

M.E. Paulaitis, J.M.L. Penninger, R.D.Gray, H.W.P. Davidson:

Chemical Engineering at Supercritical Fluid Conditions,

Ann Arbor Science Publ., Ann Arbor 1983

CHAPTER 25

LIQUEFACTION OF BIOMASS
WITH SUPERCRITICAL FLUIDS
IN A HIGH PRESSURE/HIGH
TEMPERATURE FLOW REACTOR

P.Köll, B.Brönstrup,

J.O. Metzger

Universität Oldenburg

Fachb.Chemie, PF 2503

D-2900 Oldenburg, Germany

The dramatic increase of prizes for crude oil since the beginning of the seventies revived the interest, especially in the high industrialized countries, in biomass as renewable energy source and feedstock for chemical industries. This is well-documented in a number of conference reports[1] and monographs[2] on this subject. Mainly different methods of pyrolysis, hydrolysis and hydrogenolysis are described. These methods yield more or less effectively low molecular weight compounds.

The objective of our own work was to disintegrate biomass completely into its single components in an environmentally safe way and to obtain these components in a state, which would allow further chemical treatment and usage. Furthermore we searched for methods, which would allow controlled degradation of biopolymers to low molecular weight compounds of high value.

Firstly, our interest focused on wood and its single components hemicellulose, cellulose and lignin. Secondly on peat, which is very abundant in some parts of the northern hemisphere; thirdly on chitin, which forms the skeleton of crustaceans but is also part of the cell walls of molds and mushrooms and fourthly on sewage sludge, the disposal of which is a severe environmental problem in certain parts of Europe. The mentioned examples of biomass are readily available and are altogether not used normally as food. Therefore their chemical usage would not directly compete with food production.

In our search for transforming these products in

an efficient way to interesting chemicals, we found, that the special properties of fluids at high temperatures, in our case mainly organic solvents, allowed us to develop an alternative degradation procedure for biomass of different kinds.

The experimental part of this development has been performed in a high pressure/high temperature flow apparatus ("HP-HT-apparatus"), which has been described in detail by us in the literature [3,4] and which is largely made up of commercially available HPLC equipment and a GC furnace to heat the tubular reactor. The only modification necessary is to use a preparative HPLC column (V = 50 ml) as reactor. The biomass sample (1 - 20 g) is transferred into this reactor, which withstands temperatures up to 400°C and pressures up to a few hundred bars.

Thus it is possible to degrade cellulose in supercritical acetone almost quantitatively [3], with anhydrosugars as the main reaction products (see Figure 1). Glucosan 1, 1,6-anhydroglucofuranose 2, dianhydroglucose 3 and levoglucosenone 4 amount to nearly 50%. For comparison the results of typical pyrolyses are shown in Table I [5].

Table I . Products from pyrolysis of cellulose at 300°C (data taken from [5])

	Nitrogen 1 bar	Vacuum
Char	34.2(%)	17.8(%)
Tar	19.1	55.8
Glucosan <u>1</u>	3.6	28.1
1,6-Anhydrogluco- furanose <u>2</u>	0.4	5.6

The advantages of the degradation procedure employing supercritical fluids are obvious. The high amount of residue left, called "char", is a characteristic of pyrolytic methods. This is almost totally avoided by our procedure : only 2 % residue was left and 98 % of the cellulose was liquefied. (Reaction conditions : 18 g cellulose, microcrystalline, temperature 250°C raising to 340°C within 10 hours, flow rate 4,5 ml acetone/min.).

The comparatively smooth degradation with supercritical organic solvents is also observed with chitin [3]. Again with acetone as solvent (flow rate

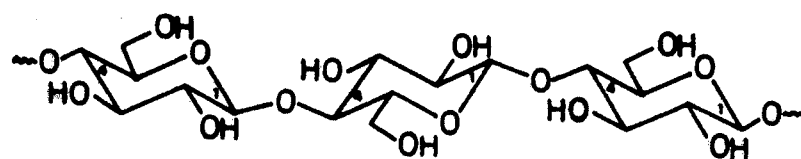
5 ml/min; temperature up from 250°C to 340°C within 7.5 hours, pressure 250 bars) 85 % were liquefied. In the tar obtained, interestingly the amino analogue 5 of glucosan 1 is found in preparatively interesting amounts (see Figure 1). 5 has never been reported as pyrolysis product of chitin and, in fact, this also was our experience in pyrolyzing chitin[6]. The main reaction product in both cases, besides water of course, is acetamide[3,6]. The remaining degradation product consists of a very complex mixture of mainly oxygen- and nitrogen containing heterocycles[7].

