Glycoconjugate Journal (1997) **14:** 669–676

EGC1

Cellulose depolymerization to glucose and other water soluble polysaccharides by shear deformation and high pressure treatment

Arnis Kokorevics* and Janis Gravitis

Latvian State Institute of Wood Chemistry, 27 Dzerbenes St., LV-1006 Riga, Latvia

The simultaneous action of shear deformation and high pressure (SDHP) creates changes in the structure of wood and its main components (cellulose, hemicelluloses, lignin). The formation of water and alkali soluble polysaccharides under SDHP action, proceeds in seconds in the solid state, without the use of any reagents and solvents. Therefore, SDHP seems to be a technologically safe method and friendly to the environment. The amorphization of cellulose crystallites and depolymerization of cellulose chains were observed under a wide range of pressures (1–6 GPa), both for cellulose samples and the cellulose part of wood. Similar depolymerization occurs in the hemicellulose part of wood. The decomposition of polysaccharides under SDHP causes the formation of the water soluble part, whose content increases with pressure and the applied shear deformation. A maximum solubility of 40% and 55% was registered at 6 GPa following treatment of cellulose and birch wood samples. A higher output in the case of wood can be explained by a specific role of lignin under SDHP, which acts as a 'grinding stone' during cellulose and hemicelluloses destruction. As shown by high-performance size exclusion chromatography, the water soluble fraction obtained from cellulose contained glucose (2.6%), cellobiose (9.6%), cellotriose (16.6%) and other higher water soluble oligomers (71%). Almost complete dissolution (98%) of the treated cellulose sample can be achieved by extraction with 10% NaOH solution. The SDHP treated birch wood was subjected to submerged fermentation (with *Trichoderma viride*), and a 13% output of proteins was obtained. In this case, the water soluble part played the role of the so called 'start sugars'.

***Keywords*: glucose, polysaccharides, wood, cellulose, lignin, high pressure, shear deformation, depolymerization, solubility, fermentation**

***Abbreviations*: ASF, alkali soluble fraction; DP, degree of polymerization; EC, energy consumption; HP, high pressure; LMWS, low molecular weight sugars; MC, moisture content; MCC, microcrystalline cellulose; SD, shear deformation, SDHP, shear deformation under high pressure; SS, shear strength; WSF, water soluble fraction**

Introduction

The plant cell wall, and especially the wood cell wall, contains the largest part of the carbohydrate resources on earth. These biomass carbohydrates are in the polymeric form (cellulose, hemicellulose) and are closely associated with another natural polymer, lignin, which is a polyphenol type substance with a network polymer structure. Therefore, for plant carbohydrates utilization in the form of low molecular weight sugars (LMWS), it is necessary to solve two problems: separation of cellulose and lignin; and depolymerization of polycarbohydrates to monomers or oligomers.

In the cellulose and paper industry, the first task is usually achieved by removing the lignin component (delignification. A wide range of technologies has been developed. Many methods for the destruction of polysaccharides exist, each having specific advantages, short-comings and limitations. Taking into account the great importance of carbohydrate biomass, it is relevant to search for new methods to solve these two problems. The development of new treatment methods based on different forms of action seems to be a promising approach. In our opinion, simultaneous action of shear deformation under high pressure (SDHP) could be such a method.

The SDHP method

The SDHP method, as well as the equipment for its realization, have been developed by the outstanding American philosopher and physicist, the Nobel prize winner

* To whom correspondence should be addressed. E-mail: arniskk@edzi.lza.lv

0282–0080

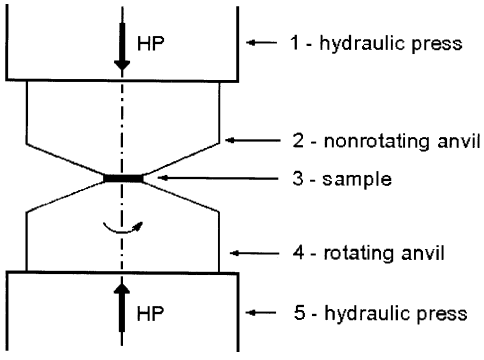

Figure 1. Schematic representation of a Bridgman anvils device (HP, applied high pressure).

P. Bridgman [1]. The best way to illustrate the essence of this method is to regard the principle of the operation of the so-called 'Bridgman anvils' (Figure 1). A thin layer of the treated sample (3) is put between two hard alloy anvil surfaces (2, 4). The anvils are placed in a hydraulic press (1, 5) which applies a high pressure (HP). The friction between the sample and the surfaces of the device protects against material outflow from the device. The rotation of the bottom anvil (4) against the upper one (2) creates shear deformation (SD) in the sample.

