CHAPTER 6

Prehydrolysis Pulping with Fermentation Coproducts

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6.1 Introduction and Background

Although the term "integrateed biorefinery" is new, the concept has long been familiar to the pulp and paper industry, where processes include biomass boilers providing combined heat and power, and byproducts of pulping include turpentine, fatty acids and resin acids. In the dominant kraft (or sulfate) pulping process, dissolved lignin and chemicals from the pulp digester are concentrated by evaporation and burned in a recovery boiler to generate steam and to recover the inorganic chemicals that are recausticized and reused as fresh pulping chemicals. In addition, prior to pulping, bark is remived from pulpwood and fed to waste fuel boilers that raise additional steam. High-pressure steam is used in a cogeration process to generate electricity for the plant, while lover-pressure steam is used for pulping process heat and paper drying. In recent years, many paper companies have added wood-fired boiler capacity and used slash from logging or wood residues from lumber mills to replace fossil

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fuels, typically requiring only natural gas to operate the lime kilns that are part of the recausticizing process.

In addition to dissolved lignin and degraded carbohydrates, the waste liquor from pulping contains a mixture of fatty acids and resin acids. While evaporating excess water to reach high enough organic solids concentration for the liquor to burn, this mixture of organic acids separates from the remaining liquor and is collected to provide products like the rosin used on the bows of violins or other stringed instruments, and diverse products including soap and the anticholesterol steroid sitostanol used in some fortified foods. In addition, while heating the wood chips at the beginning of the pulping process, a mixture of volatile products distil from the wood to provide turpentine.

Whereas the kraft process has benefited from this diverse range of byproducts for decades, the second most common type of pulping process has had a limited range of byproduct options. Mechanical pulping, chiefly thermomechanical pulping (TMP) and stone groundwood pulping, produces wood pulp used primarily in newsprint for newspapers and coated paper for magazines. These high yield pulps contain nearly all the lignin, hemicellulose and cellulose found in the original wood. High-yield pulp mills still burn bark and other wood wastes to provide steam for power and process heat, and newer processes recover additional waste heat from the thermomechanical pulping process and often with it, turpentine. Mechanical pulp mills are unable to recover the other navel stores chemicals and have very large electrical energy needs that are usually not practical to meet with available wood wastes. One way to improve recovery of potential byproducts at mechanical pulp mills is to carry out an early-stage "prehydrolysis" of wood in order to recover hemicellulose sugars, resin acids, and fatty acids.

The general concept of wood prehydrolysis is not new to the wood pulp industry. The prehydrolysis kraft process was developed commercially around 1950 in order to produce chemically pure cellulose for the dissolving pulp industry: rayon and acetate.[1,2] As shown in Figure 6.1, the prehydrolysis kraft pulping process could yield kraft pulp with nearly all the hemicelluloses and much of the amorphous cellulose removed. The companies that have used this process to produce dissolving pulps have all evaluated a fermentation product from the prehydrolysis solution, but ultimately decided that loss of heat in the digester and loss of fuel for the recovery boiler were too costly to be offset by the value of ethanol that could be produced. Mechanical pulping processes have evaluated various chemical pretreatment processes, and there are mills providing pulps prepared by first pretreating the wood with sodium sulfite or hydrogen peroxide. The thermomechanical pulping process includes a brief preheating stage that hydrolyzes some of the acetate esters in the hemicelluloses and generates an acidic pulping environment and dilute solution of hemicellulose fragments. This treatment must be minimized as extensive prehydrolysis produces lower brightness pulps that cannot be used effectively in most paper grades. The key discovery leading to a prehydrolysis capability for mechanical pulps was that the use of oxalic acid reduced this loss in brightness that rendered the

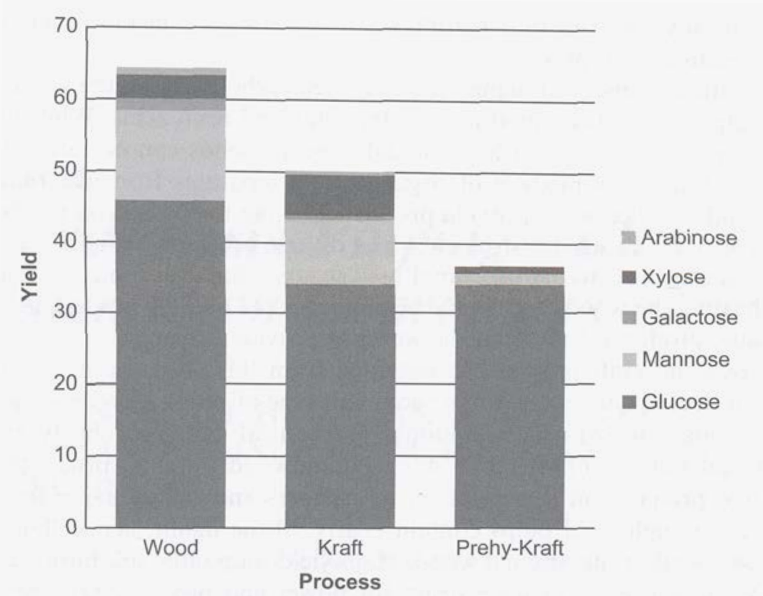

Figure 6.1 The carbohydrates in softwood and wood pulp.

pulp unsuitable for paper, and also provided a significant reduction in the amount of electrical energy needed to produce the pulp.

