

Chemical processing of lignocellulosics

H. H. Nimz* and R. Casten**

Institute of Wood Chemistry and Chemical Technology of Wood, Federal Research Centre for Forestry and Forest Products, Hamburg

Lignocellulosics can be separated into their three main components by extraction with acetic acid, containing 0.1% hydrogen chloride, at 110 °C. The residual pulp can be bleached in the same solvent with peracetic acid, which is formed in situ when adding hydrogen peroxide. Hemicelluloses and lignin are obtained in a low condensed and relatively reactive form that may be converted into valuable chemical raw materials. Some aspects of such conversions are discussed.

Chemischer Aufschluß von Lignocellulosen

Die Auftrennung von Lignocellulosen in ihre drei Hauptkomponenten gelingt durch Extraktion mit Essigsäure, die 0,1% Salzsäure enthält, bei 110 °C. Der zurückbleibende Zellstoff läßt sich im gleichen Lösungsmittel mit Peressigsäure bleichen, die in situ durch Zugabe von Wasserstoffperoxid entsteht. Hemicellulosen und Lignin werden in wenig kondensierter, relativ reaktiver Form erhalten und eignen sich für die Herstellung wertvoller chemischer Rohstoffe. Einige Aspekte dieser Umwandlungen werden diskutiert.

1 Introduction

Lignocellulosics, like wood and annual plants, consist of three main components, cellulose, hemicelluloses and lignin (Table 1). E.g. spruce wood contains 43% cellulose, 27% hemicelluloses and the same amount of lignin; beech wood consists of about the same amount of cellulose, 41%, however less lignin, 22%, and correspondingly more hemicelluloses, some 35%. These numbers are typical for European softwoods and hardwoods. Grasses, like wheat straw, contain also 35% hemicelluloses, but less lignin (18%) and cellulose (38%).

The principal drawback in any chemical processing of lignocellulosics is that it is not possible, neither technically nor on a laboratory scale, to separate these three components without changing their chemical structures. It is not only the chemical linkages between lignin and carbohydrates which hinder their separation but also their macromolecular structure. E.g., native lignin, due to its threedimensionally cross-linked structure, is insoluble in any solvent. So, in order to extract lignin from wood or annual plants, besides cleavage of covalent bonds between lignin and hemicelluloses, the lignin has to be partially degraded to lower molecular weight fragments that are soluble in the solvent. The problem, how-

Table 1. Composition of lignocellulosics

	Lignocellulosics, %		
	Spruce wood	Beech wood	Wheat straw
Cellulose	43	41	38
Hemicellulose	27	35	35
Lignin	27	22	18

ever, is that under the conditions, needed for such degradation, condensation reactions in lignin occur, which counteract the degradation.

On the other hand, it is not possible to dissolve unchanged cellulose from wood by leaving the undissolved lignin as the residue.

Currently exist two technical procedures for wood processing, wood pulping and wood saccharification. Both utilize only the cellulose, that means some 40...50% of the wood, while the lignin and hemicelluloses are lost as waste products. In the case of wood saccharification the cellulose is dissolved by degradation to glucose and the lignin is converted to a condensed insoluble product. This process is presently not applied in Western European countries because the price of ethanol, obtained from cellulose by fermentation of glucose, cannot compete with that of the ethanol from ethylene or even from other biomass like sugar cane, sugar beets or starch.

The second process, wood pulping, serves for the production of paper from wood. In this process, the lignin is dissolved by the introduction of hydrophilic groups, i.e. sulfonic acid or mercaptane groups, as well as by partial degradation. Currently the global production of chemical pulp amounts to more than 100 mio tons annually. The Federal Republic of Germany produces some 800,000 tons and imports 2.5 mio tons pulp per year, while the European Community produces 3 mio tons and imports 4.5 mio tons per year at a cost of some 2 billion ECU (Table 2).

