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Extracting Galactoglucomannans (GGMs) from Polish Softwood Varieties

Abstract
The article presents a method of extracting galactoglucomannans from conifers: spruce and larch. Galactoglucomannans (GGMs) were extracted from shavings of Polish varieties of spruce and larch, using thermal and enzymatic treatment in an aqueous environment. The composition of the extracted GGMs (depending on the extraction method) was characterized by varied content of individual monosaccharides, i.e. glucose, galactose and mannose, as well as the average particle mass. The quantitative and qualitative composition of the extracted GGMs is an important factor affecting the possibility of their wide employment in modifying cellulose fibre-containing materials in order to improve their barrier qualities, and as biological agents in plant health products. GC/MS and SEC chromatographic tests and 13C NMR analysis made it possible to establish the composition and structural changes of the acquired GGMs.

Key words: *spruce, larch, galactoglucomannans, thermal treatment, enzymatic treatment.*

List of abbreviations

GGM – galactoglucomannans,
GGM/T – galactoglucomannans after thermal treatment,
GGM/T – galactoglucomannans from spruce wood shavings after thermal treatment,
GGM/T/L – galactoglucomannans from larch wood shavings after thermal treatment,
GGM/En – galactoglucomannans after enzymatic treatment,
GGM/S/En – galactoglucomannans from spruce wood shavings after enzymatic treatment,
GGM/S/En – galactoglucomannans from larch wood shavings after enzymatic treatment.

Introduction

The basic components of wood-derived fibre resources are: cellulose, hemicelluloses and lignin. They are accompanied by smaller amounts of extraction agents and mineral compounds. Cellulose is a linear polisaccharide composed of a large number of D-glucopyranose residues, joined into chains by β-glycosidic bonds. Hemicelluloses are polysaccharides composed not only of glucose residues, but also other hexoses, such as galactoses and mannoses, as well as pentoses - xylose and arabinose. They bear names related to the most common elements, like glucomannan, galactoglucomannan, arabinogalactan. In pulp production, cellulose pulp in particular, some of the hemicelluloses dissolve and move to the digesting liquor, the composition of which depends on the wood digesting method. Hemicellulose content in softwood is 26% on average and is mostly hexosanes, while hardwood it is 20-33% with most of it being pentosanes and uronic acids [1, 2].

The galactoglucomannans, belonging to hemicelluloses, are of particular importance to numerous branches of industry (cellulose-paper, textile, pharmaceutical, food and agriculture). Their usefulness is mainly a result of the ratio of galactose, glucose and mannose residue amounts, average degree of polymerisation and their ability to settle on the surface of cellulose materials [3 - 5]. The galactoglucomannans obtained can be fully utilised as bioactive agents, e.g. for modifying dressing materials, pulps - to improve barrier qualities for air and water permeability, and for modifying plant health products [6].

Water-soluble galactoglucomannans are natural, biodegradable polymers [7]. The highest natural content of GGMs is featured in softwood wood, ranging from 10 to 20%, though their composition and structure differs depending on the plant resource. GGMs have a main chain that can be composed of D-mannopyranose and D-glucopyranose units connected by β-1,4-glycosidic bonds. This type of polymer is called glucomannans. Galactopyranose content differs depending on the raw material that the GGM is obtained from. If the ratio of galactose residues to glucose and mannose residuesis 0.1:1:4, then such a GGM is described as low-galactose GGM. On the other hand, in high-galactose content galactoglucomannans the amount of galactose residues is 0.5 - 1. The former, characterised by low galactose content, are poorly soluble in water. The latter are water-soluble GGMs with high galactose content, whose chains are composed of mannose, glucose and galactose residues, with a quantity ratio of 0.5 - 1:1:3 [7].

Extracting GGMs from plant raw materials is primarily based on thermal treatment of the material in an aqueous environment, which is a similar process to cellulose thermal treatment [8, 9]. The first phase of the GGM extraction process is based on the thermomechanical pulping (TMP) method. It consists in processing wood at 110 - 130 °C; then the material undergoes defibering in disk mills with a specific gap width. The thermal treatment aims to plastify lignin and develop fibre surface through water penetrating cell walls [5]. Up to 50% of GGMs pass into solution once the thermal treatment process is finished [1, 3].

