PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Fractionation of Lignocellulosics by Steam-Aqueous Pretreatments [and Discussion]

R. P. Overend, E. Chornet and J. A. Gascoigne

Phil. Trans. R. Soc. Lond. A 1987 **321**, 523-536
doi: 10.1098/rsta.1987.0029

Phil. Trans. R. Soc. Lond. A **321**, 523–536 (1987)
Printed in Great Britain

Fractionation of lignocellulosics by steam–aqueous pretreatments

R. P. Overend[1, 2] and E. Chornet[2]

[1] *Division of Biological Sciences, Rideau Falls Laboratory, National Research Council of Canada, Ottawa, Canada K1A 0R6*

[2] *Departément de Génie Chimique, Faculté des Sciences Appliquées, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1*

Physical processing or pretreatment of lignocellulosics concerns the ultrastructural modification of materials such as wood, straw and bagasse. The substrates produced can be subsequently converted by chemicals. The various pretreatment options will be discussed in the light of the ultrastructural, polymeric and chemical modifications that are obtained. The processes can be classified as follows: (i) steam; (ii) aqueous; and (iii) organosolvolysis treatments. All of these have their antecedents in the thermomechanical processes developed by the pulp and paper or fibreboard industries. Sequential application of thermomechanical technology leads to fractionation of the substrate into the major polymeric fractions: cellulose, hemicellulose and lignin in varying degrees of modification. A number of pretreatment concepts are now at a commercial scale and are being applied to produce foodstuffs from lignocellulosics for use by ruminant animals. The same techniques are being piloted in the energy and chemicals from lignocellulosics field.

1. INTRODUCTION

In seeking low-cost sugar from lignocellulosics for use in biotechnological routes to fuels and chemicals, much attention has been given to so-called physical techniques such as grinding, milling, irradiation and steaming. Techniques involving an obvious addition of chemicals, such as in pulping or acid hydrolysis of wood, are generally considered to be chemical processes. To date, much of the proposed treatment has focused on increasing the accessibility of the lignocellulosic substrate to enzymatic hydrolysis by cellulases with the objective of producing glucose for fermentation purposes. Before the energy concerns, essentially the same research was motivated by an interest in using low-cost lignocellulosic resources such as hardwoods, bagasse and wheat straw as feeds for ruminant animals. For example, Satter *et al.* (1981) examined the factors influencing the nutritive values of wood and forest products with respect to swelling with alkaline agents (NaOH and NH_3); delignification; steaming; acid hydrolysis; grinding and irradiation. The resistances to *in vivo* digestibility can be attributed to three major factors:

1. physical barriers due to the presence of lignin;
2. the crystallinity of cellulose;
3. lack of physical access to the substrate for the cellulase that is estimated to be ellipsoidal in shape with major and minor dimensions of 10 and 2 nm respectively (Cowling & Kirk 1976).

A more recent objective has been the fractionation of lignocellulosics to obtain each of the major components in the maximum yield and purity, thereby also maximizing income from

National Research Council of Canada contribution no. 25959.

each. In this instance, the goals to be addressed are those of extractive efficiency with minimum damage and loss of value. Thus it is to be hoped that it may be possible to obtain cellulose having characteristics allowing chemical substitution, lignin with thermoplastic and other polymer applications, and hemicelluloses for sucrochemistry.

1.1. *The ultrastructure of lignocellulosic and the fractionation problem*

Because of the research emphasis on temperate hardwood species as substrates for pretreatment, these will be used as models of the structure of lignocellulosics. Stalks from annuals such as wheat and of perennials such as sugar cane are not organized in the same way and are slightly easier to treat even though the basic structure is still a cellulose, hemicellulose and lignin composite. Softwood species are less easily treated and are usually subjected to a combined chemical and steam–aqueous treatment to be fractionated. Typically softwood chips are pre-impregnated with sulphuric acid, or SO_2 is added to the steaming cycle. Wood is composed of fibres that are the cells that form the supportive tissue of the wood. The major fibre element in softwoods is the tracheid (90%), which has dimensions of 2–4 mm length and 20–40 μm width. The wall thickness is 5 ± 3 μm. Hardwoods are much more variable and have several supporting and conductive elements. Libriform cells and fibre tracheids make up about 70% of the stem volume; storage elements such as ray parenchyma cells make up the remainder. Libriform cells are 0.8–1.2 mm in length and 14–40 μm in width. The wall thickness is 3–4 μm. (Sjöstrom 1981). Fibre separation is effected by a number of physical and chemical techniques collectively described as 'refining processes'. It is not really possible to effect further macromolecule separation by physical techniques and it is usually from this stage that various solvolysis and chemical extractions have to be performed to isolate the major polymeric families.

The lignocellulosic polymers are organized and bonded together through combinations of covalent and hydrogen bonds along with van der Waals forces. The cell walls are a composite structure with each cell encased in a primary cell wall of about 200 nm thickness composed of random and loosely organized cellulose microfibrils. The outer layer of the secondary wall S_1 is a crossed microfibrillar layer around the main cell wall S_2, which is 1–5 μm thick. The S_1 layer is composed of only a few lamellae, which can be visualized as sheets of microfibrils separated and encased in hemicellulose and lignin polymers; the S_2 layer has 30–150 lamellae according to whether the cell is part of the early or late wood of the tree. The final S_3 layer is thin (100 nm) and supports an interior 'warty' layer consisting of material left over from the life of the cell that has now become the lumen. The cells are held together by a lignin-rich layer called the middle lamella. The primary cell walls and the middle lamella 'sandwich' comprise the compound middle lamella.