With pulp and paper mills struggling to remain profitable, and with incentives of potentially higher revenues from fuel and chemical byproducts along with government incentives for ethanol production and R&D grant funds for research, the American Forest and Paper Association (AF&PA), through their research committee, the Agenda 2020 Technology Alliance, initiated a research project several years ago to evaluate a range of prehydrolysis process and processing alternatives. Assembling a management and funding consortium of more than 20 corporate sponsors and with over $1 200 000 in US Department of Energy supporting grant funds, $200 000 in grant funds from the Wisconsin Department of Natural Resources, and over $400 000 in funding support from the member companies, the consortium sponsored research at five universities and two government laboratories to evaluate pretreatment conditions, impacts on wood pulp production and quality, fermentation of the prehydrolysis filtrate, and process economics. Known as the VPP (or "Value Prior to Pulping") Consortium, it conducted research to identify potentially profitable operating conditions for prehydrolysis with both hardwood and softwood kraft pulp and TMP.

VPP Consortium research evaluated alkaline and acid pretreatments and helped to explore potential business concepts for prehydrolysis and fermentation in the context of kraft pulping for both hardwood and softwood fiber, and with TMP for use in lightweight coated magazine paper (as described below in more detail). Potential business opportunities and the feasible operating space for this technology vary with each of the options. Alkaline treatments remove carbohydrates without affecting kraft pulp yield, but the resulting prehydrolysis solution has a low concentration of sugars. Moreover, much of the sugar is present as nonfermentable carbohydrate oligomers and the high ionic strength inhibits many fermentation microbes. Acid treatments for softwoods provide acceptable yields of sugars, but have to be carefully controlled since softwood fiber is the high-strength component in most paper products and the pretreatment affects both the strength of the fibers and their ability to naturally bond, as needed to produce paper strength. The prehydrolysis treatment of hardwoods has potentially more operating space since the pulp is not relied on as heavily for paper strength. Also, hardwoods contain more hemicellulose, and it is more easily removed than for softwoods. The hardwood chips are also easier to pulp following treatment than untreated wood chips.[3]

The operating space for pretreatment in association with thennomechanical pulping is very different from that for kraft pulping. Where only about half the mass removed in pretreating wood chips for kraft pulp ends up as a yield loss of pulp with the rest as a loss of waste organics as energy, in TMP nearly 100% of the mass removed in the pretreatment is a loss of product yield. However, production of TMP requires a very large input of electrical energy in refining – nominally 2000 kWh/ton of product, and the acid (or alkaline) pretreatment can reduce this energy requirement by 25% or more. The pretreatment yield and energy savings need to be carried out in a manner that does not reduce the brightness or the strength of the pulp.

Subsequent sections of this chapter describe the research on prehydrolysis with TMP and fermentation of sugars in the hydrolysate. The research on prehydrolysis-TMP focuses on the pilot-plant studies and the process and economic modeling research. The description of fermentation research focuses on the fermentation of hemicellulose sugars to ethanol as part of the VPP research program.

6.2 Prehydrolysis Thermomechanical Pulping

Prehydrolysis-TMP can be viewed as a derivative of research that started in 1980 using fungi and fungal enzymes to enhance or replace traditional mechanical pulping methods such as TMP.[4,5] It was discovered that treating wood chips with a white rot fungus and providing sufficient time and conditions for the fungus to degrade the chips significantly decreased the electrical refining energy needed to produce pulp for newsprint or other mechanical pulp paper grades.[6] In a follow-up project to learn more about the fungal mechanism, one of the compounds exuded by the fungal hyphae was found to be oxalic acid. Although the initial thought was that the oxalic acid recruited iron from the environment and initiated a Fenton radical attack on lignin moieties, it was ultimately determined that oxalic acid alone (or diethyl oxalate as an alternative chemical for introducing the acid) was sufficient to obtain the energy savings.[7,8]

McDonough at the Institute of Paper Chemistry had previously shown that mineral acids like sulfuric acid and hydrochloric acid had much the same effect, but in that case the energy savings were not of much interest to the industry because it resulted in significant darkening of the pulp that made it impossible to recover the brightness needed for paper grades (unpublished work: Master's Thesis, Cheryl Rueckert, Institute of Paper Science and Technology, 1993). The oxalic acid treatment, discovered originally by U.S. Forest Products Laboratory and BioPulping International, did not significantly reduce pulp brightness, at least at low treatment levels. The possibility of combining energy-saving oxalic acid pretreatment with a fermentation distillation plant to process the carbohydrate residuals provided the concept of a new opportunity to create added value at TMP mills.

Another study speculated that pulp brightness stabilization with oxalic acid treatment was due either to the pK_a of the acid providing a pH 2 buffer, or by oxalic acid acting as a reducing chemical and preventing some lignin condensations. Experiments showed that sulfurous acid (H_2SO_3) also preserved the brightness of wood veneer pieces and provided somewhat lower yield loss under otherwise similar conditions.'

