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Substitution of Phenolic Components by Steam-exploded Lignin in Plywood and Self-binding Boards with Account of Energy Vecessary for Steam Explosion Treatment

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Abstract: **By using lignin extracted from steam-exploded wood as adhesive in plywood and hot-pressed fibreboards to substitute phenol-formaldehyde resins is reported. Mixtures of commercial phenol-formaldehyde resins containing 10 % lignin by weight tested as plywood binders under conditions of factory production show satisfactory cohesion. Properties of sample boards containing different amount of lignin adhesive are compared between themselves and with the EU standards for fibreboards. A strong correlation of density and form stability under humid conditions with the lignin content is found. Results of testing mechanical properties of the boards suggest that effect of lignin on mechanical strength depends on the size of particles and hot-pressing temperature. Steam explosion and hot-pressing technologies tested in the study are shown to have potential of utilizing low-quality wood and waste from forest industry to make value-added products. The estimates based on a simple model of energy flows show the energy required by steam explosion pre-treatment of biomass being within 10 % of the heat content of biomass.**

Keywords: **steam explosion (SE), SE lignin, plywood, fibreboard, SE energy evaluation**

I INTRODUCTION

Natural wood is a complex and multifunctional composite material used by humans for a vast variety of their needs from the source of energy to the stuff for arts competing successfully with other substances and modern synthetics. During millennia humans have learned to improve and modify the natural properties of wood for special needs by special treatment and selection [1]. Plywood and a variety of pressed boards are well-known composite materials widely used in building constructions and furniture. Developed technologies allow to utilize low-quality wood and waste from sawmills to make useful products.

Phenols presently are mainly derived from petrochemicals – benzene and propylene, the source of industrially used adhesives. For that reason the costs of these chemicals strongly depend on the price of oil. As the oil prices increase dramatically, the costs of wood composites rise dramatically too since the prices of phenol-based adhesive resins correlate directly with the oil market prices. Another major adhesive component – formaldehyde produced from natural gas – has been classified as human carcinogen by the International Agency for Research on Cancer in 2004 [2]. Economic considerations suggesting to reduce the costs of wood adhesives by using aromatics from renewables at stable pricing of feedstock carbon lately are raising the interest in cheap self-binding (self-adhesive) wood composites.

Since the lignocellulosic material, under the conditions of steam-explosion (SE), can provide “self-sufficient” chemical and physical transformation, both the processes - hydrolysis and defibrilization - can be achieved just by the “tools” inherent in the system itself, without any additional reagents (except steam).

An attempt to use lignin extracted from wood biomass after SE auto-hydrolysis as adhesive in plywood and the biomass itself in self-binding boards is reported paying attention to economic and energy costs of the adhesive obtained from biomass after SE pre-treatment. Results of mechanical and form-stability tests are discussed with regard to industrial EU standards for hardboards. The research was performed in cooperation of JSC “Latvijas Finieris”. Modelling the SE is represented by a preliminary analysis of energy flows.

II EXPERIMENTAL

Birch (*Betula*) wood was used as chips for obtaining SE lignin for plywood adhesive supplement and as veneer sheets for preparing plywood. Grey alder (*Alnus incana* (L.) Moench) wood chips were used for obtaining self-binding board samples. Air-dried chips of row materials were submitted to SE treatment at 235 °C temperature and 3.2 MPa pressure at 0.5 l batch reactor for 1, 2 and 3 minutes.

For obtaining the lignin following steps were done. The soluble parts were removed by adding water. Lignin was extracted from the residual by solving it in 0.4 % solution of NaOH where from it was precipitated by adding hydrochloric acid to neutralise the solution. Precipitated mass was rinsed in water to remove the remnant of sodium chloride before filtration. After drying in air the filtrate turns into powder presented as SE lignin used as the binder in the hot-pressed sample boards [3] or plywood adhesive supplement.