According to data [6, 10], hydrolysis results in a solution of β-D-mannase: β-D-glucose: α- D-galactose with a: 2 - 3:1:4 - 5 ratio. Adding organic solvent to the solution results in precipitating GGM with the simultaneous removal of oligomers and carbohydrate monomers [3, 11]. The precipitated GGMs contain small quantities of impurities, e.g. xylanes and pectins, and obtaining them without any aromatic structures or other carbohydrates is extremely difficult and involves a significant drop in efficiency [4, 10, 12, 13].

Another method of GGM extraction with their simultaneous modification is enzymatic treatment utilising the known plant biomass susceptibility to mircoorganisms [14, 15]. Due to the varied structure of

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wood and GGMs, and their susceptibility to decomposition to monomeric products, it is possible to obtain a solution containing GGM hydrolysate. However, it requires the cooperation of various enzymes, e.g. a depolimerising complex consisting of endo-1,4-β-mannanase, β-mannosidase, α-galactosidase and β-glucosidase, where the first two enzymes are the most important components of this complex. ß-mannanases catalyse the hydrolysis of the β-1,4-glycosidic bond β-D-mannose residues of the non-reducing end of such substrates as mannans, glucomannans, galactomannans and galactoglucomannans. The endomannase effect on the main chain creates short, substituted or non-substituted oligomers, mannobiose and mannose. Further hydrolysis of water-soluble oligomers and dimers into mannose is conducted by β-mannosidase. β-glucosidase and α-galactosidase, which release glukose and galactose substituents from the main mannan chain, act together with endomannanases and mannosidases [6, 16, 17].

Mannanolytic enzymes are produced from plant material on a large scale. The preparations include: Hemicell (ChemGen), Gamanase NovoNordisk, Mannaway P&G (Novozyme), Purabrite, Mannastar (Genencor), Pyrolase (Diversa) and others [17].

The aim of this work was to isolate and characterize GGMs from Polish softwood varieties using thermal treatment and enzymatic treatment of wood shavings in an aqueous environment.

An attempt was made to utilise softwood hemicelluloses to produce full-value materials, that would employ the biorefinery concept, according to which wood components (hemicellulose, cellulose, lignin, etc.) can only be fractionated using physico- and biochemical methods.

Experimental part

Raw material

Two types of softwood trees found in Poland were utilised for the purposes of the research: the spruce (*Picea abies*) and the fine-ringed larch (*Larix decidua*). The chemical composition of the studied tree species is provided in ***Table 1***.

Research methodology

GGM isolation

Before thermal and enzymatic treatment, the shavings were subjected to extraction with an organic solvent - ethyl alcohol.

Thermal treatment in aqueous environment

Wood shavings were ground in a Körner mill. Next, they were boiled in a 2 dm^3 reactor, with the liquid to wood amount ratio being (liquid ratio) 4:1, at 120 °C temperature, under the pressure of 0.22 MPa, for 60 minutes. After a pre-determined heating time, the temperature was lowered to 80 °C by adding water, lowering the suspension concentration to 5%; the whole was stirred for 30 min. The suspension was cooled to 60 °C and stirred in the reactor for 180 min. After the thermal treatment, the shavings were filtered through a Schöt funnel, thus obtaining the first filtrate. A 5% concentration suspension was made of the obtained shavings and it was again stirred in the reactor for 180 min. at 60 °C. After a pre-determined time, the shavings were filtered through a Schöt funnel, thus obtaining the second filtrate. The first and second filtrates combined were centrifuged at 1750 r.p.m. for 30 min. Next, the solution was evaporated at 40 °C in order to remove water. After the evaporation, the suspension was filtered on a glass filter with a pore diameter of 0.2 μm. After the evaporation, GGMs were precipitated by adding ethyl alcohol in an amount of 4:1 (ethanol:water). The ethanol treatment allowed for precipitating and purifying the GGM, leaving other monomeric carbohydrates in the solution. The GGM precipitate was filtered through a glass filter of a 0.2 μm pore diameter and washed successively with ethyl alcohol, methyl alcohol and methyl tert-butyl ether. The washing was done in order to purify the GGM precipitate of monomeric carbohydrate residues. The precipitate was air-dried. The dried powder was weighed and process efficiency was calculated.

In order to further purify the GGMs obtained (e.g. residual lignin), they were dissolved in water and run through a column filled with non-ionic, macroporous resin in the shape of white, non-soluble grains - Amberlite® XAD7HP. Next, the solution was concentrated and the GGM precipitated again by adding ethyl alcohol in an amount of 9:1 (ethanol:water). The precipitate was filtered and air-dried.