The individual polymers are assembled together in each of the layers. Because of the significance of the pulp and paper industry, the location and the form of the cellulose has been the most thoroughly investigated. A linear cellulose molecule may be composed of as many as 10000–14000 β-D-glucopyranose residues and may have a total length of 5 μm. These individual polymer chains are bundled together (36 or so) with the composite microfibril having regions of amorphous cellulose separating blocks of crystalline polymer. The hardwood hemicellulose is a heterosaccharide branched polymer sometimes called glucuronoxylan, *O*-acetyl-4-methylglucurono-β-D-xylan, but more often referred to simply as xylans. Typically the degree of polymerization is around 200 and xylan is easily hydrolysed by both acids and bases. Lignin is a polymer of phenylpropane units bonded through in the main aryl ether linkages and other bonds. The molecular mass of 'native' lignin is 20000. The typical composition of hardwood given in the order cellulose, hemicellulose and lignin is 40, 25, and 21%, with 39, 28, and 28% respectively for softwoods; the balance is made up of other components including extractives (Sjöstrom 1981).

The objectives of the paper maker (the user of chemical and mechanical pulps), the producer of animal fodder and the fuels and chemicals producer have much in common. The primary goal of each is to open up the initial lignocellulosic structure to something approaching the scale of an individual fibre, say 1–4 mm in length by 50 μm in width. Post-treatment (sometimes called refining) is then undertaken to meet the needs of the application: for paper manufacture the fibre should become flexible and have an extensively fibrillated surface; for animal feed the substrate is probably accessible as it is; and for the purposes of fractionation easy extraction and filterability is desired.

1.2. *Comminution*

Physical treatments such as crushing and grinding have been shown to be effective in creating accessibility to enzymes but unfortunately the treatments have to be carried out down to particle sizes passing 400 mesh screens, or less than 50 μm in size. The treatment also decrystallizes the cellulose and increases the specific surface area. As with all comminution processes there is a large energy penalty incurred in creating new surface area (typically, 0.5 mm wood particles require 100 kW h t^{-1} and 50 μm wood particles require more than 3 MW h t^{-1}). In fact, the energy and final operating costs of such treatments become prohibitive at about a particle size of 200 μm (Datta 1981).

1.3. *Refining and steaming*

The link between steam and aqueous fractionation treatments and the pulp, paper and wood products industry is very clear. Aqueous-phase prehydrolysis is used in the Kraft (sulphate) process to eliminate a large fraction of the hemicellulose before manufacturing high-purity α-cellulose (Wenzl 1970), and steaming is a critical component of most mechanical refining processes such as steamed ground-wood production and in thermomechanical pulping. The Asplund process for making fibreboard also involves steaming as a major component while the Masonite process is primarily a steam process that creates a gunstock that is subjected to a very light mechanical refiner step prior to fibreboard manufacture. Depending on the duration and temperature of the steaming stage the yield of fibre is in the range of 80–95% with the major components that are leached from the pulp being water-soluble extractives and hemicellulose fractions.

Although steaming processes have been mistakenly identified as physical processes, they are clearly chemical in nature when the changes in the ultrastructure and chemical composition of each of the lignocellulosic components is followed. At the macro-scale, however, the dominant visible effect is of fibre separation into individual fibres and bundles such that the accessibility to enzymatic attack is already much enhanced. Marchessault & St Pierre (1980) considered the steam-explosion process described in DeLong's patent (1981) to be a thermomechanical process.

2. STEAM–AQUEOUS PRETREATMENT TECHNOLOGY

The concept of steam-explosion techniques to create defibrated material with accessible cellulose or fermentable sugars can be traced to two patents lodged with the U.S. patent office in the years 1927 (Babcock 1932) and 1925 (Mason 1928). The first described experiments conducted with pine subjected to saturated steam in the temperature range 218–262 °C for between 0.5 and 5 s, explosively discharged and treated to aqueous extraction and fermentation to give a yield of 14–16 % of the initial sugar content. The second described one means by which this could be done on an industrial scale through the use of what has become known as the Masonite process gun.

2.1. *Steam explosion: batch*

The use of a Masonite process gun to effect the separation of hemicellulose and then of lignin by successive extractions with water and alcohol solvents to leave a reasonable quality cellulose is described in a patent by DeLong (1981). The apparatus is shown by Marchessault *et al.* (1983) along with a proposed extraction and fractionation scheme. Detailed patents covering modes of operation and specific operating regions have followed (DeLong 1983; Foody 1984). A variant of the explosion process specifically adapted to the pulping of non-wood species such as bagasse and wheat straw is known as the Siropulper (Mamers *et al.* 1981). In this process, an inert gas is used to drive the resulting pulp through a proprietary set of defibration bars (Mamers & Rowney 1979).

2.2. *Steam explosion: continuous*

A continuous steam treatment has been under development since 1973, initially for the animal-feed application but latterly for fractionation. The Stake system is described by Muzzy *et al.* (1983) and consists of a horizontal pressurized digester that is fed continuously by means of a patented coaxial reciprocating feeder (Brown & Bender 1981). The residence time of the biomass in the digester is controlled by the feeder and a patented discharge valve system that operates intermittently (Brown 1981). The present Stake II system with a 25.4 cm feeder is capable of treating 100 kt a^{-1} of biomass feedstock.

2.3. *Liquid-phase treatment*

The liquid-phase treatment has been carried out at a rate of 1 kg min^{-1} of 15–20 % slurries of *Populus deltoides* in water. The mechanical defibration and defibrillation is effected by means of a passage of the slurry at temperatures greater than 160 °C through a homogenizing valve with pressure differentials of 5–20 MPa. A description of the process development unit is given by Koeberle *et al.* (1985). The feedstock material is usually comminuted to less than 1 mm in length. A medium-consistency slurry is then prepared in a pretreatment loop before passage through the main homogenizing valve that is followed by a plug-flow reactor and quench system.