According to Bridgman [2], the external SD moment can cause two qualitatively different processes in the highly compressed state. If the pressure is lower than a certain critical value, the resistance between the sample and surfaces of the device is lower than the intrinsic flow strength in the sample. In this case, surface sliding takes place. The resistance increases with pressure and, at a definite moment, equilibrium is reached between the resistance and the flow strength. The surface sliding is changed by the plastic flow process in the substance volume. This process is characterized by the shear strength (SS), which depends on the sample structure and the pressure at which SDHP is realized. It is concluded that only the plastic flow regime provides conditions for effective chemical and physical processes. In some cases, if large pressure gradients are formed in different areas of the treated sample, then the rheological explosion phenomenon is possible. On the one hand, this process is undesirable, because the sample is thrown out from the device.

The SDHP method has some distinguishing features, which makes it different in principle from any other form of action used in solid state physics and chemistry [3]: Reaction rates can increase by up to three to eight orders of magnitude in comparison with similar reactions in the liquid state. Effective mass transfer and mixing proceed on the near-to-molecular level. Their formal evaluation with the 'diffusion constant' gives a value from 10 to 15 orders of magnitude higher in comparison with the processes in the solid state without SD. Processes occur only during SD. The severity of the applied SD (proportional to the rotation angle of the anvils in the 'Bridgman anvils' device) affects the SDHP process kinetics. The kinetics of the SDHP processes is less sensitive to pressure and temperature. The activation energy ($\Delta E = 4$–$6\ kJ\ mol^{-1}$) and activation volume (ΔV of the transition state $= -(1.5$–$5)\ cm^3\ mol^{-1}$) are about an order of magnitude lower in comparison with similar reactions in the liquid state. Pressure plays a rather limiting role in the SDHP processes – it governs the plastic flow of substances and allows a certain type of chemical reaction or physical transformation.

Pressure in a range of 0.1–10 GPa has usually been chosen by different researchers in their SDHP investigations. A wide range of inorganic, organic and polymeric substances have been tested under SDHP conditions [3]. In some cases, typical chemical reactions and phase transformations are also realized under SDHP, only the quantitative characterization of the processes is changed. In other cases, new changes and transformations are observed (for instance, polymerization of benzene).

Other types of equipment providing SDHP conditions have also been designed. The SDHP extruder with a rotating piston, constructed by Zharov and collaborates [4], allows the production of larger quantities of specimens and is a step towards the construction of continuous operating type SDHP devices.

The high efficiency of processes under SDHP has not yet been explained, however several theories exist, supplementing and contradicting one another [3]. It must be noted that the effect of the rise of temperature in the sample or in its local points is negligible, and cannot be responsible for specific features of SDHP.

Wood components transformation under SDHP

The object of our group's interest in the recent years has been the SDHP action on wood and its main macromolecular components – cellulose and lignin [5–9].

The investigations of the sample layers shift under SDHP indicate that the action creates a plastic flow in wood, cellulose and lignin samples. The shear strength of the plastic flow is found to be practically equal for wood and cellulose samples and higher for lignin. This indicates that the plastic flow process in wood at first occurs in the cellulose component.

Scanning and transmission electron microscopy photography shows the destruction of the cell and submicroscopical structure elements up to the formation of a glass-like mass.

Changes in the macromolecular and supermolecular structure of wood components have mainly been detected by ^{13}C CP/MAS NMR spectra (Figure 2). The spectra have been recorded at the Institute of Chemical Physics and Biophysics, Tallinn, Estonia by Dr Phys R. Teeaar.

