



Carbon materials obtained from self-binding sugar cane bagasse and deciduous wood residues plastics

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Abstract

It is demonstrated that dispersed biomass residues (bagasse, sawdust) can be processed into hard carbonaceous blocks, panels or boards with good strength and thermodynamic properties. There are two possible approaches: to mould dispersed biomass charcoal with a phenol–formaldehyde binder or to produce this material by carbonising the biomass fiberboard prepared by making use of steam explosion autohydrolysis pulp or steam explosion lignin as a binder.

In the first step, steam explosion lignin, as a modifier and a binder is introduced to the lignocellulosic biomass by impregnation or during the hot pressing process to form a hard fiberboard. By subsequent carbonisation of the fiberboard panels or blocks, carbonised panels or blocks with high bending and crushing strength and suitable thermodynamic properties are obtained due to the formation of an internal lignin reinforcement in cell lumina and impregnation of cell walls with lignin solution or molten lignin. The carbonised panels demonstrate a good dimensional stability after a standard treatment with water. The bending strength of the carbonised panels after 24 h soaking in water is 93% of that in dry state. The thermodynamic properties and porosity of the carbonised panels demonstrate their suitability for use as a building material. Lignin, a natural binder of fiberboards, has proven to be suitable for preparation of carbonaceous panels and boards.

In this respect new carbon building blocks and panels from moulded biomass and carbonised steam exploded biomass act as a concentrated form of long term carbon storage and will be a factor stabilizing the growing CO₂ concentration in the atmosphere. [Proceedings of the First Workshop of QITS, Materials Life-Cycle and Environmentally Sustainable Development, March 2–4, Campinas, UNU/IAS San Paulo, Brazil, 1998, pp. 95–101; Proceedings of the Workshop in “Targeting Zero Emissions for the Utilization of Renewable Resources”, ANESC, Tokyo, 1999, pp. 2–11.]

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1. Introduction

The current study presents a concept of carbonised board materials [1,2] production by using non-woody

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fibers—sugar cane bagasse or birch wood sawdust [3] by carbonisation of a board prepared from milled bagasse or sawdust mixed with steam explosion autohydrolysis pulp or lignin. It is only a part of the conceptual biomass refinery industrial cluster for energy and chemicals considered elsewhere [4].

Wood, as a construction material possesses excellent properties, i.e. it is a porous material with a low density and high mechanical strength and elasticity. Among the traditional construction materials, wood has a lower thermal conductivity. The majority of these attractive properties are also characteristics of charcoal. The experience obtained by the production and use of carbon materials made from coal has shown that the main properties of these materials are a low weight, a high mechanical strength, a high elasticity, a low thermal expansion coefficient, a high heat resistance as well as a high chemical and biological stability. If charcoal or materials derived from it are heated at temperatures above 800°C, the properties of such products are not inferior to those made from coal [5]. Owing to excellent absorbency and ability to withstand biological degradation, it is considered to be a future material of clean environment.

Carbon materials from biomass intended and being developed for construction purposes at present are recommended to be produced mainly from wood modified by thermoreactive polymers. Phenol–formaldehyde resins are the most popular of these polymers. Some of carbon products are prepared from fiberboard-like materials. Our intention was to replace the synthetic phenol–formaldehyde resins by biomass based products, i.e. SE self-binding lignin, its mixture with reducing substances and by SE pulp without separation of lignin from the fibrous components.

Lignin is a random network polymer with a variety of linkages, based on phenyl propane units. Lignin-based adhesive formulations have been tested for use in the plywood, particleboard and fiberboard manufacture. Lignin and phenol–formaldehyde resins are structurally very similar. The addition of lignin to phenol–formaldehyde formulations caused the premature gelling of phenol–formaldehyde resin into wood; in this case, the mechanical bond was not strong enough [6].

2. State of the art

Typically, carbonaceous panel and board type materials of biomass origin are produced from fiberboard or particleboard made from fibrous materials or chips that are bound together via a suitable heat-hardenable thermosetting adhesive under a designed pressure and temperature conditions to form the product. To ensure the properties of the carbonised end material, a medium-density fiberboard was first impregnated with phenol-based resin using an ultrasonic impregnation system in a ratio of 1:1 by weight, then hardened and carbonised in charcoal kiln [7,8] at temperatures of 800–2000°C. The carbonised specimens had the bending strength up to 25 MPa. To improve the physical properties of the carbonised materials, a great amount of phenol–formaldehyde resin was used. The main problems faced were fissures and warps, although carbonisation was carried out in a vacuum furnace. An improved dimensional stability was achieved by prior carbonisation of fine ground chips or a sawdust mixture with a small amount of oil and moulding of the char with a phenolic binder in a hot press. The dimensional stability of the products was improved, nevertheless, the expensive synthetic phenol–formaldehyde resin was used as a binder to produce carbon wall panels [9].

To produce a porous carbonaceous plate, phenol resin was mixed with sawdust in a weight ratio of about 1:1, filled in a mould, and a plate was formed at a pressure of 0.01 to 0.05 MPa. The resin was hardened, and the plate was carbonised at temperatures of above 500°C. The mechanical properties and porosity were secured due to glassy carbon formation from the phenol–formaldehyde resin [10]. By making blends of sawdust or wood meal and a mixture of phenol–formaldehyde or furan resins using a catalyst, the formation warps and fissures was precluded by an extremely low heating rate of about 3.3°C/h. At a temperature of 1000°C, a glassy carbon is formed. Due to a 25–30% resin content and a long duration of the process, the method is appropriate only for the production of electrodes or other bulky products [11].

Lignin, being phenolic in nature, is widely distributed in lignocellulosic plant materials. Lignin has been studied since the 19th century and, therefore, it has been considered as an alternative for phenol in numerous publications and patents. Recently, an

adhesive composition has been recommended that comprises product produced by the copolymerisation of one or more phenolic compounds and one or more water-soluble carbohydrates containing lignin and wood hydrolysates alone or in mixture with phenol–formaldehyde resins [12].