With this results in hand, we tried to degrade whole wood. We took birch wood for our investigations[8], because this is a tree, which grows fast even on poor soils and in cold climates and which is not high in value. Table II shows the results we obtained with different solvents under standardized conditions.

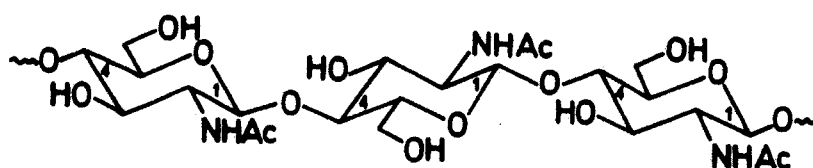
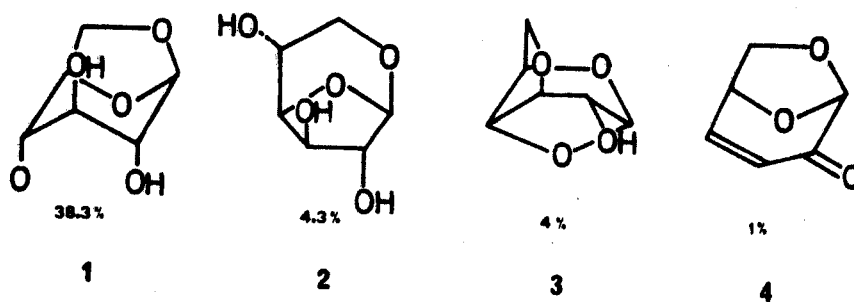
Table II. Degradation of birch wood with supercritical fluids (sample weight 3 gram, reaction time 1.0 h, pressure 100 bar, solvent feed rate 1 ml/min). Q gives the ratio of lignin to carbohydrate degradation.

Solvent	Temp. (°C)	Weight loss (%)	Residual lignin (%)	Weight loss of carbohydrate (%)	Weight loss of lignin (%)	Q
Ether	250	20.77	28.02	29.99	---	0
n-Pentane	250	24.29	34.26	38.90	---	0
2-Propanol	250	24.62	17.20	23.39	30.06	1.3
Acetone	250	22.77	19.55	23.72	18.57	0.8
Methanol	250	25.30	13.04	20.25	47.47	2.3
Ethanol	250	21.78	12.59	16.06	46.88	2.9
Ethyl acetate	270	36.76	26.55	42.98	9.44	0.2
2-Butanol	270	31.00	16.52	29.29	38.52	1.3
1-Propanol	270	32.45	11.88	26.92	56.72	2.1
2-Methyl-1-propanol	280	39.61	12.66	35.26	58.78	1.7

Column 3 ("weight loss") gives the percentage of wood degraded. All organic solvents employed dissolve 20-40 % of the birch wood within one hour. Interestingly the carbohydrates and the lignin are



Cellulose



Chitin

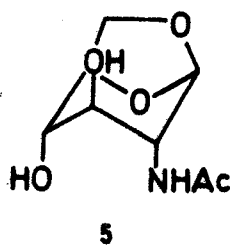


Figure 1. Products of cellulose and chitin degradation with supercritical acetone at 250-340°C.

degraded at different rates, as can be seen from columns 5 and 6. A high ratio Q of lignin to carbohydrate degradation in column 7 shows a high selectivity for lignin. Thus it can be seen that alcohols show strong preference for delignification with minor attack on carbohydrates, while ethers, esters and alkanes on the other hand preferentially attack carbohydrates at 250°C. Methanol shows a high degradation capability; ethanol has a better selectivity.

The selectivity is maintained over the temperature range from 240 - 280°C as was shown with ethanol and propanol-2 as solvents. The amount of degradation increases with temperature. But as can be seen from Figure 2, which shows the temperature influence in case of propanol-2, the ratio of Q decreases beyond 280°C, which can be explained by an increase of the pyrolytic decomposition of carbohydrates. The reaction products form nonhydrolyzable condensation products which are also analyzed as "lignin" and better should be called "humins".

Variation of pressure above critical pressure is of little influence. By increasing same from 100 to 350 bars in the aforementioned experiments the amount of degradation rises only slightly (1 - 2 %). The mass balance shows losses from 0 to 6 % due to formation of gases and low molecular weight compounds which are evaporated with the solvent and therefore escape analysis. This is contradictory to the results obtained by Calimli and Olçay[9] with the supercritical extraction of spruce wood with organic solvents. These authors performed static experiments in an autoclave and observed high losses due to formation of highly volatile compounds. Our data demonstrate clearly the advantage of a flow apparatus; sensitive compounds are quickly removed from the hot reaction zone, which apparently prevents further decomposition.

