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THE NEW ORGANOSOLV PULPS – WILL THEY OUTRIVAL STARCH AS AN INDUSTRIAL RAW MATERIAL?

Abstract

Although the separation of cellulose from lignin by solubilization of the latter via sulphur derivatives makes the production of cellulose pulp fibres independent of external energy there are strong arguments against continuation of this technology. Thus, achievements of the sulphur free isolation of pulp from wood is reviewed.

Economic factors as well as regional availability of wood lead to an outlook that new cellulose can outrival starch in the European Union. In other countries starch lends itself to symbiosis with cellulose and lignin yielding combinations of carbohydrate products at price levels competitive with petrochemistry.

P.P.

In these days enthusiasts of Richard Wagner celebrate the 120 anniversary of the first performance of the "Dawn of Gods" in Bayreuth. In Cracow we certainly can remember a more recent birthday of one of the many renowned compository contributions of our local celebrity Christoph Penderecki whom I could admire as a conductor a few months ago in my home -town Wuppertal. But of more actual interest to members of our trade surely is the "Dawn of Sulphur" as the "Leitmotiv" for the next decade when environmental protection problems will outrival probably even such burning questions as providing jobs for the "run of the mill" work force in the whole of Europe.

Let me come now to the "gist of the core":

Wherever arguments are exchanged nowadays on how to preserve the world in which we live the topic of renewable resources is focused by keen interest. Within the total biomass assimilated in the billion tonnages range every season by help of our benevolent atomic reactor called "sun" two classes of substances are of prime importance:

carbohydrates (around 75 %) and lignins (about 20 % of total biomass)

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both making up about 95 % of all organic matter, besides the 2 % each of lipids and proteins as the backbones of life.

Among the carbohydrates cellulose accounts with about 45 % for almost half of nature, complemented by another 20–25 % of hemicelluloses and a smaller share of perhaps 2–5 % of starch. The latter one is also the prominent staple in the nutrition of men, whilst ruminants and selected mammals rely on hemicellulose and to a lesser extent on cellulose as their daily diet. The growth of heterotrophic animals including mankind, however, rests solely on the proteins of their plant and vegetable food /feed for autotrophic plants alone are capable to synthesize amino acids.

The latter require the availability of nitrogen as ammonia or nitrate produced either by thunderstorms rendering nitrogen into oxides transferred to arable land by rain or as ammonia by symbiosis with micro-organisms associated with the roots of plants or trees. As global balances teach lightnings alone sustain the amino acid supply for about 2.8 billion people whilst the larger part of the surplus populations satisfies its nitrogen demands primarily by the fertilizer industry burning fossils for the conversion of nitrogen to ammonia or nitric acid. Fortunately an unknown but nevertheless essential fraction of converted aerobic nitrogen is furnished by the activity of lignin decomposites in the soil. The latter originate from the lignin transferred to the soil by dead or plowed under plants together with the total floral matter (cf. fig. 1). Various micro-organisms care for the conversion of bioorganic material proceeding most slowly for lignins from trees, less slowly for gramineous lignins and almost instantaneously for all cellulosics, lipids and proteins.

The most important feature of such partially digested lignins for the maintenance of human life is elucidated by their capability to incorporate aerobic nitrogen in such a manner that zymogenic micro-organisms can convert N_2 into NH_3, Nitrates or even heterocyclic aromatics with the latter capable to swell bentonites or other planar silicates into sandwich structures supporting moisture exchange in seedbeds. Recombination of lignin fractions with converted proteins etc. finally end up in the formation of humus maintaining a varied microflora living in symbiosis with the floral matter cultivated – including starch bearing crops.

One should memorize that the relation of C : N in living plants is enhanced from 40 : 1 to impressive 10 : 1 in the humified soil with lignin as the crucial constituent. Hence, lignin is primarily responsible to allow mankind the harvesting of food in gross tonnages so that mass populations in cities can be nourished at all.

In this context it is astonishing to note that well humified soils are capable to convert aerobic nitrogen into nitrates or ammonia in amounts up to 300 kg/ha signalizing the considerable importance of this nitrogen source [1a]. In comparison nitrogen quantities by fertilizer addition rarely exceed 50 kg/ha in spite of having been tripled since 1930. Incidentally, the application of lignin for the restauration of contaminated

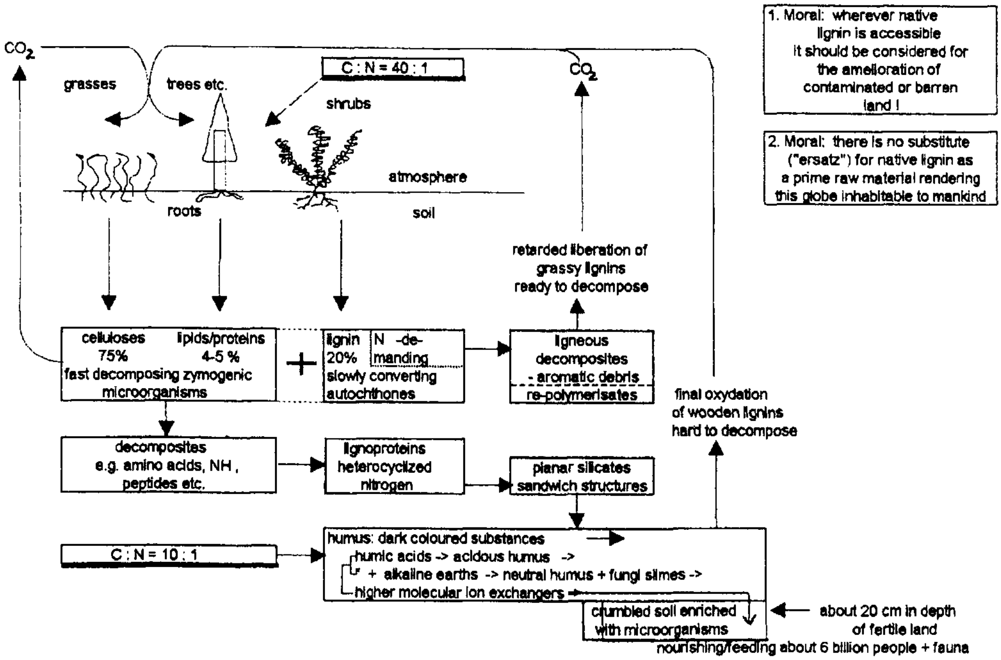


Fig. 1. The importance of lignin for the humification of soil.

soils was recently recommended by Fischer [1b] particularly after ammonolysis. Such "nitrogenized lignins" have already proven their usefulness as long-term-fertilizer furnishing nitrogen to the crop for several consecutive seasons preventing simultaneously wash out of nitrogen compounds to the underground water. – Certainly, Justus von Liebig, Haber, Bosch and Ostwald were not aware of the role of lignin and is decomposites for the assimilation of nitrogen essential for the synthesis of protein. Perhaps our ancestors surmised such contingencies for they harvested their fields only every third year after plowing under the weeds and grasses grown in the preceding two seasons – containing about 15 % gramineous lignin!