The best-known use of lignin as a binder is the steam explosion autohydrolysis process employing high-pressure steam to separate lignin from the lignocellulosic matrix—an invention of W.H. Mason [13]. The hemicellulose is hydrolysed into water-soluble carbohydrates and removed by leaching and washing with water before the lignin and cellulose fibers are made into fiberboard. The leaching and washing procedures produce enormous quantities of wastewater and the commercial Masonite fiberboard making process is currently in decline.

Industrial lignins (kraft and sulphite) have been used as binders individually or in compositions with phenol–formaldehyde resins. To increase the bonding strength, lignin demethylation products isolated as the by-products of dimethyl sulphide production [14] were treated with formaldehyde in the alkaline medium to give a resole resin. Doering [15] improved the process with a modified resole resin and an adhesive composition containing a lignin-modified phenol–formaldehyde precursor with extra formaldehyde sufficiently to provide a cumulative formaldehyde to a phenol mole ratio of 2.0–3.0, useful in bonding wood chips, veneers and sheets of plywood. A simplified process for the use of lignin binder has been suggested by Joffe et al. [16] in which powdered low molecular mass lignin was mixed with a cut up lignocellulosic material and moulded at elevated temperature and pressure. However so far the boards made with lignin binders have not been used to prepare carbonaceous materials.

Mori et al. [17] and Honma et al. [18] have suggested that carbon panels should be produced as a resistant insulation and finish building material capable of adsorbing formaldehyde, water vapour and ammonia. The previous investigations [19] had been conducted on medium density fibreboards made with a phenolic resin adhesive. Besides the known methods for production of carbonaceous building materials from fiberboard, it is recommended to use charcoal as a raw material [20].

The aim of our study was to investigate the feasibility of using fine dispersed biomass residues as a raw material for producing carbon panels as a resistant insulation and finish building material capable to adsorb formaldehyde, water vapour, ammonia and bad odour in storehouse and public premises. In our study, an attempt was made to use steam explosion autohydrolysis (SE) products as a binder and deciduous wood sawdust (birch being used as a representative of deciduous tree wood) and sugar cane bagasse as a fibrous raw material. Since formaldehyde has been recently used as a fortifying agent in tannin, lignin and carbohydrate adhesive formulations [12], we also tried formaldehyde as a fortifying agent to enhance the efficiency of SE lignin in some of our experiments.

3. Experimental section

Steam explosion treatment of birch sawdust and sugar cane bagasse: A laboratory built batch-type SE device was used [21]. The equipment included an electrically heated steam generator, a 0.5 l high-pressure reactor, a pulp collector and a condenser. The reactor was filled through the top trap and discharged through the ball valve at the bottom. Prior to being introduced into the SE reactor, the bagasse without any binder had been mechanically pressed into $1.5 \times 1.5 \times 12.0$ cm briquettes to provide a more rapid and as much as possible filling of the reaction chamber. Up to 250 g of air-dry bagasse specimens loaded into the SE reactor. Approximately 130 g of air-dry birch sawdust specimen was loaded into the same SE reactor. The SE treatment of biomass was carried out at 235°C for 3 min and explosively discharged into the collector by a quick opening of the ball valve. The resulting material (SE pulp) was separated by both one- or two-stage extractions as illustrated in Fig. 1. We preferred the handy one-stage extraction of SE pulp with 90% ethanol as a basic method for obtaining binders. The technological process for panel preparation was streamlined using SE pulp without milling and fractionation as a material making the biomass blend self-binding without any prior separation of lignin and reducing substances (RS). In this case, the cellulose fraction of the SE pulp took part in the building up of the bulk of the panels.

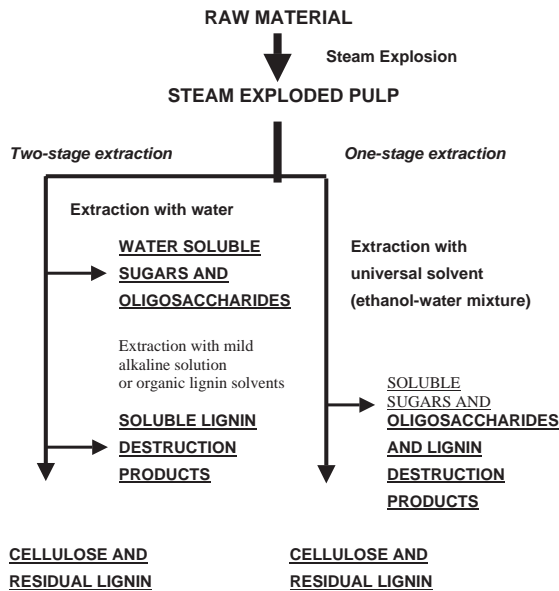


Fig. 1. Principal scheme of the separation of biochemical components after SE.

Preparation and testing of panels and blocks: From 600 to 750 g of blend o.d. was used to prepare each test panel measuring 250 × 250 × 10 mm. The blend was prepared by mixing an appropriate amount of the fibrous material (milled sugar cane bagasse or air-dry birch sawdust) with the binder (SE pulp, SE lignin). The SE pulp used was wet as obtained after preparation. The fibrous component was mixed with the binder in a double-helical mixer and dried at first at room temperature and then to a 1–2% moisture content in a drying chamber at 100–105°C. Para formaldehyde (92% formaldehyde content) was mixed with the dried blend shortly before moulding.

The mixture of SE lignin and RS, which are the water soluble carbohydrates of hemicellulose hydrolysis, was stored and used as a solution in the ethanol–water mixture. The experience of the previous research had shown that the adhesive properties of the SE lignin–RS mixture are superior to those of the SE lignin alone. If no RS are separated during the washing of SE pulp with water (the one-step leaching method), the presence of RS in the binder mixture by no means improves the quality of the binder.

