

Chapter 25

Pretreatments for Converting Wood into Paper and Chemicals

**William R. Kenealy¹, Carl J. Houtman¹, Jose Laplaza¹,
Thomas W. Jeffries¹, and Eric G. Horn²**

¹Forest Service, Forest Products Laboratory, U.S. Department
of Agriculture, Madison, WI 53726

²Biopulping International Incorporated, 2912 Syene Road,
Madison, WI 53713

Biorefining wood into paper and chemicals is not as easy as making a single traditional paper product. Paper is made from the cellulose-containing fractions of wood and processing may remove lignin and hemicellulose components. The yield and composition of the product depend upon the type of paper being produced. The paper process often alters the non-cellulose fractions, making them less suitable for conversion to other valuable products. This chapter will review methods of obtaining hemicellulosic sugars and investigate the potential for obtaining sugars by a wood pretreatment before it is made into pulp. As an example of hemicellulose removal the results of a new pretreatment using diethyl oxalate are also described. Hemicellulose removal by this system provides other benefits to the pulping process.

Biomass use is touted as a solution to the burgeoning petroleum importation of our nation and as a way to become more energy independent (1). When biomass is targeted for this purpose, carbohydrates are generally converted to products. Corn is used to make ethanol, and it is principally starch that is saccharified to glucose and fermented to ethanol. Sucrose from sugar cane is used to make ethanol in Brazil. Obtaining sugars from lignocellulose is much more difficult. Cellulose has very little solubility in water and a crystalline nature that must be overcome before it can be converted into glucose. The problem is compounded in lignocellulose when the cellulose has additional polymers such as hemicellulose and lignin that must be removed or destroyed before the cellulose is accessible.

The problems with biomass use are in part inherent in the structure of the lignocellulose and also the source of the material. Corn stover might be an easier material to convert to fermentable carbohydrates than wood, but collection, storage, and soil depletion are problems that must be solved for this feedstock. Wood is more easily transported and collected at processing sites; however, more energy is required for processing wood than for corn stover. The “Healthy Forests Initiative”(2) and Healthy Forest Restoration Act of 2003 identified small diameter woody materials that exacerbate forest fires as a problem and its solution could provide materials for biomass use. However, these materials are often located in regions where there is little transportation infrastructure and little water present in the region for local processing.

The problems with lignocellulose use are daunting, but they can be addressed. Industry has long made paper products from wood and disposed of residual material by combusting the waste to gain energy for in-plant use. While the total conversion of wood into products (such as ethanol transportation fuel) may not be widely available, the pulp and paper industry does refine wood into paper products and energy. With initiatives like Agenda 2020’s “Advancing the Forest Biorefinery” to develop “Integrated Forest Biorefineries” and obtain “Value Prior to Pulping” the industry is considering biorefining; the removal of the selected components before the paper product is made (3, 4). This is an opportunity for industry to expand its product portfolio.

Biorefineries are being considered for many different starting materials and products, not all of which consider paper as a product (5). Multiple products can be made by fermentation or chemical methods from intermediates derived from wood. In the ideal case, for paper manufacturing all of material that does not end up in the paper product would be converted into valuable products and more useful forms of energy. In reality, there are trade-offs in energy efficiency, product yields, and potential waste streams that develop into a balancing act of trying to maintain yield and paper properties while obtaining source material for other products. Kraft pulping is often used as the target for biorefining in the pulp and paper industry. The hemicellulose is burned in the black liquor, but it contributes less to the fuel value than does the lignin. Recovery of the hemicellulosic sugars in front of the pulping operation will provide new product

opportunities but may also change the operation of the recovery boilers. Research is required to evaluate the many approaches and processes that might be used.

Advances are being made in the conversion and processing of lignocellulose to useful products. When the cellulose is converted to ethanol or other products the hemicellulose must also be used since it is a significant fraction of lignocellulosic materials. If cellulose is to be a significant portion of the product, as in paper, the hemicellulose and lignin are the only materials that can provide new products. In both cases, the processing and ultimate fate of the hemicellulose is important for the economics and design of the process. In this chapter, we will consider a problem that vexes the proponents of biorefining in the pulp and paper industry: how hemicellulose is removed from wood, in a useable form, without harming the cellulose product.

Methods for Removing Hemicellulose

There are many processes that can remove hemicellulose from lignocellulose. Analytical and structural studies of hemicellulose often first isolate holocellulose obtained by oxidative means (6-8). Hemicelluloses can be removed from holocellulose and lignocellulosic materials by hot water, alkaline, and solvent extractive methods (6-15). The hemicellulose is obtained in a polymeric form facilitating the study of hemicellulose structure. Isolation of holocellulose and its conversion to chemicals and fuel would be very costly. Most studies concerning hemicellulose removal pertain to pretreatments of lignocellulose for its conversion to chemicals and fuels, and the isolation of polymeric hemicellulose is generally not a concern.

The carbohydrates present in plant cell walls depend upon the species, source, age, size, and treatment history of the material (6-13). Composition of plant cell mass is determined by isolation of polymeric forms and by determination of the sugar components in hydrolysates (10). A combination of methods shows that the glucan portion of plants is predominantly located in the cellulose, while xylan, galactan, arabinan, and mannan are located in the hemicellulose. Many extraction methods have been explored for the total conversion of lignocellulose into chemicals and fuel (16). In this latter regard, the goal of hemicellulose removal is to pretreat the lignocellulosic material so that the cellulose and hemicellulose can be converted into soluble sugars (17). Damage to the cellulose is of little concern when the purpose of treatment is to provide better access to the cellulose for enzymatic or acid digestion. Economics and prevention of process-generated metabolic inhibitors drive research into these pretreatments (17, 18). Metabolic inhibition is irrelevant when the carbohydrates are converted chemically to other products like furfural (19) and

perhaps feed additives (20), although conversion and purification processes might be affected.