Hence, the burning of lignin or its conversion to sulphur – containing soil-poisoning derivates should be abandoned as soon as possible in order to preserve this valuable prime raw material for the amelioration of available land, replacement partially wise to use it as additive to selected petrochemical plastics rendered biodegradable beyond contents of more than 40 % of native lignin.

Consequences for the pulp producers

would imply that this industry would have to change the 120 year old policy to separate celluloses from lignin by solubilization of the latter via sulphur derivates, well known under the names sulphite and sulphate cooking processes. Both introduce sulphur in reduced or oxidized form to the backbone of the principal unit of lignin which is a phenylpropane. In any case lignin and its sulphur groups are reutilized by intricate processes implying the burning of lignin and other associated incrustations like hemicellulose to make the production of cellulose pulp fibres independent of external energy. Pulp and paper people consider this as an important argument for the benevolent environmental character of their industry relying solely on energy produced by regrowing fuel without any impetus on the global CO_2-balance! This is indeed the fact but neglects the prices for the loss of lignin as the most efficient natural fertilizer to prevent the cementation of arable land of the globe or to allow the cultivation of contaminated or barren areas. Also, the preservation of lignin in the humified layer of land devoted to agriculture and forestry would represent the first sink for carbon during a period in which the imission of fossile CO_2 has become a severe threat to our global climate.

For this and other reasons the pulp industry of the future will have to play a dominant role to conserve our planet in the actual inviting conditions simultaneously influencing the fate of human beings of the generations to come. The question is whether this key industry can suffice its responsibilities in the foreseeable future.

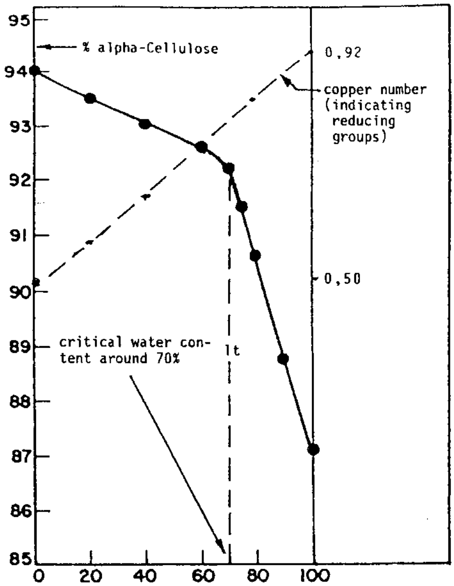
The answer is a clear "yes", for

The sulphur free isolation of pulp from wood

has been of concern to responsible researchers for about a century. As early as 1893 extraction of lignin by ethanol was tried by Scandinavian scientists, e.g. by Klason and Fagerlind. The first technological breakthrough was reported in 1932 when Th. Kleinert [1] at that time associated with the Silesion pulp industry, was granted the US-Patent 1856567 for the large – scale production of cellulose by ethanol – water cooks.

Due to circumstances Kleinert could not carry on with his interests until 1962 when he resided from the pulp and paper Institute in Montreal and became an independent college teacher (deceased 1982) directing furtheron his self-financed pertinent research projects. Several papers emerged between 62 and 76 [2] climaxed in ′71 by US-Patent 3585 104 [3]. His essential findings exhibit fig. 2 + 3 demonstrating beyond doubt that

a) ethanol-water mixtures with less than 70 % water entail only negligible cellulose-losses recommending water concentrations of 55–60 % as the most suitable liquor composition to enhance the solvent capacity for hemicellulosic oligosacharides at a level of braked hydrolysis with respect to cellulose decay.
b) an ethanol-content of 42.2 weight % approaches optimum conditions with respect to remove lignin down to residues between 2 and 4 % rendering the pulp amenable to chlorine-free bleaching operations.



ALPHA - CELLULOSE CONTENT OF ETHANOL-WATER COOKED COTTON IN % OF AIR-DRIED RAW FIBER CONTAINING ORIGINALLY 95% PURE CELLULOSE.

Experimental: 4 hours cooking in liquors of varying water contents up to 100%. Obviously at a critical water content around 70% hydrolysis proceeds at a much higher rate.

Inference: The molar ratio between ethanol and water at 70% water approaches 1 : 6 (= 19% ethanol) allowing the alcohol to cover the internal surface of all elementary fibers quantitatively with the latter accomodating ca.20% of all cellulose chains.Below this threshhold hydronium ions can attack the bridge O-atoms for hydrolysation!

(Reinterpreted from T.N.Kleinert,Das Papier 30,V18(1976)

Fig. 2. The effect of water content in ethanol-water mixtures on alpha-cellulose yield of raw cotton fibres during a four hours cook at 185°C.

Optimal pH-conditions belong to the know-how of the trade governing also the residual hemicellulose content of the bleached pulp fibres.

The physico-chemical aspects of the first Kleinert patent were first dealt with by Häusermann [4] in his ETH-thesis of 1944 on the wetting tendencies of selected plant cells by various solvents as exemplified in table 1a. Following the axiom “similia similibus solventur“ (virtually Ceasar's look at chemistry) it is almost self – evident that ethanol or 1-propanol come closest to the lipophilic character of lignin. Since ethanol is abundantly available both as a nutriment or industrial solvent also accessible by fermentation of hemicelluloses (a by-product of ethanol-water cooks) it is the preferable choice as a digesting agent for wood. Future research will probably add some modifiers to the Kleinert process as it happened to supercritical fluid extraction techniques (SFE) in the recent past.

Table 1a

Wetting capacity of mesophyllic cells derived from ascension velocities

<table>
<tr><td colspan="3">Wetting capability of mesophyllic cells (dianthus barbatus) derived from capillary ascension velocities according to lucas [a] extracted and enlarged from E. Häusermann [b]</td></tr>
<tr><th>Ascending fluid + lignin</th><th>Degree of lipophility in %</th><th>Wetting parameter : 10^6 (from wetting angles)</th></tr>
<tr><td>water</td><td>0</td><td>0.0</td></tr>
<tr><td>formic acid</td><td>28</td><td>–</td></tr>
<tr><td>acetic acid</td><td>45</td><td>–</td></tr>
<tr><td>methanol</td><td>50</td><td>24.9 ± 2.6</td></tr>
<tr><td>ethanol</td><td>66.7</td><td>31.2 ± 2.5</td></tr>
<tr><td>Lignin</td><td>70</td><td>–</td></tr>
<tr><td>1-propanol</td><td>75</td><td>42.1 ± 3.3</td></tr>
<tr><td>1-butanol</td><td>80</td><td>49.6 ± 3.5</td></tr>
<tr><td>1-hexanol</td><td>85.7</td><td>47.0 ± 4.2</td></tr>
<tr><td>1-octanol</td><td>88.9</td><td>44.1 ± 2.9</td></tr>
<tr><td>olive oil</td><td>90</td><td>42.4 ± 2.5</td></tr>
<tr><td>paraffinic oil</td><td>100</td><td>36.9 ± 0.8</td></tr>
<tr><td colspan="3">Lignin according to the ALCELL-process is made up of $C_9H_{8.5}(OCH_3)_1O_{2.5}$ – units of MW = 187.5 Dalton. Only O-atoms are considered as truly hydrophilic calling for a share of 56.0 Dalton (=3.5 O-atoms). Hence, the lipophilic section amounts to 131.5 Dalton – resulting in a degree of lypophility of 70 %! (probably 3 or 4 % more because of the limied accessibility of the O-atom in the metoxy-group!).</td></tr>
<tr><td colspan="3">Result: only polar fluids can wet wood!
Note: the plant cuticle remains undissolvable in polar fluids in spite of its amphiphilic character!</td></tr>
</table>