3. THE REACTION ORDINATE

It has been a general observation that in both the aqueous-phase prehydrolysis of the Kraft pulping process (Brasch & Free (1965) and in the steaming process (Monzie *et al.* 1984; Foody 1984) it is possible to trade duration of treatment and the temperature of treatment such that equivalent final effects (such as pulp quality or enzyme accessibility) are obtained. Implicit in this concept is the assumption that the overall kinetics follow a first-law concentration dependence and that the rate constant has an Arrhenius-type dependence on temperature, although the apparent activation energy may itself be a function of temperature. Thus time (t) and temperature (T) have been combined into a single factor for evaluating pulping processes in general. The best known of these is the 'H' factor method in which the rate at 100 °C is chosen as unity and the rates at all other temperatures are related to this standard. For a pulping process in which T varies with t, the area under the curve of relative reaction rate against time is the 'H' factor (Sjöstrom 1981). The 'P' factor of Brasch & Free (1965) is similar and will be used here as a guide in the severity of the individual treatments. The relative rate function chosen is

$$P_t = \exp\left((T_r - T_b)/14.75\right)$$

where T_r = temperature of reaction,

T_b = base temperature, i.e. 100 °C.

The product of P_t and t, the time of reaction, is the 'P' factor and has units of time. To avoid confusion of terminology, the 'P' factor will be referred to hereafter as the reaction ordinate, and will have minutes as the unit of time. The reaction ordinate should not be viewed as anything other than a means of weighting the time at reaction temperature by an arbitrary rate process, chosen simply as a device to combine T and t into a single number. In later sections of this paper, the data of several groups will be combined and represented on plots of the derived data points against the logarithm of the reaction ordinate. This is simply for display purposes to indicate trends; if some data is seen to assume a linear dependence on the reaction ordinate it should not be construed as giving mechanistic insight. As described below, the reactions in these systems consist primarily of hydrolytic depolymerizations with a small degree of pyrolysis superimposed. The observed solubilization profiles of cellulose, hemicellulose and lignin are bulk phenomena whose apparent first-order rates belie quite complex reaction and transport phenomena.

3.1. *Steam conditions to temperature conversion*

In the steam-treatment literature, saturated steam conditions are quoted in a variety of pressure units (Imperial, Metric and SI). These have all been converted to a common base of the temperature of saturated steam in degrees Celsius after conversion of the pressure units to bar† by means of the equation

$$T = 99.64 + 329.64/((11.78/\ln(P/\text{bar})) - 1).$$

This equation, which is from the EKONO company, is accurate to 0.5 % over the temperature range under consideration (160–260 °C) when compared with the standard steam tables.

4. PHENOMENOLOGY OF WATER–STEAM TREATMENTS

The lignocellulosics are complex composites of amorphous polymers, lignin and hemicellulose, with a reinforcement of crystalline cellulose. The strength of wood, the degree of swelling and accessibility to reagents such as water and pulping liquors are well known to be functions of temperature and moisture content. The extraction and fractionation of lignocellulosics leading to the isolation of the individual polymers is optimal when bulk diffusion is maximized by separating the individual fibres, and internal diffusion within the cell walls is facilitated by 'swelling' the structure.

---

† 1 bar = 10^5 Pa.

4.1. *Physical aspects*

By using isolated hemicellulose and lignins, Goring (1963) showed that the anhydrous glass-transition temperatures of these polymers is in the range 130–190 °C and that water has a plasticizing action that will reduce the softening temperature of both to less than 100 °C. Unlike hemicellulose and lignin, cellulose is not a thermoplastic but consists of zones of crystallites and amorphous or disordered areas. The thermal behaviour then depends on the effects of temperature and moisture on the amorphous zones (Back & Salmén 1982). This perspective of the polymer matrix has assisted in the interpretation of the effects of steam and temperature on the refining characteristics of wood chips (Nicholls 1970). In refining fibre for paper production, the goal is to maximize both the number of separated fibres and their length while at the same time defibrillating the cell wall. Weak or inferior-strength pulps result from poorly separated fibre bundles (shives) and broken fibres. With black spruce, Koran (1967) showed that increasing plasticity resulted in the strongest element of the composite becoming the cellulose, and as a consequence the failure then occurred between fibres by separation of the middle lamella. In well plasticized wood this mode of separation is very evident at temperatures above 160 °C, and the resulting fibres are smooth, lignin covered and unsuitable for paper but excellent for the production of fibre board. Frazier (1977) confirmed, with an *in situ* torsional pendulum experiment, that once heated to the correct softening temperature in saturated steam, the transition of the wood chip from a rigid to soft state was nearly instantaneous.

In the Asplund process of pressurized steam refining to produce fibre board, the mechanical energy is minimized at around 200 kW h t^{-1} (Back & Salmén 1982) by operating above 160 °C while in the TMP process (thermomechanical pulp) the temperature is rather less (120–130 °C) and the mechanical energy is surprisingly high at greater than 1 MW h t^{-1}. In the TMP process, the lignin is only just at its softening zone and the mechanical failure in the fibre occurs in the carbohydrate-rich cell walls resulting in the desired degree of defibration, defibrillation, extension of surface area and loss of rigidity necessary to form strong papers. Koran *et al.* (1978) investigated the Masonite pulp characteristics of a soft wood and showed, under severe steam-explosion conditions, (1 min low-temperature steaming followed by 2 min at 244 °C and 5–10 s at 284 °C, a reaction ordinate value of 70000–80000 min) that the fibres were relatively undamaged but had poor paper-making characteristics on account of their stiffness at low temperature.

4.2. *Energy consumption and heat-transfer considerations*

The reaction times in the steam–aqueous systems range over the order of hours to minutes at low and medium temperatures to only seconds at high temperatures. In the aqueous-phase system with 0.5–1 mm particles, heat-up times are likely to be very short, while in the steam system the rate of temperature rise both within the chip bed and in the individual chips is likely to be a significant rate-controlling step. Lachenal & Monzie (1985) report that with the standard industrial pulping chip (usually a slab about 3 mm thick with a face 5 cm × 3 cm and having the fibre orientation in the plane of the slab) there is indeed a significant limitation at short reaction times and high temperatures. Frazier (1977) studied the heat-up rates of western hemlock pulp chips before TMP refining and recommended a maximum chip-bed depth of 40 cm for satisfactory heat-up rates of 2 min to a temperature of 121 °C. His data suggest a thermal diffusivity 4×10^{-7} m^2 s^{-1}, greater than values reported for room temperature conditions in the literature (Holman 1981) by a factor of four. Experiments at Forintek (1985) with more massive samples of Aspen showed thermal diffusivities of 1.5×10^{-7} m^2 s^{-1}. The minimum time for reaction will be a function of the sensitivity of the various decomposition processes to temperature. The data suggest, however, that reaction times of less than 2 min at high temperatures will result in significant under-cooking of chip centres.