These pretreatments for the total conversion of lignocellulose to fuels and chemicals are good starting points for the investigation of processes to derive paper and other products from wood. Not all of these pretreatments will have applications in the biorefining of wood to a combination of paper, chemicals, and fuel. The effects of many of these pretreatments on the ability to make paper products have not been investigated. Another starting point is to examine pulping technologies that are proven to make paper products and discern if there are other products that can be obtained. While this chapter relates to hemicellulose-derived products, lignin can also be converted into products that have greater value than its fuel value.

There are three general chemical categories of hemicellulose extraction: alkaline, acidic, and solvent. Some of these methods have been used prior to making paper products; others have been developed for the purpose of facilitating total conversion of lignocellulose to fuels and chemicals. The less intensive extractions (in regards to temperature, acidity, and alkalinity) will liberate the water-soluble carbohydrates (6, 10, 14) in addition to what is liberated by the acid and base additions. Chemical methods can be used in conjunction with more aggressive treatments such as steam explosion pulping. Explosive decompression can be used with or without chemical impregnation of the chips to break apart wood fiber (21).

Alkaline Methods of Hemicellulose Removal

Efficient extraction and recovery of hemicellulose from wood by alkaline means requires finely ground wood or delignification of the wood (6-9). Grinding wood chips to extract hemicellulose prior to pulping would be cost prohibitive and damaging to the fiber, so less efficient extraction methods must be employed. The yield of extractable sugars from wood chips would be considerably less than that with ground wood or holocellulose. When the purpose of the extraction is to make paper and chemicals, the right treatment conditions can still release sugars.

Kraft pulping is the most used pulping process for making paper products. It is a high temperature alkaline process that removes both lignin and hemicellulose components from softwoods and hardwoods. The condition of the hemicellulosic materials, the complexity of the organics present, and the sulfur present in the black liquor make product development from this material very difficult. It is precisely this difficulty that has provided the incentive to explore the pretreatment of wood chips to recover the hemicellulosic fraction before pulping (3, 4). The objective is to make additional products along with the same kraft

paper product. However, the yield might be affected if significant mannose is removed (22, 23). Removal of some hemicellulose without contaminating the fraction with lignin components might be possible with gentle alkaline treatments.

Cold soda pulping is a chemimechanical process that has been known for a long time (24). This process has been used to produce corrugating board and writing paper. On hardwoods such as aspen, the process reduces the content of hemicellulose in the product and increases both the glucan and klason lignin contents. Overall there is some loss in the net glucan, xylan, and acid-soluble lignin (24). The recovery of components from the treatment liquor has not been explored, and there is significant biological oxygen demand in the spent liquor. It is likely that hemicellulosic oligosaccharides, lignin components, and acetate contribute to the biological oxygen demand. A recent patent application reported cold caustic extraction of wood chips and hardwood pulp for the production of high purity xylose (25).

Ethylenediamine and monoethylamine in alkaline solutions and other amines (26) delignify pine and produce pulps with hemicellulose contents higher than kraft with roughly the same kappa and yield (27). Treatments such as ammonia fiber explosion and ammonia recycled percolation will degrade some of the hemicellulose and alter the crystallinity and accessibility of the cellulose to digestive enzymes (17). These treatments and lime or other alkaline treatments will alter lignin structure and also delignify the material. The potential for contamination of the carbohydrate stream with lignin digestion products may limit applications of an alkaline pretreatment of wood chips for the purpose of making paper and chemicals. There are a variety of alkaline treatments that are part of solvent extractions. These processes will be discussed in the solvent extraction section.

Acidic Methods of Hemicellulose Removal

Much is known about the dilute acid prehydrolysis for making cellulose accessible to further degradation (16, 17, 28-45). Within this knowledge base is information about temperatures and acid charges that do not directly degrade the cellulose. Early experiments on water and steam (acetic acid autohydrolysis) cooking of aspen showed little damage to the cellulose (46), and similar treatments of pine (47), eucalypt (48), and sweetgum (49) provided low hemicellulose sulphate pulps. The methods to produce high alpha cellulose pulps were reviewed and significant reduction in hemicellulose content was noted with prehydrolysis (50). These reports could be a starting point for investigating the use of these processes for converting wood chips to paper products and chemicals. The knowledge base is growing and new patents are continually being

issued for both dilute acid (51-53) and strong acid hydrolysis (54, 55). However, little effect on cellulose degradation does not mean there will not be drastic effects on paper properties. Excessive temperatures will darken pulps, making them less useful for mechanical paper grades that require brightness. Small changes in the composition of the wood can dramatically affect the strength properties of the paper product. The historical data on acid prehydrolysis can be a very important starting point, but to employ this technology there must be empirical testing on the end products of interest. Both the paper product and the carbohydrate resource must be tested to prove the process is useful.

Acetic acid pulping and formic acid pulping are processes that can produce good paper products (56-58). Using performic acid in the Milox process produces a soluble carbohydrate stream from birch processing that can be separated from the lignin-containing stream. Acetic acid is an additional product recovered during the formic acid recycling (58). Since there is an appreciable degradation of the lignin during this process, problems are likely to occur with aromatic contamination of the hemicellulosic sugars; however, there is little sulfur in the product, so developing more refined uses would be less problematic than developing uses for kraft liquors.

Acetic acid pulping is an acidic method, but the use of large volumes of acetic acid and the precipitation of lignin components with ethyl acetate could also classify this as a solvent method (56, 57, 59). In some configurations, acetic acid pulping uses additional mineral acids that aid in the degradation of lignin components. The hemicellulose is increasingly degraded with higher temperatures, longer cook times, and greater loadings of acetic acid (57).