[a] Lucas R.: Über das Zeitgesetz des kapillaren Aufstiegs von Fluiden, Kolloid-Z. 23, 15, (1918).
[b] Häusermann: Über die Benetzungsgrösse der Mesophyllinterzellularen, Diss. ETH Zürich, Ber. Scheiz. bot. Ges., 54, 541 (1944).

The impressive capillary forces active in wooden tissues are set forth in table 1b. As such they are only valid for hydrophilic surfaces e.g. channels within the cellulose matrix. Hence, capillary effects are not so pronounced within suprastructures of lignin and similar incrustations. Intermediate efficiencies can be expected in contact regions between cellulosic matter and the aromatic sections of the interspersed lignin (benzene shows a surprising affinity for water! It can be mixed with absolute ethanol!) yielding shearing forces in interfacially bordering surfaces capable to sever hydrophilic from lipophilic contact zones.

The calculated ascension pressures in table 1b have obviously some bearing on practical applications. For example it could be shown recently by Stute [9] that pressures beyond 4000 bar (= 400 MPa) provoke gelatinization in various starches subject

Table Ib

Capillary effects in wooden tissues

The cohesion of so-called „water filaments" is responsible for the transport of plant juices up to the highest branches and leaves of tall trees. The corresponding cohesional tension was assessed by 0. Renner (Beih. bot. Zbl. 25(I), 183, 1919) to amount up to 300 bar equivalent to a water column of roughly 3000 meter.

Hence, one can calculate from the following ascension potentials: $h=2\gamma/\rho\cdot r\cdot g$

Radius r	Ascension power in height of water column	Bar	Pore diameter
0.1 mm = 100 μ	14.9 cm	–	0.2 mm
10 μ	149.0 cm	–	20 μ
1000 nm = 1 μ	15 m	1.5	2 μ
100 nm	150 m	15.0	200 nm
10 nm	1500 m	150	20 nm
5 nm	3000 m	300	10 nm
10.0 Å = 1nm	15 km	1500	2 nm
5.0 Å = 0.5 nm	30 km	3000	10 Å
2.5 Å = 0.25 nm	60 km	6000	5 Å

Note: rectangular pore of diagonal diameters around 5 Å accomodate micromolecules like water ($4.5\cdot4.5\cdot1.5 = 30$ Å^3) or ammonia! Hence, both of them are capable to mercerize cotton.

To be considered: ethanol decreases the surface tension from 22.3 at 22°C down to 15.5 at 100°C – which is much less than the equivalence for water (73/dyn/cm). Hence, actual capillary forces at 185°C are only a fraction of their spreading power at room temperature. A mild compensation for this loss is provided by the vapour pressure of ethanol around 22 bar at 185°C!

Scientific breakthrough: on April 25th, 1996, R. Stute (9) reported to attendants of the Int. Starch Congress in Detmold/FRG that pressures beyond 4000 bar trigger the cold gelatinization of various starches! Obviously the intensive swelling provoking this phenomenon requires the penetration of water into pores as narrow as 1nm – or to overcome bottlenecks within the porodine system of the starch supra – structure even smaller than 1 nm!

Stute's findings corroborate that the pore size distribution assessed here for wooden tissues is also valid for starch – the biological predecessor of cellulose during the evolution of plant life.

to suprastructures comparable to those met with in wood. The explanation of this surprising phenomenon lends itself by assuming that channels within the basic hinges of the starch microfibril are narrower than 1.0 nm which prevent water to penetrate voids beyond this bottleneck which can be overcome solely by higher pressures.

It is surprising that the Kleinert pulping process stirred up only limited interest in the Northamerican industry, save the consulting firms of Eli Cowan and the Pulmac Services in Montreal combining their financial efforts to carry out autoclave trials confirming and extending Kleinert's patent of 1971 to cover also lignin separation. Kleinert's financial resources were exhausted after the total sale of his real estate in the mid-seventies. In fact he was virtually deprived of his patent in '78 when the CP-Associates claimed a patent by Diebold et al. [5].

