

## CHEMICALS AND BIOFUELS FROM HARDWOODS, FUEL CROPS AND AGRICULTURAL WASTES

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### Introduction

Viewing the biorefinery in terms of its role in eco-restructuring, biomass becomes the major raw material for synthesis of industrial chemicals and related materials using biomass-based production systems (BPS). It is analogous to petroleum as the basic feedstock for the oil refinery. For the case of replacement petroleum refinery with biorefinery (1) 3R approach (reduce, reuse, recycle) is modified to 4R (replace, reduce, reuse, recycle) (Figure 1). Strategies of replacing petroleum products with non-polluting chemicals from biomass include direct substitution, indirect substitution and substitution with principally new product. However for full elimination of pollution and organization of industrial cluster, a fourth – Zero Emissions strategy is necessary (2).

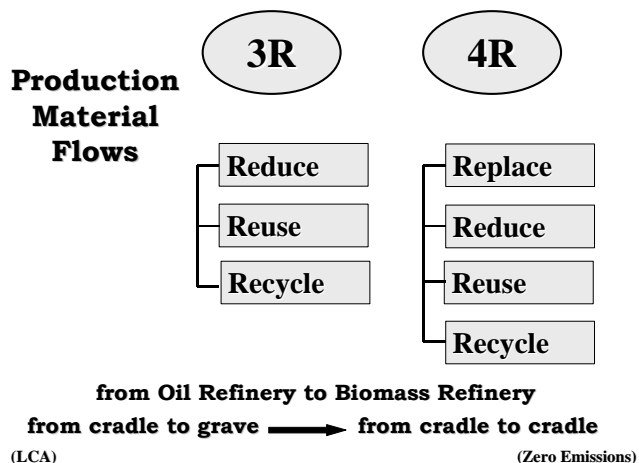


Figure 1. Shift from 3R to 4R approach (3).

Complementary biorefinery technologies utilize organic waste materials from agriculture, forestry, fishery, cities and industries while simultaneously cleaning the environment and reducing chemical risk factors. In contrast with many products made from oil, biochemicals and biomaterials have low toxicity and high biodegradability. The biorefinery concept would also facilitate carbon dioxide sequestration and reduce its emissions. Biorefinery technologies convert multi-purpose lignocellulosics into chemicals, biofuels and microbiological feedstocks. From the economic viewpoint the biorefinery creates a new economy – the lignocellulosics economy (in analogy to the petrochemicals economy) – because biofuels and biochemicals as industrial materials slowly become competitive in cost with oil based industries (2).

### Biomass-based production systems

The integrated scheme (Figure 2) of wood and non-wood biomass processing is based on methods and technologies developed or mastered at the Latvian State Institute of Wood Chemistry (Riga, Latvia) and Institute of

Industrial Science of the University of Tokyo (Japan) and is realized in the framework of the Zero Emissions Biorefinery approach developed at the Institute of Advanced Studies of the United Nations University. The treatment of biomass by steam at high temperature in the presence of small amounts of concentrated catalyst (primary process) provides the hydrolysis of pentosans and dehydration of pentoses. In parallel, furfural and acetic acid are obtained. The remaining lignocellulose bulk is used for further processing according to one of several versions (secondary processes). A part of the lignocellulose bulk as well as the whole pyrolygneous vapour, non-condensable gases and surplus lignin are burned in a boiler house to provide the biomass processing process with energy, i.e. flue gases as a heat carrier and steam.

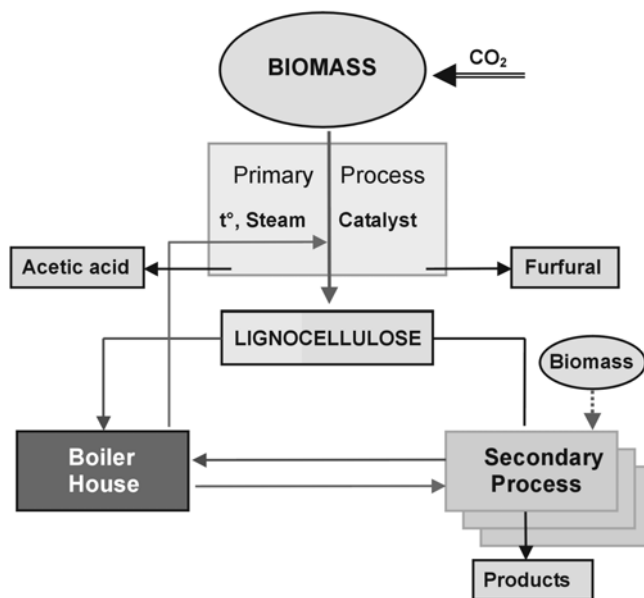


Figure 2. Biomass-Based Production System.