A gaseous source of acid has also been used. Sulfur dioxide can be introduced to the chips and sulfonic acid can be formed (33, 36, 60-62). This is an alternate way of introducing acid that does not involve impregnation of the chips. The extent of treatment can be varied by altering the time or the temperature, providing flexibility in the treatment (63). Sulfur dioxide treatment makes the sugar more accessible to digestion and has been used with wood chips in animal feed tests (20). With sulfur dioxide and steam explosion there is better recovery of the sugars when the chip size is increased (64). This is probably due to the increased damage to the lignocellulose components, which results from treating smaller chip sizes where the sugars are converted further from monosaccharides into derivatives. This is in contrast to alkaline extraction, where the extraction is much better with smaller material.

Solvent Methods of Hemicellulose Removal

Dimethyl sulfoxide (DMSO) is a solvent that has been used in the study of hemicellulose structure (65, 66). This solvent system extracts the hemicellulose

and does not cleave the acetyl esters, allowing for the determination of the structure of the hemicellulose. DMSO is used on holocellulose and to extract hemicellulose from pulps. The use of this solvent for applications in pulping would be expensive and there would be potential hazard problems with handling large volumes of the solvent.

Many solvents have been reported that cause wood to swell (67). Swelling is apparently due to interactions with the cellulose component of the wood. Solvents that swell the wood might be useful in pretreatments that will allow access to various components of the wood, provided that the solvent can be displaced without shrinkage and the solvent can be recovered. Other solvents have been tested for the ability to make pulps; alcohols (68-71), phenols (69, 72), esters (59), and combinations of solvents with acidic (73-77) and alkaline additions (26, 27, 68, 70). The objective in most of these solvent pulping systems is to remove lignin from the lignocellulosic material, leaving the cellulose-containing fractions for paper making. In general, the hemicellulose is retained partly in the cellulose-containing fraction and partly in the degraded lignin fraction. Ethanol and methanol are the primary alcohols used in organosolv processes. These processes use aqueous alcohol solutions at elevated temperatures to degrade and remove lignin fractions. Many additions and modifications have been made to these solvent processes.

Ethanol and methanol are the most often used solvents. Phenol and butanol can delignify pine meal (69). Other alcohols have been tried, but the results have not been better than those obtained with ethanol and methanol (27, 68). There are many variations on using alcohols in the pulping process. The addition of compounds such as neutral alkali earth metal salts (73, 75) indicates that divalent cations are better than monovalent and trivalent cations when liberating softwood fibers. In these studies, lignin concentrations were reduced in the product but no characterization of the extract was made.

Hemicellulose Removal with Pulp and Paper Production

Biorefining for the pulp and paper industry is envisioned as the removal and use of material that does not contribute to the paper product. At present, there is little data in the published literature that indicates how much material can be removed and how to remove it without altering the paper product. The primary target for application of biorefining is in kraft pulping since it is the largest segment of the paper industry and has a low product yield of ~50%. This provides the potential for more carbohydrate to be removed for other uses. Low yield chemical pulps have the greatest potential, but there have been studies on the pretreatment of mechanical pulps that relate to the topic of biorefining.

Mechanical and thermomechanical pulps are high yield pulps. Generally the conversion of the wood chips to paper products is in the range of 90-95% by weight. There are losses in the process and these are generally from extractibles, water soluble carbohydrates and hemicellulose. It may not be possible to economically recover these small amounts of released materials with a stand alone pretreatment process. Waste disposal costs could be decreased, but without other advantages the recovery of hemicellulosic sugars from thermomechanical processes would be costly.

Mechanical pulps generally have low strength and the product specifications often require greater strength. To increase the strength, additives such as chemical pulps or starch are blended with the pulp. If the process that recovers the hemicellulosic sugars prior to pulping delivers a stronger product, the economics improve by saving on chemical pulp or other additions. There are also high cost factors in the production of mechanical pulps. One of the highest costs in the production of mechanical pulps is the electrical energy required for refining. If the energy of producing pulps can be lessened by a process of hemicellulosic sugar removal, the economics also improve.

Oxalic acid pulping is a process that pretreats wood chips for thermomechanical pulping, saves electrical refining energy, and delivers a product with increased strength (78, 79). We have recently determined that oxalic acid pulping also releases hemicellulosic sugars from the chips (80). The combination of electrical refiner energy savings and stronger pulps puts forth an economic argument for the use of oxalic acid pulping with a reasonable repayment for the investment (79). The addition of carbohydrate recovery and conversion to additional products should enhance the use of the process.

Oxalic acid pulping should be viewed as a dilute acid prehydrolysis. Since the process has been developed for thermomechanical pulping, the extent of Carbohydrate extraction must be balanced against the electrical refiner energy savings and the paper properties, such as strength and brightness. In general, dilute acid Pretreatments may be beneficial to thermomechanical pulps. The degree of hydrolysis must be controlled to be able to show a benefit. The hydrolysis can be affected by the amount of acid used, the time for which the wood is treated, and the temperature of treatment.

Mineral acids, oxalic acid, sulfur dioxide, diethyl oxalate, and acetic acid have all been used in dilute acid pretreatments. The oxalic acid and diethyl oxalate pretreatments are examples of processes that have been proven effective for thermomechanical pulps and are able to generate hemicellulosic sugar hydrolysates. Other methods may be applicable. However, most of the work on mineral acids is performed as a pretreatment to total carbohydrate conversion, and most of the work on hot water extraction (involving autohydrolysis via acetic acid) is directed towards kraft pulp since the temperatures used (160°C to 170°C) have detrimental effects on the brightness of thermomechanical pulps.