Figures 3 and 4 show results obtained by prolonged treatment of birch wood at 250°C with propanol-2 and 94 % ethanol respectively as solvents. In both cases an initial high reaction rate is observed. Further degradation (after 1 hour) proceeds at lower rate. Lignin degradation reaches in Figure 4 almost 80 % of the theoretical level after 4 hours. In principle total degradation of wood can be achieved with all solvents tested but this requires an increase of the temperature. Acetone for instance dissolves 92.5 % of wood within 12 hours with a simultaneous temperature increase slowly up from 250 to 340°C.

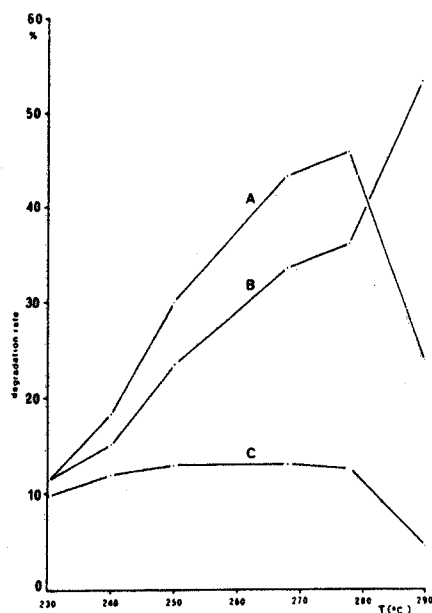


Figure 2. Influence of reaction temperature on degradation of birch wood with propanol-2 (standard conditions: sample weight 3g, solvent feed rate 3 ml/min, reaction time 1 h at 100 bar). Curve A: lignin; B: carbohydrates; C: ratio A:B x 10.

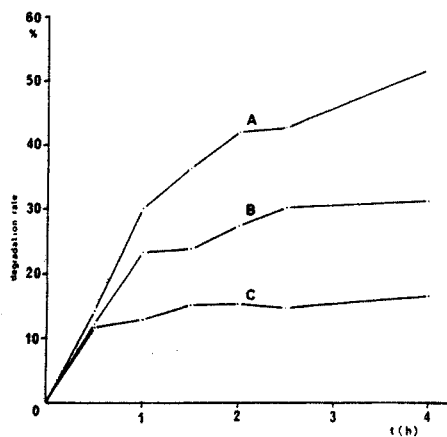


Figure 3. Time dependence of degradation of birch wood with propanol-2 at 250°C (sample weight 3g, solvent feed rate 1 ml/min at 100 bar, reaction time 1 h, Curve A: lignin; B: carbohydrates; C: ratio A:B x 10.

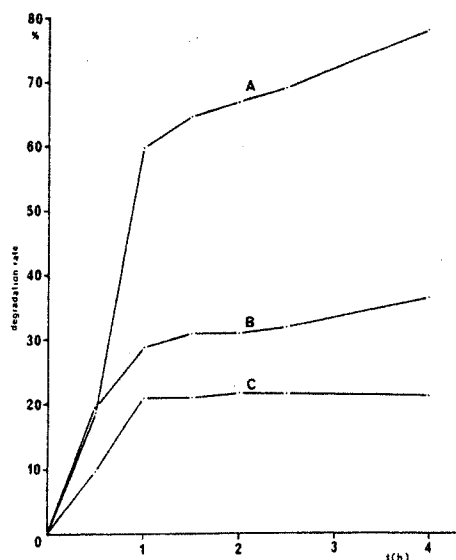


Figure 4. Time dependence of degradation of birch wood with ethanol (6 % water content) at 250°C (sample weight 3g, reaction time 1 h, solvent feed rate 1 ml/min at 100 bar). Curve A: lignin; B: carbohydrates; C: ratio A:B x 10.

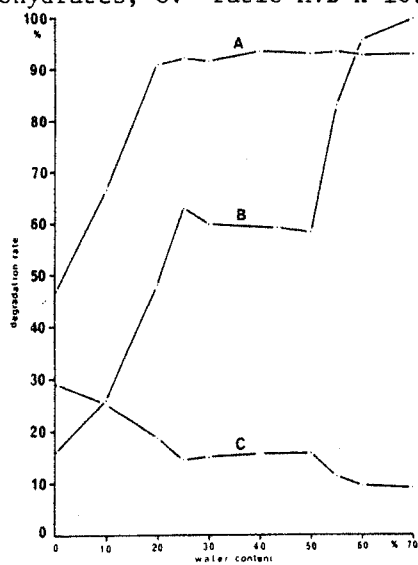


Figure 5. Birch wood degradation in dependence of water content (v/v) of ethanol (sample weight 3g, solvent feed rate 1 ml/min, reaction time 1 h at 100 bar and 250°C). Curve A: lignin, B: carbohydrates; C: ratio A:B x 10.