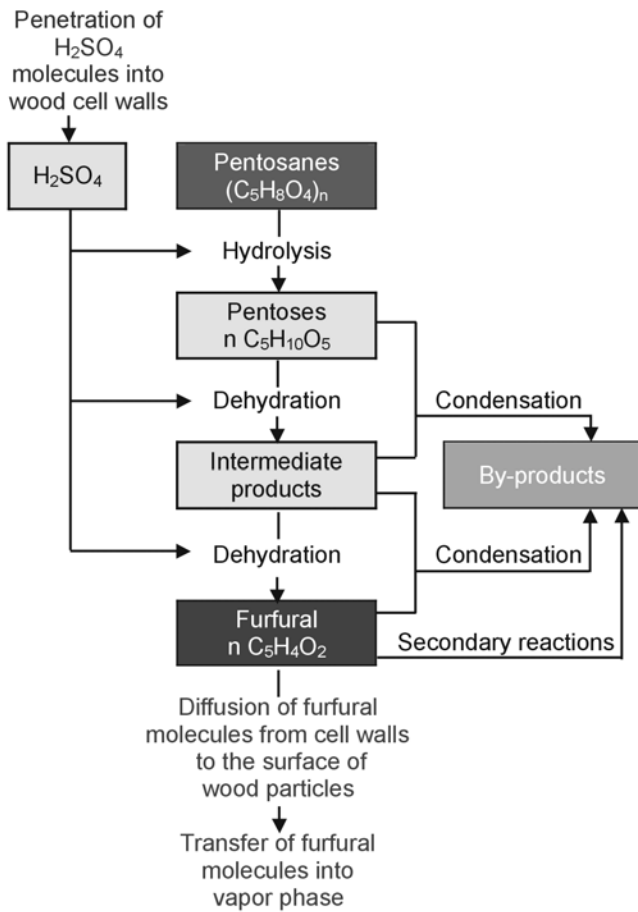
**Furfural Production.** In the conventional dilute sulphuric acid catalyzed percolation process, the plant raw material containing pentosans is mixed with dilute sulphuric acid, and, in the first step, pentosans are hydrolyzed to pentoses ( $C_6H_{10}O_5$ )<sub>n</sub>, which are then cyclodehydrated to furfural in the second step. The furfural formed is recovered by steam distillation and fractionation (Figure 3).

The rate of the first step of the furfural production process, hydrolysis reaction, in average is about 50 times higher than that for the second step, the dehydration reaction (4). Hence, the furfural formation process limiting stage is the dehydration reaction. For commercial-scale biomass conversion, the most important target is a maximal generation of pentoses and minimal loss of cellulose.

It is theoretically possible to obtain furfural as a monomer for organic synthesis and bioethanol as a motor fuel. However, in fact, up to now, the production of these two chemical intermediates using dilute acid catalysis has been considered impossible because of close values of kinetic rate constants for furfural formation and cellulose destruction.

Another problem was a comparatively low yield of furfural not exceeding 55% from the theoretical one due to secondary reactions. The mechanism of the process had to be changed in order to solve both problems simultaneously. It was realized on the basis of a new non-traditional approach, the theory of differentiated catalysis, and practically, the hydrolysis and dehydration reactions were performed simultaneously in one apparatus.

According to Vedernikov's new theory (4), hydrolysis of pentosans and dehydration of pentoses in a one-step furfural production from the plant raw material in the presence of small amounts of concentrated catalyst solutions are accelerated differentially by acetic and sulphuric acid (or other strong catalysts) (Figure 4).

