Opportunities for the Forest Products Industries

Alan W. Rudie

Abstract

The concept of sustainable harvests is not new to lumber and paper companies—they have been concerned about it and been practicing it for decades, long before it became the headline in a newspaper article. After decades of static products and markets, the industry is offered an opportunity to add products in a new business sector—fuels and chemicals. Although paper companies have a long association with the naval stores chemical business, this new market will see larger volumes and more numerous product opportunities. As with all new markets, this will create turbulence and there will be winners and losers, but the real change is that now there can be true winners. Companies must have two capabilities to be among the winners. Every major forest products industry already has mastered the first—they know where the wood is and how to get it. Forest products companies can integrate procurement into their quality needs and product value streams. Competitors from outside the forest products industry have not mastered this—yet. The second capability is commercial experience with thermal or biochemical conversion of biomass into chemical products. This is a fair competition. No one has a product, no one has a process, and everyone has the opportunity to start at the same time. The industry must use the integration of forest biomass technologies to maximize its strategic advantage and, more importantly, minimize competition for the higher value timber. This paper discusses potential forest biomass markets for fuels and higher value chemicals.

Alan W. Rudie is Supervisory Research Chemist with USDA Forest Service, Forest Products Laboratory, Madison, Wisconsin.

Introduction

In recent decades, traditional forest products have been adversely impacted by new materials—plastic replacing the paper grocery bag, steel 2×4's penetrating the dimension lumber market, TV and electronic media displacing printing and writing papers, and plastics and mineral–plastic composites penetrating the panel and wood laminate markets. The petroleum shortages of 2007 and concerns over the impact of burning fossil fuels on the earth's climate have renewed interests in wood-based fuel and chemical products. This is an opportunity for the forest products industries to go on the offensive and enter new markets in specialty chemicals, pharmaceuticals, and polymers. Forest products, including wood-based chemicals and polymers, are well positioned to be carbon neutral (or carbon negative), sustainable, and green solutions to global problems. A number of potential new forest products are listed in Table 1. The table is far from comprehensive; for more complete lists see Werpy and Petersen (2004) and Hajny (1981). These potential products have been selected as examples of chemicals and process possibilities. Several are established markets, already produced from agricultural-based feedstocks.

The first five products in the table represent an extensive group of chemicals that have glucose as a common intermediate. They are products that can be produced using chemical and biochemical processes and are categorized by the U.S. Department of Energy (DOE) as sugars platform chemicals. Ethanol is obviously used as a fuel and fuel oxygenate. It has also been used to produce ethylene and butadiene. Diols

Table 1: Select potential new products from wood.

Product[a]	Business	Status[b]	Prediction	Driver
Ethanol	Commodity	Pilot	Likely	Fuel, incentives
diols	Specialty	Lab	Probable	Glucose cost
Lactic acid	Specialty	Lab	Probable	Glucose cost
HMF	Specialty/commodity	Lab	Unknown	Yield
PHA	Specialty	Lab	Probable	Glucose cost
CNC	Specialty	Lab	Probable	Compatibility
MFC/NFC	Specialty	Commercial/lab		Compatibility
Diesel fuel	Commodity	Pilot/commercial	Probable	Scale/cost
Methanol	Commodity	Pilot	Probable	Cost

[a] PHA, polyhydroxyalcohols; CNC, cellulose nanocrystals or whiskers; NFC, nanofibrillated cellulose.
[b] Status of product production from lignocellulose. Production of diols, lactic acid, and PHAs from starch is commercial.

are used in polyesters and in products as diverse as deicing chemicals for commercial airplanes and cosmetic products. Lactic acid is used to produce polylactic acids as a renewable and compostable plastic that among other applications can replace the polystyrene used in clear clamshell food containers. These three chemicals are normally produced by fermentation-like processes in which microorganisms consume glucose and release the chemical product as a lower energy byproduct. Hydroxymethyl furfural (HMF) and related chemicals, such as 2,5-dihydroxy furan and 2,5-furanedicarboxylic acid, are produced by chemical dehydroxylation of six-carbon sugars. Polyhydroxyalkanoates are a polyester food storage polymer produced directly from sugars by a number of bacteria. Most notable are the copolymers of 3-hydroxybuterate and 3-hydroxyvalerate sold under the trade name Biopol (Monsanto, St. Louis, Missouri).

The next two products in the table, cellulose nano-crystals (CNC) and micro- (or nano-) fibrillated cellulose (NFC), are largely perceived as reinforcement materials in fiber-reinforced composite products. As a notable example, a composite produced from fibrillated cellulose using phenol-formaldehyde resin provided strength properties nearly identical to magnesium alloy with a 10% savings in weight (Nakagaito and Yano 2005).

The final two chemical products, diesel fuel and methanol, are produced by first gasifying biomass to produce hydrogen and carbon monoxide and then reforming the gas into chemical products. Most international interest is in straight-chain hydrocarbons for diesel fuel (Fischer–Tropsch) and methane for synthetic natural gas. DOE also has interest in catalyst reforming into methanol, longer chain length-mixed alcohols, and a fermentation process that produces ethanol from the product gas.

The paper focuses first on the processes—hydrolysis to produce sugars and gasification to provide synthesis gas for reforming. It then reviews the status for each of the products listed in Table 1. Much of the DOE focus is on agricultural residuals. Wood-sourced biomass behaves differently than straw and stover in both processes, and some of these differences are highlighted in the review.

Obviously, venturing into biomass-based chemical production entails considerable risk for a forest products company of any size, but it must be recognized that not taking the opportunities biomass chemicals offer also contains risks. First is the risk of persisting in commodity product businesses that are no longer growing. Of even greater concern is the impact non-forest industry companies pose to the traditional businesses. All the wood biomass estimates used by the federal government in formulating biomass fuels policy have assumed wood use will be limited to slash and thinnings produced in other harvesting or forest management activities (Perlack et al. 2005, BR&Di 2008).