From the numbers given above it can be estimated that the global production of lignin in the pulp mills amounts to some 50 mio tons per year which is more than the whole production of plastics. Correspondingly, some 30 to 40 mio tons of hemicelluloses are also produced in the spent liquors, that are mainly evaporated and burnt. It is not economically feasible to separate the lignin from the hemicelluloses in conventional spent liquors. Also, the lignin is severely condensed and contains sulfur, hindering its application on a larger scale. Only the calcium base spent sulfite liquors are

* Vortrag zum Workshop "Lignocellulosic Biomass and Processing" der Europäischen Förderation Biotechnologie in Oberursel am 10. 12. 1985

** The authors are grateful to Mrs. Carola Struck and to Dr. Othar Kordsachia for determining the pulp properties

Table 2. Lignin and hemicelluloses as byproducts of chemical pulp and cereal crop in the EEC 1982, in 1000 t

		Chemical pulp	Lignin	Hemi-celluloses
Wood ^a	prod.	3,091	1,500	1,000
	cons.	7,645	120 ^c	80 ^c
Cereal straw ^b	prod.	200	100	150
	potent.	50,000	22,500	42,000

^a VDP (1984)^b Rexen, Munck (1984)^c Estimated values

partly spray-dried and sold for various purposes (Table 7). Their amount in the EEC is about 200,000 t/y, corresponding to 8% of the totally produced spent liquors (2.5 mio t. cf. Table 2). From Table 2 it is also obvious that the EEC produces some 140 mio t of straw per year. If only 10% of this straw were pulped, it would cover more than the imported 4.5 mio t of pulp. The present problems in straw pulping by soda cooking arise from the high silica contents of the spent liquors and the inferior pulp properties.

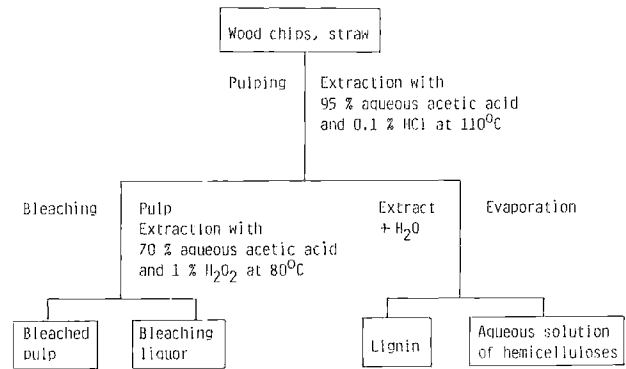
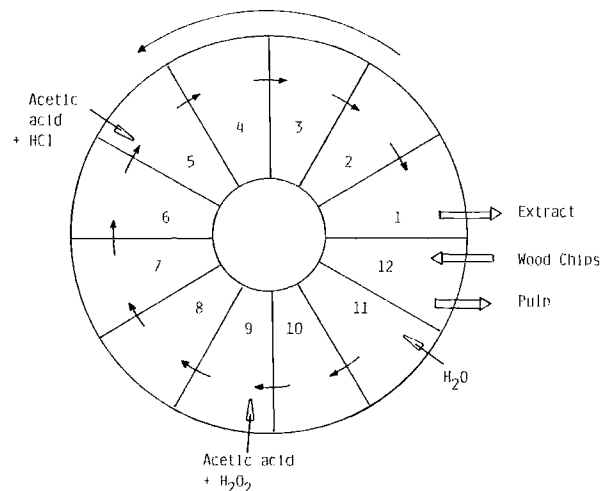
However, other pulping conditions may change these drawbacks to a point where they are less detrimental. Furthermore, van der Klashorst et al. (1985) have shown that bagasse soda lignin, which is comparable to straw lignin, condenses easily with formaldehyde and thus can be used as cold setting wood adhesive. In contrast, lignins from conventional pulping spent liquors show less reactivity towards formaldehyde, due to their highly condensed and sulfur containing structures.

2 Acetosolv-pulping

In recent years, organosolv pulping has attracted interest for reasons of environmental pollution. Though organosolv pulping has not reached technical application yet, it has the advantage that sulfur containing chemicals leading to SO₂ by burning the effluents are avoided. Furthermore, lignin is lipophilic, while the carbohydrates in wood, cellulose and hemicelluloses, are hydrophilic. For this reason lignin may be extracted from wood with organic solvents under milder conditions than with water, as it is the case in conventional pulping, where hydrophilic groups have to be introduced into the lignin under more severe conditions, in order to get it soluble in water.