From Figure 4, in connection with the results given in Table II for absolute ethanol, it can be derived, that a water content of 6 % (v/v) of the solvent significantly increases total degradation. With pure ethanol after 1 hour 16 % of carbohydrates and 47 % of lignin are dissolved (Table II) while with 6 % water content (Figure 4) 28 % and 60 % respectively are degraded. Therefore we tested the properties of different mixtures of ethanol/water systematically. The results are given in Figure 5.

We found - and that corresponds with results obtained by Kleinert already some fifty years ago [10] - that there exists a broad range of mixtures of ethanol/water, where cellulose is left almost unchanged while lignin and hemicelluloses are dissolved on the other hand almost totally. If the water content is raised to 25 % (v/v) (molar ratio ca. 0.5) a dramatic increase of the degradation rates is observed for both lignin and carbohydrates to 92 % and 60 % respectively. Higher water contents of up to 50 % (v/v) (molar ratio ca. 0.8) do not change the results significantly. The extraction residue amounts to 35 %, which represents the original cellulose content of birch wood. - Can an alternative to preparing pulp for the paper or chemical industries under elimination of problematic inorganic chemicals and the related disposal problems be based on only water and ethanol? It should be mentioned in this context, that chipping or milling of the wood is almost unnecessary because of the high penetrating power of the solvents employed. But the cellulose thus obtained has an average degree of polymerization DP of 351 (that's relatively low), a content of alpha-cellulose of 87.2 % (that's low too) and a kappa number of 27.2, which corresponds to lignin left of about 4 % by weight. This is also low for wood pulp. Non hydrolyzable material (by sulfuric acid) amounts also to 4 %. These properties make our cellulose perhaps not so suitable for paper making; the Kleinert procedure [10,11] which works at lower temperatures could be a better alternative. However for chemical and for microbiological purposes the described treatment may have an advantage.

The lignin can be obtained as a fine powder. It has an average molecular weight of about 940, corresponding to 4 to 5 monomeric phenylpropane units. This indicates severe degradation of the original lignin. By gel chromatography (see Figure 6) we