As part of a timber harvest process, slash is available at significantly lower cost than pulp wood and larger diameter wood suitable for dimension lumber. But harvesting fuel wood as an independent process—basically thinning the forest to reduce fire risk or improve growth—is a high-cost process that cannot provide chemical/fuel quality wood at competitive costs
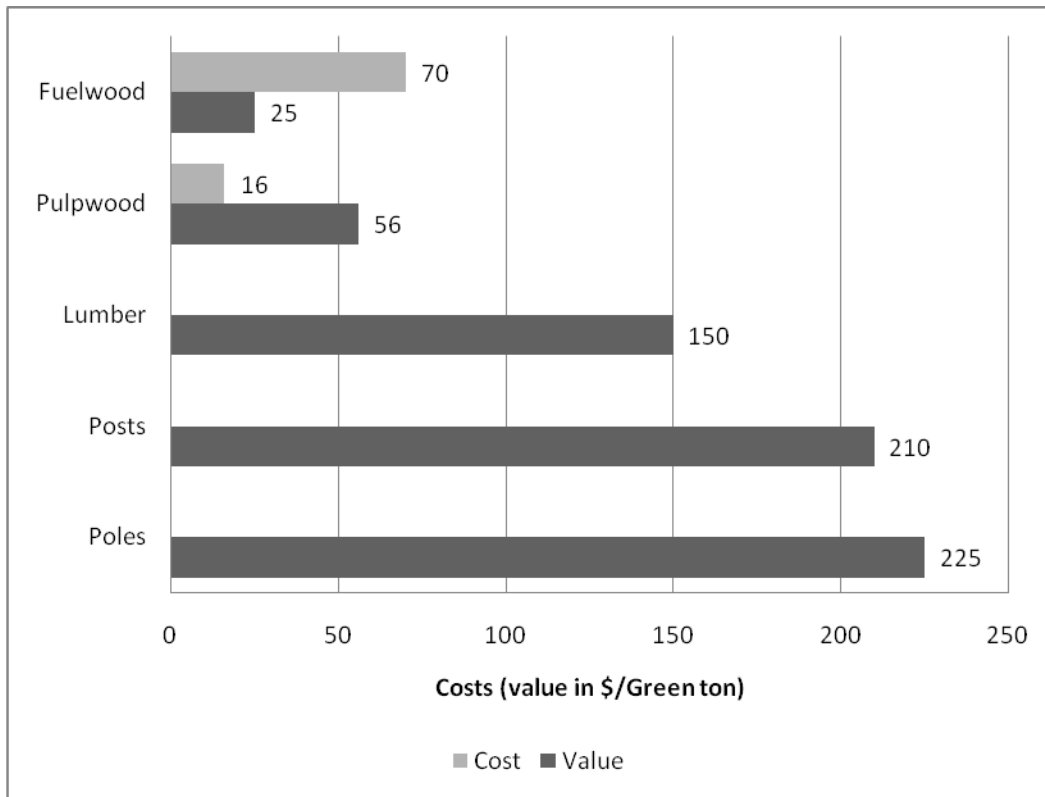
Figure 1. Estimated costs to harvest and market value of wood products. Fuelwood cost is for thinning.

(Figure 1) (USDA 2005, Bolding et al. 2009). If not integrated into a harvest operation, pulp wood is the low-cost source of woody biomass. The ultimate risk to existing forest products companies is that new entries into wood-based chemicals will not understand the market sufficiently and end up using pulpwood-quality material. The industry has already observed this trend with several electrical utilities that have entered the renewable power market. Federal incentives to promote biomass use for fuel and chemicals increase the risks because these subsidies often do not apply to traditional forest products.

This summary of possible opportunities discusses briefly the two principal conversion methods, hydrolysis to glucose and thermal decomposition to pyrolysis oil or producer gas (synthesis gas). The paper then discusses several specific products emphasizing several that are already commercial products.

Process Methods

Wood Hydrolysis to Glucose

The original lyrics to the Simon and Garfunkel song "The Boxer" contain the line "after changes upon changes we are more or less the same." Wood hydrolysis to glucose is a good example of this maxim. The discovery of cellulose as a polymer of glucose is credited to Anselme Payen (Payen 1838). Early research on the use of concentrated sulfuric acid to hy-

drolyze carbohydrates dates as far back as 1883 (Fleschsig 1883). Concentrated acids (H_2SO_4, HCl, and H_3PO_4) are effective at hydrolyzing lignocellulose to provide a mixture of sugar monomers and short-chain carbohydrate oligomers. Lignin resists the acids and is left as an insoluble polymer. Because the strong acid is energy intensive and expensive, the process could not be made viable without acid recovery (Harris 1952). Separation of the sugars from the concentrated acid and recovering acid for reuse have been the focus of most of the strong acid research, but to date there is not a commercially demonstrated acid recovery method. Blue Fire Ethanol received one of the DOE Integrated Biorefinery grants awarded in 2007 to evaluate hydrolysis with concentrated sulfuric acid using an acid recovery process developed by Arkenol (U.S. Patent: 5,597,714) and currently under pilot evaluation by JGC Corporation in Izumi, Japan. Concentrated acid hydrolysis also persists in the Klason lignin method used to determine the lignin content of wood and wood pulp (Klason 1908).