The estimated thermal-energy requirement to heat wood chips to the reaction temperature is a function of the initial moisture content and the final temperature, and ranges from 0.31 kg of steam at 9% moisture content to 0.70 kg of steam at 50% moisture content (total mass basis) per kilogram of dry wood at a temperature of 220 °C. The aqueous-slurry technique at 15% consistency requires 0.6 kg of steam per kilogram of dry wood with about 0.5 kW h kg^{-1} of pumping energy. For the purposes of commercial plant estimates, a steam consumption of 1 kg is assumed. Because this is a significant operating-cost element, it could probably be reduced to half that value by means of heat-recovery technology such as vapour recompression.

Water is a reactant in the system as well as a heat-transfer reagent, and experiments with superheated steam at 100 kPa total pressure at a temperature of 250 °C did not result in extractable pentosans as in the other treatments (Forintek 1985). The equilibrium moisture content (EMC) of wood material diminishes with temperature, such that in going from saturated steam pressures equivalent to 100 °C to those of 170 °C, the EMC of beech falls from 21% to 17% (total mass basis) (Engelhardt 1979). Conversely, with superheated steam at 100 kPa and 149 °C, the EMC falls to a value of only 3% for mountain ash (Kaufman 1956).

4.3. *Polymeric family transformations*

The available data come from several sources, and for convenience, these will be labelled as follows: PULS, a detailed study of the behaviour of Birch under laboratory conditions in a steamer–defibrator approximating the Asplund process (Puls *et al.* 1983, 1985; Wiegel & Puls 1985); FORINTEK, data obtained for Poplar in a 2 l, batch explosion gun approximating a Masonite procedure (Forintek 1985); CTP, the work of several laboratories with a 50 l volume Masonite gun, situated at CTP Grenoble (Lachenal & Monzie 1985; Barnet 1984; Monzie *et al.* 1982; Robert & Bardet 1985); GIT, the Georgia Institute of Technology operating at a scale of 1 t h^{-1} with a continuous Stake-type reactor (Colcord & Bery 1984; Muzzy *et al.* 1983); Chua & Wayman (1979) also report on work conducted in a Stake-type reactor; and finally UdeS/NRC work under liquid phase reaction conditions in a PDU at 60 kg h^{-1} treatment scale. The materials used by these groups are mainly northern hardwood species. Somewhat similar trends will be followed by plant residues, although the values of the reaction ordinate and the final yields of fractions will be very different.

4.3.1. *The carbohydrate fraction*

During the process, the lignocellulosic is continuously solubilized or 'autohydrolysed' with increasing values of the reaction ordinate. The amount of carbohydrate solubilized after water extraction of the residual pulp is a continuous function of the degree of conversion as illustrated in figure 1. The solid line shows a generalized correlation developed by Heitz *et al.* (1986), with the data of the several investigations added. The correlation holds very well for all of the data with the exception of the GIT data, which most probably reflects the difficulties of working at an industrial scale rather than any significant deviation. Because the initial materials consist

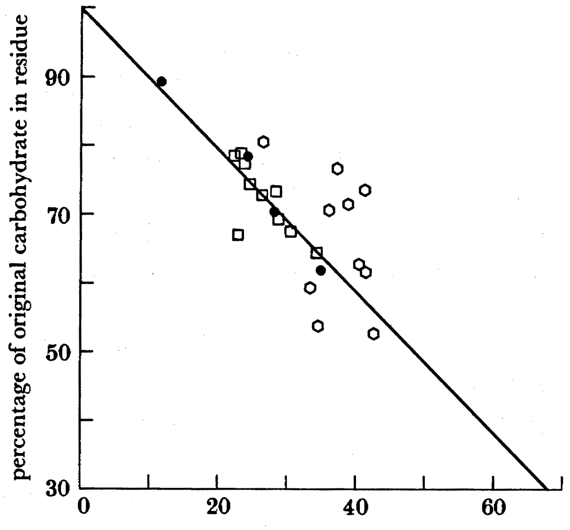

FIGURE 1. Correlation of carbohydrate solubilization with degree of conversion. ——, UdeS/NRC; ●, PULS; □, FORINTEK; ○, GIT.

of approximately 20% lignin, this suggests that lignin is also liquefied to some extent in the initial stages. The first carbohydrate to be extracted is essentially the hemicellulose that begins to be solubilized at low values of the reaction ordinate of 1000 min, and is essentially all removed from the solid residue by a value of 20000 min. The cellulose is not significantly solubilized until a value of 10000 min, pointing to the fact that the techniques can effect a separation between the carbohydrate fractions of temperate hardwoods and of the lignin to a lesser degree.

4.3.2. *The hemicelluloses*

Figure 2*a* shows the trend for both the residual hemicellulose in the pulp fibre and the value for the pulp and the aqueous extract combined when measured either as pentosan or xylose. Despite the scatter, the broad trend shows that the hemicellulose is hydrolysed at very low severity. With increasing severity, the total mass of hemicellulose-derived material diminishes as the soluble material is progressively converted to furfural and/or incorporated into what is known as pseudolignin by condensation reactions. At very high severity, almost all of the hemicellulose is destroyed. The maximum recovery of hemicellulose in the extract is of the order of 70% at reaction ordinate values of less than 10000 min. The work of Conner (1984) for several species in batch liquid-phase experiments shows that the amount of material extracted is a strong function of species; for a quaking aspen sample, the curve that would have been derived from his kinetic data for 171 °C would be parallel to the line shown but approximately 13 percentage points higher. The chosen line, that for red maple, approximates the points for hemicellulose in the fibre and illustrates the general form of a kinetically derived curve under the assumptions of the reaction-ordinate concept. The two slopes of the linear sections are presumed to reflect differing accessibilities of hemicelluloses.