Enzymatic treatment and modification of GGMs in aqueous environment

Wood shavings were initially heated in water at 80 °C, for 180 min, at 5% concentration of the suspension.

Conditions of enzymatic treatment of spruce and larch wood shavings: before moving on to enzymatic treatment, the shavings were ground in a planetary ball mill (Retsch PM100), at 120 and 130 r.p.m.

- Reaction environment – 0.05 M, pH 4.5 - 5.6 acetic buffer;
- Shaving concentration in reaction environment: 2.5% (w/v);
- Reaction time: 4 and 24 h;
- Temperature: 40 and 50 °C;
- Enzymes: enzymatic complex *Aspergillus niger* from the Institute of Technical Biochemistry of the Lodz University of Technology, with carboxymethylcellulose (CMC) – endo-β-1,4-glucanase activity – 249 U/cm^3; FPA (Filtrate Paper Activity) – 45 U/cm^3; endo-β-1,4-xylanase – 4043 U/cm^3; β-glucosidase – 190 U/cm^3; commercial enzyme - Hemicellulase (Sigma Aldrich) with an activity of 0.3 - 3.0 U/cm^3, enzyme/substrate module E/S of enzyme application: 200 - 1000 U/g of shavings.

After enzymatic treatment, GGM was precipitated from the solution in the same way as described above in the case of the GGM solution obtained after thermal treatment.

GGM and wood analysis

Wood characteristics

The chemical composition of wood shavings was tested according to Polish Standard - PN-92/P-50092 Raw Materials for the paper industry. Wood. Chemical analysis.

The polymerisation degree (DP) of the GGMs obtained was tested according to - ISO 5351:2010 Pulps - Determination of limiting viscosity number in cupriethylenediamine (CED) solution.

Characteristics of the GGM precipitate obtained

GC/MS chromatography

The quantitative and qualitative composition of the GGMs obtained was tested using GC/MS chromatography, determined using the method developed by Pszonka and Stupińska [18]. Hewlett Packard 5890, II/5972 series

GC-MS equipment was utilised. A full carbohydrate separation was performed on a capillary column DB-5 (60 m × 0.25 mm × 0.25 μm) in the following conditions of device operation: gas chromatography device: T_{dos} - 275 °C, T_{det} - 280 °C, $T_{furnace}$ = 45 (1 min) 20 °C/min do 170 °C (2 °C/min) do 230 °C (20 min). Carrier gas flow He = 0.9 cm^3/min (in T_p = 45 °C). A quadrupole mass spectrometer in SCAN (qualitative determination) and SIM (quantitative determination) was used to identify and determine the amount of separated analytes. Quantitative determination was performed using the internal standard method. Myo-inositol was used as the internal standard. The method's detection threshold is 5 μg/g for each monosaccharide, and the standard relative deviation is up to ± 10%.

Size exclusion chromatography SEC

The GGM molecular mass was determined by size exclusion chromatography, using an Agilent chromatography device with triple detection: Refractive Index (RI), Right Angle Light Scattering (RALS) and Viscometer (DP), equipped with three TSK GEL columns. A water/NaN_3 system was used as the solvent.

Nuclear magnetic resonance ^{13}C NMR

Evaluation of structural changes in the GGMs obtained was performed by ^{13}C NMR analysis. The analysis was performed on a Bruker Avance III 400 MHz spectrometer. The spectra for ^{13}C nuclei were obtained at 100.61 MHz frequency in a MAS BB DVT wide-band probe.

Research results discussion

Isolation and characteristics of GGM/T - thermal treatment

The studied wood types were characterized by high α-cellulose content (so called cellulose determined in holocellulose), in excess of 65%, as well as high hemicellulose content – about 30% (***Table 1***), in comparison to an average chemical composition of Polish softwood tree species. The other detected chemical components, such as the content of holocellulose, cellulose, lignin or organic compounds were at levels typical for those wood types.