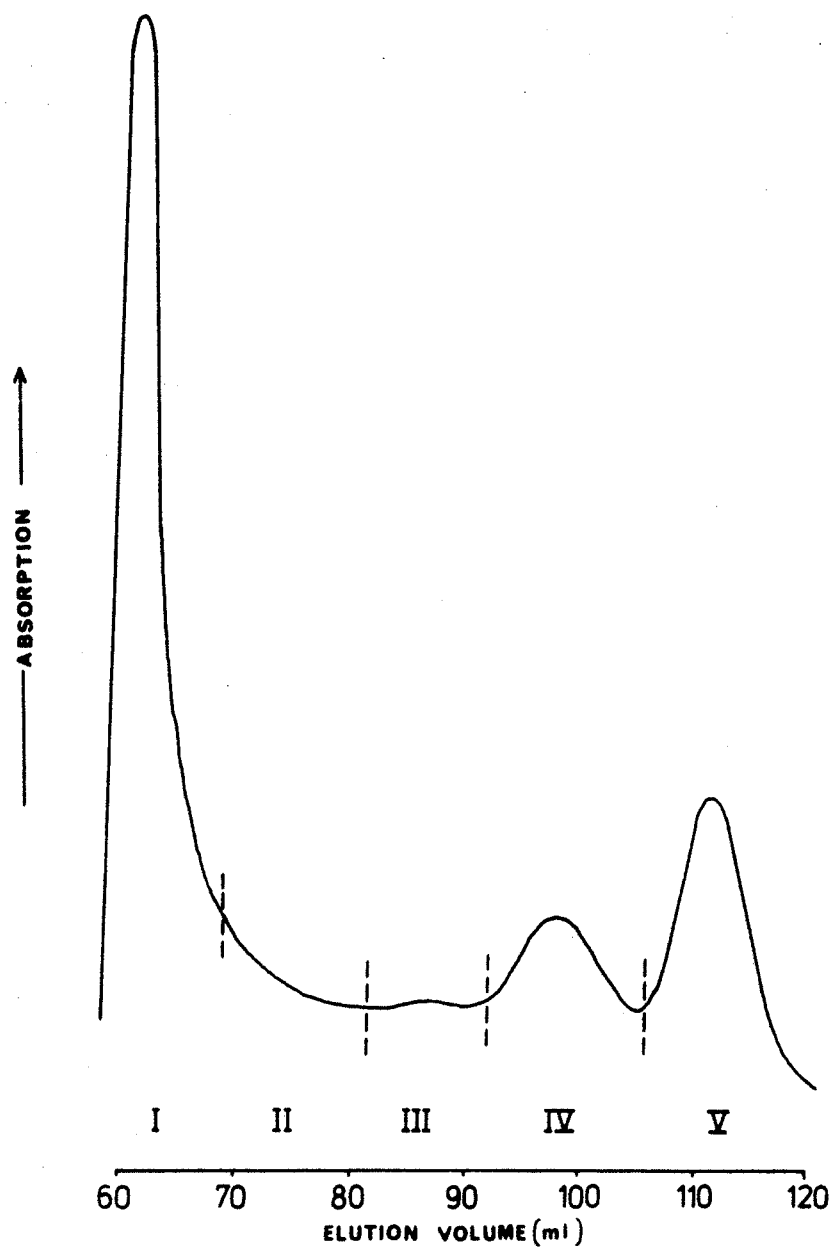


Figure 6. Gel chromatogram of dissolved lignin (Sephadex LH 20 in DMF). Weight of fractions I-V = I 52.5 %, II 12.6 %, III 5.6 %, IV (dimers) 12.9 % and V (monomers) 16.4 %.

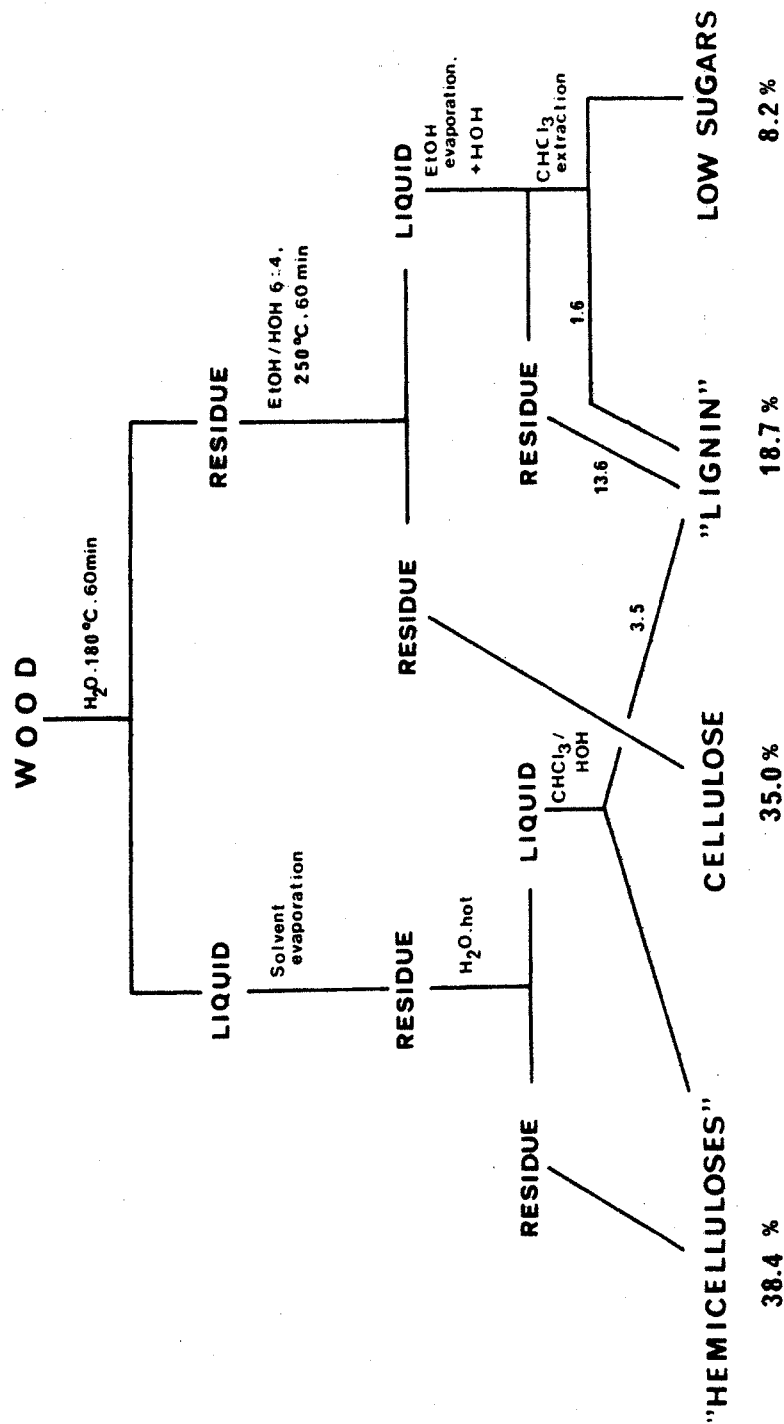


Figure 7. Mass balance of birch wood degradation with water/ethanol mixtures including prehydrolysis with water.

could show that monomeric and dimeric phenols are already present in the extract amounting to almost 30 %. Vacuum distillation of this lignin, which in itself is an interesting product gives more than 50 % yield of mostly monomeric phenols and some dimers.