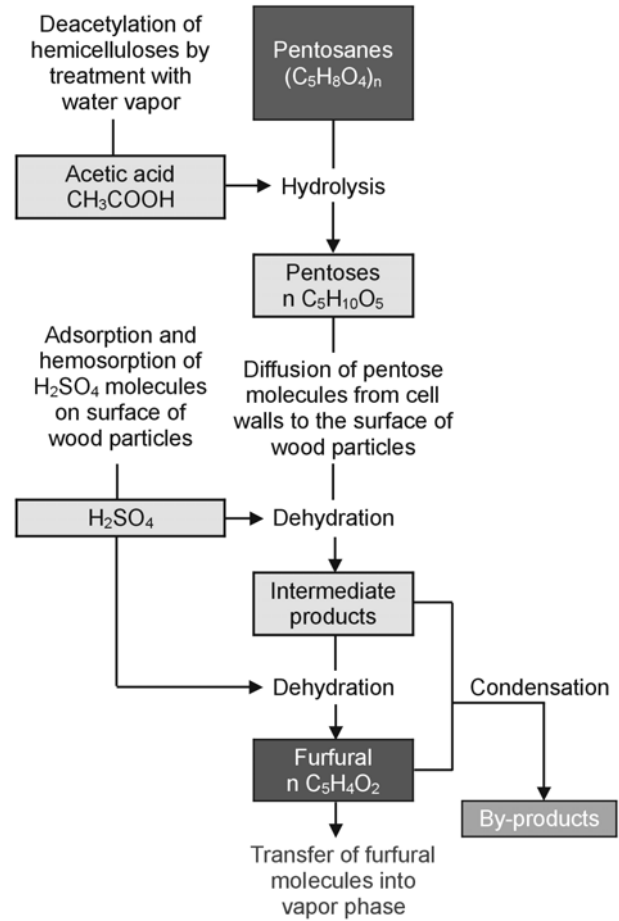


**Figure 3.** The mechanism of furfural production in the presence of dilute sulphuric acid.

Acetic acid, formed through treatment of wood with steam and uniformly distributed in the particles, catalyzes the hydrolysis of pentosans to monosaccharides. Further conversion of pentoses into furfural directly in the cell wall does not occur because acetic acid is too weak as a catalyst for dehydration at a low temperature. The pentoses formed in the process diffuse to the surface of particles where their dehydration to furfural occurs under the influence of sulphuric acid. Studies on the process kinetics (5) have confirmed that a higher concentration of sulphuric acid increases the rate of pentoses dehydration more markedly in comparison to hydrolysis of pentosans (Table 1). This allows to decrease the surplus of pentoses in the reaction system, reduces the possibility of side reactions, enhances the selectivity of the process.

**Table 1. Changes in the rate constants of pentosan hydrolysis ( $k_1$ ) and furfural formation ( $k_2$ ) in dependence on concentration of sulphuric acid**

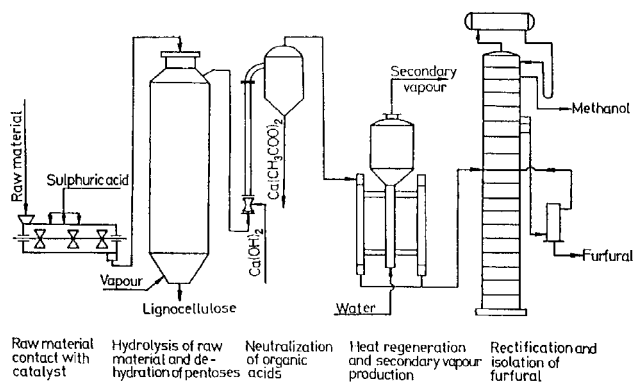
Concentration of $H_2SO_4$ , (%)	$k_1 \cdot 10^2$ , $min^{-1}$	$k_2 \cdot 10^2$ , $min^{-1}$	$k_1/k_2$
10	14.58	0.251	58.1
20	15.76	0.816	19.3
30	16.50	1.024	16.1
60	15.84	1.450	10.9
90	16.17	1.954	8.3