As a result of wood shaving thermal treatment, a solution was obtained that could contain hydrolysed cellulose and residual lignin, besides hemicelluloses. This is indicated by their lowered content (for both wood types) in the shaves left over after boiling (***Table 1***). A white GGM powder was precipitated from the obtained solution using ethyl alcohol. The precipitated GGM was washed with ethyl alcohol, methyl alcohol and methyl tert-butyl ether in order to remove any potential oligomeric and monomeric carbohydrates. The polymerisation degree of GGM in spruce wood shavings was 245 units, while in larch wood shavings it was substantially lower - 127 units (***Table 2***). The determined polymerisation degree of GGMs is close to DP values for softwood hemicelluloses [19]. The fact that the powder obtained was GGM was confirmed by its composition, determined using GC/MS chromatography. Mass ratio of individual carbohydrates, i.e. glucose, galactose and mannose showed that galactose was the dominant carbohydrate in both wood types, while glucose and mannose content was at the same level (***Table 2***). Such large amounts of galactose may indicate that it separated from wood shavings more quickly than glucose and mannose during thermal treatment. The higher galactose content in GGM of larch wood could have resulted from the presence of residuals of arabinogalactan, which that type of wood contains. The low yield attained is connected to the fact that most of the native GGMs probably remained in the wood. The yield of GGM from spruce wood was 0.76%, and from larch wood - 5.68%. The higher yield for spruce wood shaving GGMs can be explained by a looser structure of this wood type, a typical quality of fast-growing trees. Such structure makes it significantly easier for water to penetrate between individual wall layers of a wood cell. For a GGM/T/S sample the molecular mass was Mm – 39,253 Da, and for a GGM/T/L sample Mm was– 42,495 Da (***Table 2***). The share of macroparticles of a given molecular mass for the GGMs isolated from both wood types was varied. In the case of GGMs isolated from larch, carbohydrate macroparticles were more uniform than in the case of galactoglucomannans obtained from spruce shavings, which is demonstrated by the shape of distribution curves for individual molecular mass (***Figure 1***).

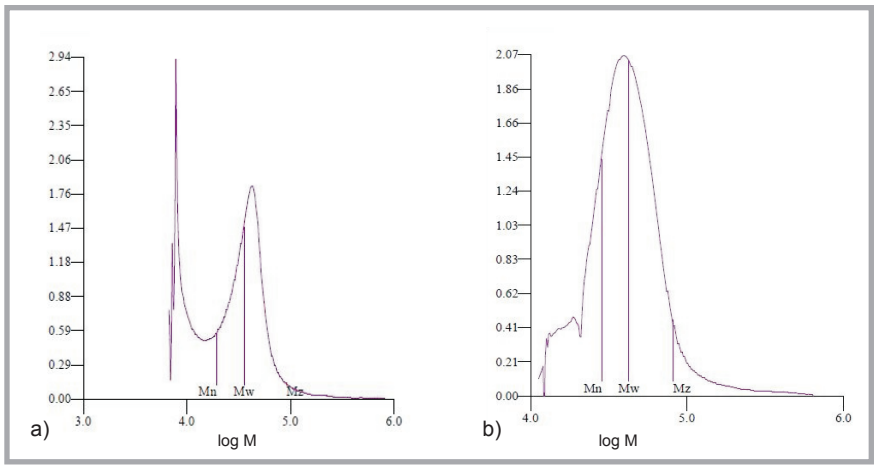

Figure 1. *Molecular mass distribution Mm for GGM/Ts obtained from spruce and larch wood shavings.*

Thermal treatment allowed for isolating GGMs from the studied wood types. The GGMs obtained had a higher galactose content in comparison with glucose and mannose quantity, and similar molecular mass values, with a polymerisation degree comparable to the DP values of hemicelluloses of softwood. The susceptibility of both wood types to GGM passing to solution was different; this is demonstrated by a substantially higher (5.68%) yield attained for GGMs obtained from larch wood shavings, compared to spruce wood shaving GGMs.

Isolation, modification and characteristics of GGM/En - enzymatic treatment

Research was conducted on galactoglucomannans isolation (after initial heating in an aqueous environment) using enzymatic preparations. Enzyme use was intended to weaken the bonds connecting GGMs to other wood components while degrading them in a gentle manner.