The VPP Consortium then sponsored research to evaluate the effects on TMP of oxalic acid pretreatment and sulfurous acid pretreatment relative to untreated controls. The overall objective was to evaluate three wood species, spruce, the most common species used at TMP mills in the Northeast and Midwest regions; aspen, a hardwood often used because it provides high starting brightness and high opacity; and red pine, a common and readily available wood species in the Midwest that normally requires high energy and provides slightly lower brightness than spruce. Process modeling and economic evaluation focused on the case of a mill producing lightweight coated paper that consisted of about 26% bleached softwood kraft pulp (used mainly for sheet strength), 30% TMP that provides both smoothness and opacity, 30% groundwood pulp, and 15% coating material that provides a gloss surface for printing. Such paper is made to meet strength requirements for high-speed printing presses (used to publish weekly magazines).

Typically, mills with wood species that provide higher strength can increase the amount of TMP, coatings or fillers, whereas mills with lower pulp strengths will require more softwood kraft to maintain critical product qualities. The bleached softwood kraft pulp is the most expensive major component in the paper, considered as purchased market pulp for this analysis, followed by the TMP produced on-site at approximately half the cost, with the clay-coating materials and groundwood pulp as lower-cost components. If prehydrolysis causes a loss of strength in the TMP, it would have to be compensated by purchase of additional kraft pulp. Thus, the research became an effort to identify prehydrolysis conditions where there is no loss in TMP strength and brightness, but significant savings in electrical energy, while also considering the potential for fermentation of prehydrolysis sugars.

6.2.1 Experimental Prehydrolysis-TMP

Experimental work was carried out using a pilot-plant scale Sunds Defibrator CD-300 woodchip refiner operating at 1.2 kg per minute feed rate. The CD-300 consists of a chip hopper with steaming bin and metering screw followed by a plug screw feeder with a compression ratio of 4 to 1. The plug screw feeder compresses the wood chips into a plug of compressed and macerated wood chips to form a steam seal for the pressurized reactor, and also feeds the wood into the PREX chemical mixing system. The PREX is a pair of vertical feeder screws that receive and break up the wood plug from the plug screw feeder. The PREX operates with the wood plug immersed in the chemical treatment solution. As the plug breaks, the wood chips expand, filling the fiber lumens with the treatment solution and providing a very uniform distribution of the acid throughout the wood chips. Typically, one kg of wood (dry weight) absorbs about one kg of water and chemicals in the PREX immersion zone. The PREX screws lift the wood chips out of the treatment solution and drop them into the pressurized preheater, which is operated to maintain a steady chip level and residence time. Pressurized treatment was at 130 °C for 10 min. Acid strength was varied to control the yield.

The pressurized preheater discharges *via* a second metering screw at the bottom of the reactor, which feeds a plug-screw discharger, again with a 4:1 compression ratio. Chips are dewatered to 65–70% solids in the plug screw feeder before the PREX immersion zone, and again dewatered to 65–70% solids by the discharge plug screw following the preheater. Liquor take-up in the PREX is 2–3 liters per minute providing a reactor concentration of about 28% solids and a filtrate (sugar) recovery by the plug screw discharge of 75%. The plug from the discharger is broken up in a pressurized transfer auger that feeds the first-stage pulp refiner. The CD-300 refiner is a pressurized disk mill with a 12″ (300 mm) flat disc zone plus a 4″ (100 mm) conical refining zone at the periphery of the plates. The refiner plate gap was adjusted to provide a first-stage specific refining energy loading of 1.1 kWh/kg. Pulp was blown from the refiner to an atmospheric cyclone and collected in 55-gallon drums. Second-stage refining was carried out in a Sprout Waldron 12″ atmospheric disk refiner using adjustments in plate gap, and multiple passes to provide a variety of specific refiner energy loadings, and degrees of fiberization. The initial quality control test for TMP is a drainage test known as freeness with a target refiner freeness value of 150 mL. Experimental results indicated that the spruce TMP was quite responsive to the oxalic acid treatment, providing a 25% reduction in specific refiner energy (SRE) using just 0.15% oxalic acid on starting wood (dry weight basis). Red pine was much less responsive to the prehydrolysis treatment, and aspen responded poorly and suffered a noticeable brightness loss before achieving even a 15% reduction in SRE. Similar experiments carried out using sulfurous acid did not provide as much energy savings and did not protect brightness as well as anticipated.

The carbohydrate removal was largely independent of species, although aspen on average provided slightly more sugar for a given treatment severity. Two aspects of aspen contribute to this outcome. The most readily removed hemicelluloses are the arabinogalactans followed by xylan. Arabinogalactan is a minor constituent of both hardwoods and softwoods, but aspen contains about 16% xylan compared to just 7% in white spruce.” The pretreatment had little impact on the tear strength of the pine pulp, actually resulting in a slight increase that persisted to treatment with an oxalic acid charge of 1% on wood. Spruce also showed a minor increase in tear strength, but went through a maximum with the optimum treatment at about 0.2% oxalic acid on wood. Aspen lost 0.5 to 1 mN m^2/g tear strength under all pretreatment conditions. Hardwood TMP does not contribute much tear strength to a sheet, but this is about a 30% loss from the tear strength of untreated aspen and would have a significant effect on the paper furnish.

6.2.2 Experimental Fermentation of Hydrolysate Sugars

Fermentation research at the U.S. Forest Products Laboratory (FPL) includes biomass conversion to value-added products such as ethanol biofuel from carbohydrates, as well as the production. of polyhydroxyalkanoate (PHA) bioplastics from lipids and carbohydrates by fermenting bacteria, shown in Figure 6.2, natural and synthetic fermentation enzymes, and fermentation inhibitors in extractives that could be used as antibacterial, antifungal, or pesticide agents.

