalone we wcześniejszych badaniach parametry czasu i amplitudy fali ultradźwiękowej, przy których proces rozwłókniania drewna osiągnął największą dynamikę. Jako środowiska doświadczeń wybrano roztwory wodne: 1% H_2SO_4 oraz 8% NaOH.

Stwierdzono, że niezależnie od środowiska doświadczeń, najbardziej podatnym na degradację ultradźwiękową składnikiem drewna jest lignina. Celuloza jest odporna na degradujące działanie fal ultradźwiękowych, a wielocukry niecelulozowe ulegają jedynie częściowemu rozkładowi. Związane z polem akustycznym zjawiska fizyko-chemiczne sprzyjające rozkładowi przechodzących do roztworu cukrów ograniczają możliwość wykorzystania fal ultradźwiękowych do stymulacji procesów hydrolizy węglowodanów.