A comparison of enzymatic preparations' effects was assumed, as well as obtaining

Table 1. *Spruce and larch tree components before and after thermal treatment in water environment.*

Parameter	Holocellulose, %	Cellulose, %	Hemicelluloses, %	Lignin content, %		α-celullose in holocellulose, %	Organic compound content, %
				insoluble in H_2SO_4	soluble in H_2SO_4		
	Spruce shavings (S)						
Initial material	85.00	53.42	31.58	30.02	0.03	68.25	3.62
After thermal treatment	78.07	47.37	30.70	28.07	0.02	66.64	---
	Larch shavings						
Initial material	66.20	46.70	22.50	25.32	0.04	65.23	3.78
After thermal treatment	59.84	39.63	20.21	23.73	0.01	63.54	---

Table 2. *Qualities of GGMs isolated from spruce and larch wood shavings using thermal treatment in aqueous environment*

Symbol	GGM, DP	Efficiency, %	Mw average particle mass, Da	Carbohydrate content - mass ratio		
				Glucose	Galactose	Mannose
	Spruce shavings (S)					
GGM/T/S	245	0.76	39,253	1	13	2
	Larch shavings					
GGM/T/L	127	5.68	42,495	1	34	2

Table 3. *Conditions of enzymatic processing of GGM/En from spruce and larch wood shavings; Constant conditions: pH 4.8 acetic buffer, concentration 2.5% (w/v); *Endo-1,4-β-glucanase (CMC) activity.*

Sample symbol	Conditions of shaving enzymatic treatment					GGM qualities					
	Enzyme type	E/S Module, U/g	Temp., °C	Time, h	Stirring, r.p.m.	Carbohydrate content - mass ratio			Mw, average particle mass value, Da	Efficiency, %	GGM, DP
						Glucose	Galactose	Mannose			
	Spruce shavings (S)										
GGM/S/En/1	*A. niger* complex	1000*	50	24	130	1	2	2	10,938	15.80	175
GGM/S/En/2	Hemicellulase	1000	50	24	120	163	2	1	80,102	33.75	159
GGM/S/En/3		500	40	4	120	90	1	1	82,516	22.04	134
GGM/S/En/4		1000	40	4	120	206	1	1	113,316	50.31	170
	Larch shavings (L)										
GGM/L/En/5	*A. niger* complex	1000*	50	24	120	2	2	2	25 368	40.62	113
GGM/L/En/6	Hemicellulase	1000	50	24	120	125	2	2	72,397	31.92	118
GGM/L/En/7		200	50	4	120	60	1	1	106,922	7.56	78
GGM/L/En/8		500	50	4	120	75	1	1	101,382	21.61	92
GGM/L/En/9		1000	50	4	120	130	2	2	92,469	47.61	103

GGMs of a changed composition, compared to the thermal treatment. GGMs isolated this way can be employed to modify fibre materials, which can allow creating a material with lowered moisture permeability, for example.

Enzymatic treatment was performed on spruce and larch tree shavings under different process conditions (***Table 3***). During the tests, two different preparations obtained from *Aspergillus niger* were utilised: the commercially available Hemicellulase preparation, and an experimental *Aspergillus niger* enzymatic complex from ITB of LUT. Hemicellulases (present both in the commercial preparation and in the enzymatic complex) were to be responsible for isolating GGM from shavings. In order to develop the area of enzyme activity, the shavings were ground in a planetary ball mill, as attempts at GGM extraction conducted in analogous conditions (without grinding) did not provide the expected results.

As a result of utilising the *Aspergillus niger* enzymatic complex and the commercial Hemicellulase, GGMs in the form of white powder were obtained. In comparison to GGM/T, they were characterised by higher yield, lower polymerisation degree and the quantitative composition of individual carbohydrates, i.e. glucose, galactose and mannose. The polymerisation degree of the isolated GGMs remained below 200 units for spruce wood shaving GGMs, and was up to 100 units for GGMs of larch wood shavings (***Table 3***), which is a typical value for softwood hemicelluloses [19]. A change in quantitative composition of individual carbohydrates was also noted. Utilisation of the Hemicellulase commercial enzyme (spruce and larch shavings), with the E/S module of 1000 U/g, resulted in glucose being the dominant carbohydrate in the GGMs obtained, which was confirmed by GC/MS chromatography. A slightly lower glucose content was observed when the E/S module was 500 U/g.

When the *Aspergillus niger* enzymatic complex was introduced, completely different results were obtained. The GGMs obtained (from both wood types) had a comparable quantitative content of glucose, galactose and mannose, which was probably caused by the presence of glucosidases and glucanases in the utilised enzymatic complex.