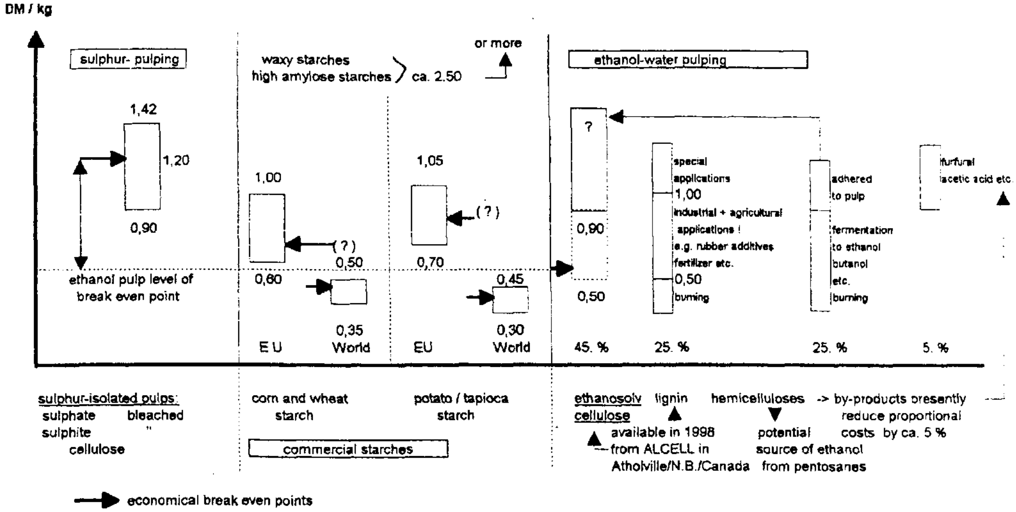
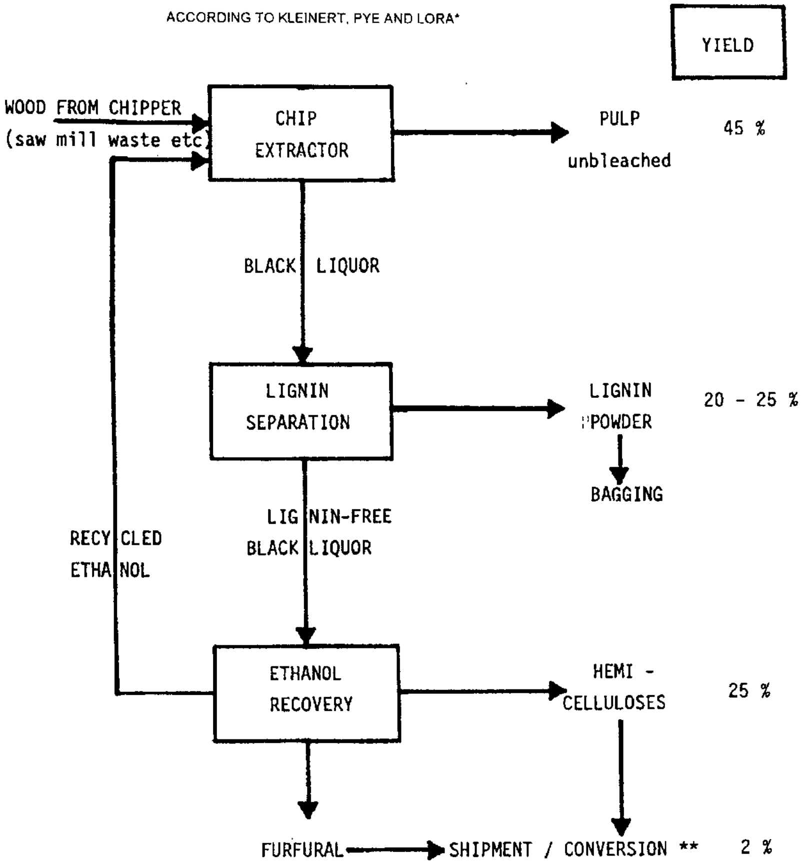


Fig. 3. Removal of residual lignin during a 60 minutes cook in a water mixture with 42.2 weight % ethanol at 185°C. Note: the concurrent loss of cellulose is negligible!

Realizing his situation Kleinert approached Bavarian authorities in 1976 who helped to finance a pilot-plant project in cooperation with MD Paper Mills in Dachau under Dr. M. Baumeister. Only four years later Baumeister reported in Baden-Baden that the Kleinert process could now be recommended for mill scale production – when he got a better position in another company. Apparently his successors saw everything from different point of view and replaced ethanol by methanol obsoleting also Kleinert's patent. But they failed to separate lignin from cellulose (as expected when comparing the wetting parameters in table 1) and required support by NaOH-extraction in a second step of their "Organocell"-process. In cooperation with a brilliant press campaign they succeeded to mobilize about 550 million marks to reconstruct the Kelheim pulp works equipped with a continous Kamyr-imitated digester to extract the lignin in a single step process applying methanol and sodiumhydroxide simultaneously. The result of taking so much risk at once was indeed shocking and agonizing : the mill was bankrupt in 1993 for the pulp was virtually unbleachable due to insufficient lignin removal and to channel formation in the 67 metre tall extractor. Another cause was perhaps the limited supply of development funds : only 15 million DM were provided to run the Munich pilot plant engineered for a ca-



* extracted and enlarged from J.H.Lora,US-Patent Nr. 5 196 460 (23.3.93)

** Burning - feed - fermentation

Fig. 4a. Schematic flow chart of ALCELL-ethanosolv cooking of hardwoods resulting from contributions by Kleinert, Pye and Lora.

pacity of only three tons per day. The blow-up of such facilities by a factor beyond two orders of magnitude is obviously beyond human control or assessment.

It is regrettable, however, that “Organosolv“-processes gained a bad reputation after the disaster of Kelheim – undeservedly, for the Kelheim procedure was really a “modified aquosolv-sodium-process“ – for methanol is more of a methylated water than a hydroxylated methane!

A much better fate experienced the perfection of Kleinert's and Diebold's patents on the American continent, where General Electric became interested in 1983 in the ethanol-water process in their pioneering research laboratory in Valley Forge/Virg. under Dr. Pye. GE bought the mentioned CPA patent and sold their Biological Energy

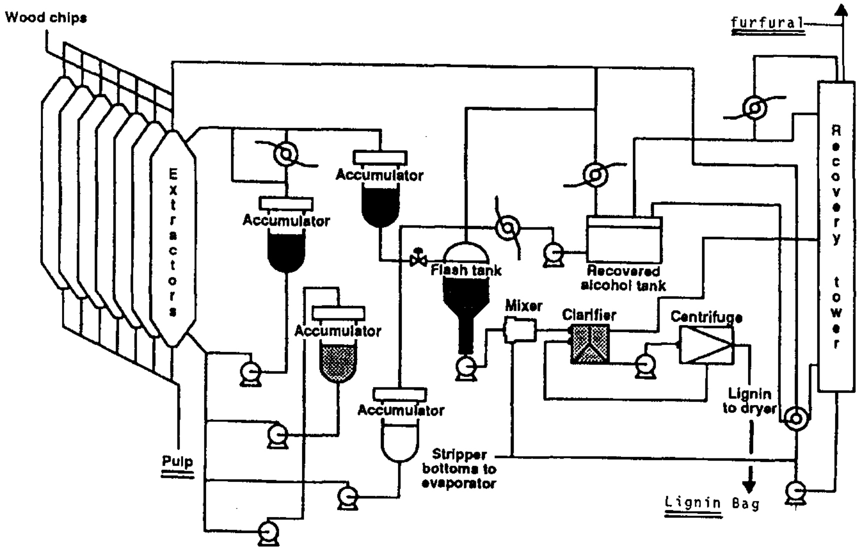


Fig. 4b. Semi – commercial flow chart of ALCELL demonstration plant in Newcastle/N.B./ Canada; Capacity per day: 10 - 15 t pulp, 5 - 6 t of native lignin.