The sulfuric and acetic prehydrolyses are normally performed by suspending the wood chips in a given volume of water or acid and running the reaction. Oxalic acid is used in solution (0.3% wt/vol) and impregnated into the wood chips; the bulk of the solution is then drained away (78, 79). Diethyl oxalate (DEO) is injected into a digester containing preheated wood chips (80, 81). When DEO contacts water at temperatures around 140°C, there is a rapid hydrolysis of the ester, depositing oxalic acid in the water within the wood chip. Further heating hydrolyzes the carbohydrates. After the reaction, carbohydrates are extractable into water in a separate process step. As Figure 1 indicates, for both aspen and pine chips, increasing the amount of DEO added to the wood chips increases the amount of Carbohydrates released from the chips. Similar carbohydrate extractions are also obtained by oxalic acid pulping (80).

The residual wood chips are enriched in cellulose and lignin relative to the control wood chips. The carbohydrates released represent the hemicellulose present, with the cellulose undegraded. If the duration of the treatment is extended, more carbohydrate is released. Figure 2 shows the amount of carbohydrate removed relative to the electrical refiner energy required to process the wood chips to thermomechanical pulp. The decrease of energy required to process wood could be related to the strength of the wood chips themselves. Wood strength has been correlated to the loss of arabinan or galactan components (82, 83), and these components are removed from the wood chips prior to any cellulose damage. The pulps from these studies have produced handsheets with strength properties (burst, tensile, and tear indexes) equal to or better than that of the control handsheets for chips with carbohydrate removal (total of arabinan, galactan, glucan, xylan, and mannan) up to 6% of the original wood chip weight. The electrical energy saved is generally between 30% and 50% for these pulps, and the handsheets show enhanced strength with brightness similar to the controls.

The relationship between carbohydrate extracted from the chips and electrical refiner energy savings may hold for other acid prehydrolysates. If so, the vast amount of literature on dilute acid hydrolysis might be mined for conditions that will produce a level of extractable carbohydrate under temperature conditions that will produce high quality bright paper.

Characterization of Hemicellulosic Extracts

The extraction of hemicellulosic sugars by an acidic prehydrolysis produces sugars that are mostly monosaccharides and small oligosaccharides. Acetyl esters normally present on the hemicellulose are partly cleaved, leaving some esters still attached to the sugars (80). This complicates a detailed analysis of the

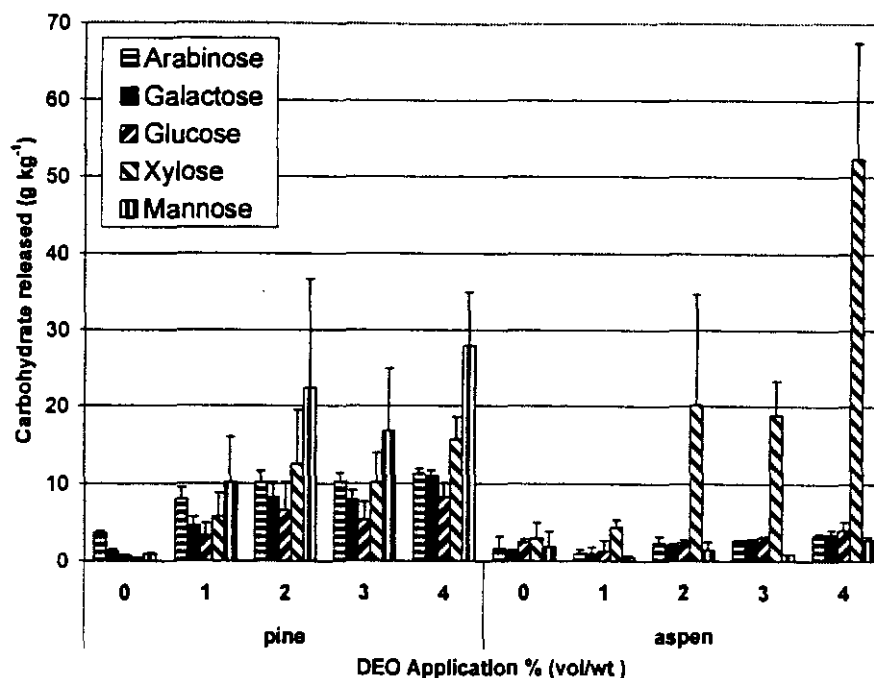


Figure 1. Carbohydrates released into aqueous solution from wood chips treated with DEO (0, 10, 20, 30 and 40 mL kg⁻¹ wood) at 135 °C–140 °C for 30 min. Results represent the average and error bars the standard deviation for at least two treatments and extractions as described (80).

sugars present and necessitates a secondary hydrolysis in the analysis of the total carbohydrates present.

A second hydrolysis is even more important for the identification of the carbohydrate composition when the hemicellulose is extracted by an alkaline system. Here the hemicellulose comes out as a polymeric material and the acetyl esters as acetate. Polymeric oligosaccharides are easier to separate and concentrate from the aqueous solutions by neutralization and ultrafiltration. The acetate could be recovered as a salt, but if acetic acid is the desired product then acid addition will be required.

The separation of acetic acid and sugars can be accomplished with membrane filtration and has been proposed as a part of ethanol production from wood (84, 85). Reverse osmosis membranes can facilitate both separation and concentration of the carbohydrates. Systems have been configured for concentrating sugar solutions in industrial settings. One example is to recycle wash water from rinsing trucks that ship high fructose corn syrup (86). The sugar is recovered, the rinse water is reused, and the heat in the wash water is retained facilitating further cleaning.