Scientists at FPL have conducted pioneering research on fermentation of hemicellulose to ethanol for over 20 years, promoting lignocellulosic biomass as a way to meet increasing global energy demands. The research led initially to the adoption of a unique xylose fermenting yeast, *Pichia stipitis*, shown in Figure 6.3, commonly found in the gut of a bark beetle. The research has included the isolation of enzymes and genes responsible for fermentation of xylose by *Schefersomyces stipitis*, the complete genome sequencing of *S. stipitis*,[11] metabolic engineering of *S. stipitis* for improved fermentation and development of patented strains of *S. stipitis* for commercial applications. The research has included evaluation of ethanol production from biomass hydrolysates.[12] An example of experimental laboratory research is described here involving the fermentation of hemicellulose to ethanol as part of the VPP

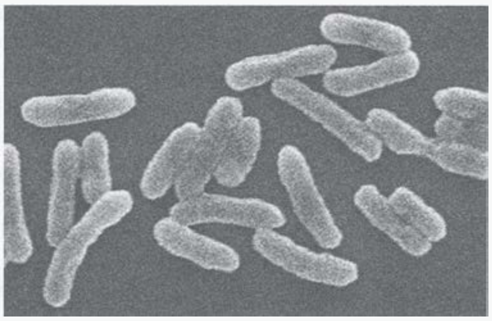

Figure 6.2 PHA producing bacteria *Pseudomonas pseudoflava*.

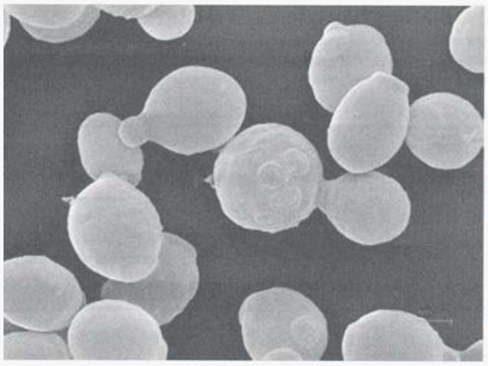

Figure 6.3 Ethanol producing yeast *Pichia stipitis.*

Table 6.1 Total sugars and pH of hydrolysate samples.

		Sugars concentration	
Hydrolysate	*pH*	*before hydrolysis*	*after hydrolysis*
Maple	~2.14	~80 g/L	~ 132 g/L
Loblolly Pine	~1.3	~60 g/L	~ 106 g/L
MSHW	~4.16	~60 g/L	~ 136 g/L

research program. In this case the experimental hydrolysate was typical of that which could be obtained in prehydrolysis kraft pulping.

Hemicellulose was extracted from pulpwood of maple (a northern hardwood species), southern pine (loblolly), and mixed southern hardwood (MSHW) species by a hot-water extraction method followed by a membrane separation process to remove water and acetic acid. The resultant hemicellulose fraction was hydrolyzed with 4% H_2SO_4 and autoclaved for 15 min. Total sugar content was determined by high-pressure liquid chromatography (HPLC) techniques, and measures of the total sugar content before and after acid hydrolysis and the final pH of hydrolysates are shown in Table 6.1. Individual monosaccharide concentrations are given in Tables 6.2, 6.3 and 6.4, along with concentrations of the microbial inhibitors furfural and HMF, as determined also by HPLC.

In the fermentation experiment, *S. stipitis* fermented 100% of the xylose, glucose, galactose and mannose to ethanol in the maple, pine and MSHW hydrolysates. Complete fermentation of the xylose required about four days. *S. stipitis* successfully fermented monomeric sugars in the pine and MSHW extracts, although the hydrolysates contained such low amounts of sugar that ethanol yields were low.

In addition to the sugar monomers, some oligomers in the maple extract were hydrolyzed and the resultant sugars fermented to ethanol by *S. stipitis*, which is known to have an enzyme with the potential for hydrolysis of oligomers. Nutrient requirements were low and are expected to be inexpensive. Biotin and thiamine are the only known essential vitamins for the cultivation of these

Table 6.2 Analysis of maple hydrolysate.

Hydrolysate ID:	*Hot-water pretreated maple hydrolysate*						
SugarAnalyses, Unit: g/L							
Original	*Glc*	*Xylo*	*Gal*	*Rham*	*Arab*	*Man*	*Total CHO*
HP87P HPLC	10.48	63.65	7.31	N.A.	N.A.	3.84	85.28
HP87H HPLC	1.15	71.3	ER	ER	3.3	ER	75.75
NREL HPLC	8.73	72.81	8.63	N.A.	4.47	8.63	107.52
NREL H^1-NMR	3.95	104.5	4.65	3.8	3.65	8.6	129.15
Posthydrolysis	*Glc*	*Xylo*	*Gal*	*Rham*	*Arab*	*Man*	*Total CHO*
NREL HPLC	6.00	99.65	8.60	N.A.	4.72	13.33	132.27
Inhibitor analyses, Unit: mg/L							
	HMF	*Furfural*	*Acetic acid*				
Original	N.A.	1.25	1.22				

Glc = glucose; Xylo =Xylose; Gal = Galactose; Rham = Rhamnose; Arab =Arabinose; Man = Mannose; Total CHO = total carbohydrate.
ER - galactose, rhamnose, mannose cannot be separated from xylose peak.