Hemicelluloses are easily separated from lignin if they are simultaneously extracted from wood, but it is also possible to extract separately with more or less degradation all components from wood. This is shown in Figure 7. Beginning with water alone at moderate temperatures of about 180°C only hemicelluloses are extracted ("prehydrolysis"); by subsequent use of a water/ethanol mixture at temperatures of around 250°C lignin is extracted and cellulose is left unchanged. The mass balance approaches 100 % and demonstrates that only a small amount of gaseous products is formed.

From Figure 5 follows that ethanol/water mixtures with more than 60 % water content attack cellulose too. Thus it is possible to liquefy birch wood quantitatively within 1 hour at 250°C. The optimum seems to be in the range of a 70 % water content. Pure water is a bad degradation medium and imposes experimental difficulties because of poor solubility of reaction products in water. It should be mentioned that in most cases the experiments with ethanol/water mixtures have been performed at temperatures below the critical temperatures of these mixtures.

Cellulose degradation has been optimized with respect to low molecular weight compounds[12]. Figure 8 shows the time dependence of the conversion of microcrystalline cellulose ("Avicel") at 250°C with a 4:6 (v/v) ethanol/water mixture. After 2 hours conversion reaches 95 %. Glucose analyzes for 31 %. Besides it are found 13.5 % ethyl glucosides, 7 % anhydrosugars and 10 % hydroxymethylfurfural (HMF).

From Figure 9 the influence of temperature and the variation of water content on conversion rates and combined yields of monomeric sugars can be derived. The analyses of these products are summarized in Figure 10. By further variation of solvent flow rate the results of Figure 11 can be reached. At 260°C cellulose is hydrolyzed to a degree of 96 % within 1 hour with a 3:7 (v/v) ethanol/water mixture. Combined monosaccharides (including HMF) analyze for about 75 % of theoretical value. Glucose alone are 56 % of theoretical. This opens new ways

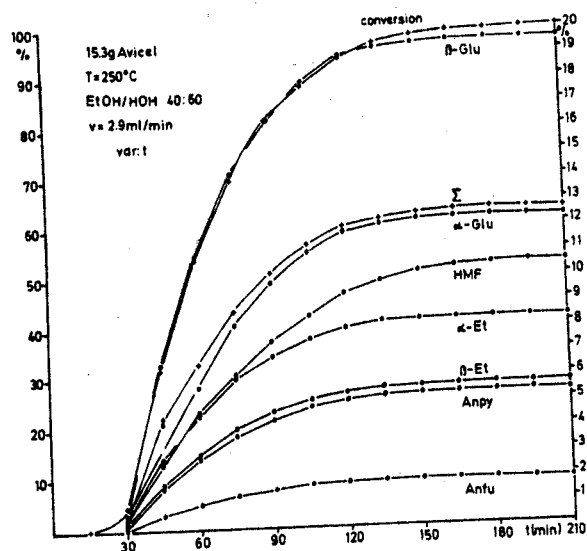


Figure 8. Time dependence of cellulose degradation with an ethanol/water mixture (4:6 v/v). Left-hand scale: conversion and sum of analyzed products (Σ). Right-hand scale: yields (based on charged cellulose) of β -glucose (β -Glu), α -glucose (α -Glu), hydroxymethylfurfural (HMF), ethyl α -glucoside (α -Et), ethyl β -glucoside (β -Et), glucosan (Anpy) and 1,6-anhydroglucofuranose (Anfu).

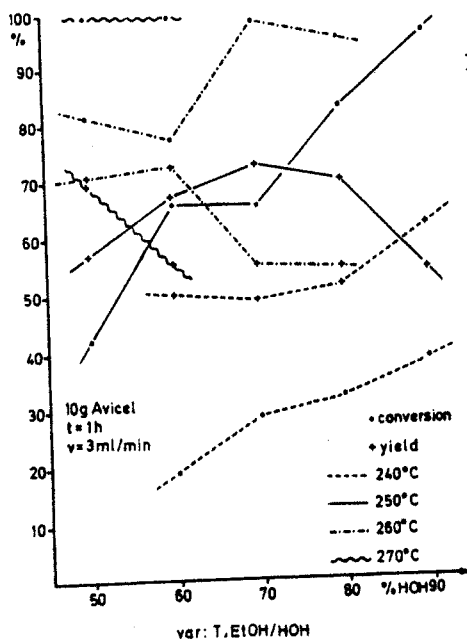


Figure 9.