SE mass materials were studied by following instrumental methods. An L&W Fibre Tester analyser was used to determine such fibre parameters as *length*, *width*, *shape factor* (the ratio of projected to actual length), *coarseness* (mass per unit length), and ratio of *fines* (fibres less than 0,2 mm), of the SE wood fibre mass and extracted cellulose. A Mettler Toledo TGA/SDTA851 thermal gravimeter and a Mettler Toledo DSC822 differential scanning calorimeter were used to detect thermal effects, loss of mass and glass transition temperature (T_g) of the extracted lignin samples. The lignin "finger-prints" in hot-pressed board samples were evaluated from infrared spectra in range from 450 to 2000 cm^{-1} recorded by a Perkin Elmer "Spectrum One" Furrier transform spectrometer. The Spectrum 5.0.1 (Perkin Elmer Instruments LLC) software was used for correction of the base line and normalisation of the spectra. All SE lignins have been characterized by analytical methods using group content value. The methoxyl content is determined_by classical Zeisel-Vieböck-Schwappach method based on quantitative reactions [4]. Content of OCH_3 groups in lignin samples is calculated from an equivalent amount of iodine determined by titration with $Na_2S_2O_3$. Phenol and carboxyl OH groups in lignin extracted from SE mass is determined by conductometric titration on a „Radiometer Analytical" CDM210 Conductivity Meter the measuring equipment accessories being provided by MeterLab.

The plywood samples were prepared from three birch veneer sheets of the size 600 x 900 x 1.5 mm bonded by 3 different kinds of adhesives spread uniformly over the surface of a veneer sheet prior to covering it with the next sheet to be glued at right angle between the directions of fibres of adjacent sheets. Commercial phenol formaldehyde resin adhesive (PF_{com}) was taken for two samples (P1). Adhesive for other two samples (P2) was made of mixture of the PF_{com} resin with SE lignin in the proportion of 9:1 of absolutely dry masses of the components. Adhesive for one more sample (P3) was made mixing PF_{com} resin with SE lignin solution in 0.4 % NaOH (25 % lignin and 75 % NaOH) in the dry substance weight proportion of 9:1. Amount of adhesive consumed was within the range of 165 – 195 g/m^2. The packets of veneer sheets were put under pressure of about 0.1 MPa for 15 – 30 min to flatten the layers before binding under higher pressure (1.8 MPa) at 127 °C temperature during 4 min in "Raute" 4 stage press. The plywood binder adhesion was evaluated at testing machine ZWICK/Z100 on test pieces of the size 25 x 150 mm after 4 hours boiling-20 hour's drying-4 hours boiling pre-treatment according to the standard [5]. Modulus of elasticity and bending strength properties were evaluated at the same testing machine by loading the test specimen of size 150 x 50 mm at the rate of 1 mm per minute.

The SE non fractioned air-dried grey alder fibre mass with moisture content of 4–5 % was pressed in a single stage hydraulic hot press at 170 and 190 °C temperature and 5 and 8 MPa pressure during 10 min. The hot-pressed board samples were left in the press to cool down for more than one hour while the pressure decreased. After the board samples were cut into various test pieces density, thickness swelling [6], water absorption, modulus of elasticity and bending strength [7], and internal bonding [8] properties were determined and compared with European standards for hardboards [9]. The specimens in size 30 x 30 mm were immersed in deionised water for 24 hours, and then thickness and mass measured for determining of thickness swelling and water absorption. Mechanical properties of hot-pressed fibreboard samples were tested by the same universal machine for testing material resistance ZWICK/Z100. For the bending strength testing the specimens size were 30 x 95 mm; the distance between supports 74 mm and the test speed 1 mm min^{-1}. For the internal bond testing the board specimens in size 30 x 30 mm were bonded to hardwood plywood testing block by PVAC glue and then after conditioning for at least 72 h tested with test speed of 3 mm min^{-1}.

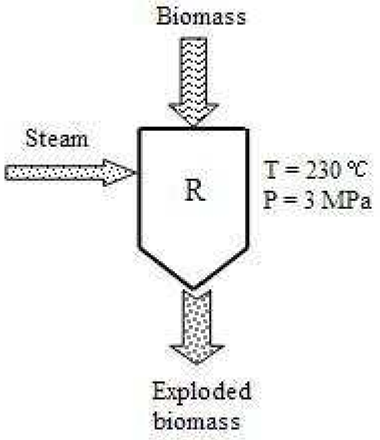

Fig. 1. The model of steam explosion evaluation

The model (Fig. 1) used to calculate the cost of SE treatment in terms of energy [10] showed essential dependence of the energy consumption on the energy content of the biomass being processed.