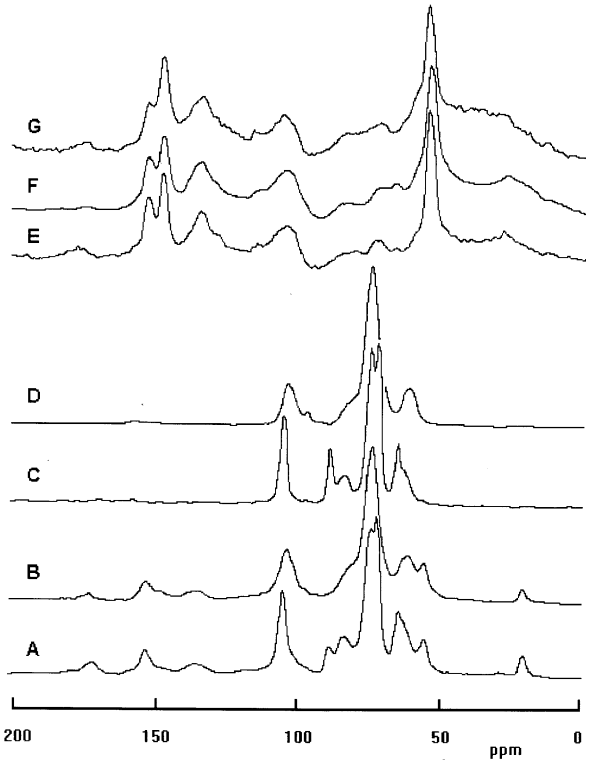

Figure 2. ^{13}C CP/MAS NMR spectra (Bruker CXP 200 spectrometer with a home-built MAS probehead with double bearing): (A) initial birch wood; (B) birch wood after SDHP (360°, 6.0 GPa); (C) initial microcrystalline cellulose; (D) microcrystalline cellulose after SDHP (360°, 6.0 GPa); (E) lignin isolated from aspen; (F) aspen lignin after SDHP (SDHP extruder, 2.6 GPa); (G) aspen lignin after SDHP (360°, 6.0 GPa).

Both cellulose component in wood and isolated cellulose samples exhibit the amorphization of native cellulose I crystallites (disappearance of the signals at 89 and 65 ppm), the broadening of the cellulose chain unit conformer distribution range (a significant decrease in the spectral resolution of cellulose signals) and chain depolymerization (with the shoulder at 97 ppm for the signal at 104 ppm). These transformations are observed over the whole range of the pressures under study (0.7–6.0 GPa), even at a small anvils rotation angle (10°, 6.0 GPa) and in cellulose specimens with different initial structure: microcrystalline cellulose (MCC), sulphite cellulose, and filter paper.

The amorphization of cellulose crystallites is also confirmed by small and wide range X-ray analysis. The comparison of wide angle X-ray measurements by supercomputer simulations [7] shows that partially destructed cellulose chains have a conformation in the amorphous phase near to that of cellulose II crystallites. The recrystallization in cellulose II crystallites is observed in the presence of water for SDHP treated wood and cellulose specimens.

Lignin transformations under SDHP are sensitive to the pressure range and vary for isolated lignin samples and lignin in wood. At 2.6 GPa, additional crosslinking of the lignin network in isolated samples occurs (the widening of all the signals attributed to lignin), while lignin in wood remains unchanged. At 6.0 GPa, the breakage of β-O-4 linkages is observed both for the lignin sample and the wood lignin component (a decrease in the intensity of the signal at 152 ppm, and an increase in the intensity of the signal at 148 ppm).

EPR spectra show a considerable increase in radicals after SDHP (360°, 6.0 GPa) in the lignin sample and also appear in the birch wood sample, but no formation of radicals is detected in cellulose. This allows the conclusion to be made that the homolytic splitting of lignin bonds proceeds both in wood and isolated specimens. We cannot make conclusions about the bond splitting in cellulose, because our sample preparation method (SDHP treatment at room temperature and subsequent freezing in liquid nitrogen for 10–45 min.) probably did not allow the detection of such radical formation. It must be noted that radical formations during cellulose milling at the liquid nitrogen temperature has been previously described [10].

Based on proton spin-lattice relaxation times (using ^{13}C CP/MAS NMR spectra), it has been detected that the naturally formed compulsory compatibility between cellulose and lignin macromolecular components in wood is destroyed under SDHP, and a new one is not created. The SDHP action provides the formation of partially destructed cellulose chains and a lignin fragment mixture in the amorphous phase at the near-to-molecular level. Also taking into account the disappearance of the other thermodynamically unequilibrium element of wood structure – cellulose I crystallites – it can be concluded that the SDHP action shifts wood as a thermodynamic system towards the equilibrium state.

The aforementioned changes of structure have been summarized and considered from the viewpoint of the wood cell wall fractal model elsewhere [11, 12].

Experimental

SDHP realization

SDHP experiments in a pressure range of 1.0–6.0 GPa were performed using a home-built 'Bridgman anvils' device (Figure 1). The experiments were characterized by the anvils' rotation angle and the pressure value. Anvils with a working surface diameter of 9.1 mm were used as the standard (in other cases, the rotation angle was recalculated according to this standard). The amount of sample which could be handled in one experiment was approximately 10 mg. The quantities of the sample necessary for further analysis and treatment were collected in a set of SDHP experiments. In cases where rheological explosions were detected during treatment in the device, the specimens

produced were not included in the set. The SDHP treatment was done at room temperature and air atmosphere.

Using a pressure range of 2.0–2.6 GPa, the SDHP process was also carried out in an SDHP extruder with a rotating piston. These experiments were characterized only by the pressure value used. The applied SD was dependent on the cylinder rotating speed (270° min^{-1}) and the gap between the cylinder and the extruder wall (0.1 mm), but were not calculated numerically. Therefore, it was difficult to compare the SD severity in these two types of SDHP equipment.