The SE lignin–RS mixture solution with the concentration 0.1–0.2 g/ml was mixed with an appro-

priate amount of the fibrous component of the blend in a double-helical mixer the wet blend was dried first at room temperature, then at 100–105°C in a drying chamber to obtain 1–2% moisture content. A blend with phenolic alcohols was prepared in a similar manner but drying was realised in a vacuum drying chamber at 40–50°C to prevent the premature polymerisation of resoles.

Phenol–formaldehyde resins are common adhesives for water-proof board production. Therefore phenolic alcohols were chosen as the reference for comparison with the novel binders—the mixture of SE lignin and reducing substances and SE pulp. The test panels measuring 250 × 250 mm were prepared at various pressures typical for the fiberboard industry.

Test blocks (15 × 15 × 120 mm) were prepared in a stainless steel die designed for simultaneous moulding of two specimens. Since plugs and female dies fitted tightly, only a negligible amount of water vapour and gases could escape during the moulding. The die of a hydraulic press had an electrical heater connected with a wiring through a transformer for moulding temperature adjustment. The experimental conditions were as follows:

Initial moisture content (% on the wet basis) 1–2; Pressure (MPa) 80.0; Temperature (°C) 170–180; Pressure time, 1 min/mm—corresponding to the specimen's thickness.

At the end of the thermal treatment, the press was released and the resulting blocks were cooled to room temperature. The prepared two portions of the blend (usually 30 g each) were filled in preheated female dies, and the moulding process continued.

Test panels 250 × 250 mm were made on a hydraulic hot plate press. The platens had electrical heaters connected with the wiring through a transformer for platen temperature adjustment. Thermocouples and a vertical face recorder were connected with the platens to control the pressing temperature during the moulding process.

The calculated amount of the blend was gradually filled in a mould, and each portion thoroughly levelled. Before moulding, the platens were heated to the temperature about 20°C higher than the actual moulding temperature. Moulding time was calculated assuming 1 min per millimetre (1 min/mm) of the panel thickness.

Carbonisation of specimens: The test blocks were carbonised in a 2 l capacity retort heated in an electric oven at temperatures up to 900°C.

The panels measuring 250 × 250 mm were cut into two pieces: 250 × 150 mm and 100 × 250 mm. The 250 × 150 mm panel was carbonised in a laboratory reactor (Ø 410 mm, length 350 mm) with electrical heating. The maximum temperature was 700°C.

The left piece of the panel (100 × 250 mm) was used to test the physical properties of the panels before carbonisation.

Bending strength was determined by the centre loading parallel to the moulding force according to the standard test on the boards 45 mm wide prepared from test panels and carbonised test panels. The test blocks of cross section 15 × 15 mm and the carbonised test blocks were tested without any preliminary processing. Prior to measurement, the samples were conditioned for 1 week at a 50% relative humidity and 23°C. The span length was 50 mm for carbonised specimens and 50 or 100 mm for the test panels and test blocks before carbonisation, respectively.

Water absorption and thickness swelling were determined according to ASTM D-1037, except that the size of the specimens was only 50–100 mm by 45 mm. This resulted in a less favourable relation of the edge length to the surface area and, consequently, in a lower water resistance.

The crushing strength of the carbonised specimens was tested on a universal testing machine “1253Y-2-2 NIKIMP”. The testing specimens were prepared from carbonised panels by grinding accurate parallelepipeds.

The thermodynamic properties of the panels were tested on an ITH-2106 measuring device for measuring of heat characteristics at the Institute of Polymer Mechanics of the Latvian University. The specimens measuring 100 × 100 mm were at least 5 mm thick.

4. Results

To obtain preliminary information about steam explosion products as binders, SE pulp, SE lignin and phenolic alcohols were chosen to make blends of test specimens. The results of the experiments are shown in Table 1. The bending strength of the test blocks before and after carbonisation at the maximum tempera-

ture 900°C was chosen to be the basic criterion for the quality of the blend and the block tested. The results given in Table 1 demonstrate that, before carbonisation, the specimens made with phenolic alcohols possessed the highest bending strength. In this case, the difference is significant. SE pulp is a good binder at 25% concentration based on the o.d. blend mass. The bending strength of the carbonised specimens demonstrates quite a different pattern. The best indexes are demonstrated by specimens with SE pulp as a binder. The most remarkable decrease is shown by specimens with phenolic alcohols.

The yield of carbonised specimens is slightly higher with phenolic alcohols and they demonstrate the smallest degree of shrinkage. In general, the yield of carbonised specimens by weight of the specimens with binders is somewhat higher than the corresponding specimen without a binder (Table 1).

The effect of temperature and the premix of paraformaldehyde are shown in Table 2. It is evident that, at the moulding temperatures below 180°C, the effect of formaldehyde on the bending strength of carbonised blocks is negative, in uncarbonised blocks it is negligible. On the contrary, at 180°C, the effect of formaldehyde is significantly positive.

Table 1 shows that the yield of the carbonaceous materials from the biomass plastics is only about 30% of the o.d. plastics' mass. Therefore, changes in the panel dimensions were considerable. To eliminate this defect we tried to make carbonaceous blocks of bagasse and birch sawdust charcoal. It was ascertained, that in this case SE lignin does not demonstrate binder properties. For that reason, in the further experiments phenolic alcohols were used as binders. Table 3 shows the results of moulding and heating of charcoal blocks. Changes in the dimensions were minimal after heating to 900°C. An insignificant increase in the thickness of the blocks was due to the formation of an inner cracked structure in a plane perpendicular to the moulding force. The bending strength of the blocks was good and could be improved by developing an appropriate technology for moulding birch charcoal.

