

TAPPI JOURNAL

WWW.TAPPI.ORG

THE PULP AND PAPER INDUSTRY'S TECHNICAL RESOURCE

BONUS ISSUE MARCH 2008



**BONUS
ISSUE**

BIOREFINERY

4

The Integrated Forest Biorefinery: The Pathway to Our Bio-Future and the Range of Product Possibilities

Eric Connor

CELLULOSIE APPROACH

10

Evaluation of Wood-Based Biorefinery Options for Pulp and Paper Mills

Theodora Retsina

NON-WOOD STRATEGIES

23

A Biorefinery Process Suitable for Non-Wood Fibers

*E. Kendall Pye, Michael Rushton,
and Alex Berlin*

LIGNIN CONVERSION

44

A Biorefinery Approach: Non-Sulfur Pulping with Partial Lignin Recovery and Conversion

*Todd S. Bolton, R. C. Francis,
and Thomas E. Amidon*

TABLE OF CONTENTS

3 EDITORIAL

Welcome to your first bonus issue of *TJ*

Jan Bottiglieri

4 BIOREFINERY

The Integrated Forest Biorefinery: The Pathway to Our Bio-Future and the Range of Product Possibilities

Eric Connor

10 CELLULOSIE APPROACH

Evaluation of Wood-Based Biorefinery Options for Pulp and Paper Mills

Theodora Retsina

23 NON-WOOD STRATEGIES

A Biorefinery Process Suitable for Non-Wood Fibers

E. Kendall Pye, Michael Rushton, and Alex Berlin

44 LIGNIN CONVERSION

A Biorefinery Approach: Non-Sulfur Pulping with Partial Lignin Recovery and Conversion

Todd S. Bolton, R. C. Francis and Thomas E. Amidon

Vice President, Operations

Eric Fletty efletty@tappi.org

Product Analyst & E-Publishing Team Lead

Lisa Hightower lhightower@tappi.org
+1 770 209-7313 | f: +1 770 446-6947

Editor Jan Bottiglieri jbottiglieri@tappi.org
+1 847 466-3891

Managing Editor

Tricia Krizner triciakriz@sbcglobal.net
+1 440 944-8908

Webmaster Karen Roman kroman@tappi.org
+1 770 209-7416

TJ EDITORIAL BOARD

Raimo J. Alén, University of Jyväskylä, ralen@cc.jyu.fi, +358-14-2602562

James W. Atkins, Atkins, Inc., jatkinsinc@yahoo.com, +1 908 806-8689

David J. Bentley, Jr., RBS Technologies, Inc., dbentley@unm.edu, +1 505 299-6871

Terry L. Bliss, Hercules Inc., Wilmington, DE tlbliss@aol.com, +1 302 995-3523

Brian N. Brogdon brian.brogdon@gmail.com, +1 678 581-9114

Jere W. Crouse, JWC Consulting, cj522@inwave.com, +1 608 362-4485

William S. Fuller, Weyerhaeuser Co., consult4frm@aol.com, +1 253 279-0250

Peter W. Hart, Westvaco Corp., pwh3@meadwestvaco.com, +1 409 276-3465

Kasy King, Papermaking Process Consulting, LLC, kasyking@new.rr.com, +1 920 991-9102

Ted McDermott, McDermott Consulting Services, tedmcd@earthlink.net, +1 847 934-6386

Nick G. Triantafillopoulos, ROHM NOVA, LLC, nick.triantafillopoulos@omnova.com, +1 330 794-6249

Paul Wiegand, NCASI pwiegand@ncasi.org, +1 919 941-6417

Subscribe to TAPPI JOURNAL

Available in electronic form (via email) or electronic + print (via mail.) TAPPI Members—1 year (11 issues): Print + electronic, US\$132; electronic only, US\$29. Non-members: Print + electronic, US\$376; electronic only, US\$262. International mailing charge: US\$14. Visit www.tappi.org to subscribe, or contact TAPPI's Member Connection Center at 1 800-332-8686 (USA); 1 800-446-9431 (Canada); or +1 770-446-1400.

TAPPI, 15 Technology Parkway S., Norcross, GA, 30092, publishes TAPPI JOURNAL monthly.

ATTENTION PROSPECTIVE AUTHORS: All papers published are subject to TAPPI JOURNAL's peer-review process. Not all papers accepted for review will be published. Before submitting, check complete author guidelines at http://www.tappi.org/s_tappi/doc.asp?CID=5&DID=552877.

Statements of fact and opinions expressed are those of individual authors. TAPPI assumes no responsibility for such statements and opinions. TAPPI does not intend such statements and opinions or construe them as a solicitation of or suggestion for any agreed-upon course of conduct or concerted action of any sort.