Dilute acid hydrolysis methods are nearly as old, with patent literature dating back to 1920. Because dilute acids are much slower, the treatments were normally carried out at elevated temperatures (160–220°C) and pressures. Probably most significant in dilute acid development was the Scholler (1935) process patented in 1935 and used in Germany during WWII to supplement fuel needs with lignocellulosic
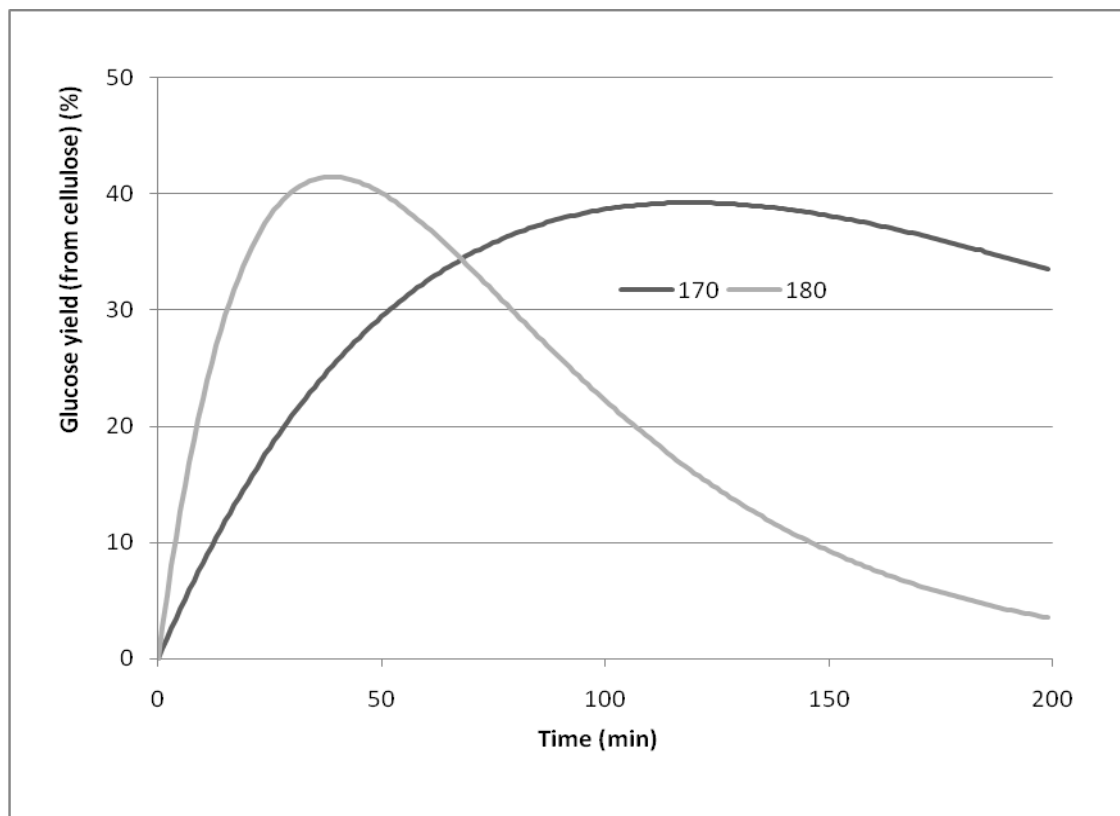
Figure 2. Effect of competing reactions for glucose formation from cellulose, and glucose decomposition to hydroxymethylfurfural on overall glucose yield in dilute acid hydrolysis of wood. The kinetics favored high temperature (180° C vs. 170° C) and short retention times to increase glucose yield.

ethanol (Faith 1945). In the United States, the Madison process was developed by the Forest Products Laboratory (Harris et al. 1945) and used to construct a full-scale plant in Springfield, Oregon, completed in 1946 (Katzen and Schell 2006). Under the high temperatures of dilute acid treatments, the product glucose is unstable and dehydrates to 5-hydroxymethylfurfural and levulinic acid (McKibbins et al. 1962). Furthermore, the kinetic rate slows significantly once the amorphous cellulose is hydrolyzed. The combination of the slower rate and decomposition reactions leads to a kinetic rate limited process yield of about 50% of the available cellulose (Figure 2) (Saeman 1945, Mok et al. 1992) The term recalcitrant cellulose was later coined for the reduced reaction rate of crystalline cellulose and resulting maximum yield of glucose in dilute acid treatments. Nonetheless, the Madison process was able to produce optimized yields of glucose leading to 60–68 gallons of ethanol per U.S. short ton of wood and achieved 50 gallons per ton in the commercial plant before it was shut down at the end of WWII (Katzen and Schell 2006).

Due to the limitations of dilute acid treatment, it was eventually abandoned by DOE and most research switched to the use of fungi or fungal enzymes to hydrolyze cellulose to glucose. DOE has put significant resources into producing more effective enzyme mixtures that convert cellulose to glucose, with emphasis on improving rates and reducing the cost of the enzymes. The results have been an approximate doubling of the process rate (down from about 4 days to 2 days) and five-fold decrease in enzyme costs. Many of the enzymes used come from a very effective fungus, *Trichoderma reesie*, discovered in the south Pacific during WWII (Tolan 2006). The major advantage of enzymes is highly selective conversion that produces glucose without significant decomposition to other products. This allows high yields of cellulose conversion with longer treatment times and higher enzyme doses, but as with dilute acid, enzyme conversion rates slow dramatically after about half the cellulose is hydrolyzed, reinforcing the concept of recalcitrant cellulose (Figure 3). Although cellulose crystallinity may have some part in the reduced reaction rates, other chemical factors also appear to be involved (Yang et
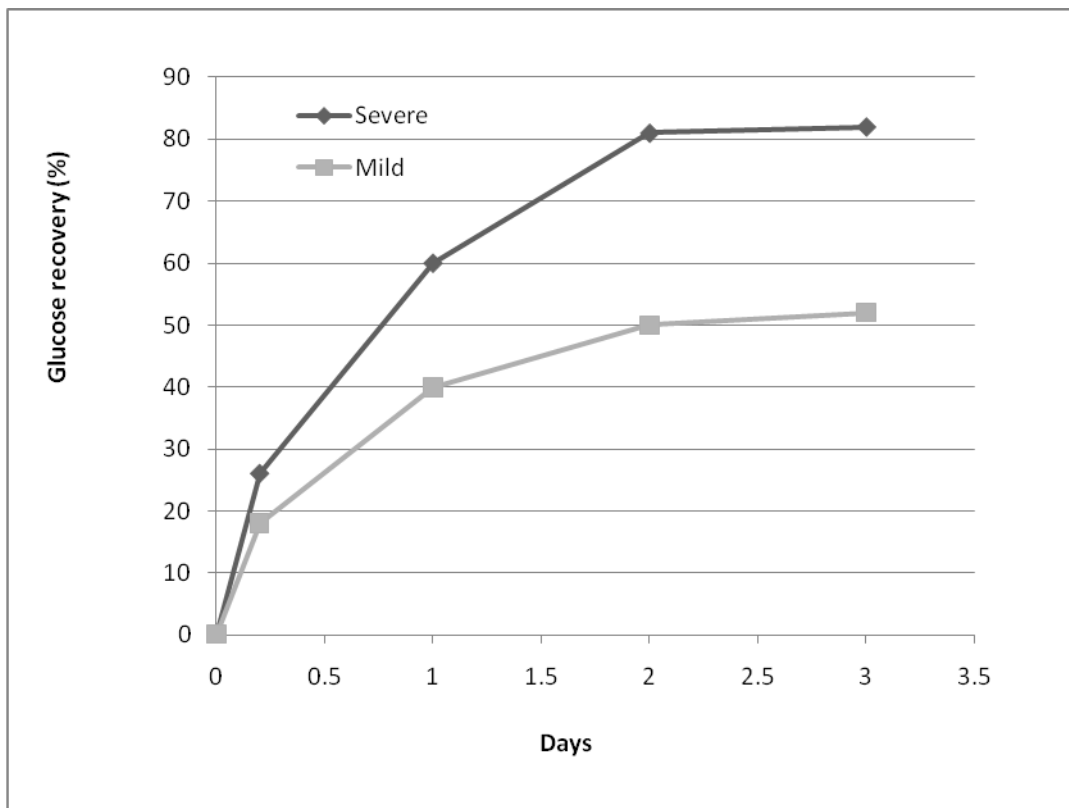
Figure 3. Effect of pretreatment and decrease in rate of conversion for enzyme hydrolysis of biomass.