Puls (1985) has established that the initially solubilized hemicellulose material has a high DP and retains a very high degree of acetyl substitution. At high values of the reaction ordinate, the amount of monomeric material increases significantly. The 4-*O*-methylglucuronic acid side

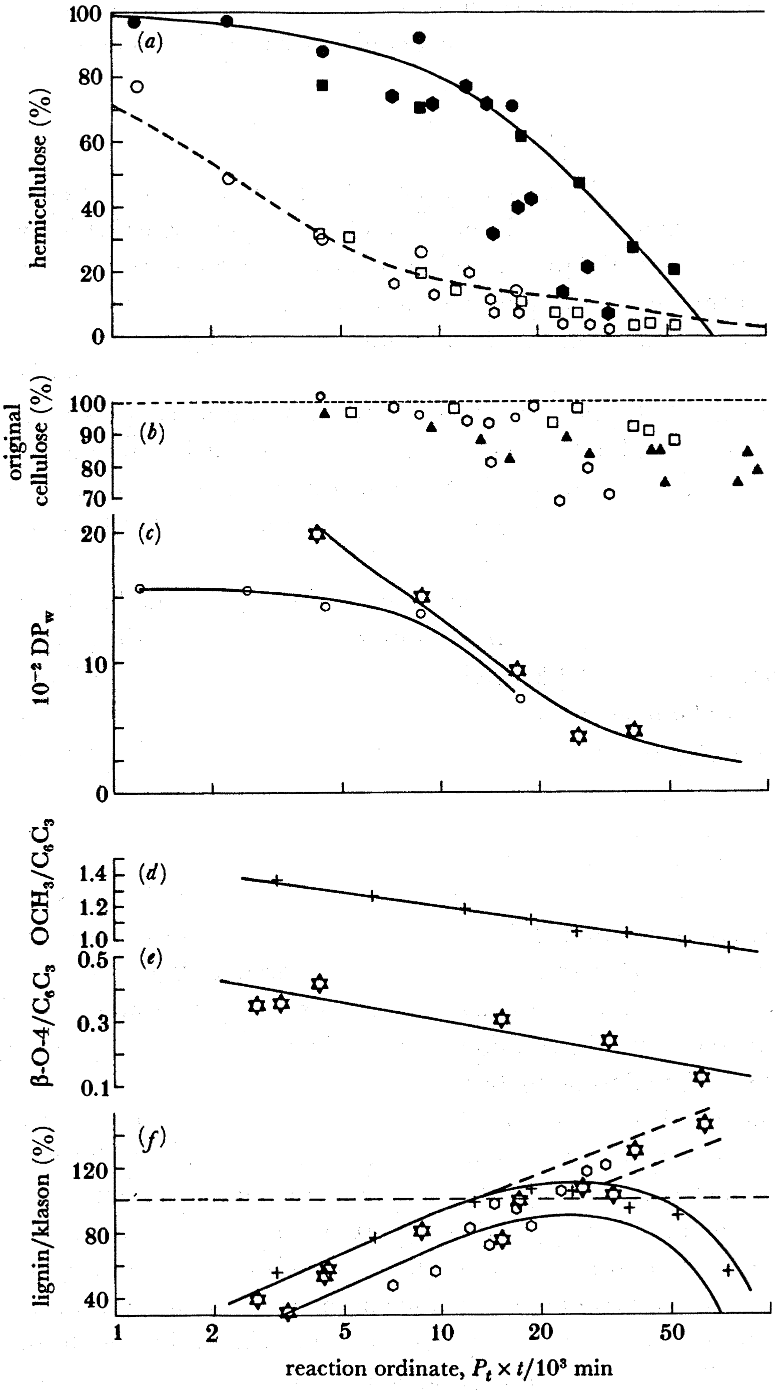

FIGURE 2. Polymeric family behaviour in steam–aqueous treatment. Solid line in (*a*) shows trend for hemicellulose in solid and extract; broken lines show trend for hemicellulose remaining in solid. Symbols: ○, PULS; □, FORINTEK; ○, GIT; +, Wayman & Chua; ✡, CTP; ▲, Sawada & Nakamura. See text for details of (*b*)–(*f*).

groups on the xylan chain do, however, hydrolyse rapidly. The high molecular mass material is easily post-hydrolysed under mild acid conditions. Several workers have found that, in steam treatment, the aqueous extract contains a toxic factor that has limited both enzymatic action and microbial growth (Saddler 1985).

4.3.3. *Cellulose*

Until reaction ordinate value of 10000 min, the cellulose appears to be intact (figure 2*b*). Data for two series of experiments in which the trend of degree of polymerization was followed are shown in figure 2*c*. Evidently the glycosidic bonds are progressively hydrolysed with increasing severity and the $\mathrm{DP_w}$ trends towards the LODP (level-off degree of polymerization) found in acid hydrolysis experiments. Despite the wide scatter in values for cellulose solubilization, it is evident that the majority of the cellulose is retained in the pulp residue until very high severities are attained. The work of Sawada & Nakamura (1985) with *Larix leptolepis* was carried out to a reaction-ordinate value of 897705 min, at which point the cellulose value is only 45%. Marchessault & co-workers (1980, 1983) have shown that the crystallinity of cellulose is preserved under the conditions of DeLong's patent claims (1981) that correspond to a reaction ordinate value of 3000–10000 min.

The accessibility of the cellulose to enzymatic degradation to glucose has been extensively studied as a route to the production of ethanol. Pulps having large quantities of residual lignin are easily hydrolysed to about 80% yield of glucose for reaction-ordinate values of 10000–50000. A patent claim suggests that the optimum value is 30000, although the data supporting this show a wide range of acceptable values in which the total conversion to glucose exceeds 80%.