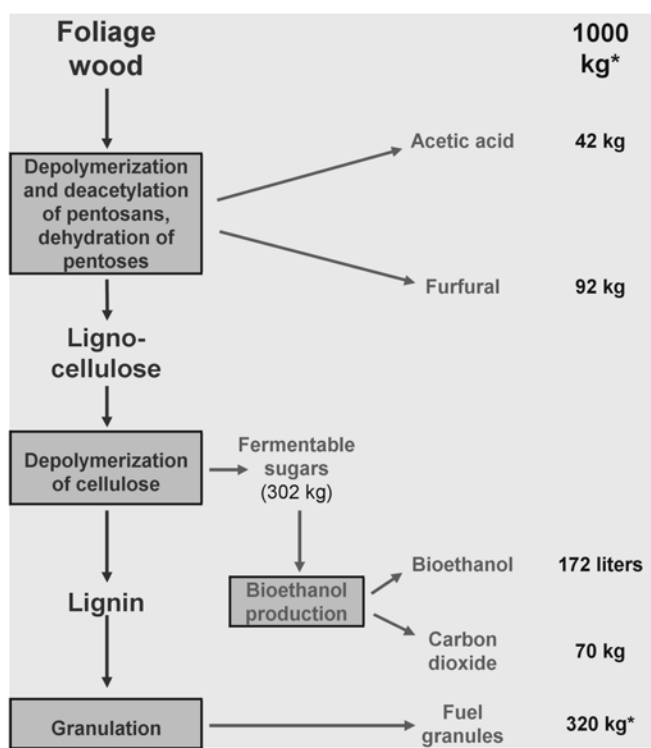
**Figure 4.** The mechanism of furfural production in the presence of concentrated sulphuric acid.

To realize the furfural production process (6), an original construction of a two-shaft helix shaped blade mixer of continuous action and an air-disperser has been developed. The optimum lay-out diagram of the blades on the mixer shafts, their configuration, shaft distance as well as the number of their revolutions have been experimentally determined. The optimum combination of these parameters has provided an uniform distribution of the catalyst in the raw material mass. The mixer was incorporated in the technological scheme of furfural production (Figure 5).

The aimed change of the mechanism of the process has permitted to solve two problems simultaneously: to make increase the furfural yield from 55% up to 75% from theoretical and to diminish 5 times degree of the cellulose destruction (4). The production process does not create any solid waste products. Since 1997 for the first time in the world's industrial practice the new technology yielding furfural and fermentable sugars further processed into bioethanol has been realized in Russia with capacity 4 300 t/a of furfural and 8 800 t/a of bioethanol. The solution of the problem of simultaneous obtaining of furfural and bioethanol would permit in the near future to use the low quality foliage wood and agricultural wastes as alternative to oil as chemical raw material (Figure 6). The technical and economic characteristics of the process are summarized in Tables 2 and 3.



**Figure 5.** Flow diagram of furfural production using small amount of strong catalysts.



**Figure 6.** The manufacturing scheme and output of furfural, bioethanol and other products from foliage wood.

**Table 2. Production of furfural from low quality deciduous wood: product, energy, labor and materials capacity**

Materials, energy and personnel	For 1 t furfural production	For 5000 t furfural production
Raw materials	25 m <sup>3</sup>	125 000 m <sup>3</sup>
Sulphuric acid	0.22 t	1100 t
Power	650 kWh	3250MWh
Factory personnel	-	70 employees

**Table 3. Production of furfural from low quality deciduous wood: average production cost**

Expenses	Unit of measurement	Amount for production of 1 metric ton	Price, USD	Total, USD
Raw material	m <sup>3</sup>	25	12.00	300.00
Technical water	t	0.22	60.00	13.20
Purification of sewage	m <sup>3</sup>	69	0.35	24.10
Power	m <sup>3</sup>	34	0.49	16.70
Sulphuric acid	kWh	650	0.15	97.50
Mean salaries (500 USD/month)				84.00
Taxes for social maintenances (34%)				28.50
Depreciation and other expenses				181.20
By production: thermal energy	Gcal	8.17	25.60	-209.10
Prime cost				536.10

Besides acid hydrolysis of lignocellulose, there are several options of lignocellulose use.

**Obtaining of levoglucosan from lignocellulose.** There are several techniques of levoglucosan (1,6-anhydro-β-D-glucopyranose) production. It has been demonstrated by one of the authors (J. Zandersons) of present study earlier, that birch lignocellulose obtained upon furfural production by the method developed by Vedernikov is the best raw material for levoglucosan (7). However, from the practical point of view, fast pyrolysis in a cyclone type reactor presents some problems to be overcome. Firstly, the cyclone type thermoreactor can be used if the biomass to be processed lacks the tendency towards plasticity and adhesion to the inner surface of the reactor wall (e.g. the birch lignocellulose mentioned above).