Table 6.3 Analysis of loblolly pine hydrolysate.

Hydrolysate ID:	*Loblolly Pine*							
SugarAnalyses, Unit: g/L								
Original	*Glc*	*Xylo*	*Gal*	*Rham*	*Arab*	*Man*	*Total CHO*	
HP87P HPLC	4.18	9.88	*low*	22.70	2.66	17.42	56.84	
HP87H HPLC	3.20	35.43	ER	ER	17.77	ER	58.10	
Dionex IC	3.11	15.95	9.15	0.44	17.22	9.94	55.81	
4% H_2SO_4, 15 mins								
HP87P HPLC	21.7	33.14	31.1	16.0	15.62	23.24	140.8	
HP87H HPLC	10.2	70.32	ER	ER	15.3	ER	95.82	
Dionex IC	13.17	25.82	17.47	0.73	18.14	31.33	106.66	
Cation – ICP Unit: mg/L								
	Al	*Ca*	*Cr*	*Cu*	*Fe*	*Mg*	*Ni*	*Zn*
Original	1.17	6.82	52.70	1.39	185.83	91.99	2.66	0.29
Inhibitor analyses, Unit: mg/L								
	HMF	*Furfural*	*Acetic acid*					
Original	5	2.5	1.33					

Glc = glucose; Xylo = Xylose; Gal = Galactose; Rham = Rhamnose; Arab =Arabinose; Man = Mannose; Total CHO = total carbohydrate.
low - below the detection limit.
ER - galactose, rhamnose, mannose cannot be separated from xylose peak.

Table 6.4 Analysis of mixed southern hardwood hydrolysate.

Hydrolysate ID:	*Mixed Southern Hardwood*						
Sugar Analyses, unit: g/l							
Original	*Glc*	*Xylo*	*Gal*	*Rham*	*Arab*	*Man*	*Total CHO*
HP87P HPLC	18.3	51.74	*low*	*low*	6.76	10.94	87.74
HP87H HPLC	7.8	44.2	ER	ER	4.7	ER	56.7
Dionex IC	11.16	30.81	7.15	3.09	1.31	6.62	60.14
4% H_2SO_4, 15 min							
HP87H HPLC	18.4	107.1	ER	ER	10.5	ER	136
4% H_2SO_4, 30 min							
HP87P HPLC	18.1	101.6	ER	ER	10.4	ER	130

Cation Analyses, ICP-MS unit: mg/l								
	Al	*Ca*	*Cr*	*Cu*	*Fe*	*Mg*	*Ni*	*Zn*
Original	13.1	1418.8	2.9	0.2	1061.8	807.7	3.4	11.0

Inhibitor analyses, Unit: mg/L			
	HMF	*Furfural*	*Acetic acid*
Original	*low*	*low*	*low*

Glc = glucose; Xylo = Xylose; Gal = Galactose; Rham = Rhamnose; Arab = Arabinose; Man = Mannose; Total CHO = total carbohydrate.
low – below the detection limit.
ER - galactose, rhamnose, mannose cannot be separated from xylose peak.

organisms. During the ethanol fermentation process, *S. stipitis* also produced a byproduct xylitol, a sweetener used in the food industry.

In summary, laboratory experiments showed that *S. stipitis* can successfully ferment monomeric sugars in maple, pine and MSHW hydrolysates, although in the experiments pine and MSHW hydrolysates contained such low amounts of sugar that ethanol yields were low. The xylose-metabolizing yeast *S. stipitis* strain CBS 6054 is a good candidate for commercial development of hot-water extracted maple hydrolysates, because the strain has promise for oligosaccharide hydrolysis while fermenting subsequent monomeric sugars to ethanol. For a commercial scale-up of ethanol production, a minimum of 10-15% sugar concentration in hydrolysate would be needed for best ethanol production, at least 6% (wt) ethanol with 1 g ethanol/L per hour. A xylose fermenting microorganism like *S. stipitis* is required to reach these levels.

6.2.3 Modeling Prehydrolysis-TMP and Fermentation Process Concept

Addition of a prehydrolysis and fermentation process to an existing pulp and paper mill would impact overall mill operations, so we take the “whole-mill’’ approach to modeling prehydrolysis pulping and fermentation process concepts. For example, at a typical mill producing lightweight coated paper using TMP blended with purchased kraft pulp, the pretreatment of wood chips will remove hemicellulose and increase the moisture content of chips fed to the TMP refiners, while reducing specific energy required in the refiners, which in turn will allow the production of higher quality and higher volumes of TMP pulp at the same energy input, offsetting some of the more expensive purchased kraft pulp input.

To model this prehydrolysis-TMP and fermentation process concept, FPL researchers developed models of overall pulp and paper mill operations, using energy and mass balance equations. The energy and mass balance equations were designed with sufficient detail to predict operational impacts of prehydrolysis on overall mill-wide operations. While the energy and mass balance equations were implemented in Microsoft Excel, the results for several cases were validated by comparing with more complete WinGEMS models. WinGEMS is the pulp and paper industry's premier process simulation tool that has been used for many years to model pulp and paper production processes.