Materials

Birch wood (*Betula pubescens*) powder (<0.2 mm) with a moisture content (MC) of 6–8% in an air dry sample. Specimens were extracted with a benzene/ethanol (2 : 1 by volume) mixture for 10 h and subsequently with hot water for 10 h to remove the extracts.

Spruce wood (*Picea abies*) powder (<0.2 mm) with 5–6% MC. The extraction procedure was the same as described.

Microcrystalline cellulose (MCC)–PH101 (Avicel, USA), finely powdered with 4.4% MC.

Filter paper sheets with 5.1% MC.

Sulphite cellulose chips with 4.8% MC.

Other experimental details (the treatment procedures, analysis tools, etc.) have been briefly described in the text or references.

Results and discussion

Formation of water soluble sugars under SDHP

LMWS were detected after the SDHP action on wood and cellulose samples, and their quantity was evaluated as the content of the water soluble fraction (WSF). The quantity of WSF was measured depending on: (1) the pressure at the fixed value of the applied SD (360°) (Figure 3); and (2) the applied SD at a constant pressure (3.0 and 6.0 GPa) (Figure 4).

The yield of WSF was also detected for other samples, different methods of specimen preparation and for SDHP in the SDHP extruder with a rotating piston (Table 1). For comparison, the numerical values of WSF from the previous experiments are also included in Table 1.

The content of WSF increased with pressure and the applied SD and a higher content of WSF was observed for the samples obtained from wood rather than cellulose. There are several phenomena which are connected with the wood components transformation process during SDHP thereby illustrating this process.

The yield of WSF increases rapidly with the applied SD up to 360–540° of the anvils' rotation angle (Figure 4). Further application of SD is less effective, and the output of WSF leads to some asymptotic limit. Therefore, for a certain

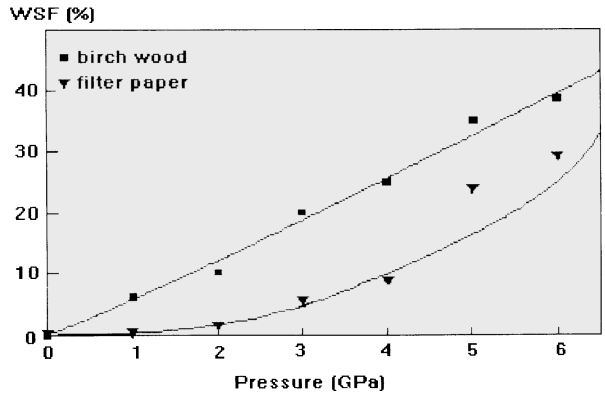

Figure 3. The content of WSF dependence on pressure (360° of the anvils' rotation angle).

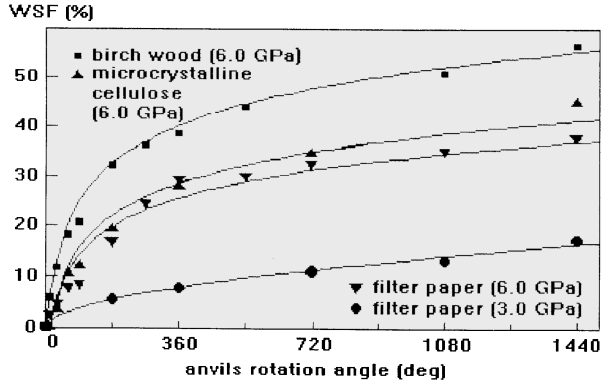

Figure 4. The content of WSF dependence on the anvils' rotation angle.

Table 1. The content of WSF.

Sample	*SDHP treatment conditions*	*The content of WSF*
Birch wood	360°, 6.0 GPa	38.7%
cellulose		
MCC	–''–	27.9%
Filter paper	–''–	27.7%
Sulphite cellulose	–''–	30.3%
The insoluble part of SDHP treated MCC specimen	–''–	33.1%
MCC	In two stage process 2 * [360°, 6.0 GPa]	54.0%
Filter paper		
Air dry [4.5% MC]	180°, 6.0 GPa	16.6%
Vacuum dry [0% MC]	–''–	43.1%
Wetted	–''–	1.7%
Birch wood	SDHP extruder, 2–2.6 GPa	22.8%
Spruce wood	–''–	18.5%
MCC	–''–	0%

sample with its plastic flow characteristics at a certain pressure, a limit of WSF exists which can be achieved by SDHP. This phenomenon is observed clearly both for wood and cellulose samples (MCC and filter paper) at 6.0 GPa. At a pressure of 3.0 GPa, this effect is less and the asymptotic limit was achieved at a higher SD value.