al. 2006). Different pretreatment processes that result in differences in lignin content, surface area, and hemicellulose content can have dramatic effects on the rates of final conversion. In a commercial sense, however, time is money and most lignocellulose biorefinery concepts based on enzymatic conversion abandon some of the yield to reduce capital costs. Of seven DOE-supported lignocellulosic plants in the Integrated Biorefinery grants and 1/10-scale biorefinery grants, projected yields range from 70 to 85 gallons of ethanol per ton.

Enzyme hydrolysis concepts generally require a pretreatment to remove some of the hemicellulose and increase the exposure of the cellulose to enzymes. For agricultural residuals, this is often just a hot water treatment or steam explosion process. Hardwoods can be pretreated with similar technologies but are a little harder to break up into small particles and the wood structure does impede the pretreatment. Often hardwoods are treated with dilute acid to accelerate the hydrolysis of hemicellulose. Softwoods are generally considered hard to treat and saccharify, although there are numerous research papers where this has been accomplished (Zhu et al.

2009). Grinding (size reduction) can be performed either before or after pretreatment, but there is considerable energy savings if the grinding is carried out after the wood chips have been treated with acids. The severity of pretreatments varies widely. Mild conditions may remove 15% or less of the original biomass but, at least in some cases, result in slower enzymatic hydrolysis rates and a lower overall yield. Stronger conditions increase the amount of biomass hydrolyzed in pretreatment and usually provide faster enzymatic conversion and higher enzymatic conversion yields (Figure 3), but the acid conditions often degrade some of the sugars. This can also reduce overall yield (Boussaid et al. 2000). There are more exotic pretreatments that have been proposed. Sulfite (sulfurous acid) has been used for nearly a century as a pulping process and is effective as a pretreatment acid (Wayman et al. 1984, Boussaid et al. 2000, Zhu et al. 2009). Oxalic acid has been promoted by the Forest Products Laboratory and has several unique advantages, but it is more costly than sulfuric acid and unlikely to get serious attention in any application except pretreatment in pulping processes (Swaney et al. 2003). The Lignol Innovations project, one of the
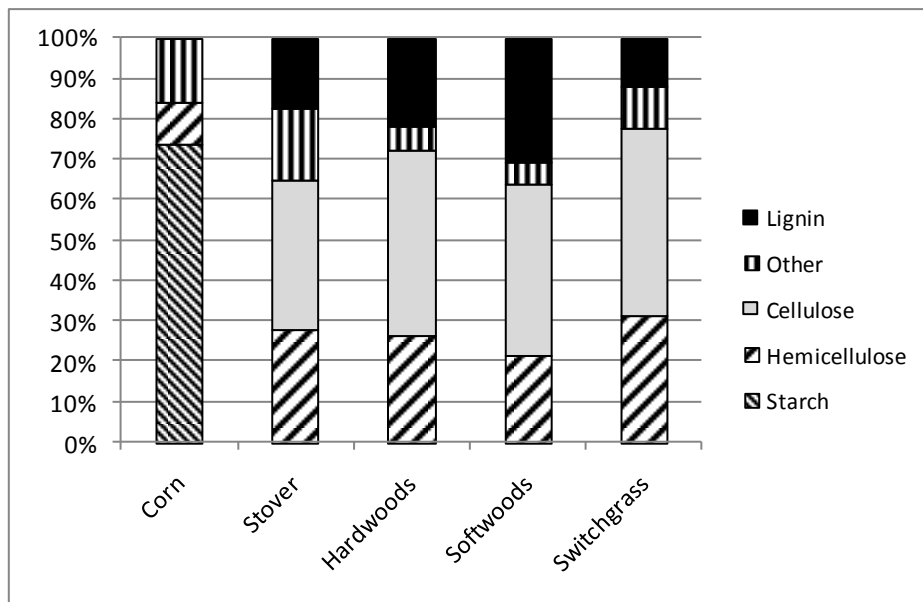
Figure 4. Contribution of major polymers to the composition of typical biomass.

10% validation grants issued by the DOE, planned to use a mild version of a solvent pulping process as pretreatment for ethanol production. Other papers have suggested supercritical water, molten salts, and even ionic liquids as pretreatments. A key feature of any successful pretreatment method will have to be low cost. Fuel is still a low-value commodity. The potential 100% yield product value per ton of wood from a fuel ethanol or butanol plant about equals product value from a market pulp mill and is half that of an integrated pulp and paper mill. Product value simply cannot support an expensive pretreatment process.

Much of the materials removed in the prehydrolysis treatments are sugars and oligomers from the hemicelluloses fraction of the biomass carbohydrates. Although the major focus is on cellulose conversion, lignin and hemicelluloses constitute almost half of most biomass (Figure 4). Lignin content is low in grasses and other herbaceous biomass, 15%, rising to almost 30%, in some softwoods. Hemicellulose is typically 20% to 30% of the biomass. Hemicellulose in grasses, corn stover, and hardwoods is rich in xylans, a group of polysaccharides that contain xylose as part of the backbone chain of the polymer. Xylose is significant in that it is a five-carbon sugar that is not fermented by common brewers yeast (*Saccharomyces cerevisiae*). As almost 20% of grasses and hardwoods, xylose is a significant secondary sugar that can contribute to the viability of a lignocellulosic biorefinery.

Xylose has its own list of potential products, including furfural and xylitol, but can also be fermented to ethanol by some yeasts. This goal has also received considerable DOE support and currently there are at least four native or genetically modified organisms capable of fermenting xylose to ethanol. Verenium is planning a separate fermentation step for sugars removed in prehydrolysis using their proprietary organism for fermenting xylose to ethanol (Patrick 2008).