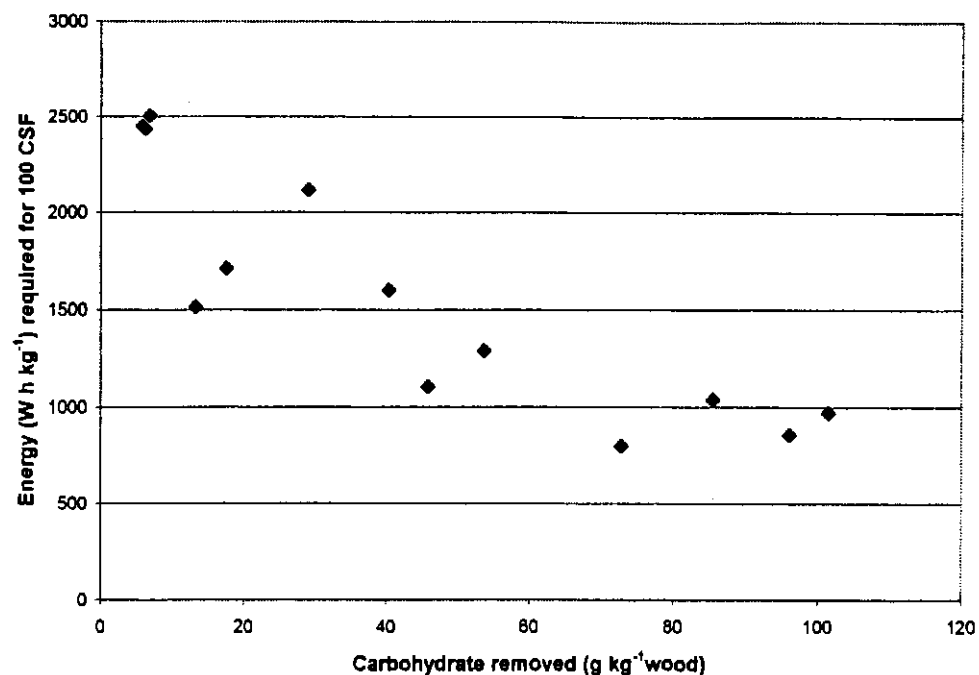


Figure 2. Energy required to process pine wood chips to 100 mL CSF. Chips were processed with DEO at 135 °C–140 °C as described (81). Carbohydrate was calculated by the sum of identified sugars removed from wood chips and corrected for water of hydrolysis. Energy at 100 CSF was calculated from a power function fit of a plot of energy used in pressurized and atmospheric refiners for at least three pulps vs CSF.

Acidic pretreatments and hydrolysis are known to produce inhibitors of yeast that metabolize the sugars to ethanol (87). Little work has been performed to characterize inhibitors of metabolism produced by alkaline extraction methods. There are many post-extractive treatments for cleaning inhibitors from the extraction liquids (87, 88). Enzymatic (89), chemical (87, 88), and adsorbent methods (90, 91) can remove inhibitors and allow more extensive and faster conversion of the sugars to the product. The adsorbent methods may be particularly interesting because they offer the potential to recover other defined products from the adsorbent.

For the work on DEO pretreatments, we tested the raw extract for the metabolism of the sugars to determine if large concentrations of inhibitors were present. Ethanol production will require higher concentrations of sugars, which may result from different extraction procedures or reverse osmosis filtration. Figure 3 shows the result of a test of a supplemented DEO pine extract and metabolism by *Pichia stipitis*. The sugar concentrations were determined by

HPLC (92) and are reported in the figure as monosaccharides. There was some delay in the metabolism of the sugars, and then almost all the monosaccharides were consumed, with glucose, galactose, and mannose appearing to be used simultaneously, followed by xylose and then arabinose. A secondary hydrolysis was also performed, so the sugar derivatives could also be followed. The proportions of individual sugars that were present as monosaccharides in the extract were as follows: 89% arabinose, 38% galactose, 25% glucose, 56% xylose, and 30% mannose. By the end of the incubation, the following proportions of the total sugar present were consumed 80% arabinose, 45% galactose, 66% glucose, 93% xylose, and 48% mannose. In all cases except arabinose, more sugars were consumed than could be accounted for by the monosaccharide content, indicating an ability of *P. stipitis* to metabolize sugar derivatives present in the extract.

A similar experiment was performed with *Saccharomyces cerevisiae*. Using the same extract and the conditions described above for *P. stipitis*, *S. cerevisiae* consumed the following percentages of the total sugar present: 5% arabinose, 46% galactose, 44% glucose, 6% xylose, and 35% mannose. *S. cerevisiae* does not normally use pentoses, and *P. stipitis* readily uses pentoses. These experiments also indicated that there might be some benefit in treating the extract with enzymes that might target mannose, galactose, and glucose derivatives so better conversion of the hexoses could be accomplished. The DEO and oxalic acid pretreatments have good potential in biorefining and thermomechanical pulping. Extending the reaction conditions by increasing heat, chemical loading, or time of pretreatment might also make these useful pretreatments for chemical pulps.

Summary

There are many methods of removing hemicellulose from lignocellulose. Acidic extraction results in short oligosaccharides or monomeric sugars. Alkaline and solvent methods provide more polymeric material. Polymeric material is easier to concentrate, using precipitation or ultrafiltration. If the extraction method does not deliver concentrated sugars, then reverse osmosis can be used. At the same time, reverse osmosis can separate the acetic acid from the sugars. Alkaline methods produce acetate, which will require acid addition and salt formation to derive acetic acid.

Acidic pretreatments are being used in commercial start-up ventures for the total conversion of lignocellulose to chemicals and fuels. The pretreatments are followed by further acid or enzymatic hydrolysis. The predominant product in these ventures is ethanol for use as a fuel. Acidic pretreatments are valuable in thermomechanical processes where electrical refiner energy savings and stronger