It may be assumed that the accumulation of short chains (oligomers) and LMWS in the system creates a steady-state condition of the plastic flow. In such a state, only the mixing of the existing components occurs, without further destruction of long chains to short chains and short chains to monomers. Such a proposal is supported by several observations. SS measurements of MCC and birch wood show that this characteristic remained unchanged during SDHP. Therefore, the reaction reagents and products which differ in principle only by the degree of polymerization (DP), have an equal SS value. In such conditions, there is no mechanism that can concentrate the SDHP action on less destructed cellulose chains. However the removal of the more transformed part of the mixture – WSF and repeating the SDHP action on the residual part allows more WSF to be obtained (Table 1). Therefore, in such a two stage process, a higher output of WSF can be obtained. Experiments with β-D(+)-glucose, D(+)-cellobiose and D(+)-raffinose under SDHP (360°, 6.0 GPa) did not exhibit destruction to monomers or polymerization, as detected by HPSE chromatography (a Gilson liquid chromatograph with a refractive index detector (RI 131) (France) and a Trisacryl GF05 column (30 and 0.8 cm) (Sweden)). IR spectra also confirm, that these substances are unchanged under SDHP up to 6.0 GPa, except for the modification of crystallinity.

As can be seen from Table 1, using cellulose samples with different supermolecular and macromolecular (differences in DP) structure:

(1) MCC – containing only cellulose I crystallites;

(2) filter paper, sulphite cellulose – containing amorphous and crystalline (cellulose I) parts;

(3) the insoluble part of SDHP treated cellulose – containing mainly the amorphous part and recrystallized cellulose II crystallites; all exhibited very similar values for WSF yield. ^{13}C CP/MAS NMR spectra after SDHP treatment are also almost identical for these cellulose specimens. Therefore, the WSF output is limited by the formation of a certain types of chain in the steady state and not by the supermolecular and macromolecular structure of the material. The rapid amorphization and depolymerization of these longer chains and further depolymerization in the amorphous phase continues up to the steady state.

A higher output of WSF is available from wood. Therefore, up to approximately 3/4 of the birch wood non-lignin part can be utilized as water soluble sugars. As shown by SS measurements, the lignin sample has a higher value of SS (0.53 GPa) compared with the cellulose sample (0.45 GPa). It is well known from SDHP investigations [3], that the components with a higher SS concentrate the SDHP action on the component with a lower SS value in mixtures. Therefore, in wood, lignin acts as 'grinding stones' against polysaccharides (cellulose and hemicellulose). Such features make wood and other lignin containing plant materials more attractive for LMWS production. WSF may be obtained from these materials not only in larger quantities but also in a lower pressure range. While a remarkable output of WSF from cellulose is observed at only 3 GPa, such quantities are obtained from birch wood at 1 GPa (Figure 3). This allows the use of SDHP devices, which provide a lower range of pressure. The operation with an SDHP extruder with a rotating piston allows WSF to be obtained from two species of wood (Table 1), while cellulose transformation does not reach the level necessary for WSF formation. Experiments with the SDHP extruder were carried out at the Institute of Organic Chemistry, Moscow, in collaboration with Professor A. Zharov.

A vacuum dried filter paper sample (0% MC) exhibited an approximately two times higher yield of WSF compared with air dry samples in the same conditions (180°, 6.0 GPa) (Table 1). It must be noted that many realizations of a vacuum dried sample are accompanied by rheological explosions. We consider that the absence of water in the system changes the intrinsic flow characteristics and thereby plastic flow conditions. More detailed investigations (SS measurements, WSF output related to the applied SD and MC) are suggested for the future. The opposite case – the filter paper sheets wetted thoroughly in water showed the formation of insignificant quantities of WSF, and each experiment was accompanied by rheological explosions during SDHP or pressure release.

Formation of alkali soluble polysaccharides under SDHP

To evaluate the less destructed cellulose and hemicellulose chains, it was partly solubilized in a 10% solution of NaOH (the alkali soluble fraction – ASF) was measured. The 10% NaOH solution has the capacity to provide the maximal solubility of cellulose chains [13]. The cellulose chains with DP 200–250 can be dissolved in this solvent at room temperature, while, for cellulose specimens with a disturbed intermolecular order, even up to three times longer chains can be dissolved. The content of ASF, in a similar manner to WSF, was determined depending on: (1) the pressure at a fixed value of the applied SD (360°) (Figure 5); and (2) the applied SD at a constant pressure (6.0 GPa) (Figure 6).