In the preliminary experiments of choosing an appropriate set of binders, sufficient binder properties were demonstrated by both SE pulp and SE lignin (Tables 1 and 4). The best concentration of SE lignin was 15% on the o.d. blend mass basis. SE pulp as a

Table 1

Properties of carbonised blocks of bagasse and birch sawdust (moulding time 1 min/mm; pressure 96.0 MPa; hot-plate temperature 170–180°C; maximum carbonisation temperature 900°C)

Composition of the blend		Properties of specimens before carbonisation				Properties of carbonised specimens					
Fibrous material	Binder	Binder content (%)	Density (g/cm ³)	Bending strength (MPa)	Yield (%) on o.d. basis	Dimensions (%) ^a		Density		Bending strength	
						Thickness	Width	g/cm ³	% ^a	MPa	% ^a
Milled bagasse	Steam explosion pulp of bagasse	25	1.276	34.2	28.3	66.2	75.2	0.941	73.7	17.9	52.3
		50	1.268	28.0	30.0	69.0	73.5	0.903	71.2	17.9	63.9
	Steam explosion lignin of bagasse	12	1.222	26.1	28.0	67.9	74.4	0.871	71.3	10.5	40.6
		25	1.140	23.4	30.2	78.2	77.4	0.785	68.9	8.3	35.5
		12	1.214	64.3	29.2	94.5	75.5	0.665	54.8	9.4	14.6
Phenolic alcohol	25	1.240	63.7	31.7	86.8	75.0	0.724	58.4	8.5	13.3	
	Birch sawdust	Steam explosion pulp of birchwood; treated 3 min at 235°C	25	1.252	33.0	27.2	67.9	75.9	0.903	72.1	13.4
50			1.281	29.6	28.2	66.2	73.3	0.835	65.2	17.1	57.8
Steam explosion pulp of birchwood; treated 5 min at 220°C		25	1.302	34.4	27.2	68.6	74.8	0.907	69.7	13.6	39.5
		50	1.234	25.4	27.2	69.6	74.0	0.833	67.5	11.4	44.9
Milled bagasse	Without binder	—	1.210	13.6	25.5	69.3	73.0	0.753	62.2	7.9	58.1

^aBased on the properties of the corresponding specimens before carbonisation.

Table 2

Effect of temperature and formaldehyde premix upon the density and bending strength of bagasse blocks made with SE lignin binder (moulding pressure 80 MPa)

Hot-plate temperature (°C)	Formaldehyde premix (wt% on o.d. SE lignin basis)	Uncarbonised blocks			Carbonised blocks	
		Density (g/cm ³)	Bending strength (MPa)	Density (g/cm ³)	Bending strength	
					MPa	% on bending strength of uncarbonised blocks
140	none	1.075	12.0	0.682	6.1	50.8
	2.5%	1.096	10.9	0.640	5.6	51.4
160	none	1.200	21.9	0.837	13.6	62.1
	2.5%	1.260	24.7	0.899	6.1	24.7
180	none	1.192	21.9	0.884	6.6	30.1
	2.5%	1.285	27.0	0.929	17.9	66.3

Table 3

Dimension, mass and density alterations of carbonaceous blocks after carbonisation (moulding pressure 80.0 MPa; heating temperature 900°C; heating rate 1.6°C/min)

Blend composition	Length	Width	Thickness	Volume	Mass	Density	Density (g/cm ³)	Bending strength (MPa)
	%, based on the properties of uncarbonised blocks							
Birch charcoal 85%	97.2	97.4	104.1	98.5	80.5	82.2	0.922	5.4
Phenolic alcohols 15%								
Birch charcoal 80%	99.4	100.0	102.9	102.0	85.2	85.4	0.956	7.6
Phenolic alcohols 20%								
Bagasse charcoal 85%	97.3	100.0	101.0	98.3	83.4	79.0	0.893	14.5
Phenolic alcohols 15%								

binder insured a sufficient bending strength of the test blocks, but also a good bending strength of the carbonised specimens. The results of experiments with a paraformaldehyde premix have discrepancy. In some experiments, the bending strength of the test blocks and especially of the carbonised ones was greatly improved (Table 2). In other cases its effect on the carbonised block strength was negative. Therefore, it was decided to use a formaldehyde premix only in blends where SE pulp was used as a binder.

In fiberboard industrial production, a moulding pressure of 6.0–8.0 MPa is used for hard fiberboard. A pressure of 8.0 MPa was chosen to mould the test panels measuring 250 × 250 mm. The physical properties of the panels are given in Table 4. The bending strength of bagasse test panels meets the bending strength requirements of medium density and hard fiberboards.

The bending strength values of the uncarbonised panels show that the phenolic alcohols in the amount used in our investigations surpass SE pulp in bonding efficiency. If moulding pressure is 8.0 MPa, the bending strength of the uncarbonised panels made with phenolic alcohols is considerably higher than with SE pulp binder. However after carbonisation the panels made with SE pulp retained their bending strength better and its values equalised up (Table 4). The formaldehyde premix increased the bending strength in our experiments with birch sawdust, although its effect on milled bagasse is not clear (Table 5). The formaldehyde premix somewhat increased the density of the panels both in sugar cane bagasse and birch sawdust panels.

Table 4 shows that the absolute values of the bending strength of carbonised panels are close for the specimens in the dry state and after a 24 h soaking in

Table 4
Physical properties of panels before and after carbonisation

Fibrous Binder material	Amount of binder on o.d. blend mass basis (%)	Moulding temperature (°C)	Density (g/cm ³)	Thermal conductivity (W/mK)		Heat capacity (kJ/kgK)		Bending strength in dry state	Bending strength after 24 h swelling in water		Retained bending strength after swelling (%)
				Uncarbonised	Carbonised	Uncarbonised	Carbonised		Uncarbonised	Carbonised	
Milled bagasse	20	170	1.113	0.237	—	1.093	—	32.3	29.2	—	90.4
				0.848	—	1.093	—	32.3	29.2	—	90.4
Phenolic alcohols + RS	15	220	0.764	0.185	0.150	1.308	1.438	13.6	6.7	49.3	41.2
				0.601	0.150	1.308	1.438	13.6	6.7	49.3	41.2
SE pulp	50	210	0.933	0.245	0.147	1.299	1.366	12.0	5.6	46.7	58.3
				0.738	0.147	1.299	1.366	12.0	5.6	46.7	58.3
Birch sawdust	20	170	1.155	0.270	—	1.068	—	39.7	35.6	—	89.7
				0.734	—	1.068	—	39.7	35.6	—	89.7
Phenolic alcohols	50	205	0.841	0.197	0.155	1.391	1.507	12.9	1.5	33.3	11.6
				0.618	0.155	1.391	1.507	12.9	1.5	33.3	11.6
SE pulp	50	205	0.841	0.197	0.155	1.391	1.507	12.9	1.5	33.3	11.6
				0.618	0.155	1.391	1.507	12.9	1.5	33.3	11.6