4.3.4. *Lignin*

The water extraction that isolates, in the main, the hemicellulose derivatives at reaction-ordinate values of less than 20000 min also removes a certain proportion of water-soluble lignin. In the case of the steam treatments, almost 10–15% of the original lignin is water soluble. In the aqueous systems, 30–40% of the original lignin is extracted in water. Marchessault & St Pierre (1980) observed that the distribution of the lignin in the pulp residue was appreciably changed over that of the original wood material. It appeared that the lignin had coalesced into small spheres of less than 5–10 μm diameter. These are easily soluble in aqueous organic solvents such as ethanol–water and dioxane–water, and the lignin can be recovered by evaporating the solvent. The final product is a thermoplastic material. An alternative extraction technique (Muzzy *et al.* 1983; Wayman & Lora 1983) is the use of dilute sodium hydroxide (0.4% by mass) followed by precipitation from aqueous solution by addition of dilute acid.

The extent of extraction is a function of the value of the reaction ordinate and is illustrated in figure 2*f*. Data from these research groups are illustrated in the form (extracted lignin)/(original Klason lignin). At values of reaction ordinate greater than 15000 min, there is an apparent increase in the total amount of lignin to values exceeding that of the original lignin. The incremental amount is often described as pseudolignin and behaves as Klason lignin the analytical determination. It is believed that its origin is in degraded pentosan or hemicellulose compounds and as can be seen from figure 2*a* its appearance is correlated with the large increase in 'missing' hemicellulose that occurs at around 15000 min.

In the process, the primary chemical effects are the hydrolysis of the easily broken ether type of linkages, both inter and intra to the basic phenylpropane (C_6C_3) moieties of the lignin structure. Figure 2*e* illustrates the decrease in the number of β-*O*-4 linkages per C_6C_3 unit as a function of reaction ordinate according to ^{13}C NMR measurements by Robert & Bardet (1985). Chua & Wayman (1979) demonstrated that the methoxyl (OCH_3) content decreased constantly with the reaction ordinate as shown in figure 2*d*. The hydrolysis product, methanol, has been shown to be present in the hydrolysis washings and there is a concomitant increase in the ring phenolic groups as shown by ^{13}C NMR measurements (Robert & Bardet 1985).

Relative to milled wood lignin samples of the same species, the lignin is significantly depolymerized. Chum *et al.* (1985) found that the mass-average molecular mass of alkali-extracted steam-treated aspen (at 12500 min) was 2100 with a polydispersity of 2.7. The same workers found that solvent extractions of the same material had lower mass-average molecular masses of 1050 and 920 g mol^{-1} for ethanol and methanol respectively; the OCH_3:C_6C_3 ratio was lower for the solvent-extracted lignin than for the alkali-extracted material. Glasser *et al.* (1983), working with alkali-extracted steam-treated aspen and poplar (reaction ordinate unknown), found mass-average values of 2300 and 3000 g mol^{-1} (polydispersivities of 2.9 and 3.3) respectively. Chua & Wayman (1979), working with aspen, found a bimodal molecular mass distribution for dioxane–water-extracted material. The ratio of the high-molecular-mass fraction to the low-mass fraction increased up to an apparent extraction efficiency of 100% (reaction ordinate value of 15000–25000 min). The data were interpreted in terms of competitive depolymerization and recondensation kinetics. Because of an extremely high value of molecular mass for the heavy fraction (196000 g mol^{-1}), the polydispersivity of the samples was extremely high and the mass average considerably greater than those found by other workers.

5. Fractionation

The steam and aqueous treatment processes are reasonably well understood for temperate zone hardwood species such as aspen, poplar, and birch. They are also applicable to sugar-cane bagasses and to annual plant residues, such as straws. The experience to date with softwood species suggests that chemicals will have to be added to develop more efficient fractionation. Continuing with the discussion on the basis of the hardwoods, it is possible to envisage a number of fractionation processes based on a steam or aqueous pretreatment process of the types described above.

The primary treatment process is to reduce the feedstock wood material to a particle size, such that the process can mechanically cope with it, and to obtain a morphology, such as a chip, that allows simultaneous heat and mass transfer under the conditions of the relatively rapid process. In the aqueous treatment, the options include using chips under conditions similar to present-day hydrolysers or working with medium-consistency slurries (10–15%) of material milled to less than 1 mm in short-time, high-temperature treatments. The steam-treatment process functions well with standard-size pulp chips. The preferred treatment conditions appear to be in the reaction ordinate range of 10000–30000 min, which will result in the removal of the majority of the hemicellulose from the pulp residue after water extraction. Adjustment of this parameter will lead to the maximum recovery of hemicellulose in the extract. The majority of process flow sheets envisaged include a water extraction of this fraction composed mainly of hemicellulose-derived material and 10–20% of the original lignin and a certain amount of extractive material (a function of species). The cellulose-rich pulp obtained

(70–75%) can then be treated in three ways: alkali extraction of the lignin; solvent extraction of the lignin; or direct hydrolysis by either acid or cellulase enzymes to yield a glucose stream and residual lignin.

5.1. *Hemicellulose*

The classical options for the hemicellulose fraction have been to carry out the acid catalysed conversion of the C_5-fraction to furfuraldehyde, or to hydrogenate the material to manufacture xylitol. Neither of these are commodity chemicals and their current markets are relatively small. An alternative approach has been to sell an aqueous concentrate of hemicelluloses as an animal feed (Galloway 1975). It has also been proposed that this fraction be used as a base for SCP production or, in the context of energy, be further hydrolysed to monomeric sugar and converted to ethanol through the use of *Pachysolen spp.*, which appear capable of directly fermenting xylose to ethanol.

5.2. *Cellulose*

Under the preferred conditions for maximum recovery of hemicelluloses, the cellulose has undergone a significant degree of depolymerization and appears to be trending towards the LODP value. This precludes the material finding markets that depend on fibre quality if the treatment process has greater than 5000 min of treatment on the reaction ordinate. The present-day largest markets for non-fibre cellulose are those of regenerated celluloses and derivatives based on processes dependent on a high-DP base material. Recent work in Finland (Eckman *et al.* 1983) has shown a cellulose carbamate process that can utilize LODP material in a novel and less-polluting way than the present-day viscose process.