Another problem is a decline in the amount of the heat carrier used to pass all the fine lignocellulosic biomass particles through the thermoreactor in a heat carrier flow. These problems could be solved by use of a tubular thermoreactor equipped with a rotating helical band mixer to loosen the coarse fraction of milled lignocellulose and move it forward. A pilot scale reactor measuring 150 mm in diameter and 9 m in length with a capacity of 40 to 60 kg o.d. lignocellulose per hour has been developed and constructed at the Latvian State Institute of Wood Chemistry (Figure 7). Test runs have demonstrated that the modulus of heat carrier could be lowered to 2.9 parts of the heat carrier on the weight unit of lignocellulose. Experimental data are summarized in Table 4.

**Table 4. Products yield during fast pyrolysis of birch lignocellulose in a pilot scale tubular thermoreactor**

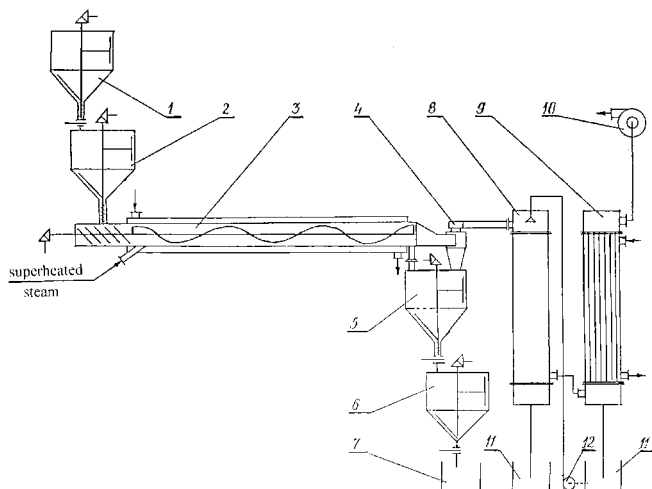
Temperature in the thermoreactor (°C)	Modulus of heat carrier (kg/kg)	Yield from cellulose mass in lignocellulose (%)		Levoglucosan/Thermolysis tar (%)
		Reducing substances	Levoglucosan	
350	3.7	6.8	28.2	73.7
375	2.9	8.6	42.8	78.5
380	3.5	11.8	39.5	71.4

A somewhat lower yield of levoglucosan can be attributed to the threefold shorter residence time of lignocellulose particles in the high temperature zone of the tubular thermoreactor in comparison with the case of the cyclone type reactor. Hence, the length of the reactor should be enlarged. Anyway, this type of tubular thermoreactor may be regarded as a prototype of fast pyrolysis industrial scale apparatuses.

A single-effect vacuum evaporator was used to obtain a water soluble tar containing 10% of water, the technical levoglucosan was isolated by the

acetone method and purified by selective extraction with ethanol and crystallization (7). To prepare a high-purity levoglucosan (m.p. 178-180 °C), a method of fractional distillation of levoglucosan sililderivatives was used (8).

To gain a provisional idea of the possible cost of levoglucosan before its production is started on an industrial scale, we calculated the total sum of the expenditures related to materials, chemicals, fuel and power costs to produce 1 t of purified levoglucosan (95-96% purity, m.p. 173-175 °C) and its by-products (water-soluble tar and carbonaceous residue). The expenses, calculated in the present economic situation of Latvia, are summarized in Table 5.



**Figure 7.** Flow sheet of a pilot scale fast pyrolysis unit with a tubular thermoreactor: 1 – upper reloading receptacle; 2 – loading bunker; 3 – fast pyrolysis reactor; 4 – cyclon; 5 – reloading receptacle; 6 – discharge bunker; 7 – container of carbonaceous residue; 8 – scrubber; 9 – condenser; 10 – ventilator; 11 – shut-off receiver; 12 – pump.