The FPL models were constructed using hypothetical but realistic mill parameters and scales that were thought to be "typical" of commercial operations. The objective of the modeling was to determine conditions under which an investment in prehydrolysis pulping might be a good business decision. The models include capital costs that are considered to be accurate within perhaps ±30%, and in general there remains some uncertainty about actual production performance of the process itself, so the analysis is accompanied by sensitivity analysis and stochastic risk analysis, recognizing the variability and uncertainties related to underlying parameters. The models are tools that can help to identify opportunities for commercial development, but actual investment decisions will require more detailed analysis supported by more precise engineering estimates of capital costs and operating parameters.

FPL researchers recently developed preliminary estimates of financial performance for various prehydrolysis-TMP investment scenarios with projected financial cash flow worksheets linked to process energy and mass balance equations that were developed in Microsoft Excel.[13,14] The resulting VPP-TMP process and economic model is also available for download at the VPP website maintained at SUNY-ESF (www.esf.edu/pbe/vpp/). In addition, stochastic simulation was incorporated into the VPP model as a way to show variability in the predicted financial returns in relation to probability distributions of specified engineering and financial parameters.

The VPP-TMP model computes an incremental investment analysis based on differences in projected cash flows for whole pulp and paper mill operations, between what is called the "process" case with VPP, and the "base" case without VPP (*i.e.* the existing mill without prehydrolysis and fermentation). The differences or "incremental" cash flows are used to compute measures of financial performance for the hypothetical VPP investment, including internal rate of return and discounted net present value. These measures may be used to evaluate the financial feasibility of the business concept. The Excel model computes the financial performance measures in three ways: before tax and finance, before tax, and after tax (the latter two options include the effects of capital financing or borrowing). Internal rates of return are calculated both on a "nominal" basis, which includes inflation, and on a "real" basis, which removes inflation.

For VPP/TMP the base case mill is assumed to be currently processing 300 oven dry metric tons per day (OD MT/day) of chips into thermomechanical pulp, with a specific refiner energy input of 2.1 MWh/MT. This TMP is blended with groundwood pulp and bleached kraft pulp. The blended pulp is used to make lightweight coated paper. The boundary of the VPP-TMP model starts with clean chips entering the primary TMP refiner and ends with the dried coated paper product. Full steam recovery from the refiners is implemented. The financial model suggests that if the base case TMP mill's initial capital investment was $620 million (the cost of a new mill) the after-tax internal rate of return over a 20-year lifetime would be 6.7%, but more typically an existing mill would be an older mill with smaller and depreciated capital costs.

The FPL VPP-TMP model uses engineering parameters estimated from VPP-TMP experimental results.[13] In addition, the model incorporates recent historical price data for pulp, wood, chemicals and electricity. The projected financial performance of the VPP business concept was estimated for aspen, spruce, and pine. Oxalic acid was presumed to be used as the primary pretreatment chemical. The level of oxalic acid was chosen to be the maximum level that would not significantly degrade the strength or optical properties of the wood pulp.

In the cases of aspen and pine the pretreatment was estimated to improve the strength properties of the resulting TMP pulp. The power load of the refiner was assumed to be limited at its current level, and the paper production also limited to its current level by market demand. For all the wood species analyzed the specific energy for refining would be reduced as a result of pretreatment. Thus, while maintaining the total electric power load on the refiners, the mill could increase the throughput of TMP. Since the overall paper production was also held constant it was determined that a lower amount of groundwood pulp and/or bleached kraft pulp would be used for blending with TMP. Table 6.5 displays the major operating parameters for the base case (the existing mill without prehydrolysis and fermentation) and the three different process cases involving prehydrolysis pulping and fermentation for each of three different wood species.

In the model, the cash-flow analysis worksheet provides calculations of the after-tax net present values and internal rates of return for the three process cases. We assumed a pretax nominal discount rate of 11% with Federal and state income taxes at a combined effective rate of 41.5%. Table 6.6 shows key model results and assumptions, including projected financial performance for the three process cases (after-tax net present value, NPV, and internal rates of return, IRR, on both nominal and real dollar basis), ethanol production, and the capital costs of ethanol production and pretreatment facilities. Ethanol capital costs vary among the three cases because of varying levels of wood-sugar recovery and fermentation. Projected real IRRs of 16–27% across the three cases indicate positive expected financial performance. The main source

Table 6.5 Operating parameters for TMP cases.

Process Parameters	*Base*	*Aspen*	*Spruce*	*Pine*
Wood moisture content (% total weight)	50	50	50	50
OA loading (% on wood weight)	0.00	0.85	0.07	0.90
Sulfur Dioxide (% on wood weight)	0.0	1.0	0.0	0.0
Hydrogen Peroxide (% on pulp weight)	2.0	1.5	2.0	3.0
Sodium Bisulfite (% on pulp weight)	0.50	0.00	0.50	0.75
Hemis removed, total (% total available)	0	10	3	20
Extractives removed (% total available)	0	50	50	50
Acetic acid removed (% wood treated)	0	1.5	0.25	0.25
Primary specific energy (MWh/m.t.)	1.12	0.83	0.78	0.78
Secondary specific energy (MWh/m.t.)	0.70	0.52	0.49	0.49
Rejects specific energy (MWh/m.t.)	0.70	0.52	0.49	0.49
Kraft pulp (% fraction total pulp)	30	24	30	24
Groundwood pulp (% fraction total pulp)	35	30	21	28
LWC coating weight (% of paper weight)	15	15	15	15
Conversion monosaccharide to ethanol (%)	0	46	46	46
TMP mill process labor (workers/day)	24	24	24	24
Ethanol plant process labor (workers/day)	0	12	12	12

Table 6.6 Financial performance of incremental investment for various VPP/TMP cases.