The Mw average molecular mass for GGMs (spruce shavings) obtained as a result of Hemicellulase treatment was high and ranged from 80,102 to 113,316 Da, depending on process conditions. For the *Aspergillus niger* enzymatic complex, on the other hand, it was lower – 10,398 Da

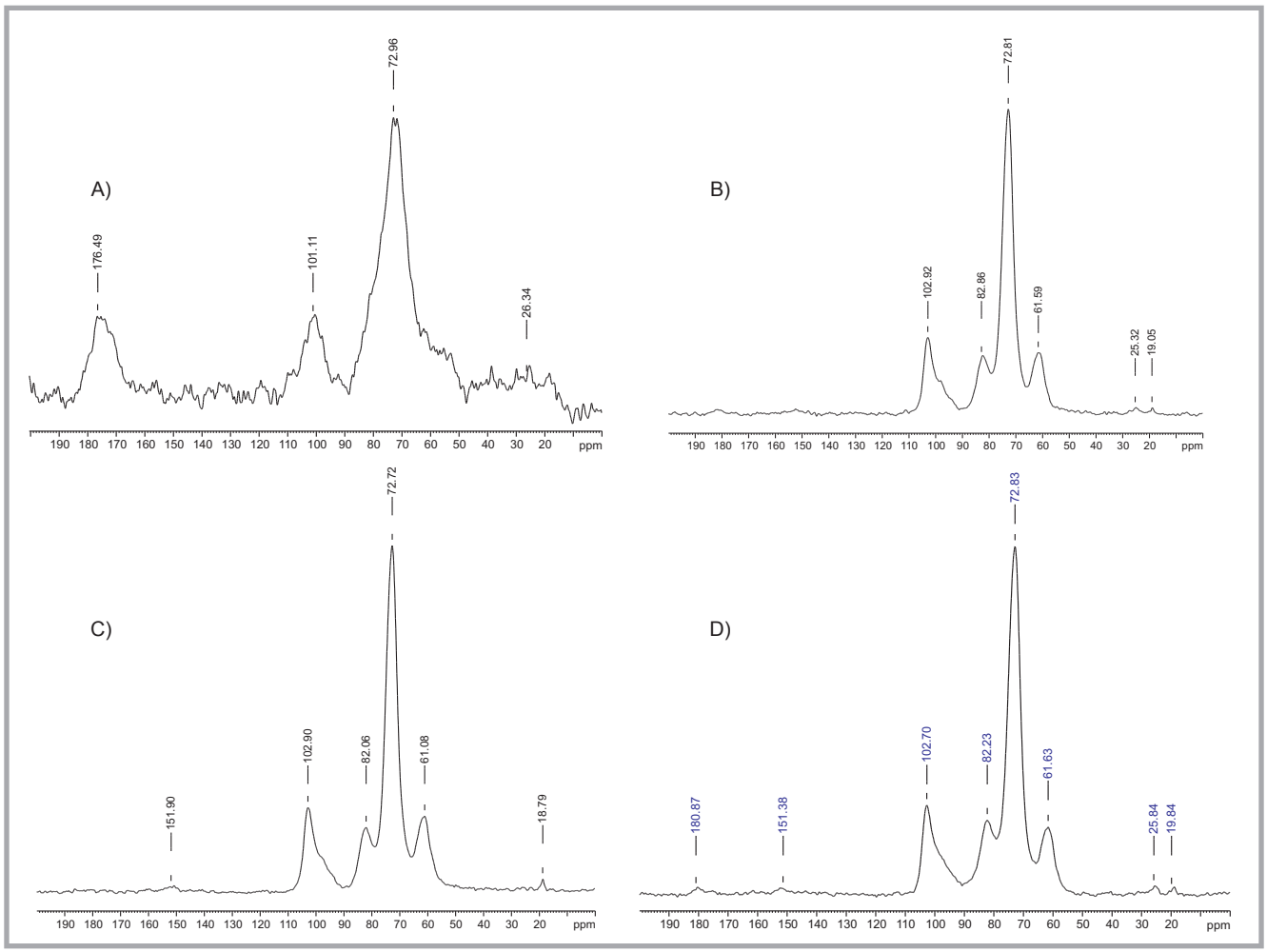

Figure 2. *^{13}C NMR spectrum images for GGM/S/En.* ***Samples****: A) GGMS/En/1; B) GGMS/En/2; C) GGM/S/En/3; D) GGMS/En/4.*

(***Table 3***). A similar tendency was observed for GGMs obtained from larch wood shavings, where the addition of the *Aspergillus niger* enzymatic complex resulted in obtaining GGMs with an identical mass ratio of glucose, galactose and mannose – 2:2:2, with a low average molecular mass at the same time – 25,368 Da (***Table 3***). However, it is worth noting that the hemicellulose molecular mass is different depending on wood type, ranging from 700 to 150,000 Da [19].