For the MCC specimen, with increasing pressure and applied SD, the yield of ASF is rapidly approaches 100%. A smaller quantity of ASF obtained from wood, compared with a cellulose specimen, was connected with the lignin part which, as described previously, was more stable in SDHP. The fact that the output of ASF from birch wood can exceed the content of the non-lignin part at a pressure of

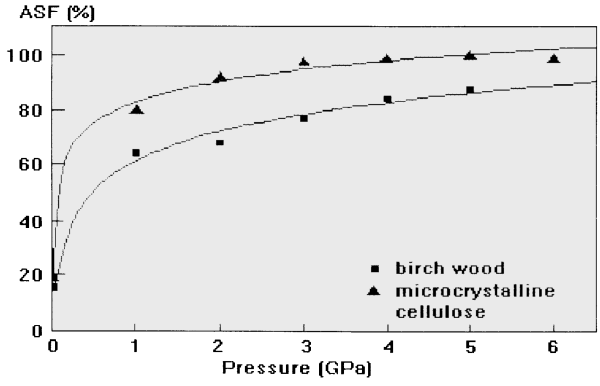

Figure 5. The content of ASF dependence on pressure (360° of the anvils' rotation angle).

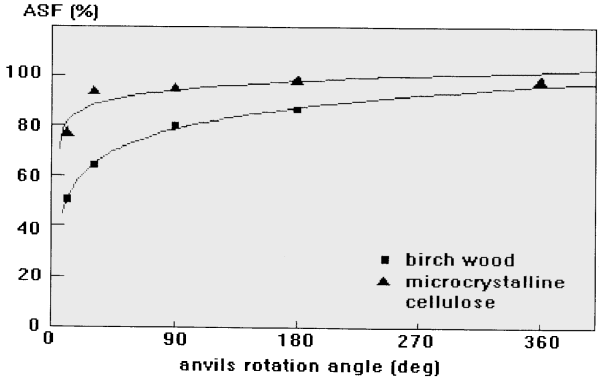

Figure 6. The content of ASF dependence on the anvils' rotation angle (6.0 GPa).

4 GPa (360°) or an anvil rotation angle of 90° (6.0 GPa) is surprising. A hypothesis can be made that in addition to polysaccharide products lignin destruction products also acquire the capacity to dissolve in alkali.

Composition of the water soluble fraction

The WSF obtained from MCC under SDHP (360°, 6.0 GPa) was chosen for further analysis. Its HPSE chromatogram exhibits four peaks (Figure 7). The last three of these agreed precisely with that of the model compounds: β-D(+)-glucose, D(+)-cellobiose and D(+)-raffinose. The wide signal with a maximum at 11.67 min was assigned to water soluble sugars – tetramer and larger oligomers. Unfortunately, model compounds were not available to us. The areas of these peaks were 2.7%, 9.6%, 16.6% and 71% for monomer, dimer, trimer and higher oligomers, respectively. Note that the peak, at 16.8 min, does not reflect compounds smaller than glucose, but is connected to the buffer salts effluence effect.

The ^{13}C NMR solution spectra of WSF and its fractions (fractionated by HPSE chromatography) also confirmed

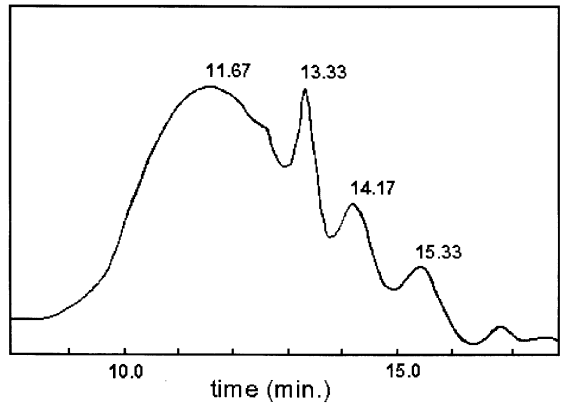

Figure 7. HPSE chromatogram of WSF obtained from MCC under SDHP (360°, 6.0 GPa). The chromatography system – 'Gilson' with the refraction coefficient detector RI 131 (France); the column – LKB-TSK G2000PW (30 and 0.75 cm) (Sweden).

that WSF consists of glucose and its oligomers [8]. Additionally cellobiose and cellotriose, cellotetraose, cellopentaose and cellohexaose were also detected. The spectra of WSF and its fractions have a group of signals which cannot at present be identified [8].