	Aspen	*Spruce*	*Pine*
After-tax NPV ($ million)	48.2	32.7	26
After-tax nominal IRR	30%	26%	20%
After-tax real IRR	27%	23%	16%
Ethanol production (million gal/yr)	1.01	0.59	1.92
Ethanol capital cost ($ million)	10.1	5.9	19.2
Pretreatment capital cost ($ million)	25.4	25.9	26.9

of the positive financial performance is a combination of significant specific energy savings and strength improvement of the TMP pulp, which allows for a reduction in expensive kraft pulp.

In an effort to further understand the factors that control the financial performance in the model, sensitivity analysis was performed by sequentially increasing various process parameters by 1%, one at a time. The results of sensitivity analysis varied across the different process cases, but in general the parameters to which the model was most sensitive are shown in Table 6.7, along with "reasonable" expected values of those parameters, and a range in their expected values from more "pessimistic" to more "optimistic". When the ranges of parameter values that are shown in Table 6.7 are introduced into the model it determines the sensitivity of projected financial performance (*e.g.* the sensitivity of NPV) to expected variation in process parameters. The parameters associated with the pulp blend are found to be the most important in terms of their impact on financial performance in the model. Pretreatment capital cost is next. Absent from this list is electrical power cost because in this

Table 6.7 Parameter values used for sensitivity analysis.

	Pessimistic	*Reasonable*	*Optimistic*
Per cent kraft pulp (%)	26	24	22
Per cent groundwood pulp (%)	32	30	28
Kraft pulp price ($/MT)	700	743	800
Groundwood pulp price ($/MT)	400	423	450
Pretreatment capital cost ($MM)	23	21.5	20
Primary specific energy (MW hr/MT)	0.90	0.83	0.70
Wood chips price ($/MT)	70	64	60

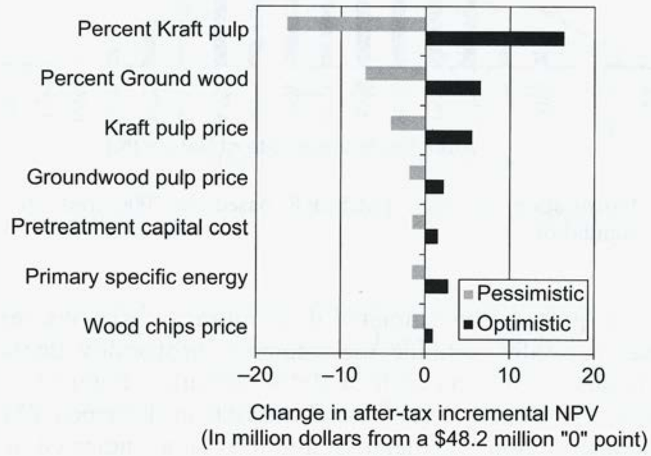

Figure 6.4 Sensitivity analyses of NPV for the aspen prehydrolysis TMP process case.

analysis the total electrical demand was held constant and thus removed from consideration in sensitivity analysis.

Figure 6.4 shows the results of the sensitivity analyses of NPV for the aspen prehydrolysis-TMP process case. The figure shows for the important process parameters how the estimated after-tax Net Present Value varies as the parameters are varied from "pessimistic" to "optimistic" values. Similar results are obtained for the other two wood species. For aspen, the after-tax incremental NPV was $48.2 million, and changing the kraft pulp blend by just 2% can change the NPV by $1 5 million. Changing the kraft blend has by far the greatest impact on NPV when compared to the other parameters. However, even if all the parameters are set to their "pessimistic" values, the NPV still remains positive.

A more holistic way to evaluate the financial risk is to assign probability distributions to the values of multiple engineering and financial parameters in the model (*e.g.* ethanol yield, washing efficiency, pulp prices, *etc.*) and then run model simulations by choosing values randomly from these distributions and using a large number of simulations to derive estimated probability distributions of financial performance. The results of such multivariate stochastic

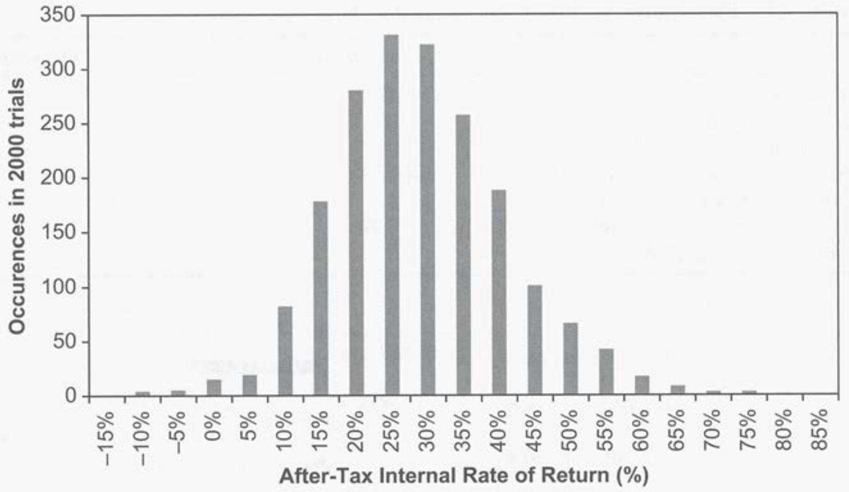

Figure 6.5 Distribution of aspen TMP IRR based on 2000 trials of a stochastic simulation.

simulations can provide the estimated distribution of after-tax real IRR for example, that naturally combine the estimated probability distributions of underlying model parameters with model sensitivities. Figure 6.5 shows the results of such a stochastic simulation of the IRR in the aspen TMP case. As expected, the distribution is centered at about 27%, as indicated in Table 6.6. Analysis of this distribution indicates that a 95% confidence interval for after-tax IRR is between 5% and 55%.