Three of the DOE demonstration ethanol plants plan to use wood as all or part of the feedstock for the process. Pacific Ethanol plans to use a mix of wheat straw, corn stover, and poplar; Lignol plans to use a mix of hardwoods and softwoods. Verenium Biofuels plans to start their system on bagasse and intends to use energy cane and wood chips as well. There are two projects on prehydrolysis with the residual wood used in traditional pulp and paper products. Red Shield Environmental received a 1/10-scale grant from DOE to restart an idle pulp mill in Old Town, Maine. The proposal is to pretreat wood chips to extract hemicellulose sugars and ferment the sugars to produce ethanol as a co-product. The residual wood chips will be kraft pulped to produce bleached kraft market pulp. CleanTech Partners of Madison, Wisconsin, and a partnership of paper companies organized by the American Forest and Paper Association received a DOE research grant to evaluate water and acid prehydrolysis of wood with project tasks to evaluate prehydrolysis hardwoods, prehydrolysis softwoods, and prehydrolysis thermomechanical pulp. This project has been completed, with final reports submitted to DOE. Although details have not been released publically, it is known that several implementation scenarios projected profitable operations, but it is not clear that the predicted financial returns were sufficient for any of the project partners to take on the investment risks.

Gasification and Pyrolysis of Wood

When heated with sub-stoichiometric levels of oxygen, wood or other biomass degrades into a liquid referred to as pyrolysis oil, or a mixture of low-molecular-weight gases—predominately hydrogen,

carbon monoxide, carbon dioxide, and water—often called producer gas. There has been considerable research on both processes, but applications with gasification appear to be closer to commercial practice. The gases can be recombined to form hydrocarbons, or alcohols. Two processes already have considerable commercial experience using product gas from coal gasification. The Fischer–Tropsch process was developed in Germany before WWII and used to supply diesel fuel when Germany began to suffer from fuel shortages later in the war (Anderson et al. 1952, Schulz 1999). It was picked up by a South African company—SASOL—and has been used in South Africa for the same purpose since 1955. Experience with methanol also dates back to the early decades of the last century (Tijm et al. 2001). Notable U.S. experiences with methanol from coal gasification are the Eastman Chemical Company and Air Products and Chemicals Inc. plants in Kingsport, Tennesse (Vaswani 2000, Tijm et al. 2001). There are still a number of research concerns with biomass gasification and gas reforming, but the two main processes required have to be considered relatively mature technologies.

Nano-fibrilated cellulose and cellulose nanocrystals have synthetic or manufacturing processes that are unique to the product and are discussed in the section on these two products.

Ethanol

Most of the current commercial scale-up activity with biorefineries is targeting ethanol as a transportation fuel and fuel oxygenate. The main advantages of this are that the commercial-scale fermentation processes already exist, and as a fuel product, the market is established and large enough to absorb new ethanol production. But ethanol is not an ideal fuel. Most existing internal combustion gas engines were assembled with seals and hoses that are not compatible with high concentrations of ethanol. The result is that gasoline was limited to an ethanol content of 10%, recently raised to 15%, in order to avoid damaging the existing fleet of vehicle engines. The vast majority of ethanol manufactured in the United States is produced in the grain-belt region of Iowa and surrounding states. Because ethanol is not compatible with other petroleum uses, it is not allowed in the distribution pipelines and has to be distributed by rail. The result is that both U.S. coasts have little incentive to use any more than the minimum ethanol required for fuel oxygenate. Even though overall ethanol production capacity in the United States may be

in line with expected need, the distribution of capacity has resulted in a glut of ethanol in the central states, lower use on the coasts, and depressed pricing that is considerably noticeable during times of lower crude petroleum costs. This is an advantage for wood-based processes, which would often be located in regions where there is little corn-grain alcohol production and that can benefit from lower transportation costs to the sizable east and west coast markets. Additional drawbacks of ethanol are lower overall density and a lower energy content that translates to fewer miles per gallon for cars using ethanol as part of the fuel mix.

There are considerable government incentives and macro-economic incentives to advance cellulosic ethanol production capabilities in the United States. Currently, this is a $1.01 tax incentive paid to the ethanol blender. To put $1.01 into perspective, this equates to $40 per barrel of petroleum and means that at $50 per barrel for a petroleum world market price, a cellulosic ethanol producer could potentially operate at over $80 per barrel production cost and still be profitable. Because most of the DOE-supported semicommercial scale plants are planning to produce ethanol, it is a good bet several of these will be operating within the next decade. These companies are gaining considerable pilot-scale experience with cellulosic ethanol, and it is reasonable to expect that Iogen, Poet, and Verenium will proceed to commercial scale. Several other companies are also intent on building commercial-scale processes but appear to be a bit behind these three in pilot experience.

Ethanol being largely a commodity, its biggest impact on forestry is potential use of wood as raw material. Because a modern-scale 50 million gallon per year ethanol plant will require almost 2,000 ovendried tons per day of biomass, it would be worthwhile for forest products companies to become involved to make sure the plant scale and feedstock requirement will not exceed the available supply of fuelwood. Considering risk, risk avoidance, and potential reward, the major issue to the forest products industry is risk avoidance. With 10 years or more in grain-ethanol production, it is not clear that a company proposing a corn ethanol plant could make a useful determination of financial reward simply because of the volatility in fuel cost; doing this for a lignocellulosic production process is even more difficult.

Recent emphasis has drifted away from ethanol because of the limitations of this liquid as a fuel. Much of the current focus has shifted to butanol, which can also be produced by fermentation of glucose and therefore is proposed as an easy conversion for a fermentation-based plant. Butanol has higher energy

density and has less effect on seals and hoses in the existing vehicle fleet. Proponents claim that it can be distributed in existing pipelines. The main organisms able to produce it are the clostridium family of bacteria, which consume sugar to produce a mixture of butanol, acetone, and ethanol. The two biggest problems with butanol are that the organisms produce a mixture of products and the butanol is sufficiently toxic that the bacteria go dormant at low concentrations. Most proposals to produce butanol use membrane processes or solvent extraction to remove butanol *in situ*, but these are all added cost and risk.