As can be seen from the chromatogram, higher oligomers prevail compared with the smaller ones and especially with glucose. This effect can be explained in a similar way to the existence of the WSF output limit during the application of SD and the phenomenon that, under the SDHP (360°, 6.0 GPa) action, the splitting of cellobiose and raffinose is not observed. The depolymerization of longer chains is more likely in the presence of oligomers during plastic flow. Shorter chains are prevented from further destruction to glucose and its dimer and trimer. Hence, there is obviously a limit of glucose and smaller oligomers which are accessible to the SDHP treatment. The dependence of this limit on SDHP conditions is an object for further investigations. The impossibility to obtain only glucose output cannot be regarded as a drawback of the method. On the one hand, further splitting is possible by other methods (hydrolysis) while, on the other hand, the high output of water soluble oligomers is also very attractive.

Submerged fermentation of SDHP treated wood

Obtaining proteins and other energy carriers from wood material requires a special pretreatment. Conventional pretreatment methods require considerable quantities of reagents, washing agents (water) and time. SDHP can be viewed as an attractive method for the pretreatment of wood and other biomass material for microbiological use.

Birch wood pretreated by SDHP (360°, 6.0 GPa) was subjected to submerged fermentation with *Trichoderma viride* in a bulb laboratory shaker [14]. The 12.9% true protein output of absolutely dry substrate was obtained

after a 72 h cultivation time (the biomass productivity $0.05\,g\,l^{-1}\,h$).

It is interesting that, compared with submerged fermentation of the wood pretreated by other methods: (1) A good yield can be obtained without lignin removal. Therefore, the lignin or its products did not act as a ferment poison or an effective inhibitor. (2) There is no need for the addition of so called 'start sugars' (usually, 2% of sacharoze). These are provided by glucose and other sugars of the WSF formed under SDHP.

Energy consumption during SDHP

To evaluate the prospects of SDHP action in the field of wood chemistry, it is important to know the energy characteristics of the process. Since SS measurements are done at a pressure of 5 GPa, energy consumption (EC) is also calculated at this pressure [6]. When applying SDHP, it is necessary to ensure two stages: (1) the achievement of the necessary pressure; (2) the realization of SD in the compressed state, where EC is proportional to the anvils' rotation angle.

For the first process, as compared to the second ($MJ\,kg^{-1}$ range), EC is insignificant (for cellulose, $43\,KJ\,kg^{-1}$ [6]), and for further SDHP characterization, only EC at the second stage is used (Figure 8). The EC of birch wood and MCC samples are equal. Figure 8 also shows an EC used in several conventional mechanochemical technologies in the pulp and paper industry [15].

Undoubtedly, such a comparison is only approximate, because SDHP is characterized only by the energy necessary to provide the physical processes, while the characteristics of industrial processes exhibit real EC, including the loss of energy in the equipment employed. At small quantities of the applied SD, where noteworthy amounts of WSF are observed and the ASF formation is high, the SDHP treatment EC is comparable with the EC in conventional technologies. An increase in the rotation angle allows the application of the quantities of energy which are several times higher compared to any mechanochemical treatment method.

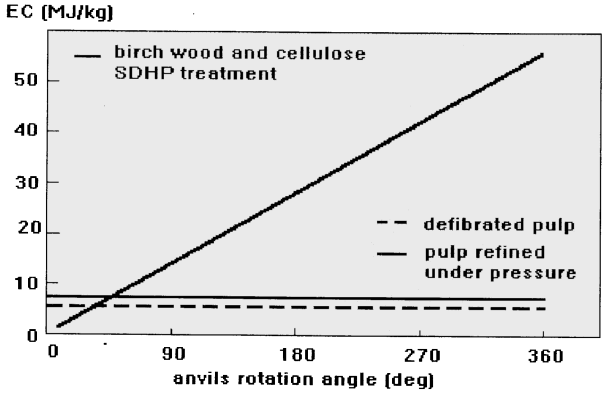

Figure 8. Energy consumption during the SDHP treatment of birch wood and cellulose specimens, dependence on the anvils' rotation angle and energy consumption used in technologies of the mechanochemical treatment of wood materials.

Conclusions

The SDHP method provides chemical reactions and phase transitions of macromolecular components of wood without the use of reagents (or their addition in minimal quantities), without large amounts of solvents and the preliminary sample treatment required by other methods. The reactions are realized at room temperature in a short period of time (seconds). The use of lignin containing materials is very promising, because lignin has a specific action as 'grinding stones' against polysaccharides. Taking into account the fact that polysaccharide destruction proceeds more easily compared with the destruction of lignin, and the part remaining after water and alkali extraction is enriched with lignin, the SDHP method can be characterized as 'decellulofication' rather than delignification.

There are some similarities between SDHP and the mechanochemical action on wood and its components: (1) destruction of the morphological structure of wood; (2) cellulose amorphization and depolymerization; (3) higher transformation rates in wood (in the presence of lignin) as compared with the cellulose sample; (4) a decrease in the transformation rates during the process, when the products of transformation are accumulated in the system.