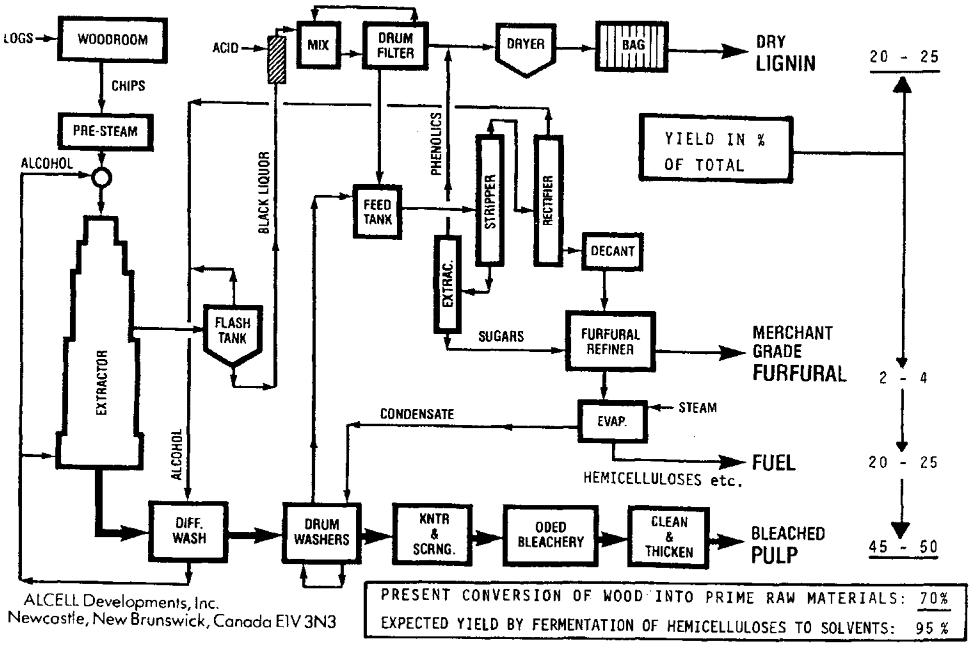
Corporation BEC a year later to G.S. Petty's REPAP company active in pulp and paper in Canada and the U.S.

In 1988 J.H. Lora et al. [5] were granted U.S. patent No. 4764596 concerning primarily the separation of the lignin suspended in ethanol-water which turned out as the decisive key to render the Kleinert – process as economically unbeatable – denoted meanwhile as REPAP's ALCELL (alcohol and cellulose) achievement. For it is now the first time in the history of pulping that digesting of wood can be carried out without taking resort to sulphur and moreover utilizing the chips to 70 % (much more is in the offing!) by adding to the usual 45 % cellulose another 22 % of lignin as an extremely valuable native prime raw material (besides furfural, acetic acid and other byproducts).

A schematic flow chart of ethanosolv cooking as perfected by Pye and Lora [5] is illustrated in fig. 4a yielding two prime raw materials (pulp and lignin) and one byproduct (furfural for the petrochemical industry). As soon as sufficient external energy is available fermentation techniques converting hemicelluloses to solvents (ethanol, aceton, butanol etc.) could push up the total yield to about 95 % of wood fed to the "extractor" replacing the classical digester.

With the accumulated know-how in their hands REPAP started a pilot plant for 95 million dollars in Newcastle/N.B. with a capacity of up to 15 tons/day of pulp and more than five daily tons of native lignin; the pertinent flow chart shows fig. 4b. In the past seven years more than 6000 cooks were performed – and not a single one failed

!!! Hence, one decided to re-model an idle sulphite mill in Atholville/N.B. scheduled to operate in 1998 with a capacity of about 130,000 t.p.a. pulp and 60,000 t.p.a. of sulphur-free-ALCELL-lignin. The flow chart of this continuously operated mill exhibits fig. 4c.



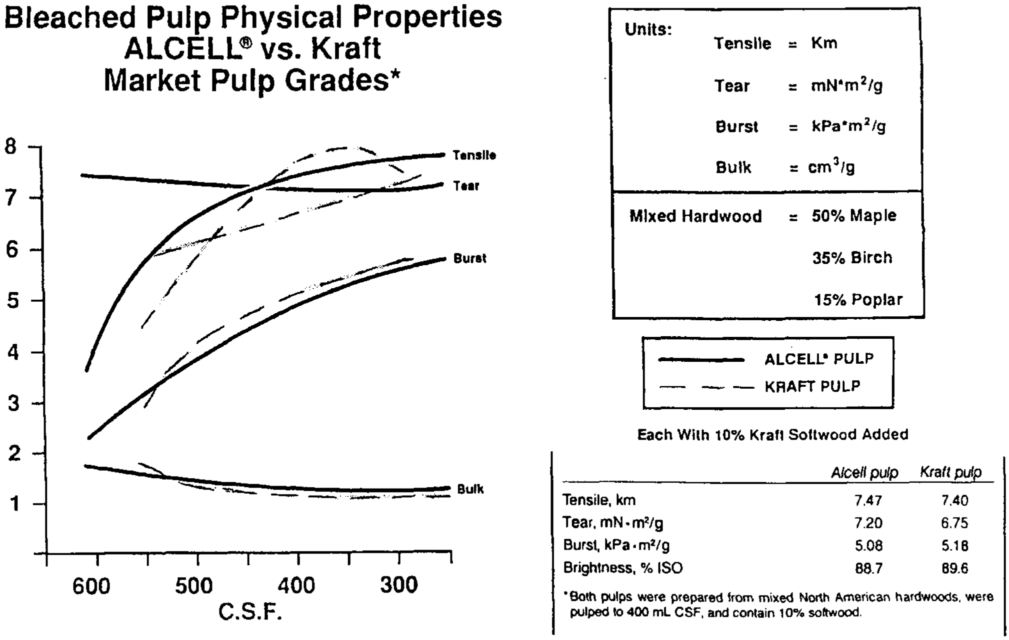
* presently erected in ATHOLVILLE/N.B./CANADA (scheduled for operation in 1998)

Fig. 4c. Flow chart of continuous ALCELL pulping in Atholville/N.B. Capacity per annum: 130 000 t of hardwood pulp, 60 000 t of native lignin.

This event will mark the beginning of the new age of converting trees into the prime raw materials cellulose and lignin and also ring the death-bell for the sulphate mills furnishing at present 90 % of the global pulp supply. For ALCELL-products can well compete with the qualities of kraft pulp as demonstrated by fig. 5.

As the comparison of the meaningful parameters tensile strength, tear, burst and specific volume prove quality differences between the two pulps cooked without and with sulphur respectively do not exist, for the mixture of chips was identical in both cooks. The addition of 10 % softwood considers the experience that any harvesting method for hardwood stands will always include a share of 10 % softwoods enhancing slightly the average fibre length.

Another benefit of ethanol pulping could count even more:



Units:
Tensile = Km
Tear = mN*m²/g
Burst = kPa*m²/g
Bulk = cm³/g

Mixed Hardwood = 50% Maple
35% Birch
15% Poplar

Each With 10% Kraft Softwood Added

	Alcell pulp	*Kraft pulp*
Tensile, km	7.47	7.40
Tear, mN·m²/g	7.20	6.75
Burst, kPa·m²/g	5.08	5.18
Brightness, % ISO	88.7	89.6

*Both pulps were prepared from mixed North American hardwoods, were pulped to 400 mL CSF, and contain 10% softwood.