Up to now, ethanol and methanol are the main solvents used for organosolv pulping. In the Munich-Dachau-(MD)-procedure, which has now reached demonstration plant scale, wood chips are first treated with 50% aqueous methanol at 190 °C for 15 min and thereafter with 30% methanol in the presence of sodium hydroxide and anthraquinone at 170 °C for some 30 min.

Last year in our laboratory we have developed a pulping procedure using acetic acid (Nimz, Casten 1984) instead of alcohol (Fig. 1). In this case, wood chips or straw are extracted with 95% aqueous acetic acid containing 0.1% hydrogen chloride at 110 °C for 3...5 hours. In contrast to conventional sulfite pulping, pine wood can also be delignified to a kappa number below 30. When compared with the MD procedure, no pressure vessels, sodium hydroxide or anthraquinone are needed. The only chemicals, acetic acid and hydrogen chloride, are recovered by evaporation of the extract. The residue, when poured into water, yields lignin as

**Fig. 1.** Acetosolv pulping and bleaching**Bild 1.** Acetosolv-Aufschluß und -Bleiche**Fig. 2.** Carrousel extractor for acetosolv pulping and bleaching**Bild 2.** Karussell-Extraktor für Acetosolv-Aufschluß und -Bleiche

an insoluble precipitate, which may be filtered off, while the aqueous filtrate contains the hemicelluloses. The lignin is free from carbohydrates, due to the mild pulping conditions little condensed and soluble in many organic solvents.

Another advantage of our procedure is that we can bleach the pulp in the same solvent by the addition of hydrogen peroxide at the end of the extraction. The hydrogen peroxide combines with the acetic acid under the formation of peracetic acid, which is known to be a powerful and selective delignification and bleaching agent.

In conventional as well as organosolv pulping with alcohols one gets a pulp with a kappa number of or below 30, which has to be bleached in 3 to 5 steps with chlorine, hypochlorite and/or chlorine dioxide. Correspondingly, the bleaching effluents contain chlorinated organic compounds, which currently cause the main environmental problems in pulp mills.

Figure 2 shows a possible carousel extractor for pulping and bleaching consisting of 12 sectors. The extractor moves counter-clockwise with a speed of e.g. one sector per hour, while the acetic acid flows clockwise (small arrows). There are three zones, a washing zone, a bleaching zone and a pulping zone. The washing zone (sectors 10 and 11) contains water, which is added into sector 11, the bleaching zone (sectors 9 to 6) contains 70–90% acetic acid with hydrogen peroxide, added into sector 9, and the pulping zone (sectors 5 to 1) contains 90–95% acetic acid with 0.1% hydrogen chloride. The fresh wood chips are filled into sector 12 and are released after a full rotation of the extractor as washed pulp from the same sector.

Table 3. Pulp properties after 4 h pulping with 95% acetic acid at 110 °C at various concentrations of HCl

	Spruce	Spruce	Spruce	Beech	Pine	Wheat straw
HCl	0.05	0.1	0.2	0.1	0.1	0.1
Yield	51.3	46.7	44.0	41.4	49.6	37.7
Fines	50.5	46.3	43.2	41.3	37.1	36.6
Shive yield	0.8	0.4	0.8	0.1	12.5	1.1
Kappa-number	38.3	30.2	22.5	7.7	61.0	25.0
DP _w	2,516	2,309	2,861	3,218	–	2,413
Beating degree	47.5	30.5	47.0	74.0	52.0	76.5
Beating length	11,220	9,860	10,270	8,155	8,292	7,188
Tearing strength	51.2	62.9	67.6	42.5	50.1	37.0
Burst area	69.7	58.2	60.6	53.6	58.6	42.3
Folding endurance	3,529	3,599	3,902	5,845	1,808	746

Table 4. Pulping and bleaching of beechwood chips

No.	Pulping time h	Bleaching		Pulp yield	Brightness % ISO
		% H ₂ O ₂	time, h		
31	3	1	4	42.2	75.8
30	4	1	4	40.9	79.3
36	5	1	4	39.1	80.5
34	4	1	8	41.5	84.0
37	5	1	8	40.0	85.2
35	4	2	4	40.2	85.7

The acetic acid used for the bleaching flows further to the pulping zone and leaves the extractor in section 1, together with the other acetic acid, added in sector 5. In this way less than 5 liters of acetic acid are needed per kg of wood.