III RESULTS AND DISCUSSION

Particle size statistics was studied with fibres of air-dried SE fibre mass (F1), residue of the SE fibre mass after extraction of the components soluble in water and 0.4 % solution of NaOH (F2), and ground residue (F3). The obtained results are summarised in Table 1. As seen in the table, the average length and width of the fibres decreases, but the amount of smaller particles increases after further treatment – rinsing with water and solution of NaOH, grinding [3].

Since the average ratio of length to width of undamaged fibres in the natural aspen and birch wood are equal to 1.2/0.033 and 1.2/0.024 mm, respectively [11], the length of fibres after SE is smaller the width being the same as of natural fibres. Compared with dimensions of industrial fibres [11] the dominating fibre length is 1 mm in both cases the length of industrial fibres reaching 12.8 mm while the length of SE fibres does not exceed 7.5 mm.

The glass transition temperature T_g of the alder-wood SE lignin determined by calorimetric test of the samples was found to be in the range of 137-157 ºC. The T_g of air-dry SE lignin is lower than that of absolutely dry lignin sample. The thermo-gravimetric (TG) analysis showed that the 1 min treated SE air-dry lignin sample (SE1L) loss of mass occurred earlier at increasing temperature comparing with the lignin obtained after 2 min SE treatment (SE2L) different than in the case of Differential Scanning Test where the glass transition temperature T_g of the SE2L lignin sample is lower than T_g of the SE1L lignin.

Infrared spectra of lignin, extracted from the SE fibre mass showed that intensity of the IR carbonyl band at 1702 cm^{-1} is growing in spectra of the SE lignin samples with the increase of duration of SE treatment of the mass from which lignin is extracted.

TABLE 1

DETERMINED FIBRE PARAMETERS OF THE SE FIBRE MASS. ASPECT RATIO – AVERAGE LENGTH/AVERAGE WIDTH

Sample	**F1**	**F2**	**F3**
Number of fibres	14502	20042	20014
Temperature at testing, °C	40.5	40	39.3
Average length, µm	855	799	637
Average width, µm	30.9	26.4	29.6
Shape, %	84.8	85.9	86.3
Fines, %	10.2	11.6	29.9
Coarseness, µg/m	339	172	225
Aspect ratio	27.7	30.3	21.5

TABLE 2

MECHANICAL PROPERTIES OF PLYWOOD SAMPLES

Sample	**Adhesive**	**Shear strength, N mm^{-2}**	**Bending strength, N mm^{-2}**		**Modulus of elasticity, N mm^{-2}**	
			along fibres	across fibres	along fibres	across fibres
*	PF$_{comm.}$ + hardener	≥ 1	23	75	500	10 000
P1	PF$_{comm}$	1.8 ± 0.3	30 ± 2	163 ± 7	1 284 ± 86	17 940 ± 840
P2	PF$_{comm.}$ + SE lignin	1.9 ± 0.3	32 ± 2	133 ± 23	1 200 ± 70	16 370 ± 1340
P3	PF$_{comm.}$ + SE lignin:NaOH	1.3 ± 0.2	31 ± 2	153 ± 14	1 275 ± 110	18 200 ± 1020

* Requirements of Joint Stock Company "*Latvijas Finieris*".

Content of OCH_3 groups of SE lignins decreased with increasing SE treatment time (1, 2, 3 min) and are in range from 16 to 15 percent. Total content of both phenol and carboxyl OH groups of the extracted SE lignin increases with increasing SE treatment time and are in range from 7 to 9 percent.

Results of plywood samples tests are presented in Table 2.

As seen from the results of testing shear strength, admixture of SE lignin to commercial phenol-formaldehyde resin up to 10 % does not affect the quality of adhesion. Using the sodium hydroxide solvent for better mixing of lignin into the resin has not improved cohesion, as one may see comparing shear strength of samples P1 and P3. Adhesion in all the samples comply with the requirements for products of the Joint Stock Company "*Latvijas Finieris*". More studies are necessary to find conditions for rational use of SE lignin as substitute for PF resins in plywood production.