Fig. 5. Relevant parameters for papermakers of two pulps made from identical hardwoods mixtures cooked as ALCELL and SULPHATE market pulp grades for comparison pulped from 600 to 300 C.S.F. Facit: as Tensile, Tear, Burst and Brightness bear out after pulping to 400 ml CSF differences in quality are not discernible.

As long as kraft pulping has been applied on mill scale its emitted odours have been considered as molestations not accepted in densely populated areas as met with in middle Europe. As table 2 bears out ethanol cooking outrivals the sulphur cook by impressive lower emissions particularly with respect to malodorous reduced sulphur compounds. No doubt that true organosolv pulping will never touch the limit concentrations of any emissions imposed by environmental legislation. As to chlorinated organic substances there exists even a gap of an order of magnitude in favour of ALCELL pulp, also a factor of five with respect to the limit prescribed by authorities. Certainly environmental protection will soon become the major argument when it comes to the collection of investment capital in order to finance ethanol pulping mills of which ten are required each year to satisfy the rising demand of two million tons due to mounting consumption of paper all over the globe.

However, the most convincing argument has been money ever since mankind relied on coins when trading. A comparison of production costs bears out that the proportional expenditures to produce one ton of pulp will amount two almost 500 DM/t for sulphate pulp. Ethanol pulping will require an additional 2 or 3 % due to

Table 2

Emission of SULPHATE and sulphur-free ALCELL pulping process in relation to environmental legislation

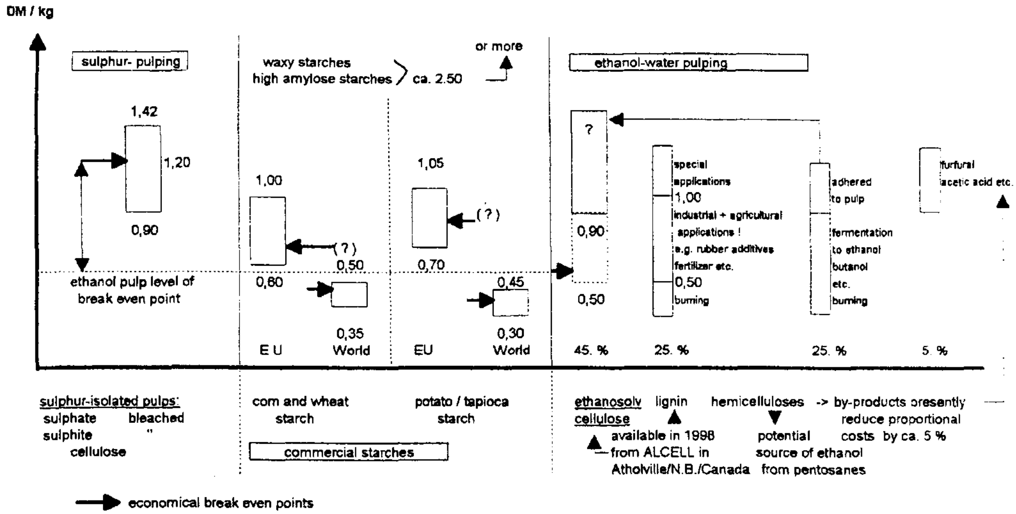
Emissions per ton of air-dry pulp for ALCELL- and sulpate cooking			
Emission into	ALCELL	SULPHATE	CANADIAN LEGISLATION
1. Air in mg/m^3 as			
a) reduced sulphur · (H_2S/mercaptanes)	0	0.22	0.18
b) dust	9	15.0	13.0
2. Water in g/m^3 as			
a) suspensoids	5	10	11.3
b) BOD	5	6	7.5
c) COD	7–12	10–12	?
d) AOX	0.3–0.5	3–5	2.5
Facit: The AOX-emission of the Alcell-process is by an order of magnitude smaller than in case of the sulphate procedure! Consequently the ALCELL-technology can be considered as the cleanest pulping cooking ever invented and will meet any target of any environmental legislation anywhere!			

higher capital investment for acid-proof steel. What matters more are the sales prices for the two varieties, which perambulate within an astonishing range below and above the break-even-equator as illustrated in table 3 comparing also the band width of prices paid during the last decade for commercial starches. In view of the fact that the novel ethanosolv-pulp makes use presently of two thirds only of the total wood upgraded to commercial products, we will experience for the first time in the history of pulp making since A. Mitscherlichs first sulphite production in Kelheim, that this process will be profitable in spite of the agonizing ups and downs of pulp market prices because the break even point of the ethanol pulping will be lower than the meanest price levels ever experienced. This situation will further improve when the actual conversion of 70 % of wood thanks to the added 20–25 % of salable lignin will be further enhanced by the utilization of the 25 % hemicellulose fraction for fermentative upgrading to ethanol and other solvents.

Total utilization of the wood implies that a sufficient share for mill-based energy production by burning of wood fractions is no longer available. Hence, the process depends on external energy supplies primarily from electric power stations. Fortunately this shortcoming is outweighed multifold by the earnings on hitherto lost lignin. If nuclear energy is available the replacement of sulphur-based pulp productions by

Table 3

Price levels for standard carbohydrate commodities since 1985 compared to expected sales revenues from ALCELL prime raw materials



Note: The economical break even point for ethanosolv-pulp is highly competitive with starch prices within the EU. Outside this community the combination of ethanosolv-cellulose with starches at world market conditions could outrival even petrochemical products – a boon to the environment!

ethanosolv mills could render a serious contribution to the reduction of the climate threatening emissions of CO_2 provoked by the consumers of car and heating fuel – besides the reduced supply of nitrogen fertilizer to the soil.

There is yet another decisive advantage of ethanosolv pulping:

Because the process requires no intricate recovery boilers for black liquor etc. save the relative simple redestillation of alcohol from water such mills can be operated successfully at much lower scales than sulphur consuming units yielding already profits at capacities of only 100,000 to 150,000 t.p.a. . This extra advantage minimizes also logistics of wood supplies shortening transportation distances.

The outlook of ethanol-pulping

is even brighter then anticipated so far. For the horizon will clear up further when the considerably higher profits allow larger assignments to R & D enabling researchers to tackle all experiments forbidden so far for lack of funds. As to the novel kind of pulp cooking there is still a drawback to be overcome for the proven technique can handle only hardwoods with an admixture of up to 15 % softwoods. Hence, the first objective will be to master also softwoods cooks "unpurified" by considerable admixtures of hardwoods. One approach in this direction was recently undertaken [7] and seemed to open up new prospects. Along this alley further trials should be envisaged to remove the residual lignin around 28 Kappa – number by physical extraction techniques – not by chemical bleaching!

The advent of a sulphur – free regenerating technique for cellulose by dissolving the undivided chain molecule in NMMNO some 15 years ago by American Enka researchers [8] and meanwhile practized by Courtaulds on a 20,000 t.p.a. scale (Tencel) suggests investigations as to the filtering off of the remnants of lignin by modern filtering techniques (accurel membranes etc.) rendering also chemical treatments superfluous. Last not least should endeavours be undertaken to marry truely dissolved cellulose with polysaccharides as filler – e.g. with micronized starch!