water. It means that, at this point, the panels before carbonisation substantially differed from the carbonised panels. The mean bending strength of uncarbonised panels after 24 h of soaking with water was only 11.6–58.3% of those in the dry state. For carbonised panels, this ratio was 82.8% and 100% for bagasse and birch sawdust, respectively. As can be seen from Table 4, if the uncarbonised panels made with phenolic alcohols were compared with those made with SE pulp, the bending strength before soaking and the bending strength after soaking the specimens in water was significantly greater in the case of phenolic alcohols. There were no substantial differences in bending strength among the carbonised panels with different binders, when panels prepared at 8.0 MPa moulding pressure were compared (Tables 4 and 5).

The crushing strength values demonstrate no definite trend and all the binders tested may be estimated as equal if the criterion is this physical property (Table 6).

4.1. SEM and XRD analysis

Materials with a widely developed porous structure were obtained after the carbonisation of the bagasse plastics. For materials obtained after the carbonisation (up to 900°C) of the plastic prepared from 75% bagasse and the 25% SE bagasse lignin binder, the porosity of two levels can be seen on SEM micrographs, i.e. the cell lumens and cavities between the cell blocks (Fig. 2A). The cells surface was covered with a film (Fig. 2B), the film bridges between the cell walls can be detected in the close-up view (Fig. 2C). Changes in the carbonisation conditions (up to 800°C, vacuum) resulted in more compact cell blocks and narrow cavities between the cell blocks and the film on the cell surface, and also the existence of film bridges between the cell walls (Fig. 2D). The carbonised material prepared (up to 900°C) from a binderless bagasse plastic exhibits more dense cell blocks (Fig. 3A). Unlike the previous specimens, a fragile rupture of cell walls (Fig. 3B), separated cells, well survived vessel elements and lots of fines can be detected; the cell wall looks swollen. After the carbonisation (up to 900°C) of the plastics prepared from 75% bagasse and a 25% phenolic alcohol binder, more dense cell blocks with a uniform mass and less individual cross-sections are visible in SEM images, and the cavities are deep

Table 5
Physical properties of sugar cane bagasse and birch sawdust panels and the corresponding panels made with the SE pulp as a binder (wt. ratio 1:1; moulding pressure 8.0 MPa and time 1 mm/min; maximum temperature of carbonisation 670°C)

Raw material	Panels							Carbonised panels				
	Formaldehyde premix	Moulding temperature (°C)	Density (g/cm ³)	Bending strength (MPa)		Thermodynamic properties		Density (g/cm ³)	Bending strength (MPa)		Thermodynamic properties	
				in dry state	after 24 h swelling in water	Thermal conductivity (W/mK)	Heat capacity (kJ/kgK)		in dry state	after 24 h swelling in water	Thermal conductivity (W/mK)	Heat capacity (kJ/kgK)
Bagasse	None	200	0.808	10.6	5.0	0.185	1.295	0.718	5.7	5.2	0.175	1.371
		210	0.933	12.0	7.0	0.245	1.299	0.738	5.6	4.6	0.147	1.366
	2.5% on o.d. SE pulp mass	170	0.948	14.2	3.4	0.236	1.328	0.732	4.3	4.4	0.165	1.567
Birch sawdust	None	200	0.915	7.4	0.8	0.208	1.314	0.643	3.1	2.2	0.152	0.746
		205	0.830	11.3	3.6	0.182	1.196	0.615	4.0	4.0	—	—
	2.5% on o.d. SE pulp mass	205	0.841	12.9	1.5	0.197	1.391	0.618	4.3	4.4	0.155	1.507
		215	0.868	13.8	5.2	0.198	1.285	0.664	6.8	7.3	0.185	1.368
		215	0.899	27.7	7.0	0.220	1.367	0.719	7.9	6.0	0.180	1.331

Table 6

Crushing strength of carbonised panels (moulding pressure 8.0 MPa; maximum temperature of carbonisation 670°C)

Raw material	Conditions of panel moulding		Density of carbonised panels (g/cm ³)	Crushing strength, MPa	
	Binder amount (% on o.d. blend mass)	Temperature (°C)		to the moulding force	⊥ to the moulding force
Milled bagasse	SE lignin + reducing substances—15%	225	0.500	6.0	9.9
	SE pulp 50%	200	0.718	6.2	7.7
	SE pulp 50%; formaldehyde 2.5%	170	0.732	6.4	8.1
	Phenolic alcohols 20%	170	0.848		12.0
Birch sawdust	SE pulp 50%	205	0.615	17.7	14.6
	SE pulp 50%; formaldehyde 2.5%	215	0.664	4.1	10.7