It is not surprising, since mechanochemical devices also serve, to some extent, for the application of SD and HP. SDHP provides better transformations in a short period of time.

Our investigations were done using a laboratory scale device mostly at a pressure of 6 GPa. It allowed the detection of the transformation of wood and its components under SDHP as completely as possible and exhibited the maximal potential of the method. The feasibility of scaling-up the SDHP process to a pilot stage and further on to a technological process is essential. The use of a 'Bridgman anvils' type device has some drawbacks: (1) the small quantity of specimen treated; (2) the cyclic operation; (3) the need for hard alloy materials for the anvils design; (4) the rapid wear of the device and its working parts – anvils.

For the treatment of larger quantities of material under SDHP, the problem of process realization in a lower pressure range needs to be addressed. This will decrease the EC and the device's wear. Also, the use of other types of SDHP devices (extruders with conical ferule, extruders with twin screws, mills, etc.) which can be operated continuously. The pressure in these devices is moderate, compared with 'Bridgman anvils', so this use could be worthwhile. The SDHP extruder with a rotating piston [4] can be regarded

as the more promising device. Our investigations show that this type of equipment allows the successful application of severe structural transformation, especially in the case of wood specimens. To increase the effectiveness of the SDHP process in a moderate pressure range, the following could be utilized: (1) the addition of minor amounts of reagents; (2) the variation of plastic flow characteristics (an increase of the SS value). This will be the object of future study.

Acknowledgements

The SDHP investigations were done in close collaboration with: Professor A.A. Zharov (Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia) – the development and operation of the SDHP equipment, the discussion of results; Dr Phys. R. Teeaar, Proffessor E. Lippmaa (Institute of Chemical Physics and Biophysics, Estonian Academy of Sciences, Tallinn, Estonia – NMR investigations; Dr Habil. Chem. U. Kallavus (Material Research Center, Tallinn Technical University, Tallinn, Estonia) – scanning and transmission electron microscopy investigations; Professor T. Paakkari, Dr R. Serimaa, Dr S. Vahvaselka (Department of Physics, University of Helsinki, Helsinki, Finland) – small and wide angle X-ray analysis, supercomputer simulation of the cellulose chain conformation; Dr Biol M. Zeltina (Institute of Microbiology, Latvian Academy of Sciences, Riga, Latvia)– submerged fermentation experiments.

This research was supported by the Latvian Council of Science via grant No 585.

References

1 Bridgman PW (1935) *Phys Rev* **48**: 825–47.
2 Bridgman PW (1946) Rev Mod Phys **18**: 1–146.
3 Zharov AA (1984) *Usp Khim* **53**: 236–50 (in Russian).
4 Zharov AA, Shakhovskoi GP, Zhulin VM, Bogdanov AY (1988) *Instrum Exp Tech Engl Transl* **31**: 1061–62.
5 Gravitis J, Kokorevics A, Teeaar R, Zharov A, Lippmaa E (1991) *J Pulp Paper Sci* **17**: J119–23.
6 Kokorevics A, Gravitis J, Zharov A, Teeaar R, Kreituss A (1992) *Wood Chem* **N6**: 20–25.
7 Serimaa R, Vahvaselka S, Kokorevics A, Teeaar R, Gravitis J, Pakkari T (1992) *Univ Helsinki Rep Ser Phys* **HU-P-259**: 1–29.
8 Teeaar R, Lippmaa E, Gravitis J, Kokorevics A, Kreituss A, Zharov A (1994) *J Appl Polym Sci* **54**: 697–708.
9 Gravitis J, Kokorevics A, Vaivad A, Teeaar R (1994) In Third European Workshop on Lignocellulosics and Pulp. Extended Abstracts. Stockholm, Sweden, 187–91.
10 Hon DN-S, Srinivasan KSV (1983) *J Appl Polym Sci* **28**: 1–10.
11 Gravitis J (1994) *Lignin Newslett* **N2**, 2–4.
12 Gravitis J, Kokorevics A, Andersons B, Kallavus U, Teeaar R (1995) In The 8th International Symposium on Wood and Pulping Chemistry. Proceedings. Helsinki, Finland, 93–100.
13 Rogovin ZA (1972) *Cellulose Chemistry* Moskva: Khimiya (in Russian).
14 Zeltina M, Kokorevics A, Gravitis J (1992) *Wood Chem* **N6**, 94–95.
15 Fengel D, Wegener G (1984) *Wood Chemistry*, *Ultrastructure*, *Reactions* Berlin: Walter de Gruyter.