,Finally, as a method for comparing distributions, the cumulative probability distributions were calculated for the three wood species, with results shown in Figure 6.6. The curves in Figure 6.6 can be interpreted as the probability of achieving an after-tax IRR value or better. For example, for the pine case the probability of achieving an IRR greater than 10% is about 70%, while the probability of achieving an IRR greater than 20% is about 30%.

In summary, all of the prehydrolysis-TMP cases were estimated to offer positive financial performance, with incremental after-tax IRRs of 16-27%. However, the stochastic risk analysis indicated that there is a relatively wide range of possible IRRs. For example, the 95% confidence interval for the aspen case includes estimated IRRs that range from 5% to 55%. It is also interesting to note that the IRR in all the cases goes up by 3% when the ethanol plant is removed and only the pretreatment is implemented, indicating that the primary economic benefit of prehydrolysis pulping in the case of TMP is the improvement in pulping and papermaking (chiefly reduced purchase of kraft market pulp as TMP output increases).

These results suggest that at current and projected ethanol prices (based on projections from the 2010 U.S. Annual Energy Outlook), the ethanol plant revenue cannot support its capital investment as well as the pretreatment

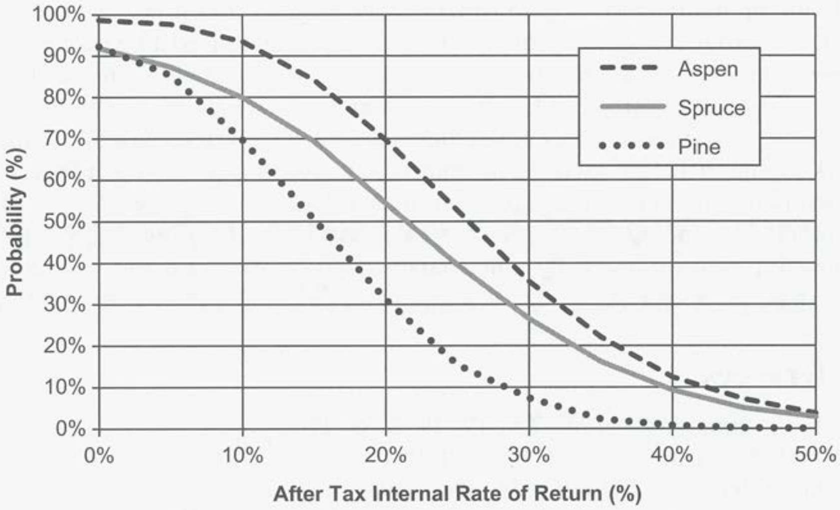

Figure 6.6 Cumulative distribution of TMP IRR based on 2000 trials of a stochastic simulation of each of the cases.

process itself. In other words, the VPP pretreatment process may be desirable by itself (without ethanol fermentation) based on the cost reductions for the pulp mill, and given the reductions in specific energy consumption, which may provide some mitigation of rising energy prices.

6.3 Summary and Path Forward

The research on prehydrolysis pulping and fermentation has identified important signposts that point the path forward in biorefining and forest products research. One important finding is that the quantities of carbohydrates that can be extracted from wood chips prior to pulping are limited, and recovery may not be justified if the carbohydrates are fermented primarily into low commodity value fuel ethanol. Thus, one signpost on the path forward is to seek higher-value carbohydrate derivatives or fermentation products to improve the commercial feasibility of prehydrolysis pulping concepts. The ability of Pichia to produce xylitol as well as ethanol is a notable example. Another important finding is that process synergies with an existing pulp and paper mill can vary substantially depending on the type of mill, and can vary even within one particular type of mill, depending on process assumptions, as shown in the VPP-TMP results. Thus, another signpost on the path forward is to seek process and mill synergies that enable biorefining to enhance overall mill performance, and to explore the role of prehydrolysis pulping in various mill contexts. such as various types of kraft pulp and paper or paperboard mills. Lastly, the finding in the case of VPP-TMP that the estimated IRR goes up by a further 3% when the ethanol plant is removed and only the pretreatment is implemented clearly suggests that it may be better in some cases to focus more attention on the improvement of existing pulping and papermaking processes than trying to repurpose existing facilities unless clearly higher financial rewards can be obtained from such repurposing. Although the pulp and paper industry may have entered an era of slower growth or declining markets, nevertheless there is an enormous global demand for paper and paperboard products, which still have high value, and thus the challenge for biorefining technology is to develop an ability to extract yet higher value from pulpwood than produced by pulp, paper, paperboard or existing biorefining concepts.

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