**Table 5. Calculation of joint production costs of 1 t of purified levoglucosan, 1.5 t of soluble tar and 5 t of charcoal**

Expenditure items	Unit of measurement	Consumption	Average price, USD (in Latvia)	Production costs, USD
Lignocellulose (moisture w=10%)	t	11.10	30.00	333.00
Acetone	t	0.22	900.00	148.00
Ethanol	t	0.34	790.00	270.00
Fuel Oil	t	3.75	330.00	1238.00
Steam (saturated)	Gcal	61.75	33.00	2038.00
Power	1000 kWh	2.1	44.00	84.00
Technological water	1000 m <sup>3</sup>	1.9	24.00	46.00
Totally				4207.00

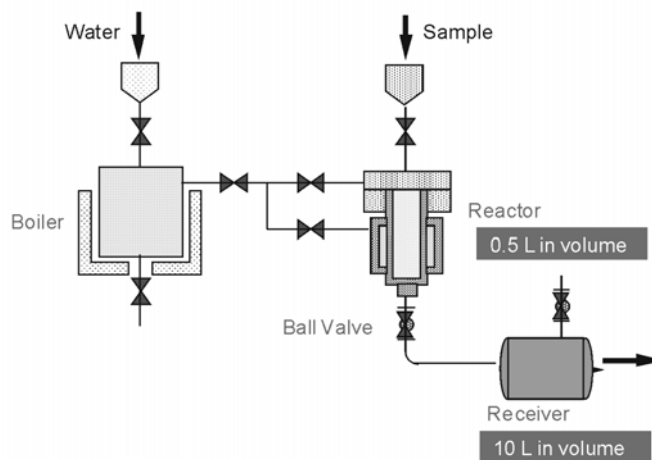
The water soluble tar is a residue of levoglucosan crystallization containing 19 to 20% levoglucosan and 10 to 13% hydroxyl groups (o.d. tar basis). It was tested as a hydroxyl groups-containing component for the preparation of a rigid polyurethane foam with an increased softening temperature (up to 150 °C). Hence, the water-soluble tar can substitute the glycerol or xylitol in these compositions and can be sold at the wholesale price of glycerol 1500 USD/t.

The yield of the carbonaceous residue of lignocellulose is 50 to 60% from o.d. lignocellulose mass. Its elemental composition is C = 63.9%; H = 5.1% and O = 31.0%. The lower combustion heat 23.5 MJ/kg. As a raw material of fuel briquettes production, it could be sold at a price of 75 USD/t. All prices and costs are given including the value-added tax (18% in Latvia). The levoglucosan share of the production costs is : 4207 – (2250 + 375) = 1582 USD/t.

However, the fuel oil costs to superheat the steam are high. Therefore, it is reasonable to substitute fuel oil with the carbonaceous residue. In parallel with the excluding of fossil fuel from the process heat balance and thereby improving the carbon dioxide emission balance, the cost share of levoglucosan is also substantially reduced: 4207 – 1238 – 2250 = 719 USD/t of levoglucosan.

**Steam-explosion autohydrolysis.** Steam-explosion (SE) autohydrolysis (Figure 8) is another way to process the lignocellulose remaining after prehydrolysis of deciduous wood chips for furfural production. The steam-explosion autohydrolysis treatment has been proposed as a method to obtain various value-added products from lignocellulosic biomass (9) such as wood, corn cobs, sugar cane bagasse as well as lignocellulose of furfural production. During the process, a wide range of chemical transformations occurs: the functional groups are cut off, and thereby acid molecules are formed in the system (for example, acetyl groups in hemicelluloses provide the formation of acetic acid) (Figure 9). A two-stage extraction (with hot water and subsequently with 90% ethanol) or a one-stage extraction with 90% ethanol allowed separation of reducing substances (mono- and oligosaccharides) and the lignin portion of the material obtained after SE treatment. The remaining matter is a partly destructed fiber material, which can be used to prepare various products, e.g. microcrystalline cellulose.