Another possible technique uses separated pulping and bleaching towers by recycling the extract with intermediate defibration of the pulped chips, which reduces the bleaching time and the amount of hydrogen peroxide.

Table 3 shows the properties of some pulps before bleaching. After four hours extraction of spruce wood chips with 0.1% hydrogen chloride the kappa number is 30 at a pulp yield of some 46%. Strength properties are comparable to those of sulfate pulp. Beech wood chips under the same conditions give kappa numbers around 8, DP values above 3,000 and a beating length of some 8,000 m. The results with pine wood in this case were not satisfying, but in the meantime we have found conditions by which pine wood chips can be pulped too. Straw gives also pulp with reasonable strength properties. The results, given in Table 3, are only of preliminary value, because they were obtained from 50 g wood samples.

Table 4 shows the results after bleaching of beech wood chips. With a 1% hydrogen peroxid solution an 84% brightness degree is obtained after eight hours bleaching time. These results were obtained with not defiberized pulp, so that the bleaching time and the consumption of hydrogen peroxide may be further reduced.

Our present work is dealing with optimization of the pulping and bleaching conditions as well as properties and utilization of all three wood components, pulp, lignin, and hemicelluloses.

3 Products derived from hemicelluloses

The key products derived from hemicelluloses are furfural from pentosans and hydroxymethylfurfural from hexosans (Fig. 3). A great variety of chemicals may be obtained from

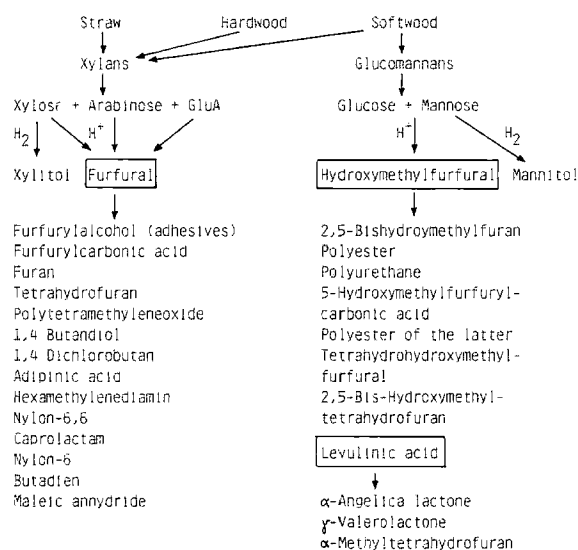


Fig. 3. Main products derived from hemicelluloses
Bild 3. Hauptprodukte aus Hemicellulosen

furfural. Furfural and its reduction product, furfurylalcohol, can be used as adhesives and substitute formaldehyde in particleboard glues. However, currently it cannot compete with the price of urea-formaldehyde and similar resins, due to its price of about DM 2.70/kg. The price of furfural depends on the concentration of xylans in the substrates from which it is obtained with strong mineral acids. In oat hulls and corn cobs the concentration of xylans is close to 30% while the aqueous solutions obtained from hardwood chips after extraction with acetic acid contain some 70% xylans. From straw, besides xylose, some arabinose is obtained which also yields furfural on acidolysis.

In the case of softwoods, the hemicelluloses consist mainly of glucomannans which on treatment with strong mineral acids give hydroxymethylfurfural (HMF). This compound is relatively unstable and the yields are low. According to Szmant and Chundury (1981) the highest yields (42%) were obtained from glucose in DMSO with borontrifluoride as catalyst after 48 h at 100 °C. However, these yields were determined in solution, without isolation of the products. It is well known that the main losses occur during isolation by distillation. For this reason Stenzenberger and co-workers (1983) have proposed acetylation of HMF to acetoxyethylfurfural (Bicker 1983), which is more stable and can be distilled without decomposition. Simultaneously, Dadgar and Foutch (1983) have claimed to get 40% yield, based on cellulose, of HMF from sawdust by a multistage extraction process. HMF actually is only an intermediate in the