The yield of GGM (Hemicellulase commercial enzyme) is of particular note, being much higher in comparison to GGM/T and ranging from 22.04% to 50.31% for spruce wood shaving GGMs, and from 7.56% to 47.61% for larch wood shaving GGMs (***Tables 2*** and ***3***). A high GGM yield was also attained for the *Aspergillus niger* enzymatic complex, equalling 15.80% for spruce wood shaving GGMs, and for larch wood shaving GGMs – 40.62%.

Treatment and modification with the *Aspergillus niger* enzymatic complex resulted in observing a clear presence of the carbonyl group at 170 - 180 ppm in the ^{13}C NMR spectrum image. This phenomenon pertained to the GGM/S/En/1 (***Figure 2.A***) and GGM/L/En/5 (***Figure 3.E***).

The presence of the carbonyl group was not observed in samples where the commercial Hemicellulase enzyme was used. Spectrum characteristics for the studied wood types were similar, with a visible content of aliphatic carbon atoms. No aromatic structures were observed in the spectrum images, which, therefore, indicates that the GGM obtained were purified of the so called residual lignin to a high degree.

The action of the *Aspergillus niger* enzymatic complex changed the structure of the isolated GGMs, which is connected to the carbonyl group appearing. The carbonyl group presence may significantly influence the GGMs' sorption capability relative to cellulose fibres, e.g. in dressing materials and in cellulose pulp used in paper manufacturing [5].

Hemicellulases, present in the Hemicellulase commercial preparation and in the *Aspergillus niger* enzymatic complex, extracted the GGMs from wood shavings. The apparent differences in the content of individual carbohydrates (for the studied wood shavings) were connected to the presence of glucosidases and glucanases in the enzymatic complex, which probably removed some of the glucose residuals from the GGMs, both from the end of the chain (β-glucosidases), and from the middle (Endo-1,4-β-glucanases). The GGMs obtained were characterised by an average polymerisation degree in excess of 100 units, which is a typical result for hemicelluloses present in softwood. The utilised enzymatic preparations allowed for extracting GGMs with a high efficiency, which averaged above 35%. It is worth noting that no aromatic structures were observed in the ^{13}C NMR spectrum images, which, therefore, indicates that