Influence of water content on degradation of cellulose with ethanol/water mixtures at different temperatures. Conversion curves show amount [%] of degraded cellulose. Yield curves give sum of analyzed products (glucose, ethyl glucosides, anhydroglucoses and HMF) related to amount of degraded cellulose.

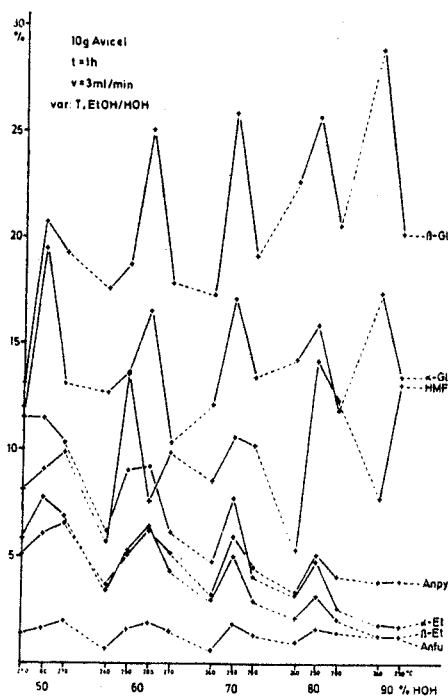


Figure 10.
Influence of temperature on sugar yields in degradation of cellulose with four different ethanol/water mixtures. Yields of β -glucose (β -Glu), α -glucose (α -Glu), hydroxymethylfurfural (HMF), glucosan (Anpy), 1,6-anhydroglucofuranose (Anfu), ethyl α -glucoside (α -Et) and ethyl β -glucoside (β -Et) based on amount of degraded cellulose.

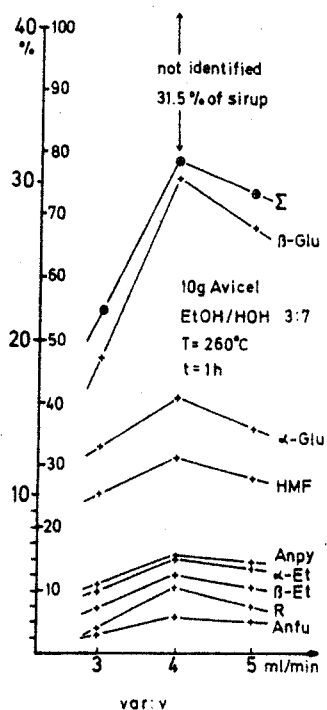


Figure 11.
Influence of solvent feed rate on sugar yields in degradation of cellulose near optimum conditions. Outer left scale gives yields (based on charged cellulose) of β -glucose (β -Glu), α -glucose (α -Glu), hydroxymethylfurfural (HMF), glucosan (Anpy), 1,6-anhydroglucofuranose (Anfu), ethyl α -glucoside (α -Et) and ethyl β -glucoside (β -Et). R = amount of residual cellulose. Inner left scale gives sum (Σ) of analyzed products. Total yield of degradation products obtained as sirup exceeds 100%.

for wood saccharification.

The same ethanol/water mixture was used for peat degradation[13]. Table III gives the results for white peat (low degraded, experiments No. 1 - 4) and black peat (high degraded, experiment No. 5). While almost 90 % of white peat can be dissolved, only 30 % of black peat is degraded under comparable conditions.

Table III. Degradation of peat with an ethanol/water mixture 3:7 (v/v). Experiments No. 1-4: white peat. No. 5: black peat. "Extr". = Extract weight %.

Experiment No.	Reaction Conditions				Results	
	Temp. (°C)	Flow Rate (ml/min)	Press. (bar)	Time (min)	Weight loss (%)	Extr. (%)
1	265	1 - 2	150	30	68,0	not d.
2	265	7	150	60	79,8	75,6
3	265	8	150	120	89,9	85,1
4	265	7	150	30	84,3	80,7
	275			30		
5	275	6 - 7	150	30	29,5	14,9
	285			30		

Higher weight losses (up to more than 60 %) are also attainable for black peat with solvents of higher ethanol content. The losses due to formation of gases are considerably higher for black peat than for white peat. In neither case the degradation products are liquids (or tars) but solids, which are partly water soluble (up to 55 %).