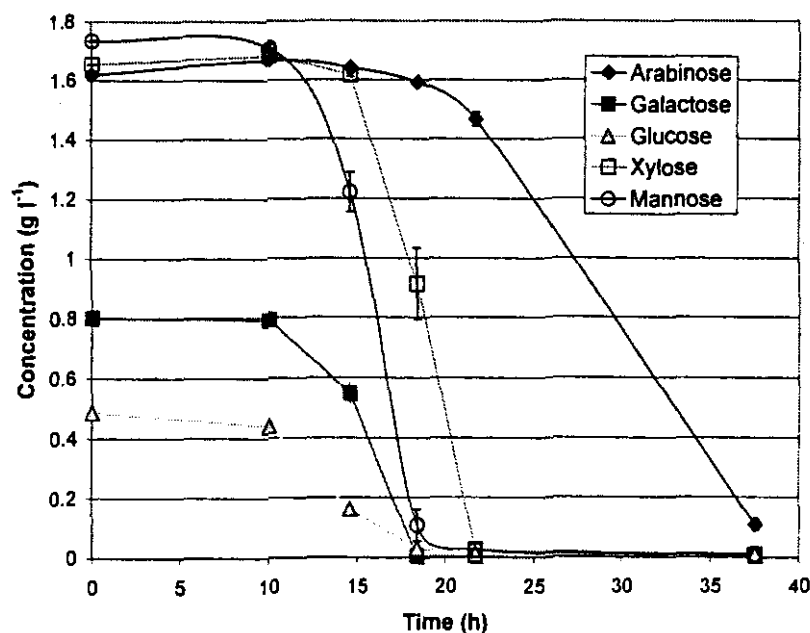


Figure 3. Carbohydrate usage (monosaccharide content) by *Pichia stipitis* (CBS6054) in 40-mL DEO kg⁻¹ treated pine extract + yeast nitrogen base (pH 6.0). Data are average of two experiments, error bars represent standard deviation.

products are a result that is correlated with hemicellulose removal. Testing of other pretreatments might provide similar benefits. Pretreatments that are of value in thermomechanical pulping might also be of value in chemical pulping, and investigation of these techniques is underway.

References

1. Perlack, R.; Wright, L. L.; Turhollow, A. F.; Graham, R. L.; Stokes, B. J.; Erbach, D. C. *Biomass as feedstock for a bioenergy and bioproducts industry: The technical feasibility of a billion-ton annual supply*; Oak Ridge National Laboratories: Oak Ridge TN, April, 2005.
2. *Healthy forests; an initiative for wildfire prevention and stronger communities*; August 22, 2002.
3. Raymond, D.; Closset, G., *Solutions!* **2004**, (September), pp 49-53.
4. Thorp, B.; Raymond, D., *PaperAge* **2004**, 120(7), pp 16-18.
5. Kamm, B.; Kamm, M., *Appl. Microbiol. Biotechnol.* **2004**, 64, pp137-145.

6. Baeza, J.; Freer, J., In *Wood and cellulosic chemistry*, ed.; Hon, D.; Shiraishi, N., Marcel Dekker, Inc.: New York, 2001.
7. Timell, T. E., In *Advances in carbohydrate chemistry*, ed.; Wolfrom, M. L.; Tipson, R. S., Academic Press: New York, 1964; 19, pp 247-302.
8. Timell, T. E., In *Advances in carbohydrate chemistry*, ed.; Wolfrom, M. L.; Tipson, R. S., Academic Press: New York, 1965; 20, pp 409-483.
9. Jacobs, A.; Dahlman, O., *Biomacromolecules* **2001**, 2, pp 894-905.
10. Pettersen, R. C., In *The chemistry of solid wood*, ed.; Rowell, R., American Chemical Society: Washington, DC, 1984; pp 57-126.
11. Aspinall, G. O., In *Biogenesis of plant cell wall polysaccharides*, ed.; Loewus, F., Academic press: New York, 1973; pp 95-115.
12. Aspinall, G. O., In *Advances in carbohydrate chemistry*, ed.; Wolfrom, M. L.; Tipson, R. S., Academic Press: New York, 1959; 14, pp 429-468.
13. Sun, X.-F.; Sun, R.; Fowler, P.; Baird, M. S., *Journal of Agricultural and Food Chemistry* **2005**, 53, pp 860-870.
14. Willfor, S.; Holmbom, B., *Wood Science and Technology* **2004**, 38, pp 173-179.
15. Adams, G. A., In *Methods in carbohydrate chemistry*, ed.; 1965; 5, pp 146-147.
16. Wyman, C.; Dale, B.; Elander, R. T.; Holtzapple, M.; Ladisch, M.; Lee, Y. , *Bioresource Technology* **2005**, 96, pp 1959-1966.
17. Mosier, N.; Wyman, C.; Dale, B.; Elander, R. T.; Lee, Y. Y.; Holtzapple, M.; Ladisch, M., *Bioresource Technology* **2005**, 96, pp 673-686.
18. Eggeman, T.; Elander, R. T., *Bioresource Technology* **2005**, 96, pp 2019-2025.
19. Rowell, R.; Hajny, G. J.; Young, R. A., In *Introduction to forest science*, ed.; Young, R. A., John Wiley & Sons, Inc.: 1982; 4, pp 451-469.
20. Hajny, G. J. *Biological utilization of wood for the production of chemicals and foodstuffs*; USDA Forest Service Forest Products Laboratory: Madison WI, 1981; 65.
21. Kokta, B. V.; Ahmed, A., In *Environmentally friendly technologies for the pub and paper industry*, ed.; Young, R. A.; Akhtar, M., John Wiley & Sons, Inc.: New York, 1998; pp 191-214.
22. Vaaler, D.; Syverud, K.; Seem, B.; Moe, S. T., *Tappi Journal* **2005**, 4(4), pp 23-27.
23. Copur, Y.; Makkonen, H.; Amidon, T. E., *Holzforschung* **2005**, 59, pp 477-480.
24. McGovern, J. N.; Springer, E. L. In *History of fpl cold soda cmp process*, TAPPI Pulping Conference, New Orleans, October 30-November 2, 1988; TAPPI Press: New Orleans, 1988; pp 641-648.
25. Svenson, D. R.; Li, J. United States 2005.