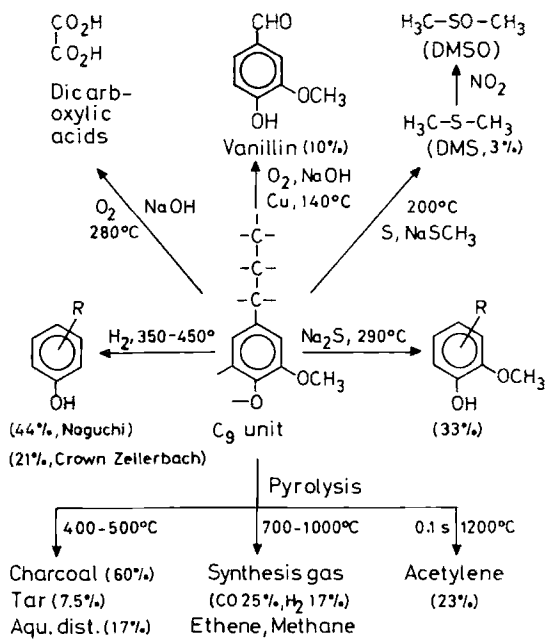


Fig. 5. Products derived from lignin by degradation

Bild 5. Abbauprodukte des Lignins

water as a solvent in order to get a cold setting wood adhesive. This shows that the pH plays an important role for the effectiveness of the gluing.

Another possibility is lignin degradation to low molecular weight chemicals. Out of the many products that may be obtained from lignin (Fig. 5) so far only vanillin and dimethylsulfoxide (DMSO) are commercially produced on a small scale. Yields are, however, low and actually exists no market for higher amounts of vanillin.

Hydrogenolysis at 350...450 °C in the presence of catalysts leads to a mixture of alkylated phenols. The Japanese Noguchi process consists of two steps by which the spent sulfite liquor is first desulfonated and separated from inorganic salts and sugars and thereafter mixed with phenol in order to get a homogeneous mixture for the hydrogenation step. The process was repeated by Crown Zellerbach in the early sixteenth, who found lower yields of phenols (21%) than the Japanese authors had published (44%). In the case of ACL a one-step procedure would be sufficient, because no salts or sulfur have to be removed before the hydrogenation step.

The conditions are similar to those used in the PERC or LBL procedures for the liquefaction of wood by catalytic hydrogenation (Esnouf 1985; Moffatt, Overend 1985). In these processes the whole wood (not just the cellulose) is transformed to liquid fuels. The main problems in wood liquefaction, however, are high costs for the grinding of wood and hydrogenation of the carbohydrates. Lignin contains some 20% less oxygen than cellulose and hemicelluloses and 15% less than wood. This means that the hydrogenation of lignin consumes much less hydrogen and no grinding energy, which makes acetosolv lignin a much more attractive candidate for liquid fuels than wood. Furthermore, no transportation costs arise if the hydrogenation plant is built close to a pulp mill.

Similar considerations are valid for the pyrolysis of lignin to synthesis gas or to acetylene (Fig. 5). The latter is obtained either from wood or from lignin above 1,200 °C, if the reaction time is very short (flash pyrolysis). The technology of this process is known from the industrial production of acetylene from hydrocarbons. Crown Zellerbach Corp. had built a pilot plant for the production of acetylene from lignin

and wood in the 1970th. The highest yield obtained from kraft lignin was 23%. It was calculated that, in order to become economical, the yield should be higher than 30%, at a capacity of 150 t/d. If one starts with pure, sulfur-free organosolv lignin, this aim should be reached easier than with either kraft lignin or wood.

5 Conclusions

In general any chemical processing of lignocellulosics first to deal with the separation of its three main components, cellulose, hemicelluloses, and lignin. The easiest way, extraction of one or two components with an appropriate solvent, is not possible, because each component is insoluble in any solvent due to its macromolecular structure and covalent chemical bonds between lignin and hemicelluloses.

Conventional chemical pulping procedures introduce sulfur containing functional groups into lignin in order to get it soluble in the aqueous reaction medium. However, lignin, according to its chemical structure, is a hydrophobic compound, while cellulose and hemicelluloses are hydrophilic. This means that organic solvents are more selective than water for the extraction of lignin from wood and for the bleaching reactions, in which a highly selective reactivity of lignin is required.