1,3 Propane Diol (PDO)

There are two propane diols with similar properties. 1,2-propane diol is readily available and can be produced from propylene. It is used as a solvent and in some cosmetic and pharmaceutical applications. 1,3-propane diol is useful in polyesters but does not have convenient synthetic routes from petroleum-based chemicals. To fill market needs, Shell Oil company has been producing 1,3-PDO using a more complicated route. E.I DuPont de Nemours and Co. has an interest in 1,3-PDO because the polyester has specific properties making it a valuable carpet material. They partnered with the UK-based agricultural product company Tate and Lyle on genetic engineering *Escherichia coli* (*E. coli*) to produce the 1,3 isomer. This is now a commercial process using glucose from corn as raw material and with the carpet yarn sold under the trade name Sorona. Because the process technology has been developed in industry, there is less known about how the PDO is manufactured or progress in developing the market for the diol. But 1,3-PDO is a great example of a higher value chemical that has existing markets. The intellectual property is controlled, offering some protection from competitive pressures. Obviously, DuPont and Tate and Lyle will control the ability of another company to partner with them in cellulosic production of this chemical. They do not need processing or fermentation expertise but can benefit enormously from the expertise of a company that understands biomass supply, how volume impacts availability and price. On the risk vs reward scale, it is probably lower risk than many other products. Product and process already exist, product value is higher, offering more operating room to remain profitable, and the intellectual property controls entry into the market. If the next partner is a forest products company, it is good business for the industry and it would be good business for DuPont and Tate and Lyle. But as the third party into the venture, the price

could be high. 1,3-propane diol demonstrates a process for which the production capability is controlled and the product market already exists. There are other product markets that can be developed just as DuPont and Tate and Lyle pursued this one. But if companies as large as DuPont take on partners to develop biomass-based products, a smaller forest-products-based company might also consider this as a good business strategy.

Poly Lactic Acid (PLA)

The major new product introduction in this area is Ingeo, a polylactic acid produced by NatureWorks LLC, a wholly owned subsidiary of Cargill. It provides a useful contrast to the DuPont, Tate and Lyle joint venture. NatureWorks was a joint venture of Dow Chemical and Cargill. Successful at developing Ingeo, Dow later sold its share to Cargill. Organisms that ferment glucose to lactic acid are common and there are other companies producing lactic acid and polylactic acids. Although NatureWorks has proprietary technologies, the presence of competing technologies (Sreekumar and Thomas 2008) reduces the value of a partnership. Both Sorona and Ingeo are competing against other products, but Sorona is reported to have some advantages over other carpet yarn fibers, whereas Ingeo is considered a direct replacement for petroleum-based plastics, such as the polystyrene used in clamshell packaging. Ingeo also appears to have too low of a softening temperature for many applications. These issues seem to have resulted in a slower market penetration for Ingeo than initially expected. Ultimately, bio-based products are nice, but the consumer puts greater value on price and performance. Lactic acid represents a case of a higher value chemical for which production technology is available and a market already exists. It could be pursued as an independent with an off-take contract or in partnership with an existing producer.

Polyhydroxyalkanoates (PHA)

Poly lactic acid is one example of a polyhydroxyalkanoate. There are other polymers using longer chain hydroxyalkanoates, but of particular interest is poly(β-hydroxybutyrate) (PHB), or more specifically, the copolymer of PHB with 3-hydroxyvalerate (PHBV) (Sreekumar and Thomas 2008). PHAs are produced by nearly 100 different bacteria as a food storage polymer (Sudesh et al. 2000, Poirier et al. 1995). This is regarded as a fermentation process converting sugars to PHB. Poly(hydroxybutyrate) is the most common
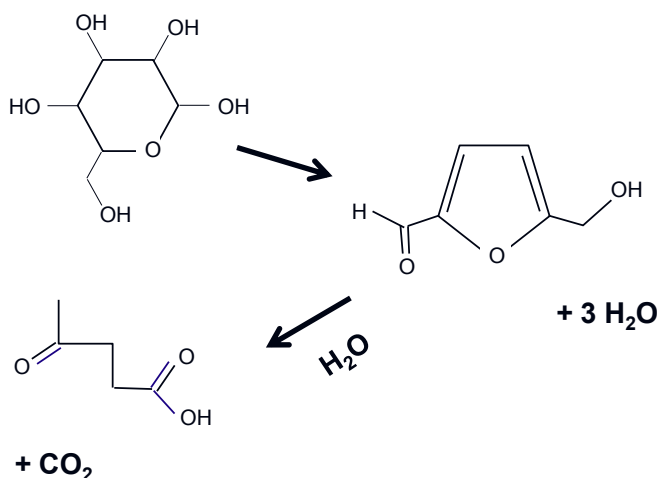
Figure 5. Dehydroxylation of glucose to 5-hydroxymethylfurfual and decomposition of HMF to levulinic acid.

PHA but is not particularly useful as an industrial plastic (Sreekumar and Thomas 2008, Poirer et al. 1995). The addition of propionic acid to the glucose solution results in the hydroxyvalerate co-polymer, which is more easily processed. The PHBV copolymer is marketed by Monsanto under the trade name Biopol. Using genetic engineering methods, microbiologists have been able to express various PHAs in recombinant *E. coli* and in the plant Arabidopsis. Current efforts in this area are focused at having the PHA expressed in oil seeds such as rapeseed or sunflower (Poirier et al. 1995). PHAs represent a potential broad class of polymers produced directly by the fermentation organism or potentially as a food storage polymer in plants. Again, there are existing processes and products and potential partners to reduce risk in entering a new market.

5-hydroxymethylfurfural (HMF)

The furfurals are dehydroxylation products of sugars that are formed as decomposition products during the high-temperature dilute acid hydrolysis of cellulose. The five-carbon sugars xylose and arabinose form furfural, which is sufficiently volatile to be distilled out of solution as it forms. Six-carbon sugars such as glucose, mannose, and galactose decompose leaving a -CH$_2$OH group on the 5-carbon of the furan ring, and this results in considerably lower volatility. The proposed reaction pathway is that the six-carbon

sugars dehydoxylate to 5-hydroxymethylfurfural, which further decomposes to levulinic acid (Figure 5). This continued decomposition is a major problem in trying to obtain high yields of HMF. Levulinic acid is also a potential chemical feedstock or fuel (Werpy and Petersen 2004) and an active target of research. A process producing both HMF and levulinic acid will need a separations step and will require that markets be developed for both chemicals.

HMF is not necessarily the target compound as an industrial feedstock chemical. Using oxidizing conditions, it can be turned into the 2,5-dicarboxylic acid (Partenheimer and Grushin 2001) which has properties similar to terephthalic acid used in polyester. Under reducing conditions, the aldehyde functional groups can be reduced to an alcohol to give 2,5-dihydroxymethylfuran. This can function as the diol in polyesters. Under hydrogenation conditions, the diene in the furan is reduced to the corresponding tetrahydrofuran, to give 2,5-dihydroxymethyltetrahydro-furan. This also can provide a diol for polyesters. All these compounds are potential targets for chemical products and more stable products that if formed *in situ* should reduce decomposition to levulinic acid and increase the product yield.