The dawn of sulphur remodels also the viscose industry!

Similar simplifications with virtually comparable improvements of the environment situation are presently achieved in the regeneration of cellulose for the large scale production of man – modified textile and technical fibres. As just mentioned 20 Kt of staple fibres p.a. have conquered the market recently whilst the biggest viscose producer, the Lenzing Fibres in Upper-Austria, are now embarking on a continuos filament production close to Vienna utilizing also the Tencel experiences based on NMMNO with the latter produced by Chemische Werke Hüls in North-Rhine-Westphalia.

Fig. 6 illustrates the effects of streamlining cellulose regeneration when disposing of sulphur implying also an improvement of the quality of such rayon. The latter approaches almost polyester fibres with respect to textile parameters. With the process still in his infancy one can almost predict substantial improvements within the next decade which hopefully leads to a replacement of the many hydrophobic petrochemical fibres which by their very nature are not real textile fibres for a breathing human skin, restricting their future to technical applications. All this will make the industrialized states a little more independent from Near East oil and help bridle CO_2 emissions.

The new cellulose – can it outrival starch?

The breakthroughs in the production of sulphur free pulp will not remain without impact on the starch industry. One example is particularly striking:

During the past two decades the demand of the paper industry for starch as an additive to the stock increased steadily in order to reduce the fall-through on the wire of a paper machine by better retentions of fines and to obtain cleaner waste water particularly due to the action of added cationic starch derivatives. Actually the

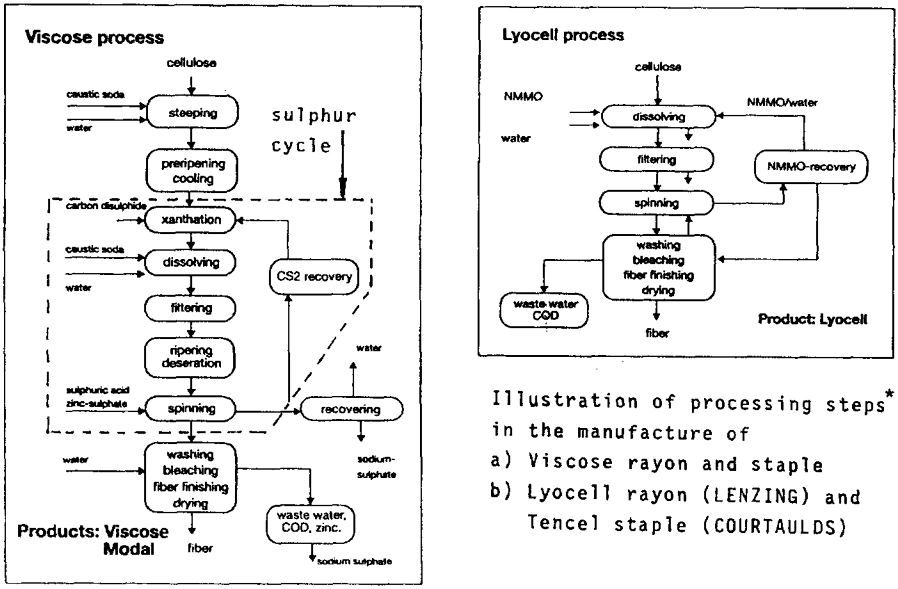


Illustration of processing steps*
in the manufacture of
a) Viscose rayon and staple
b) Lyocell rayon (LENZING) and
Tencel staple (COURTAULDS)

Note: sacrificing the sulphur cycle for the xanthation of cellulose streamlines the regeneration by NMMNO recoverable by 99% !

* Extracted and modified from R.Kampf and W.Schaumann,Lenzinger Berichte 75, 91 - 96(1996).

Fig. 6. The classical viscose process entailing the intermediate xanthation of cellulose was cut down to a few steps by renunciation on sulphur stages for the monomeric dissolution of cellulose in NMMNO.

consumption of starch by the paper industry exceeds a third of the total starch production allotted for upgrading in the industry, perambulating around 400 000 t of starch annually for the German paper and board production close to 15 mio tons in 1995.

The papermakers will probably be a moderate customer of starch producers in the future for two reasons:

Ethanol pulp can be cooked so that the pulp retains a predeterminable share of hemicellulose responsible for the fibre to fibre bonding governing the paper strength. Hence, hemicellulose can replace starch at lower costs!

It was recently demonstrated by Rahm [9] that the present policy to foster recycling of paper increases the CO_2 – load in the atmosphere due to the enormous energy consumption during deinking, sorting , bleaching and other efforts to maintain the required whiteness of the paper. From this point of view recycling can be recommended only for high – quality waste papers so that most of the collected waste paper (approaching 60 % in some western countries) should be better burnt - preferably right in the paper mills where people are experts in judging paper qualities. For waste paper still has the heating value of brown coal and does not add to the CO_2 balance!

The renunciation on waste paper on a larger scale will naturally increase the demand for primary fibres. The question arises:

Can our forests supply enough wood to produce paper from virgin fibres?

A reliable forecast can be dared at present only for the forests in the Federal Republic where only 35 million m^3 are harvested annually – just half the quantity of 65 mio m^3 growing, equivalent to a growth of 2.3 % or 6.75 m^3/ha. The official figures for Poland seemingly underrate the assets of the local forest industry. Therefore, table 4 has been submitted to pertinent Polish Institutes asking for correction and actualization.

Table 4

Wood resources in Poland and Federal Republic

<table>
<tr><th></th><th>Federal Republic[*]</th><th>Poland[**]</th></tr>
<tr><td>Total area of forests</td><td>9.6 mio ha</td><td>8.7 mio ha</td></tr>
<tr><td>Wood stock available per ha
country total</td><td>302 m^3/ha
$2.9 \cdot 10^9$ m^3</td><td>172 m^3/ha (250 m^3/ha ?)
$1.5 \cdot 10^9$ m^3 ($2.4 \cdot 10^9$ m^3 ?)</td></tr>
<tr><td>Total annual growth</td><td>65 mio m^3 = $\underline{6.75}$ m^3 / ha } 30 mio m^3 left in the forest</td><td>36 mio m^3 = $\underline{4.13}$ m^3/ha (?)</td></tr>
<tr><td>Current annual harvest</td><td>35 mio m^3</td><td></td></tr>
<tr><td>Current timber harvested</td><td>23 mio m^3</td><td>18.3 mio m^3</td></tr>
<tr><td>Wood allotted to pulp and paper[Δ]</td><td>9 mio m^3 (= 26 % of harvest)</td><td>3.6 mio m^3 (=10% of harvest)</td></tr>
<tr><td>Share of state forests</td><td>47 %</td><td>83 %</td></tr>
<tr><td>Share of Coniferous forests</td><td>67 %</td><td>79 %</td></tr>
<tr><td>Share of mixed woods</td><td>unknown</td><td>unknown</td></tr>
<tr><td>Waste paper recovered to paper consumed</td><td>56 %</td><td>31 % (only one deinking unit operating)</td></tr>
<tr><td colspan="3">Inference: the Federal Republic could easily convert almost 25 mio m^3 presently rotting in the forests into about 5 mio t of pulp and 2.5 mio t of native lignin (to be used as filler for plastics or as natural fertilizer to increase the assimilation of nitrogen in the soil) rendering her independent from pulp imports and allowing simultaneously to reduce the share of recycling waste paper from 60 % to perhaps 25 % excluding inferior grades serving in future as fuel for paper mills. – Probably similar marginal conditions prevail also in Poland.</td></tr>
</table>