26. Abbot, J.; Bolker, H. I., *Svensk Papperstidning* **1984**, 87(12), pp R105-R109.
27. Green, J.; Sanyer, N., *Tappi Journal* **1982**, 65(5), pp 133-137.
28. Maloney, M. T.; Chapman, T. W., *Biotechnol. Prog.* **1986**, 2(4), pp 192-202.
29. Maloney, M. T.; Chapman, T. W.; Baker, A. J., *Biotechnology and Bioengineering* **1985**, 27, pp 355-361.
30. Springer, E. L., *Industrial and Engineering Chemistry Product Research and Development* **1985**, 24, pp 614-623.
31. Springer, E. L., *Tappi* **1966**, 49(3), pp 102-106.
32. Springer, E. L.; Harris, J. F., *Svensk Papperstidning* **1982**, 85(15), pp R152-R154.
33. Springer, E. L.; Libkie, K. A., *TAPPI* **1980**, 63(7), pp 119-120.
34. Springer, E. L.; Zoch, L. L., *Tappi* **1968**, 51(5), pp 214-218.
35. Comer, A. H.; Libkie, K. A.; Springer, E. L., *WoodFiber Sci.* **1985**, 17(4), pp 540-548.
36. Hams, J. F.; Baker, A. J.; Conner, A. H.; Jeffries, T. W.; Minor, J. I.; Pettersen, R. C.; Scott, R. W.; Springer, E. L.; Wegner, T. H.; Zerbe, J. I. *Two-stage dilute acid hydrolysis of wood: An investigation of fundamentals*; USDA Forest Service: Madison WI, 1985.
37. Harris, J. F.; Scott, R. W.; Springer, E. L.; Wegner, T. H., In *Progress in biomass conversion*, ed.; Tillman, D. A., Academic Press: Orlando, FL, 1984; 5, pp 102-141.
38. Zerbe, J. I.; Baker, A. J., In *Energy from biomass*, ed.; Klass, D., Institute of Gas Technology: Chicago, 1987; pp 927-947.
39. Comer, A. H.; Lorenz, L. F., *WoodFiber Sci.* **1986**, 18(2), pp 248-263.
40. Comer, A. H.; Wood, B. F.; Hill, C. G.; Harris, J. F., *Journal of Wood Chemistry and Technology* **1985**, 5(4), pp 461-489.
41. Carrasco, F.; Roy, C., *Wood Science and Technology* **1992**, 26, pp 189-208.
42. Brennan, M. A.; Wyman, C., *Applied Biochemistry and Biotechnology* **2004**, 113-116, pp 965-976.
43. Liu, C.; Wyman, C., *Bioresource Technology* **2005**, 96, pp 1978-1985.
44. Lloyd, T. A.; Wyman, C., *Bioresource Technology* **2005**, 96, pp 1967-1977.
45. Wyman, C.; Dale, B.; Elander, R. T.; Holtzapple, M.; Ladisch, M.; Lee, Y. *Bioresource Technology* **2005**, 96, pp 2026-2032.
46. McGovern, J. N.; Brown, K. J.; Kraske, W. A., *TAPPI* **1949**, 32(10), pp 440-448.
47. Simmonds, F. A.; Kingsbury, R. M.; Martin, J. S.; Mitchell, R. L., *TAPPI* **1956**, 39(9), pp 641-647.
48. Meller, A., *TAPPI* **1950**, 33(5), 248-253.
49. Simmonds, F. A.; Kingsbury, R. M.; Martin, J. S., *TAPPI* **1955**, 38(3), pp 178-186.

50. Richter, G. A., *TAPPI* **1955**, 38(3), pp 129-150.
51. Torget, R. W.; Padukone, N.; Hatzis, C.; Wyman, C. US 6,022,419, 2000.
52. Nguyen, Q. A.; Tucker, M. P. US 6,423,145 B1, 2002.
53. Schmidt, A. J.; Orth, R. J.; Franz, J. A.; Alnajjar, M. US 6,692,578, 2004.
54. Lightner, G. E. US 6,258,175 B1, 2001.
55. Farone, W. A.; Cuzens, J. E. US 5,726,046, 1998.
56. Young, R. A., In *Environmentally freindly technologies for the pulp and paper industry*, ed.; Young, R. A.; Akhtar, M., John Wiley & Sons, Inc.: New York, NY, 1998; pp 133-156.
57. Young, R. A.; Davis, J. L., *Holzforschung* **1986**, 40, pp 99-108.
58. Sundquist, J.; Poppius-Levin, K., In *Environmentally freindly technologies for the pulp and paper industry*, ed.; Young, R. A.; Akhtar, M., John Wiley & Sons, Inc.: New York, NY, 1998; pp 157-190.
59. Aziz, S.; Mcdonough, T. J., *TAPPI* **1987**, 70(3), pp 137-138.
60. Boussaid, A.; Cai, Y.; Robinson, J.; Gregg, D. J.; Nguyen, Q. A.; Saddler, J. N. *Biotechnol. Prog.* **2001**, 17, pp 887-892.
61. Soderstrom, J.; Galbe, M.; Zacchi, G., *Biotechnol. Prog.* **2004**, 20, pp 744-749.
62. Pan, X.; Zhang, X.; Gregg, D. J.; Saddler, J. N., *Applied Biochemistry and Biotechnology* 2004, 113-116, pp 1103-1114.
63. Overend, R. P.; Chornet, E., *Phil Trans R Soc Lond A* **1987**, 321, pp 523-536.
64. Cullis, I. F.; Saddler, J. N.; Mansfield, S. D., *Biotechnology and Bioengineering* **2004**, 85(4), pp 413-421.
65. Hagglund, E.; Lindberg, B.; McPherson, J., *ACTA Chemica Scandinavica* **1956**, 10, pp 1160-1164.
66. Bouveng, H. O.; Lindberg, B., *Methods in Carbohydrate Chemistry* **1965**, 5, pp 147-150.
67. Mantanis, G. I.; Young, R. A.; Rowell, R., *Holzforschung* **1994**, 48, pp 480-490.
68. Aziz, S.; Sarkanen, K., *Tappi Journal* **1989**, 72(3), pp 169-175.
69. April, G. C.; Kamal, M. M.; Reddy, J. A.; Bowers, G. H.; Hansen, S. M., *TAPPI* **1979**, 62(5), pp 83-85.
70. Dahlmann, G.; Schroeter, M. C., *Tappi Journal* **1990**, 73(4), pp 237-240.
71. Lonnberg, B.; Laxen, T.; Sjoholm, R., *Paperija Puu* **1987**, 69(9), pp 757-762.
72. Sakakibara, A.; Edashie, Y.; Sano, Y.; Takeyama, H., *Holzforschung* **1984**, 38, pp 159-165.
73. Pasmer, L.; Behera, N. C., *Holzforschung* **1985**, 39, pp 51-61.
74. Pasmer, L.; Cho, H. J., *TAPPI* **1989**, 72(2), pp 135-142.
75. Yawalata, D.; Pasmer, L., *Holzforschung* **2004**, 58, pp 7-13.