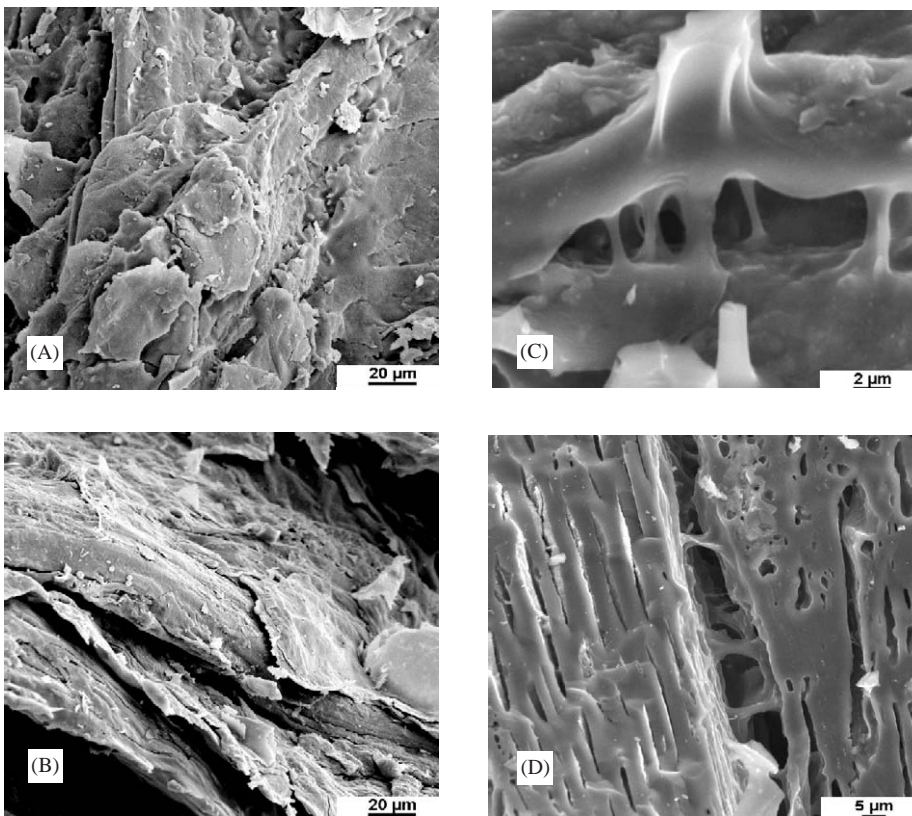


Fig. 2. SEM micrographs of plastics (moulded at 170°C; pressure—90 MPa): A—75% moulded bagasse and 25% SE bagasse lignin binder (extracted with 90% acetone in two stage extraction procedure); B—100% bagasse; C—the same as A carbonised at 900°C; D—the same as A carbonised at 800°C under a vacuum.

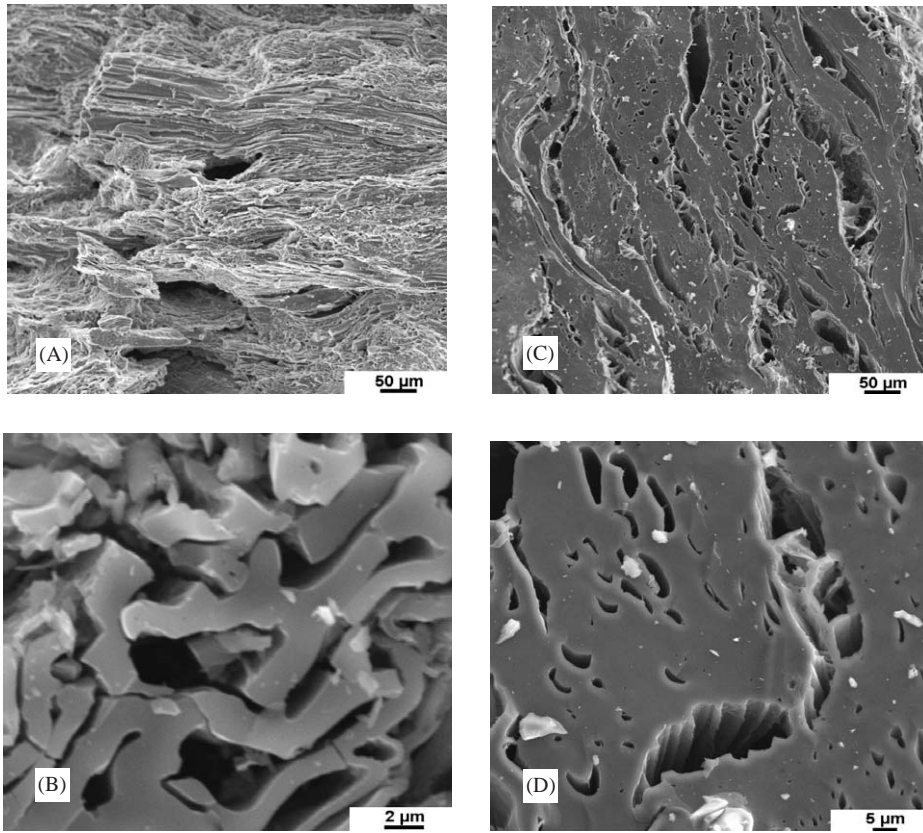


Fig. 3. SEM micrographs of carbonised at 900°C plastics: A and B—prepared from 100% bagasse; C and D prepared from 75% bagasse and 25% phenolic alcohol binder.

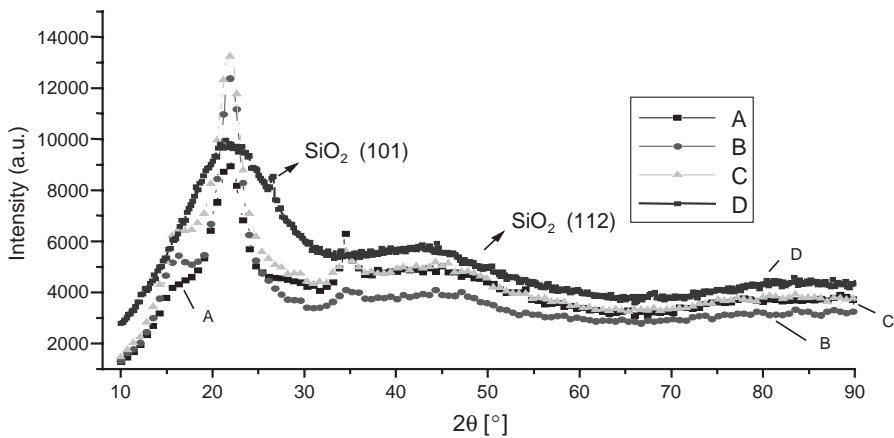


Fig. 4. XRD of bagasse plastic (moulded at 170°C; pressure—90 MPa); A—without the use of any binder; B—with 25% SE bagasse lignin binder (extracted with 90% acetone in a two-stage extraction procedure); C—with 25% phenolic alcohol binder; D—SE bagasse lignin binder (extracted with 90% acetone in a two-stage extraction procedure) itself.