Contrary to this results with peat, municipal sewage sludge treated in the same manner yields again an oil which has an interestingly high content of long chain fatty acids[14]. Advantage of this treatment is the fact, that it is not necessary to dry the sewage sludge intensively before liquefaction, which is necessary precondition in other processes and which is expensive.

CONCLUSIONS

Organic solvents in the supercritical state such as alkanes, ethers, esters and alcohols ("supercritical fluids") are suitable for biomass disintegration and biopolymer dissolution and degradation in a temperature range of 240 - 340°C. Good properties for the mentioned purposes show also ethanol/water mixtures which are employed as liquids at subcriti-

cal conditions. From this it may be concluded, that a high density, an optimum high temperature and good solution properties of fluids are prerequisite for biomass transformation irrespective whether it are supercritical or subcritical fluids. Thus wood can be totally liquefied. On the other hand it is possible to prepare cellulose by dissolving hemi-celluloses and lignin only. Obtained lignin gives high yields of monomeric and dimeric phenols by vacuum distillation. High glucose yields are obtained by cellulose degradation with ethanol/water mixtures (3:7 v/v) thus opening new ways for wood saccharification.

LITERATURE

1. Shafizadeh, F., K.V. Sarkanen and A. Tillmann, Eds. Thermal Uses and Properties of Carbohydrates and Lignins (New York: Academic Press, 1976); Tillmann, D.A., K.V. Sarkanen and L.L. Anderson, Eds. Fuels and Energy from Renewable Resources (New York: Academic Press, 1977); Jones, J.L., and S.B. Radding, Eds. Solid Wastes and Residues, Conversion by Advanced Thermal Processes (Washington, D.C.: ACS Symp. Series 76, 1978); Tomlinson, M., Eds. Chemistry for Energy (Washington, D.C.: ACS Symp. Series 90, 1979); St.-Pierre, L.E., and G.R. Brown, Eds. Future Sources of Organic Raw Materials, CHEMRAWN I (Oxford: Pergamon Press, 1980); Jones, J.L., and S.B. Radding, Eds. Thermal Conversion of Solid Wastes and Biomass (Washington, D.C.: ACS Symp. Series 130, 1980); Klass, D.L., Eds. Biomass as a Nonfossil Fuel Source (Washington, D.C.: ACS Symp. Series 144, 1981).
2. The National Research Council. "Renewable Resources for Industrial Materials", (National Academy of Sciences, Washington, D.C.: 1976); Anderson, L.L., and D.A. Tillmann, Eds. Fuels from Waste (New York: Academic Press, 1977); Tillmann, D.A., Wood as an Energy Resource (New York: Academic Press, 1978); Bungay, H.R., Energy, the Biomass Options (New York: J. Wiley a. Sons, 1981); Rider, D.K., Energy: Hydrocarbon Fuels and Chemical Resources (New York: J. Wiley a. Sons, 1981); Sittig, M., Organic and Polymer Waste Reclaiming Encyclopedia (Park Ridge,

N.J.: Noyes Data Corporation, 1981).

3. Köll, P., and J.O. Metzger, Angew. Chem. 90: 802 (1978); Angew. Chem. Int. Ed. Engl. 17: 754 (1978).
4. Metzger, J.O., J. Hartmanns, D. Malwitz and P. Köll in "Chemical Engineering at Supercritical Fluid Conditions". This book.
5. Shafizadeh, F., and Y.L. Fu, Carbohydrate Res. 29: 113 (1973).
6. Köll, P., and J.O. Metzger, Z. Lebensm. Unters. Forsch. 169: 111 (1979).
7. Metzger, J.O., D. Malwitz, and P. Köll, unpublished results (1980).
8. Köll, P., B. Brönstrup and J.O. Metzger, Holzforschung 33: 112 (1978).
9. Calimli, A., and A. Olcay, Holzforschung 32: 7 (1978).
10. Kleinert, Th. N., and K. Tayenthal, U.S.Pat.No. 1.856.567 (1932); Kleinert, Th. N., Cellulose-chemie 18: 114 (1940); Das Papier 21: 653 (1967); U.S.Pat.No. 3.585.104 (1971); Tappi 57: 99 (1974); Tappi 58: 170 (1975).
11. Schweers, W., and D. Meier, Holzforschung 33: 25 (1979) and following articles: Baumeister, H., and E. Edel, Das Papier 34: V 9 (1980).
12. Brönstrup, B., Thesis, University of Oldenburg Germany (1982).
13. Köll, P., J.O. Metzger, and B. Brönstrup, Telma, in press.
14. Schuller, D., University of Oldenburg, private communication 1980.

Financial support for part of this work was provided by "Forschungsmittel des Landes Niedersachsen".