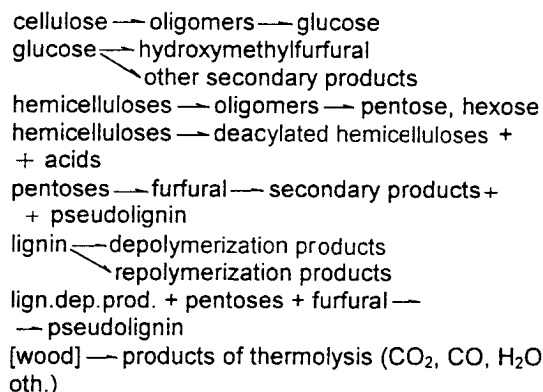
During the last decade, a new trend in processing of charcoal and carbonaceous materials has arisen, i.e. evaluation and production of carbonized fiberboard materials (e.g. wood ceramics) and slabs of charcoal fines with a phenol formaldehyde binder. We replaced the synthetic phenol-formaldehyde resins by the biomass-based SE lignin with an admixture of reducing substances obtained from ethanol-water extracts to prepare binders for fiberboard production. The further carbonization of the obtained fiberboards gives carbonaceous construction materials (11).



**Figure 8.** Scheme of steam-explosion laboratory unit (IIS, University of Tokyo).

The application of SE in combination with subcritical water treatment (high temperature - high pressure water treatment) allow processing of wide spectra of wood and non-wood biomass into value-added products. Attractive prospects for an effective utilization of agrowastes by the combination of such method are proved experimentally (Figure 10). The solid part remaining after the SE action has been subjected to high temperature - high pressure water treatment. Depending on the conditions of the subcritical water treatment process (temperature, pressure, time), a wide variety of products will be produced, such as mono- and oligosugars applicable for fermentation,

pyrolysis products (organic acids), low molecular soluble lignins applicable as resin materials, phenol derivatives (phenylpropane), the oil residue applicable as a fuel and the solid residue (carbonaceous materials).



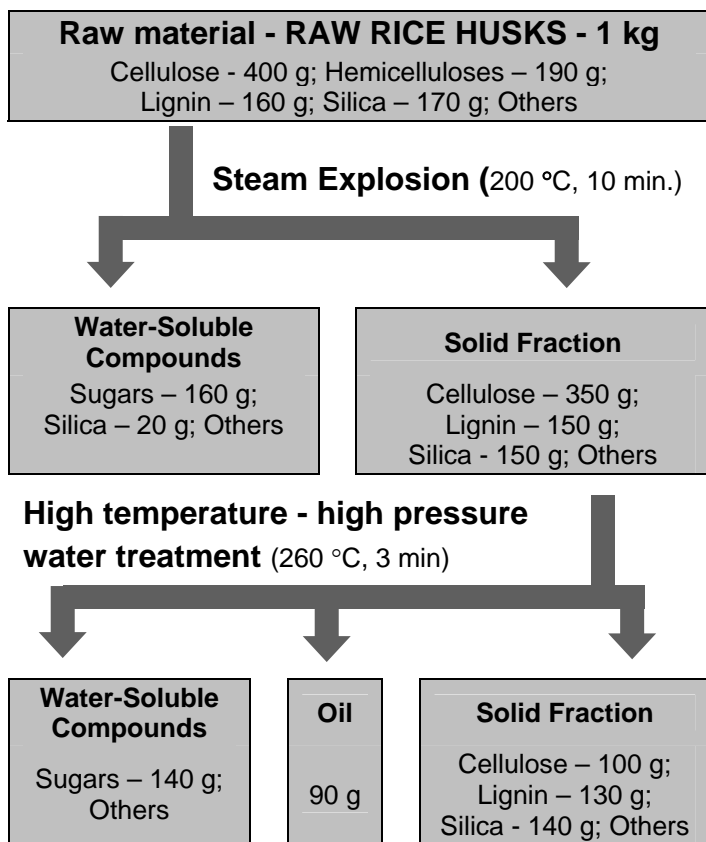
**Figure 9.** Outline of possible transformations of plant biomass components during Steam Explosion treatment (10).

**Energy supply of Biomass-Based Production System.** The pyroigneous vapour of the carbonization unit, non-condensable gases and the carbonaceous residue of the fast pyrolysis reactor as well as lignin and a portion of the lignocellulose remaining after furfural production (the latter is determined by economic considerations) are passed to a boiler house.

Depending on the structure of the industrial cluster, the energetical self-sufficiency is striven for and fulfilled as far as possible. Establishing sound ecological foundations is the prime principle guiding industrial cluster organization.

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**Figure 10.** Materials balance estimated for rice husks treatment.