[Δ] Residual wood from saw mills etc. + slim stems etc. due to forest care/supervision

[*] Datae collected by Dr. Thoma, MD Papierfabriken München (1995)

[**] Datae extracted from Z. Fornalski, Przegląd Papierniczy Special Issue 1995/96 (assessed figutes in brackets).

The facts assure beyond doubt that the Federal Republic for instance could easily make use of the 30 mio m^3 now rotting in the forests by directing the non-timber share to ethanolsolv pulp mills converting the required 25 mio m^3 to almost 5 mio t of pulp and another 2,5 mio t of native lignin. Both are primary raw materials (and no longer a waste product as the sulphur carrying lignin presently unavoidable) and could be put to use in many industrial or agricultural applications. Their reduced sales prices would further enable both products to penetrate markets hitherto dominated by petrochemical manufacturers.

Even classical paper and board application would profit from the availability of sulphur – free wood components if the favoured recycling policy of used fibres is restricted to the upper grades. For the use of virgin fibres e.g. in board or conjugated board would soon expel many packaging items made out of plastics from the market – a boon also to environment! More virgin fibres in paper would also call for fewer chemical additives in the stock and consequently entail cleaner waste waters.

Regrettably the new cellulose will threaten market segments formerly held by starch – but only in the European Union! In the by far larger "rest of the world" starch lends itself to symbiosis with cellulose and lignin yielding combinations of carbohydrate products at price levels competitive with petrochemistry.

Unfortunately, the most research contributions offered to starch congresses anywhere restrict themselves to the improvement of market – adapted products sold in limited quantities. But what the starch industry really needs is a pioneering research effort which would finally lead to a breakthrough opening markets in the million tons range.

A prerequisite would be that we are sufficiently informed about the suprastructure of starch. In this respect my coworkers have worked on two posters concerning the role of lipids in the conversion both of starch and cellulose. I am convinced that all essential informations for the cited breakthrough are contained in the literature last not least in papers written by our predecessors. For not very far from here around 1850 the Jewish grandmother of H.F. Mark was born in Lemberg (hopefully to be renamed one day!). This multiply gifted scientists found out in 1926 working at an Institute in Berlin-Dahlem that tenacity of all polymers including carbohydrates in the form of fibres, films or foils attains only a level equivalent to solely 2 % of covalent bonds. Hence, the overwhelming contribution to the work of rupture is provided by friction during elongation.

Having this in the background of our mind we should devote more of our concern to material sciences governing the performance of solid bodies – particularly of carbohydrates. In this context I remember the work of H.Frind in the late fifties who tripled the tenacity of copper rayon just by mild modifications of the stretch – spinning conditions. Unfortunately during the second half of this century the petrochemical industry has attracted the best talents in macromolecular chemistry. Fortunately this trend has changed for the better, as I mean, in recent years focusing public and political interest on problems like biomass conversion and on regrowing raw materials.

A steadily growing number of research institutes or government agencies concern themselves exclusively with polysaccharides problems as for instance the Carbohydrate Research Foundation in The Hague or the Non-Food Agro - Industrial Research Dissemination Network (NF-AIRID) headquartered in Newbury, 43 Kingsfisher Court in Great Britain and supported by 15 National Network Leaders in all European countries west of Finland and Greece. Financial support comes from Brussels and from governments in the respective countries. Interestingly, one such projects aims at the reduction of lignin synthesis in trees by transgenetic engineering resorting to antisense RNA. These researchers at the University of Toulouse hope to reduce in this way the amount of sulphur chemicals during pulping of trees to be felled in about 50 years (carried out under the ECLAIR programme). Other experts of AGROL in Guildford (England) were successful in adapting the Bacillus stearotherthermophilis to ferment the five – carbon sugars like xylose as the largest fraction of sugars in hemicelluloses from wood pulping also occurring in waste streams of maize syrup production. With the said bacillus active up to 75°C the production of bioethanol runs now as well as with glucose as substrate being on top also economical because hemicelluloses are cheaper than sugar or starch. Hence, it is foreseeable, that in the not too distant future wood and straw can be upgraded to cellulose, lignin and ethanol as a whole.

The latest developments in this respect will be reported during the Second European Biomass Forum in Graz in September 1996.

After all we live in a truly refreshing period in this time witnessing the uprise of carbohydrates and lignin as the coming raw material basis both for mankind and industry.

All we need is enthusiasm and perseverance to personify ourselves with our institutional and industrial research and development endeavours – and in case of success we often lack a generous person or agency providing the funds to get efforts protected in the form of patents involving fees not at the disposal of the ordinary scientist. What we need after all is a political force granting every citizen at least protection of one mental property – thereby enriching the country and all her citizens.

The USA give a good example concerning this dilemma: private persons and small companies asking for a patent pay only a few hundred dollars without obligation to pay fees when not put to use.

The Europeans should follow suit to benefit more from their own endeavours!

Thank you all for listening!

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NOWE PULPY CELULOZOWE Z PROCESÓW Z UDZIAŁEM ROZPUSZCZALNIKÓW ORGANICZNYCH – WYPRZEDZAJĄ ONE SKROBIE JAKO SUROWIEC PRZEMYSŁOWY?

Streszczenie

Chociaż oddzielanie celulozy od ligniny przez rozpuszczanie tej ostatniej poprzez jej rozpuszczanie w formie pochodnych siarkowych czyni produkcję włókien celulozowych niezależną od dodatkowej energii z zewnątrz, istnieje szereg argumentów przeciwko kontynuowaniu tej technologii. Dokonano przeglądu metod wydzielania celulozy bez pomocy związków siarkowych.

Względy ekonomiczne oraz lokalna dostępność drewna wskazują, że w Unii Europejskiej nowa celuloza wyprzedzi skrobię jako surowiec przemysłowy. W innych krajach skrobia pozostanie w symbiozie z celulozą i ligniną dając kombinowane produkty węglowodanowe o cenach konkurujących z produktami petrochemicznymi.