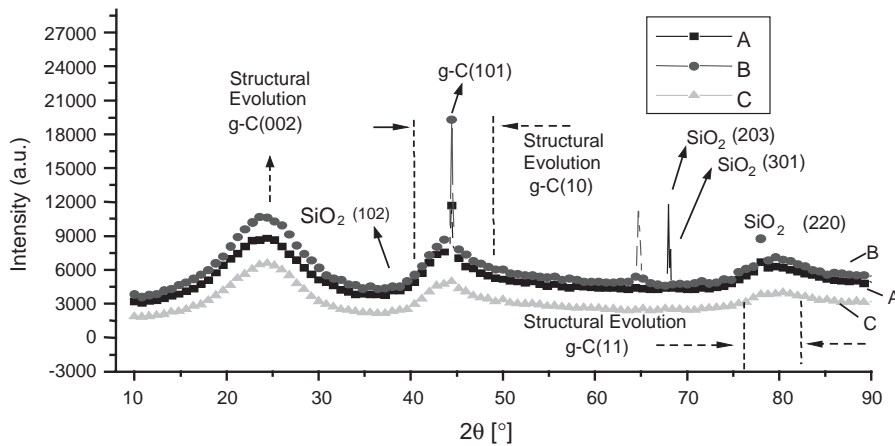


Fig. 5. XRD of bagasse plastic samples carbonised at 900°C: A—without binder; B—with 25% SE bagasse lignin binder; C—with 25% phenolic alcohol binder.

(Fig. 3C). In a close-up view, a “melted” surface of the cross-section of cells is observed (Fig. 3D).

Hence, SEM analysis indicates that the carbonised material obtained from binderless bagasse plastics, a plastic with a SE bagasse lignin binder and a plastic with a phenolic alcohols binder have different structure on the submicroscopical level. The use of the SE bagasse lignin binder allowed producing of a carbon material with a highly porous structure with film bridges between the remnants of the cell walls. It can be assumed that the film was a product of SE bagasse lignin binders transformation during carbonisation.

XRD patterns of the bagasse plastic are shown in Fig. 4. The evolution of the crystalline structure by increasing the diffraction intensity and line broadening and by the angular shifting of the lines through the graphite characteristic values [22] occurred from specimens A to C. The binder itself showed a completely amorphous structure (specimen D). These specimens, after carbonisation at 900°C (carbonised plastic) are presented in Fig. 5. It is interesting to observe the structural evolution of a random structure of carbon into a graphite-2H structure (g-C(002)), as well as the two dimensional hk (10) and hk (11) reflections for the specimens prepared without the binder and the SE bagasse lignin binder (Fig. 5A and B), respectively. For the phenolic alcohol binder (Fig. 5C), there was a substantial decrease in the evolution of the graphite structure.

4.2. Adsorption isotherms

Water and benzene vapour adsorption isotherms were recorded by a vacuum balance with quartz spirals at 295 K. The benzene adsorption isotherms were recorded only in the initial part of the relative pressure range (p/p_0), while the water adsorption–desorption isotherms were measured in a full range of p/p_0 . The calculated surface characteristics of six carbonised plastics are summarised in Table 7. All specimens, except the carbonised birch sawdust block (specimen No. 2), adsorbed benzene very slowly, which can be explained by the benzene solubility in the remnant tar (especially in the case of panels, No. 3–5). In the case of the carbonised charcoal block (No. 1) this slow process can be interpreted by the microporosity of the material. The carbonised birch sawdust and bagasse blocks (No. 2 and 6), according to water vapour sorption data, exhibited low specific surface values. Most possible, it is attributable to a low concentration of oxygen-containing groups on the materials surface. It must be noted that the carbonised charcoal block (No. 1), as well as the carbonised bagasse panel (specimen No. 5), had a highly specific surface. The carbonised birch sawdust panel with a 2.5% formaldehyde premix (specimen No. 3) might be considered as a system of medium porosity. All the rest of the specimens (No. 2, 4 and 6) were a broad porous material.

Table 7
 Characteristics of carbonised biomass plastics porosity (A—specific surface)

No	Specimen	Raw material	Binder		Moulding		Carbonisation temperature (°C)	Water vapour sorption			Benzene sorption: A (m ² /g)
			Name	Amount (% o.d. blend basis)	Pressure (MPa)	Temperature (°C)		A (m ² /g)	Pore volume (cm ³ /g)	Mean pore size (nm)	
1	Charcoal blocks	Birch charcoal	Phenolic alcohol	20	96	180	900	325	0.10	1.25	360
2	Sawdust blocks	Birch sawdust	SE lignin	25	96	190	900	110	0.12	4.35	275
3	Sawdust panels	Birch sawdust	SE pulp + formaldehyde	47.5+2.5	8	220	670	150	0.12	3.2	280
4	Sawdust panels	Birch sawdust	SE pulp	50	8	205	670	135	0.11	3.2	290
5	Bagasse panels	Sugar cane bagasse	SE lignin	15	8	225	670	255	0.14	2.2	290
6	Bagasse blocks	Sugar cane bagasse	SE lignin	30	96	180	900	135	0.11	3.25	305

5. Discussion

Steam explosion autohydrolysis is an alternative for pyrolysis to upgrade lignin to a more usable phenolic-type resin. Lignin macromolecules are broken into smaller macromolecules, lignin segments and monomeric chemicals. Due to the rupture of lignin-carbohydrate bonds, lignin can be leached from the fibrous SE pulp by organic solvents or solutions of alkalis. The solubility of SE lignin is an advantage if the lignin preparation is used not only as a binder but also as a matter to fill up the porous structure of lignocellulosic biomass and to increase the bending and crushing strength of the carbonised panels. The results of sorption studies presented in Table 7 demonstrate that a satisfactory to good porosity can be reached alongside with a good bending strength of the test specimens (Table 4).