5.3. *Lignin*

Existing lignin markets use lignin derived from the sulphite and sulphate pulping industries, and are quite large at 0.75 Mt a^{-1}. Much of the output finds markets based on the water-soluble characteristics of these derivatives in applications such as speciality dispersants. It is probable that lignins derived from steam and aqueous pretreatments are suitable for a wider range of applications. Some that have been described are as petrochemical phenol replacement in adhesives and as a thermoplastic polymer substitute.

6. CONCLUSIONS

Steam- and aqueous-phase pretreatments for temperate hardwoods, bagasse and plant residues can effect a separation of the feedstock into two fractions: an aqueous extract composed mainly of hemicellulose derivatives along with some water-soluble lignin, and a pulp composed of cellulose and an easily extracted lignin. The yield and composition of each fraction is a function of both temperature and time that can be combined into a single reaction ordinate that enables both process control and prediction of yield and quality for each fraction of a given species. Steam–aqueous pretreatment processes already exist at a commercial scale and are likely to become economical and integral components in the future biotechnological utilization of lignocellulosics.

REFERENCES

Babcock, L. W. 1932 *Method of producing fermentable sugars and alcohol from wood.* U.S. Patent no. 1825464 (26 April 1932).

Back, E. L. & Salmén, N. L. 1982 Glass transitions of wood components and implications for molding and pulping processes. *TAPPI* **65** (7), 187–110.

Barnet, D. 1984 *Autohydrolyse rapide du bois de peuplier* (*Populus Tremula*): *evolution de la composition des echantillions en function de la durée du traitment.* Thèse 3^{eme} cycle, Université de Grenoble.

Brasch, D. J. & Free, K. W. 1965 Prehydrolysis-Kraft pulping of pinus radiata grown in New Zealand. *TAPPI* **48** (4), 245–248.

Brown, D. B. 1980 *Apparatus for discharge of pressure cooked particulate or fibrous material.* U.S. Patent no. 4211163 (8 July 1980).

Brown, D. B. & Bender, R. 1980 *Feeding natural cellulose fibre into steam pressure vessel for manufacture of fodder from waste wood chips, straw, bagasse etc.* Canadian Patent no. 1070537 (29 January 1980).

Chua, M. G. S. & Wayman, M. 1979 Characterisation of autohydrolysis aspen (*P. Tremuloides*) lignins. 1. Composition and molecular weight distribution of extracted autohydrolysis lignin. *Can. J. Chem.* **57**, 2603–2611.

Chum, H. L., Johnson, D. K., Ratcliff, M., Black, S., Schroeder, H. A. & Wallace, K. 1985 Comparison between lignins produced by steam explosion and organosolve pretreatments. *International Symposium on Wood and Pulping Chemistry*: *Technical Papers, Vancouver, Canada*, pp. 223–225. Stockholm: SPCI.

Colcord, A. R. & Bery, M. K. 1984 Production of ethanol and chemicals from wood by the Georgia Tech Process. In *Liquid fuel developments* (ed. D. L. Wise), pp. 130–137. Boca Raton: CRC Press.

Conner, A. H. 1984 Kinetic modelling of hardwood prehydrolysis. 1. Xylan removal by water prehydrolysis. *Wood Fibre Sci.* **16** (2), 268–277.

Cowling, E. G. & Kirk, T. K. 1976 Properties of cellulose and lignocellulosic materials as substrates for enzymatic conversion processes. *Biotech. Bioengng Symp.* vol. 6, pp. 95–124.

Datta, R. 1981 Energy requirements for lignocellulosic pretreatment processes. *Process Biochem.* **16** (4), 15–19 and 42.

DeLong, E. A. 1981 *Method of rendering lignin separable from cellulose and hemicellulose in lignocellulosic material and the product so produced.* Canadian Patent no. 1096374 (24 February 1981).

DeLong, E. A. 1983 *Method of rendering lignin separable from cellulose and hemicellulose in lignocellulosic material and the product so produced.* Canadian Patent no. 1141376 (15 February 1983).

Ekman, K., Eklund, V., Fors, J., Huttunen, J. I., Selin, J.-F. & Turunen, O. T. 1983 Fibres by wet-spinning of cellulose carbamate solutions. In *Proceedings of the 1983 International Dissolving and Speciality Pulps Conference*, pp. 99–104. New York: TAPPI Press.

Engelhardt, F. 1979 Untersuchungen über die Wasserdampfsorption durch Buchenholz im Temperatur-bereich von 110 bis 170 C. *Holz Roh- u. Werkstoff* **37**, 99–112.

Foody, P. 1984 *Method for obtaining superior yields of accessible cellulose and hemicellulose from lignocellulosic materials.* Canadian Patent no. 1163058 (6 March 1984).

FORINTEK 1985 *Pretreatment methods for enhancing conversion of lignocellulosic material to liquid fuel.* Contract no. 54SS23216-3-6364.

Frazier, W. C. 1977 On the presteaming of chips for thermomechanical pulping. In *Preprints. 63rd Annual Meeting, CPPA*: *Technical Section*, A91–99.

Galloway, D. 1975 Growing role of wood products in the livestock feeding field. *Pulp Pap.* **49** (9), 104–105.

Glasser, W. G., Barnett, C. A., Muller, P. C. & Sarkanen, K. V. 1983 The chemistry of several novel bioconversion lignins. *J. agric. Fd Chem.* **31** (5), 921–930.

Goring, D. A. I. 1963 Thermal softening of lignin, hemicellulose and cellulose. *Pulp Pap. Can.* **64** (12), T517–T527.

Heitz, M., Carrasco, F., Rubio, M., Chauvette, G., Chornet, E. & Overend, R. P. 1986 Generalized correlations for the aqueous liquefaction of lignocellulosics. *Can. J. chem. Engng.* **64** (4), 647–650.

Holman, J. P. 1981 *Heat transfer.* New York: McGraw-Hill.

Kauman, W. G. 1956 Equilibrium moisture content relations and drying control in superheated steam drying. *Forest Prog. J.* **6** (9), 328–332.