In the proposed acetosolv-procedure much milder reaction conditions than in conventional pulping procedures are needed for an only slight lignin degradation, necessary for the solubility of lignin in acetic acid. Furthermore, acetic acid combines with hydrogen peroxide to peracetic acid, which has long been known as a powerful and selective lignin oxidant. This allows a sulfur-free pulping and chlorine-free bleaching.

Conventional pulping as well as saccharification of lignocellulosics make use only of some 50% of the raw material. Lignin and most of the hemicelluloses are waste materials, because they are severely condensed or transformed to humic substances under the conditions applied. Acetosolv pulping leads to a lignin that is less condensed and free from sulfur.

Acetosolv pulping of straw yields a typical grass lignin that is suitable as a glue for particle boards. Straw pulp is already produced in Denmark and Italy by soda cooking in low amounts. The main drawback of straw is its high content of silica which is less detrimental in acetosolv cooking, because in this case half of the silica remains in the pulp and the other half in the lignin, which must not be burnt. In case of straw-saccharification, the price of lignin would reduce the final price of ethanol.

Recently Paszner et al. (1985) have claimed that high yields of glucose may be obtained from lignocellulosics by acid catalysed organosolv means (ACOS). The process is similar to acetosolv pulping with the exception that it uses acetone instead of acetic acid and 200 °C instead of 110 °C. This results in the complete hydrolysis of cellulose in one step. The lignin may, however, be more condensed under the chosen reaction conditions. This has to be proven, because it is of basic importance for the cost calculations of ethanol obtained from the glucose. It seems to us that the concomitant utilization of lignin and perhaps the pentoses from the hemicelluloses will be an indispensable prerequisite for the production of ethanol from lignocellulosics.

Aside from the above mentioned ACOS procedure, which has to be proven yet, yields of glucose, which is the essential intermediate in ethanol production, are far less than 100% in acid hydrolysis procedures, and side products like

hydroxymethylfurfural have to be removed before fermentation of glucose to ethanol. Enzymatic hydrolysis of cellulose to glucose needs delignification in the case of lignocellulosics so that acetosolv pulping is advantageous as a pretreatment procedure.

However, ethanol is not the only liquid fuel or useful chemical that may be derived from cellulose. According to Thomas and Barile (1984) α -angelicalactone shows a better performance as a gasoline extender than ethanol and can be obtained at a lower price from lignocellulosics. Though the authors did not remove the lignin before hydrolysis of bagasse in their calculations, it might improve the yields and add lignin as an additional valuable product. The production of α -angelicalactone from cereal straw, bagasse or residual wood concomitantly with lignin and furfural from the pentosans seems to us an attractive research project.

As can be seen from Fig. 3, a great variety of valuable chemicals can be obtained from hydroxymethylfurfural (HMF). However, due to its instability, the yield of HMF from cellulose is always low, and many publications have been dealing with this problem. In our laboratory, we have started some promising research in getting stable derivatives of HMF and levulinic acid from cellulose, which may be further processed or used as fuels.

Liquefaction of wood or other lignocellulosics by catalytic hydrogenation at temperatures between 300 and 450 °C is the only process in which all three components are utilized. However, the two main obstacles hampering its technical application in the future will be the high energy needed for wood grinding and the large amount of hydrogen necessary for the transformation of carbohydrates to hydrocarbons. In contrast, lignin contains 20% less oxygen than carbohydrates and correspondingly needs much less of the expensive hydrogen for getting liquid fuels. Furthermore, lignin is already obtained as a fine powder in the acetosolv process, needing no further grinding.

Any processing of lignocellulosics has to deal with all three components in order to become compatible in price with the processing of other raw materials. However, even by doing so, some products, like liquid fuels, might be obtained cheaper from coal. Consequently, one should look for other valuable products that cannot be derived or only at a higher price from coal or crude oil. One such product is certainly pulp. Pulp does not only serve for the production of paper but also for valuable fibers and cellulose derivatives. A great variety of chemicals other than ethanol may be obtained from cellulose, which are derived from other raw materials only at higher costs. The market for such products in some cases may expand with their availability at a lower price. This might especially be possible for furfural from hemicellu-

loses. New technologies are urgently needed for getting uniform products in higher yields under less polluting conditions.

6 Literature

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