Though our intention was not to solve the problem of producing good quality fiberboard from bagasse or sawdust, we paid attention also to this aspect, because the quality of panels could influence the properties of the carbonisation products of these panels obtained with SE products as binders. The influence of the moulding process temperature on the physical properties of panels becomes apparent in bending strength, swelling capacity and water absorption values. Of course, the main cause is the melting point of SE lignin, which manifests itself in an effective binding of the fibrous raw material usually above 200°C (Table 5). On the other hand, the higher the temperature of moulding, the more distinct is the influence of the thermal degradation of lignocellulose, starting with easy-hydrolysable polysaccharides. The previous investigations [23] have demonstrated that, if birch wood is hot pressed at 200°C, the amount of extractives in the alcohol-benzene mixture reach 37.4%, which is a ten-fold increase from the starting one (3.6%). At the same time, the content of easy-hydrolysable substances decrease from 30.0% to 3.4%. The content of lignin also decreases from 19.4% to 12.1%. The yield of reducing substances is negligible. Pilipchuk [24] came to a conclusion that high temperature pressing of wood increases the reaction rate and the accumulation of high molecular products, mostly lignin. The accumulation of partly melted and insoluble high-molecular substances in the voids of capillary and submicrocapillary systems

will prevent the soaking of water into the cell walls. It inhibits the swelling and secures the water resistance of the wood-base laminate. A partial loss of the most active chemical groups provides a certain hydrophobisation of the wood plastic.

Mobarak et al. [25] studied a binderless process of composite obtained from bagasse and pointed out that a minimum of water must be present in the cell walls to obtain plastic-like products of good strength and water resistance. It was shown that the oven-dry material failed to give products of any strength. The authors stressed also that the thin-walled pith cells are more easily deformed than the relatively stiff fiber particles, thereby enlarging the contact area and facilitating the formation of bonds. The morphological factor seems to have a greater influence in this respect than the moisture content, although the presence of some water or water vapour is essential for any plastic deformation.

This opinion was backed also by Pulikowski [26], who stated that the susceptibility of wood material to binding when subjected to hot pressing was dependent mainly on the transition of wood cellulose into an amorphous state. Amorphous cellulose is capable of forming bonds under hot pressing conditions even in the absence of hemicelluloses and lignin. Maybe, the good binding properties of SE pulp are due to the modification of the submicroscopic structure of cellulose caused by steam explosion treatment. The lignin activated by steam explosion as well as changes in the cellulose structure (reduction in the degree of polymerisation), facilitate the formation of new bonds during the moulding process.

SEM analysis demonstrates that, if SE lignin is used as a binder, it causes changes in the structure of the plastic and of the carbonised plastic in the submicroscopic level (Fig. 2). The visible film bridges between the remnants of the cell walls are the product of the SE lignin binders transformation during carbonisation at elevated temperatures. The bridging of the compressed elements inside the porous structure of the carbonised panels cause good bending strength properties of the specimens made with a binder of SE lignin and reducing substances.

The bending strength of carbonised panels is, on the average, about 40% of that measured for panels before carbonisation. The corresponding indices for panels made with phenolic alcohols binders are about 25%.

As can be seen from Tables 1 and 4 the uncarbonised specimens with a phenolic alcohols binder are substantially stronger than those moulded with binders of SE origin. However, this superiority is lost when the specimens are carbonised at 900°C. The bending strength of the carbonised blocks prepared from bagasse and SE pulp or SE lignin is stronger than the specimens prepared from bagasse and a 20% phenolic alcohol binder. The carbonised plastics prepared from bagasse and a phenolic alcohols binder form dense cell blocks up to a uniform mass and less individual cross sections as shown in SEM images (Fig. 3).

Bending strength, density, porosity and thermodynamic properties are important for the materials intended for insulation, finishing and shielding purposes. The common medium-density fiberboards, as well as the finish and insulation boards should have a bending strength of no less than 15.0 and 2 MPa, respectively. The corresponding standards for density are: more than 400 and 250 kg/m³, and those for thermal conductivity 0.157 and 0.093 W/mK. The data given in Tables 4 and 5 demonstrate that these requirements are met by panels made from sawdust and milled bagasse by making use of SE pulp and SE lignin with an admixture of reducing substances.

The thermodynamic properties of carbonised panels correspond to these properties of dry pinewood. For example, the longitudinal thermal conductivity of pinewood is 0.384 W/mK, while that in a radial direction is 0.17 W/mK. The thermal conductivity values of the carbonised panels presented in Tables 4 and 5 are within these limits.

The carbonised panels demonstrate a remarkable dimensional stability after 24 h swelling in water (Table 4). The bending strength of carbonised panels after 24 h of soaking in water is, on the average, 93% of that measured before water treatment and still meets the requirements for insulation boards. This index of carbonised panels is much better than that of panels before carbonisation. The bending strength of uncarbonised panels after 24 h of soaking is only 30–40% of that measured for panels before soaking in water.

6. Conclusions

Our investigations have shown that it is possible to prepare carbonised panels strong enough to be offered

for building industry as chemically and biologically durable insulating, finish and shielding materials.

The best binder is the SE pulp if it is mixed with the fibrous material in the weight ratio 0.5:1 to 1:1. In some cases, the formaldehyde premix in the amount 2.5% on the o.d. SE pulp basis improves the quality of carbonised panels but this effect is not consistent. The preferable hot-platen temperature during moulding is 220°C to 240°C. The moulding time is 1 min/1 mm of the panel thickness. It can be concluded that the bending strength of the test block before carbonisation does not always correlates with that of the carbonised specimens.

SE lignin can be used in a mixture with the hydrolysis products of the easy-hydrolysable fraction of cellulose and hemicelluloses.

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