The yield of HMF can be increased by running the reaction in a two-phase system to extract HMF into an organic phase where it is more stable (Chheda et al. 2007, Roman-Leshkov et al. 2007). Other approaches have included the use of catalysts, conducting the reaction in organic solvents (Bicker et al. 2003), or more recently ionic solvents (Binder and Raines 2009). Although these methods increase the yield of HMF, they also increase the process cost, and none of the approaches tried has attracted commercial attention. One problem stems from the use of glucose as the starting sugar. Fructose is a six-carbon sugar like glucose, but as a ketose (as opposed to an aldose) can form a five-member ring rather than the six-member ring of glucose. The five-member ring mimics the furan ring, and not surprisingly, yields of HMF from fructose are significantly higher than the yield from glucose (Binder and Raines 2009, Chheda et al. 2007). The result is that yields of HMF from cellulose or glucose are rarely above 50% ,compared to yields around 80% when starting with fructose. Because the goal is to obtain a 5-hydroxymethylfurfural based pro-

cess direct from cellulose, an *in situ* conversion of glucose to fructose adds to the difficulty. The 5-hydroxymethylfurfual and the related chemicals are regarded as valuable chemical intermediates, and the company that discovers an efficient chemical route should have a profitable product. This group of products is higher risk because the processes are not well established and there has not been a product to help establish the market. The rewards should be equally high for the company that owns the process.

Fischer–Tropsch Hydrocarbons

Fischer–Tropsch hydrocarbons are a mixture of straight-chain hydrocarbons that can have properties ranging from liquid petroleum gas to wax (Anderson et al. 1952, Tijmensen 2000). As currently pursued in the United States, the target product is typically a component of diesel or aviation fuel. As stated in the section on gasification and gas reforming, there is considerable commercial experience with reforming the product gas from coal gasification. To minimize costs, both SASOL and Eastman built their plants near coal sources. In addition, SASOL operates on a massive economy of scale. The two main plants are each 48,000 tons per day (tpd), almost 100 times the maximum conceivable size of a biomass plant. Obviously, built next to a coal field, SASOL can operate at this scale, and it compares well to the process scale of a petroleum refinery and the country's petroleum needs. Each Fischer–Tropsch reactor is just 6,000 tpd, but this is still about 10 times the size of typical biomass processing systems like U.S. pulp mills and wood-fired utilities. This has created an interesting engineering challenge—downsizing the plant and still maintaining a favorable cost structure.

The process must be scaled to available biomass without losing profitability. There are several advantages to biomass that engineers are trying to exploit to accomplish this goal. The first is that the product gas is cleaner than the typical product gas from gasifying coal. But exploiting this requires a detailed knowledge of the gas contaminants and a cautious redesign of the gas clean-up process. The research to accomplish this is ongoing. The second opportunity is integration with existing biomass processes. Two of the DOE-sponsored 1/10-scale biomass demonstration plants are Fischer–Tropsh reforming processes integrated with pulp mills. This provides two advantages—the pulp mill can make use of the waste heat of the Fischer–Tropsch process , improving the energy economy, and the lime kiln can take "waste" product gas. The Fischer–Tropsch pro-

cess uses a catalyst to combine hydrogen and carbon monoxide into hydrocarbons and water (Anderson et al. 1952, Schulz 1999). In the traditional Fischer–Tropsch process, each pass through the catalyst bed produces a mixture of products of which 30-50% may be diesel hydrocarbons, but much of the gas is unchanged, some is low-molecular-weight hydrocarbons such as methane, and some may be long-chain hydrocarbons such as wax (Anderson et al. 1952, Tijmensen 2000). In normal practice, the desired hydrocarbons are condensed out of the product stream and the gas components are collected, compressed and recirculated through the Fischer–Tropsch catalyst bed. Newer reactor systems may have per-pass efficiencies for production of condensable products as high as 80% (Tijmensen 2000). But compressing the non-condensable components, cleaning the gas up, and recycling it are expensive parts to the process. Instead of the recirculation process, a pulp mill can take the light components and use them as fuel in the lime kiln. This approach completely changes the economy of scale metric because now the optimal scale is just sufficient to supply the kiln with the excess gas and the pulp mill with the waste heat. Both Flambeau River (1,000 bdt/day) and NewPage Corporation (500 bdt/day) are engineering small-scale processes integrated into their pulp and paper mill operations.

There are two other alternatives that are being considered to manage the required small scale of a biomass processes against the presumed need for large scale in Fischer–Tropsch reforming. Small distributed and potentially even mobile pyrolysis oil plants could be assembled to feed liquid product to a large gasification-Fischer–Tropsch plant, possibly as part of an existing petroleum refinery. This reduces transportation distances for the low-density biomass and replaces it with a much higher energy-density bio-oil. Alternatively, biomass gasifiers could be connected using a bio-gas pipeline to provide the gas volumes needed for a refinery scale Fischer–Tropsch process. The current scale of gasifiers is considerably smaller than Fischer–Tropsch processes and distributing them along a pipeline eliminates a large part of the biomass transportation cost and replaces it with the more efficient pipeline.

The process risks for gasification-Fischer–Tropsch are probably not large as long as the company does not expect the engineering to be perfect and has the financial backing to reengineer and replace parts of the process that do not work as well as planned. The product is basically diesel fuel which in today's market is not a particularly valuable product. The price variability is also not very comforting to bankers and other

equity partners who are needed to finance a plant. There is a particular disadvantage for the early installations in this case. The engineers cannot predict what sensors and controls will be most critical for running the process and recognize they have specified more instrumentation than necessary.

Other Gas Reforming Processes

Two other gas reforming processes are worth mentioning. The Netherlands has an extensive evaluation on production of methane to replace petroleum based natural gas in their existing gas pipelines (van der Drift et al. 2005). Methane can be produced at greater conversion efficiency than Fischer-Tropsch-hydrocarbons (McKeough and Kurkela 2007) and is an attractive method to switch a large network of fuel uses to renewable fuels. Methanol has been produced using the product gas from coal gasification for several decades (Hamelinck and Faaij 2002, Tijm et al. 2001). It can be used like ethanol as a gas oxygenate or substitute for gasoline. As a gas reforming process, it also has a higher conversion efficiency than Fischer–Tropsch liquids (McKeough and Kurkela 2007) and has a considerable market as a feedstock for other chemicals.