76. Goyal, G. C.; Lora, J. H.; Pye, E. K., *TAPPI* **1992**, 75(2), pp 110-116.
77. Sun, R.; Lu, Q.; Sun, X.-F., *Cell Chem. Technol.* **2002**, 36(3-4), pp 243-263.
78. Akhtar, M.; Swaney, R. E.; Horn, E. G.; Lentz, M. J.; Scott, G. M.; Black, C. C.; Houtman, C. J.; Kirk, T. K. 2002.
79. Swaney, R. E.; Akhtar, M.; Horn, E.; Lenz, M.; Klungness, J.; Sabourin, M. In *Oxalic acid pretreatment for mechanical pulping greatly improves paper strength while maintaining scattering power and reducing shives and triglycerides*, Tappi Fall Technical Conference: Engineering pulping & PCE & I, 2003; Tappi Press, Atlanta GA.: 2003.
80. Kenealy, W.; Horn, E.; Houtman, C. J.; Swaney, R. E.; Davis, M. W., *Holzforschung* **2006**, Submitted.
81. Kenealy, W.; Horn, E.; Houtman, C. J., *Holzforschung* **2006**, submitted.
82. Winandy, J. E.; Lebow, P. K., *Wood Fiber Sci.* **2001**, 33(2), pp 239-254.
83. Curling, S. F.; Clausen, C. A.; Winandy, J. E., *Forest Products Journal* **2002**, 52, pp 34-39.
84. Ethanol research breakthrough: Wood feedstock. <http://renewableenergyaccess.com/rea/news/story?id=22228>
85. Suny researchers find way to make ethanol from wood. <http://www.esf.edu/newspubs/news/2005/01.18.ethanol.htm>
86. Reverse osmosis. http://www.gewater.com/librarv/tp/691_Sweet_Solutions.js
87. Klinke, H. B.; Thomsen, A. B.; Ahring, B. K., *Appl. Microbiol. Biotechnol.* **2004**, 66, pp 10-26.
88. Palmqvist, E.; Hahn-Hagerdal, B., *Bioresource Technology* **2000**, 74, pp 17-24.
89. Khiyami, M. A.; Pometto III, A. L.; Brown, R. C., *Journal of Agricultural and Food Chemistry* **2005**, 53, pp 2969-2977.
90. Canilha, L.; Silva, J. B.; Solenzal, A. I., *Process Biochem.* **2004**, 39, pp 1909-1912.
91. Horvath, I. S.; Sjode, A.; Nilvebrant, N.-O.; Zagorodni, A.; Jonsson, L. J., *Applied Biochemistry and Biotechnology* **2004**, 113-116, pp 525-238.
92. Davis, M. W., *Journal of Wood Chemistry and Technology* **1998**, 18(2), pp 235-252.

ACS SYMPOSIUM SERIES **954**

Materials, Chemicals, and Energy from Forest Biomass

Dimitris S. Argyropoulos, Editor
North Carolina State University



American Chemical Society, Washington, DC



Library of Congress Cataloging-in-Publication Data

Materials, chemicals, and energy from forest biomass / Dimitris S. Argyropoulos, editor.

p. cm.—(ACS symposium series ; 954)

Includes bibliographical references and index.

ISBN 13: 978-0-8412-39814(alk. paper)

ISBN 10: 0-8412-3981-9(alk. paper)

1. Biomass energy. 2. Forest biomass.

I. Argyropoulos, Dimitris S., 1956—

TP339.M367 2006
620.1'.17—dc22

2006043053

The paper used in this publication meets the minimum requirements of American National Standard for Information Sciences — Permanence of Paper for Printed Library Materials, ANSI Z39.48—1984.

Copyright © 2007 American Chemical Society

Distributed by Oxford University Press

All Rights Reserved. Reprographic copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Act is allowed for internal use only, provided that a per-chapter fee of \$33.00 plus \$0.75 per page is paid to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. Republication or reproduction for sale of pages in this book is permitted only under license from ACS. Direct these and other permission requests to ACS Copyright Office, Publications Division, 1155 16th Street, N.W., Washington, DC 20036.

The citation of trade names and/or names of manufacturers in this publication is not to be construed as an endorsement or as approval by ACS of the commercial products or services referenced herein; nor should the mere reference herein to any drawing, specification, chemical process, or other data be regarded as a license or as a conveyance of any right or permission to the holder, reader, or any other person or corporation, to manufacture, reproduce, use, or sell any patented invention or copyrighted work that may in any way be related thereto. Registered names, trademarks, etc., used in this publication, even without specific indication thereof, are not to be considered unprotected by law.

PRINTED IN THE UNITED STATES OF AMERICA