Tested results of the self-binding fibreboard samples are summarised in Table 3. As seen from the Table very good form stability properties of the self-binding fibreboard samples were achieved. It's due to low porosity of SE fibres that also had low moisture content – only 4-5 % after drying in the open air. The tested mechanical properties of the board samples increase with increasing density. The best properties belong to the board samples pressed at high pressure (8 MPa) and relatively low temperature (Table 3, row 3). Interesting to mention that density of the board sample, pressed at high temperature and at lower pressure, is higher of density of the sample pressed at the same temperature and at higher pressure. This allows conclude that the fibres already destroyed during SE and then pressed at the temperature of 190 ˚C are destroyed more significant and that the pressing regime should not be useful because of low mechanical properties (Table 3, row 5).

TABLE 3

PROPERTIES OF THE SELF-BINDING GREY ALDER FIBREBOARD SAMPLES

Pressing conditions		**Board samples properties**					
T, ˚C	**P, MPa**	**ρ, g cm^{-3}**	**G_t, %**	**G_a, %**	**f_m, N mm^{-2}**	**E_m, N mm^{-2}**	**$f_{t\perp}$, N mm^{-2}**
170	8	1.34 ± 0.04	8 ± 1	7 ± 3	32 ± 5	4701 ± 1296	0.6 ± 0.6
170	5	1.27 ± 0.04	9 ± 1	10 ± 3	29 ± 5	4121 ± 1237	0.8 ± 0.6
190	8	1.24 ± 0.18	11 ± 1	17 ± 6	14 ± 5	2573 ± 1273	0.4 ± 0.4
190	5	1.30 ± 0.03	10 ± 1	11 ± 2	16 ± 1	3593 ± 332	0.9 ± 0.2

T – average temperature; P – pressure; ρ – density; G_t – swelling in thickness; G_a – water absorption; f_m – bending strength; E_m – modulus of elasticity; $f_{t\perp}$ – internal bond (tensile strength perpendicular to the plane of the board); ± – standard deviation.

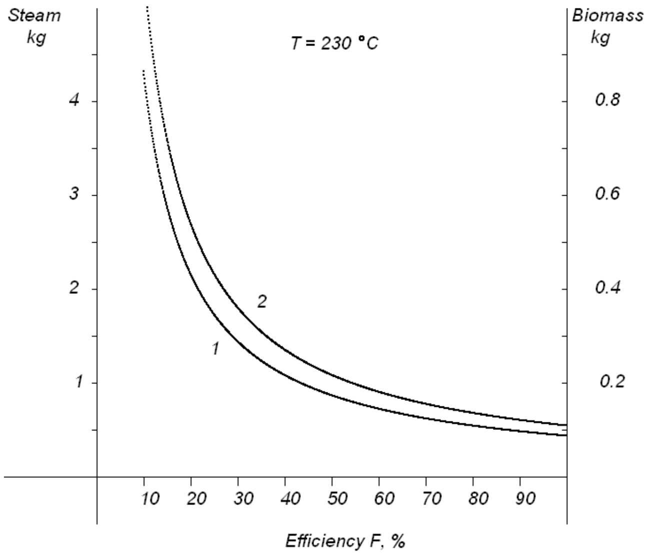

Fig. 2. Consumption of saturated steam per one kg of the dry content of biomass as function of the efficiency of energy use at steam explosion pre-treatment: 1 – 14 % moisture; 2 – 20 % moisture.

Comparing the properties with European Standard for hardboards [9] it can remark that the board samples obtained at temperature of 170 ˚C and pressure of 8 MPa comply with the requirements for load-bearing boards for use in dry conditions (type HB.LA). Because of good swelling property the board samples could be assigned to the type HB.E which belongs to boards for use in exterior conditions, but only one property – internal bond after boil test – was not tested to confirm it.

In Fig. 2 the necessary amount of steam per 1 kg of the absolutely dry content of biomass is presented as function of efficiency assuming that energy for SE treatment of biomass is supplied by condensation of saturated steam at temperature of 230 ºC with account for the mass of steam required to maintain the pressure the latter being calculated from assumption that unit mass of chipped biomass freely fits into a volume of 5 l. The vertical axis on right shows the amount of biomass to be burnt to produce the required amount of saturated steam.