Nano-Fibrillated Cellulose (NFC)

Nano-fibrillated cellulose is composed of very fine filaments remaining after the original cell or biological structure of the cellulose is disintegrated. Normal processing techniques include dispergers or grinders (Iwamoto et al. 2007), cryo-crushing (Chakraborty et al. 2005), treatment with enzymes (Henriksson et al. 2008), or tempo oxidation (Saito et al. 2009). The major limitation with any cellulose product considered as a reinforcement fiber is the incompatibility with thermoplastics that melt at low enough processing temperatures to not char cellulose. NFC has as an additional problem that the 20-nm-wide by 1-μm-long filaments are entangled, making them even harder to disperse into a polymer. Current research is focused on forming sheet with thermosetting resins like phenol-formaldehyde (Nakagaito and Yano 2005), epoxy, or acrylics (Iwamoto et al. 2007). There is considerable research interest in these materials because strength properties can be outstanding, and they can be used as reinforcing material without reducing optical clarity. The NFC-reinforced phenolformaldehyde in Nakagaito and Yano's experiments gave tensile properties matching magnesium alloy AZ91 while the composite

density at 1.4–1.5 g/cm^3 is 20% lower than for AZ91. As a new product, NFC is made from bleached hardwood pulp. It could be formed into sheets and sold as a dried product for use like carbon or glass fiber cloth used in reinforced epoxy. Although it is possible to replace the suspension water with solvents and dry it under conditions that reduce bonding, it is unlikely that the product can be dispersed into a resin for other types of fiber-reinforced composites. For NFC, like HMF, there is neither an accepted industrial-scale process nor established commercial products. A company deciding to pursue fibrillated cellulose needs to consider integrating the NFC production with captive products or collaborating directly with an existing manufacture already using advanced fiber-reinforced composites.

Cellulose Nanocrystals (CNC)

Cellulose nanocrystals (also called nanocrystalline cellulose (NCC)) are the crystalline portion of the cellulose fibril that remains after all the easily hydrolyzed amorphous cellulose is removed by acid. The standard preparation (Beck-Candanedo et al. 2005) is little changed from the process recommended 50 years before by Ranby (1952). CNC mimics the fibril structure of the starting cellulose. Typical wood cellulose provides crystals approximately 4 nm in diameter and 150 nm long. CNCs prepared from other plant sources, algae, or tunacin can be up to 20 nm and nearly a micron long (Beck-Candanedo et al. 2005). Strength properties are estimated to be even greater than NFC, but the small size has made it difficult to test directly. A modulus of 145 GPa was reported by Sturcova et al. (2005).

Cellulose nanocrystals are prepared in 64% sulfuric acid, resulting in surfaces containing sulfate ester groups. The sulfate esters provide charged surfaces to the CNC, producing naturally stabilized dispersions. Problems have been encountered transferring these dispersions to nonaqueous conditions where they can potentially be mixed into typical polymers. Some work has been reported with CNCs dispersed in styrene-butylacrylate latex (Favier et al. 1995), PHA latex (Dufresne et al. 1999), atactic polypropylene (Ljungberg et al. 2005), and polyacrylic acid (Lu and Hsieh 2009). Outcomes have not been spectacular, but electrospinning CNCs into polyacrylic acid fibers has provided good strength gains while maintaining optical clarity. Rubbery state polymers show good strength enhancement at relatively low CNC levels of ~3%. But polymer matrices below the glass transition have not shown reinforcement. Although the CNC sur-

face area is huge, the cellulose surface is not compatible with most polymers, resulting in very poor bonding between resin and reinforcement. Efforts to functionalize the surface have not been able to overcome this problem (Ljungberg et al. 2005).

It is well recognized that a CNC process can be coupled with any of the glucose-based products discussed in this paper. The process faces all the problems of the strong acid hydrolysis process, but if the reinforcement strength can be demonstrated and utilized, the product value may be sufficient to neutralize acid with limestone and dispose of the gypsum. As with the nanofibrillated cellulose, there is not an established market for CNC and any company contemplating producing this product has to solve the problems of incorporating them effectively into more common or higher performance polymers.

Summary

Renewed interest in bio-based products and chemicals offer the forest products industries many opportunities to enter into new product markets. There are opportunities to partner with other companies, as DuPont has done with Tate and Lyle and Cargill did with Dow Chemical. For some of the potential new products, this should be considered as smart business strategy. The forest products companies bring vast knowledge of biomass supply, logistics, and material handling. This knowledge can make them a valuable partner. In becoming involved they not only gain entry into new product markets, but also help to protect their existing products from costly completion for timber or pulpwood.

Several of these products do not appear to offer significant advantage to early adopters. Fuel products such as Fischer–Tropsch hydrocarbons and ethanol are examples. But markets for the reinforcing fibers NFC and CNC are not likely to be large and will reward the first companies with efficient processes and high-performance products. Other products such as 1,3-propane diol and lactic acid as examples will probably develop large enough markets for companies to establish production facilities at a later date. Where that will reduce the risks inherent in developing a new process, the third or fourth entry into the market may find it hard to break in.

One of the most intractable problems to be faced is the difference in scale for biomass processes and traditional products. Fischer–Tropsch hydrocarbons are produced at 6,000 tpd. A modern 50 million gallon per year ethanol plant will require 2,000 tpd of wood. But in most regions in the country, biomass-based processes will encounter uneconomical transportation distances if they scale beyond about 500 tpd. Solutions for the economy of scale can be found by integrating production with other products, or with concepts such as distributed pyrolysis plants or a dedicated bio-gas pipeline with distributed biomass gasification plants. The small scale will also favor smaller market products where there is no advantage to larger scale plants.

None of these processes is at a state where it can be implemented without research and without risk. But several high-value markets are available for companies that have the creativity and persistence to succeed. For every potential product mentioned in this review, there are many related products and processes that can have higher value than traditional forest products. For the forest products industries, this is the time to go on the offensive and capture new markets and renewed profitability.

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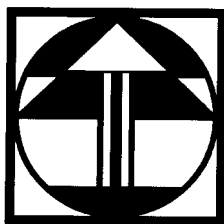
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