Koeberle, P., Meloche, F., Chauvette, G., Menard, H., Chornet, E., Jaulin, L., Heitz, M. & Overend, R. P. 1985 Prétraitement du matériel lignocellulosique par voie thermo-mechano-chimique en phase aqueuse. In *Fifth Canadian Bioenergy R & D Seminar* (ed. S. Hasnain). London: Elsevier Applied Science Publishers.

Koran, Z. 1967 Electron microscopy of radial tracheid surfaces of black spruce separated by tensile failure at various temperatures. *TAPPI* **50** (2), 60–67.

Koran, Z., Kokta, B. V., Valade, J. C. & Law, K. N. 1978 Fibre characteristics of Masonite pulp. *Pulp Pap. Can.* **79** (3), T107–T113.

Lachenal, D. & Monzie, P. 1985 The French exploded wood project. In *International Symposium on Wood and Pulping Chemistry*: *Technical Papers, Vancouver, Canada*, pp. 7–8. Stockholm: SPCI.

Mamers, H. & Rowney, J. E. 1979 *Method and apparatus for explosively defibrating cellulosic fiber.* U.S. Patent no. 4163687 (7 August 1979).

Mamers, H., Yuritta, J. P. & Menz, D. J. 1981 The siropulper – an explosive alternative for non-wood pulping. In *TAPPI Pulping Conference, Atlanta, Georgia*, pp. 261–268.

Marchessault, R. H. & St Pierre, J. M. 1980 A new understanding of the carbohydrate system. In *Future sources of organic raw materials: CHEMRAWN 1* (ed. L. E. St Pierre & G. R. Brown), pp. 613–625. Oxford: Pergamon Press.

Marchessault, R. H., Malhotra, S. L., Jones, A. Y. & Perovic, A. 1983 The wood explosion process: characterization and uses of lignin/cellulose products. In *Wood and agricultural residues* (ed. J. Soltes), pp. 401–413. New York: Academic Press.

Mason, W. H. 1928 *Apparatus for and process of explosion fibration of lignocellulosic material*. U.S. Patent no. 1655618 (10 January 1929).

Monzie, P., Pichon, M., Lombardo, G. & Schwab, Y. 1984 La technique d'hydrolyse flash; performances et perspectives. In *Bull. Liais.* (*Groupe Polyphenols*) **12**, 233–257. Plovdiv, Bulgaria.

Muzzy, J. D., Roberts, R. S., Fieber, C. A., Faass, G. S. & Mann, T. M. 1983 Pretreatment of hardwood by continuous steam hydrolysis. In *Wood and agricultural residues* (ed. J. Soltes), pp. 351–368. New York: Academic Press.

Nicholls, G. A. 1970 An interpretive view of refiner pulping. *Wood Sci. Technol.* **4**, 292–300.

Puls, J., Ayla, C. & Dietrichs, H. H. 1983 Chemicals and ruminant feed from lignocelluloses by the steaming-extraction process. *J. appl. Polym. Sci.* **37**, 685–695.

Puls, J. K., Poutanen, K. & Viikari, L. 1985 The effect of steaming pretreatment on the biotechnical utilization of wood components. In *Bioenergy-84: Biomass Conversion* (ed. H. Egnéus & A. Ellgard), vol. 3, pp. 173–180. London: Elsevier Applied Science Publishers.

Robert, D. R. & Bardet, M. 1985 Structural changes in lignin during steam hydrolysis of aspen wood. In *International Symposium on Wood and Pulping Chemistry: Technical Papers, Vancouver, Canada*, pp. 213–214. Stockholm: SPCI.

Saddler, J. N., Yu, E. K. C., Mes-Hartree, M., Levintin, N. & Brownwell, H. H. 1985 The fractionation of lignocellulosic substances by steam explosion and the subsequent conversion of the various components to sugars, fuels and chemicals. In *Energy From Biomass: 3rd E.C. Conference* (ed. W. Palz, J. Coombs & D. O. Hall), pp. 978–981. London: Elsevier Applied Science Publishers.

Satter, L. D., Baker, A. J. & Millett, M. A. 1981 *Increasing the nutritive value of wood and forest products through chemical and physical treatments in upgrading residues and by-products for animals*. Boca Raton: CRC Press.

Sawada, T. & Nakamura, Y. 1985 Effect of explosion operation for effective utilisation of plant material. In *International Symposium on Wood and Pulping Chemistry: Technical Papers, Vancouver, Canada*, pp. 31–35. Stockholm: SPCI.

Sjöstrom, E. 1981 *Wood chemistry: fundamentals and applications*. New York: Academic Press.

Wayman, M. & Lora, J. H. 1983 *Depolymerisation and extraction of lignin*. Canadian Patent no. 1147105 (21 May 1983).

Wenzl, H. F. J. 1970 *The chemical technology of wood*. New York: Academic Press.

Wiegel, J. & Puls, J. 1985 Ethanol from pentoses and pentosans by thermophillic and mesophillic micro-organisms. In *Energy From Biomass: 3rd E.C. Confeence* (ed. W. Palz, J. Coombs & D. O. Hall), pp. 670–674. London: Elsevier Applied Science Publishers.

Discussion

J. A. Gascoigne (*Cross & Bevan Laboratories, Arlesey, Bedfordshire, U.K.*). Dr Overend has mentioned explosion techniques, but this type of pulping relies on the use of expensive pressurized equipment and high temperatures; the formation of acids during the aqueous prehydrolysis also leads to corrosive conditions necessitating the use of stainless steels.

In an attempt to overcome these costly items, Cross & Bevan has been able to make a straw-based product for dual use. The heating of acid-treated straw under low liquid conditions at 80 °C is followed by an alkaline treatment at the same temperature. The semi-solid 'pulp' produced has high digestibility in the ruminant and, after washing, the 'pulp' has been used successfully in making corrugated cardboard. Utilization of the 'black wash liquor' is now being investigated. The process uses simple equipment and is being operated on a pilot scale in Suffolk (England).