The energy content of 1 kg of saturated steam at 230 ºC is equal to the heat content of about 0.2 kg of air-dry biomass. The y-axis on the right side in Fig. 2 shows the energy equivalent of biomass that needs to be burnt to provide the required amount of saturated steam. As seen from Fig. 2, at 50 % efficiency about 20 % of the available biomass has to be burnt to provide the energy necessary for steam production.

IV CONCLUSIONS

1. The length of fibres after SE treatment is smaller the width being the same as of natural fibres.
2. The SE lignin functional group analysis correlates with conditions of sample treatment.
3. More studies are necessary to find conditions for rational use of SE lignin as substitute for PF resins in plywood production.
4. The obtained grey alder self-binding fibreboard samples from SE fibres are comparable with commercially obtained hardboards.
5. At 50 % efficiency the energy necessary to produce the calculated amount of steam for treatment of biomass is equal to about 20 % of the heat content of air-dry wood.

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Jānis Grāvītis, Jānis Āboliņš, Ramūnas Tupčiauskas, Andris Vēveris, un Bruno Alksnis. Tvaika sprādzienā izdalītā lignīna izmantošana fenola komponentu aizvietošanai saplāksnī un pašsaistošās plātnēs un tvaika sprādziena apstrādei nepieciešamās enerģijas novērtējums.
No tvaika sprādzienā apstrādātās koksnes izdalītais lignīns izmantots kā fenola-formaldehīda sveķu saistvielas aizstājējs karsti presētu šķiedru plātņu eksperimentālos paraugos un ražošanas apstākļos pārbaudīta saplākšņu saistviela, kas satur 10 % lignīna piejaukumu pēc svara. Noteiktas karsti presēto plātņu paraugu mehāniskās īpašības un formas noturība pret mitrumu atkarībā no lignīna satura un salīdzinātas ar ES standartu prasībām. Konstatēta pietiekami laba adhēzija saplākšņu paraugos un cieša presēto plātņu mehāniskās izturības un formas noturības korelācija ar lignīna daudzumu. Pārbaudes rezultāti norāda uz lignīna ietekmes atkarību no daļiņu izmēriem un presēšanas temperatūras. Darbā pārbaudītās tvaika sprādziena un karstās presēšanas tehnoloģijas paver iespējas zemas kvalitātes koksnes un koksnes atkritumu izmantošanai vērtīgos produktos. Vienkāršota enerģijas plūsmu modeļa ietvaros veiktie tvaika sprādziena apstrādei nepieciešamās enerģijas aprēķini liecina, ka tā pie 230 ˚C darba temperatūras nepārsniedz 10 % no gaisa sausas koksnes siltumspējas.

Янис Гравитис, Янис Аболыньш, Рамунас Тупчаускас, Андрис Веверис, и Бруно Алкснис. Результаты замены фенольных компонент формальдегидных смол лигнином, выделенным из древесины после парового взрыва, и оценка затрат энергии.
Лигнин выделенный из древесины после парового взрыва использован в качестве клеящего вещества в экспериментальных образцах волокнистых плит и добавки к коммерческим фенол-формальдегидным смолам, употребляемым для склеивания фанер. Примесь весовых 10 % лигнина к фенол-формальдегидеым смолам при испытании склеенных в производственных условиях фанер показала удовлетворительную когезию. Механические свойства и влагоустойчивость формы образцов плит корелируют с содержанием лигнина. Результаты испытаний механических свойств сравниваются с требованиями европейских стандартов и обнаруживают зависимость влияния лигнина на механические свойства от размера частиц и температуры прессования. Испытания полученных образцов показали что использованные технологии парового взрыва и горячей прессовки обладают потенциалом для использования низкокачественной древесины и древесных отходов дря производства ценных продуктов. Оценка энергии, необходимой для обработки древесины паровым взрывом показывают что при температуре 230 ˚C она не превышает 10 % от теплоты сгорания воздушно-сухой древесины.