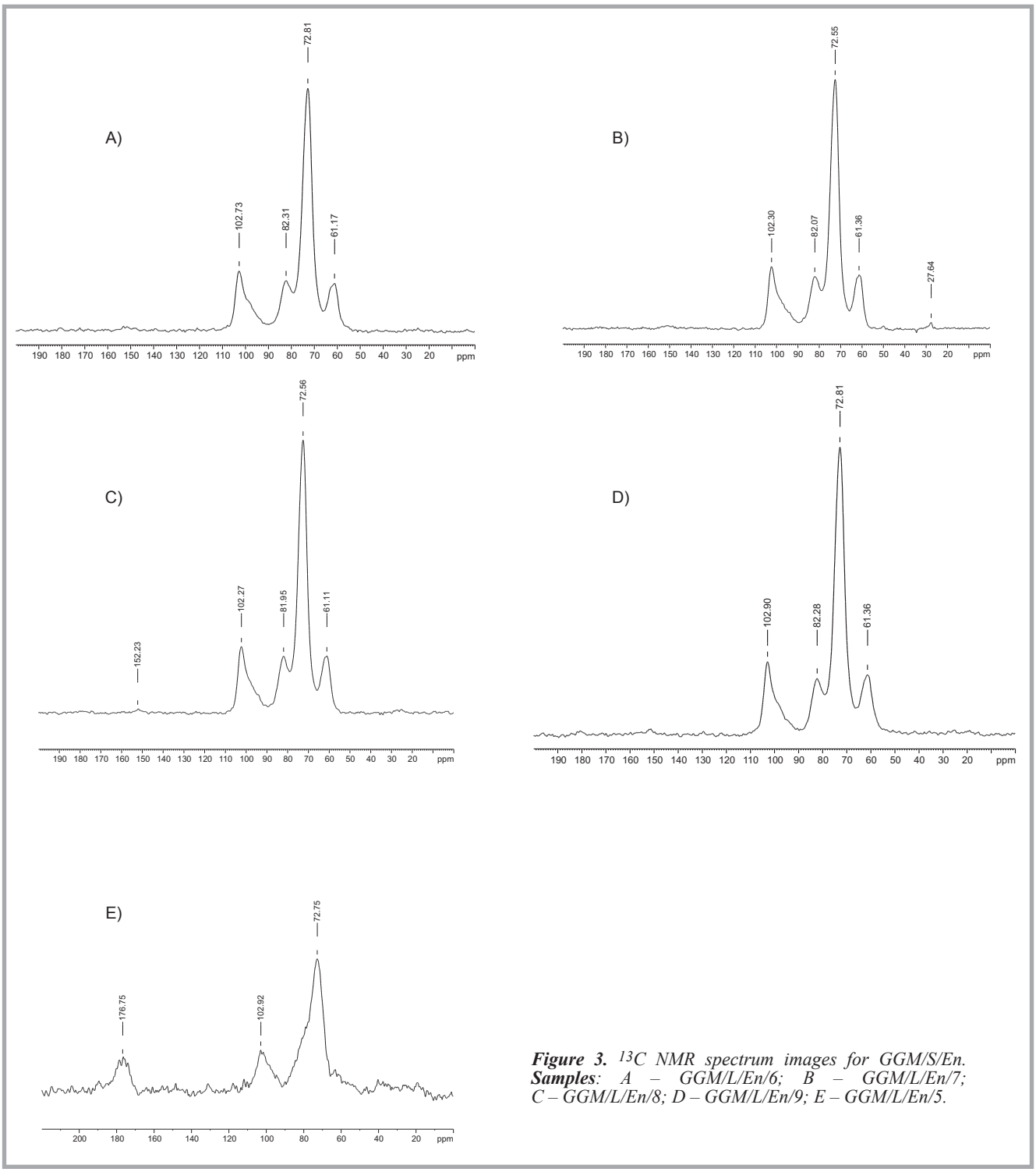

Figure 3. *^{13}C NMR spectrum images for GGM/S/En.* ***Samples****: A – GGM/L/En/6; B – GGM/L/En/7; C – GGM/L/En/8; D – GGM/L/En/9; E – GGM/L/En/5.*

the GGMs obtained were purified of the so called residual lignin to a high degree.

Conclusions

- As a result of subjecting the studied softwood varieties: the spruce and the fine-ringed larch to thermal treatment, GGMs with a glucose, galactose and mannose mass content ratio of 1:13:2 for spruce wood shaving GGMs and 1:34:2 for larch wood shaving GGMs were isolated.
- Thermal treatment resulted in a high polymerisation degree of the extracted GGMs. DP value of the GGMs was 245 (sample symbol GGM/T/S) and 127 (sample symbol GGM/T/L).
- The yield of GGM isolation (thermal treatment) from larch wood shavings was about 6%, while for GGM/Ts from spruce wood shavings - about 0.8%.
- As a result of applying treatment with the Hemicellulase commercial enzymatic preparation, the mass ratio of individual carbohydrates: glucose, galactose and mannose for GGMs isolated from spruce wood shavings was 153:1:1 on average, and 100:2:2 for larch wood shaving GGMs. In contrast, the *Aspergillus niger* enzymatic complex extracted GGMs with a comparable quantitative content of indi-

vidual carbohydrates, with the mass ratio being 2:2:2 on average.

- The efficiency of isolating GGMs from spruce wood shavings using the Hemicellulase commercial treatment was above 35% on average, and 30% for larch wood shavings. The *Aspergillus niger* enzymatic complex extracted GGMs with an efficiency of roughly 16% (from spruce wood shavings), and an efficiency of about 40% for larch wood shaving GGMs.
- The polymerisation degree of GGMs (from spruce wood shavings) obtained using the Hemicellulase commercial enzyme was 154 units on average, and 98 units for larch wood shaving GGMs. As a result of employing the *Aspergillus niger* enzymatic complex, the DP of GGMs was comparable for both wood types and averaged 144.
- The presence of the carbonyl group was confirmed in the ^{13}C NMR spectrum images for GGMs (from both wood types) extracted with the *Aspergillus niger* enzymatic complex.

Summary

As a result of thermal and enzymatic treatment of Polish softwood varieties: the spruce and the fine-ringed larch, galactoglucomannans of varied compositions of monosaccharides and molecular mass were obtained. Further research is anticipated on employing them as active agents for surface modification of paper pulps, fibre materials - including dressing materials - to improve barrier qualities for air and water permeability, and for modifying plant health products.

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