Copyright 2008 by TAPPI, all rights reserved. For copyright permission to photocopy pages from this publication for internal or personal use, contact Copyright Clearance Center, Inc. (CCC) via their website: www.copyright.com. If you have questions about the copyright permission request process, please contact CCC by phone at +1 978 750-8400. To obtain copyright permission to use excerpts from this publication in another published work, send your specific request in writing to Editor, TAPPI JOURNAL, 15 Technology Parkway S., Norcross, GA 30092, USA; or by fax to +1 770 446-6947. Send address changes to TAPPI, 15 Technology Parkway S., Norcross, GA 30092, USA; Telephone +1 770 446-1400, or FAX +1 770 446-6947. www.tappi.org



2007 EPE Conference Session

These papers were originally presented at TAPPI's 2007 EPE Conference and are being made available as a special benefit to TAPPI JOURNAL print subscribers.

Editor's Note

JAN BOTTIGLIERI | EDITOR,
jbottiglieri@tappi.org



Welcome to your first bonus issue of *TJ*

This special bonus e-issue of *TAPPI JOURNAL* includes first-look papers on one of our industry's most compelling topics: biorefinery technologies. It was compiled by Ken Patrick, *Paper360°* senior editor and veteran industry journalist. He has selected content that represents the best of the new research presented at TAPPI's recent EPE Conference—content not yet available to the general TAPPI membership.

"In the very near future, biorefin-

eries will become yet a third major component of many integrated paper industry manufacturing facilities, together with chemical and mechanical pulp mills and the papermaking operation," writes Patrick. "Today's modern pulp and paper mills are already maximizing the use of cellulosic raw materials in the production of paper and board products, but advanced bio-fuel technologies are now nearing full commercial implementation."

We're pleased to bring this

special issue **exclusively to *TJ* print subscribers** as a way to extend the value of your *TJ* subscription, and to thank you for your support. If you have colleagues, customers or other industry contacts who you feel would benefit from this type of information, please encourage them to visit www.tappi.org and begin their own print subscription to *TAPPI JOURNAL*.

Discover, first-hand, the latest advances in biorefinery technology at the

2008 TAPPI International Bioenergy & Bioproducts Conference

August 27 – 29, 2008

Being held in conjunction with the

2008 TAPPI Engineering, Pulping & Environmental Conference

August 24 -27, 2008 | Portland, Ore., USA

Today's pulp and paper mills are beginning to integrate production of bioenergy with paper and board capacity. These two events provide, for the first time under one roof, an opportunity to explore the future of this emerging development and understand its impact from a total production, market, and economic perspective.

More information on these events is available at
www.tappi.org/08epe

THE INTEGRATED FOREST BIOREFINERY: THE PATHWAY TO OUR BIO-FUTURE AND THE RANGE OF PRODUCT POSSIBILITIES

Eric Connor

ThermoChem Recovery International, Inc. (TRI)
3700 Koppers Street, Suite 405
Baltimore, MD 21227

ABSTRACT

As the pulp and paper industry moves forward the integrated forest biorefinery provides a future pathway to long term growth and profitability. This paper describes the technologies that make up the thermochemical biorefinery platform, the product optionality and flexibility that is possible, and a phased approach for implementing the thermochemical integrated biorefinery at an existing pulp and paper operation.

INDUSTRY BACKGROUND

The reliability, affordability and environmental impact of energy supplies have become the most critical issue for the world economy. While most of the initial response has been investment in producing ethanol from corn, there is common consensus that there is simply not enough corn to meet renewable energy needs. Given that consensus, as we look forward, the conversion of cellulosic biomass to fuels will be required. The U.S. Energy Policy Act of 2005 set an objective of generating 1 billion gallons per year of transportation grade biofuels from lignocellulosic sources by 2015. A primary source of cellulosic feedstocks is the pulp and paper industry – the world’s largest non-food biomass collection system. Recently, the U.S. paper and forest products industry made a commitment to increase the development of biomass fuels, with the long-term goal of developing a network of integrated “forest products biorefineries”. Forest products biorefineries represent an emerging opportunity that will have a dramatic impact on future U.S. energy supplies and on the forest products industry itself. It has been estimated that by using existing technology and moving the industry to forest products biorefineries, the U.S. pulp and paper industry could produce nearly half of the transportation fuels amount targeted by the DOE, resulting in a new high-value revenue stream for the industry while eliminating its dependence on fossil fuels.

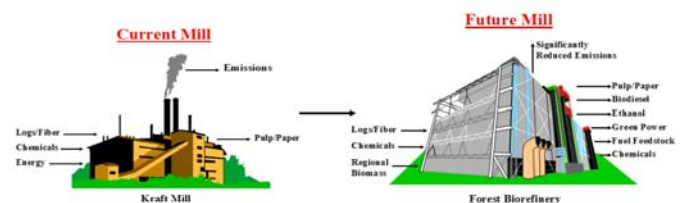
Pulp and paper mills are ideal sites for biorefineries because:

- Paper and forest products companies are efficient growers, harvesters, transporters and processors of biomass
- Pulp and paper mills are located near numerous sources of biomass, such as forest and agricultural residuals, and energy crops, and have existing infrastructure to ship finished product
 - In the U.S. alone, mills utilize over 120 million dry tons of wood per year as a raw material; additionally, these mills have ready access to a roughly equal amount of forest

residuals and an even greater amount of agricultural waste and energy crops

- Pulp and paper mills are familiar with producing power from biomass: currently they produce 60% of their power from wood residuals and spent liquors. Pulp and paper mills also have a highly trained workforce capable of operating energy and biorefinery systems.
- By integrating the integrated forest biorefinery with the existing mill operation, impressive thermal efficiencies (up to 80%) are achievable, new revenue streams are generated and operating costs are lowered

As illustrated below, the current pulp and paper mill uses logs and fiber, chemicals and energy to produce commodity pulp and paper products. Future mills, **Integrated Forest Biorefineries**, will import regional biomass instead of purchased energy. They will expand the industry’s mission from simply manufacturing low margin paper products to creating new revenue streams by producing “green” power and creating new, high-value products such as biofuels and



biochemicals, all while improving the efficiency and profitability of their core paper-making operations.

TRI provides the essential, enabling biomass gasification technology required for the development of the forest products biorefinery. Our gasification systems are uniquely capable of high-performance integration with pulp and paper facilities. Industry analysts believe the thermo-chemical pathway (gasification) is **the only currently available technology** that can process all feedstocks, be built on a large scale, achieve high conversion efficiencies and be rapidly replicated worldwide.

GASIFICATION TECHNOLOGY

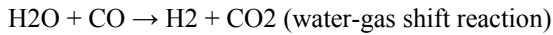
By deploying biomass gasifiers, the pulp and paper industry will be able to process not only spent liquor, but also any other biomass produced on-site and any biomass that can be economically transported to a mill, such as forest and agricultural residuals, for gasification. This gasification system will produce a synthesis gas (“syngas”) for the replacement of fossil fuels, the production of biofuels and biochemicals, and the generation of green electricity, process steam and heat for pulp and paper production.

STEAM REFORMING OF BIOMASS

The method of gasification we use is based on our proprietary indirectly-heated steam reforming. Superheated steam reacts endothermically (consumes heat) with the carbonaceous components of the biomass to produce hydrogen and carbon monoxide fuel gases (synthesis gas or syngas):

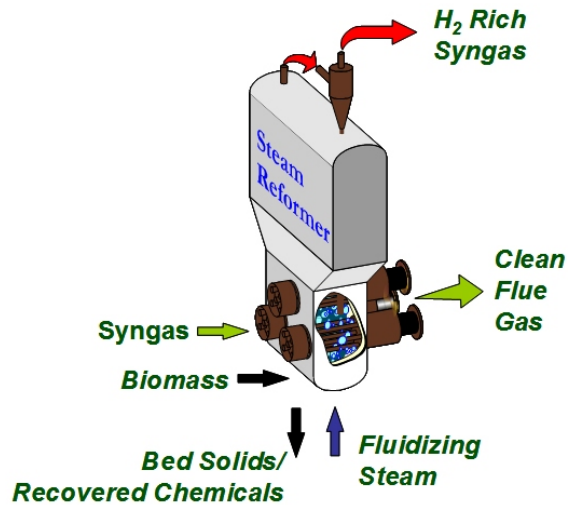


Water-gas shift reactions also occur simultaneously with the steam reforming reactions to yield additional hydrogen and carbon dioxide:



TRI's "PulseEnhanced" steam reformer is a patented technology that:

- Produces a medium Btu syngas
- Can customize the composition of the syngas to meet the needs of the downstream process
- Can process a wide spectrum of carbonaceous feedstocks
- Is energy self sufficient by utilizing a portion of the syngas produced as fuel for the proprietary PulseEnhanced heat exchangers that provide the required endothermic heat
- Is inherently stable and safe



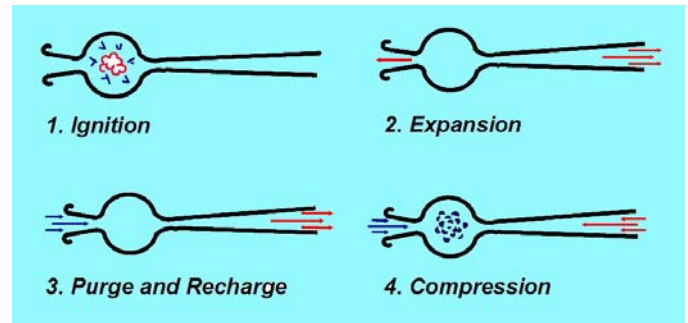
THE PULSE COMBUSTOR: HOW IT WORKS

We use a patented technology to efficiently provide the endothermic heat for the steam reforming reaction. This technology can transfer 30-40% more heat than conventional technologies, resulting in improved performance and reduced costs. The proprietary pulse combustion heater is a heat exchange device that uses pulse combustion technology to combust a wide range of fuels to provide heat to the steam reformer.

The original pulse combustor was developed by the Germans in World War II as the propulsion system for the V-1 buzz

bomb. This technology has been modified to provide high heat transfer instead of thrust.

Pulsed Heater Operation Principle



In the simplified pulsed heater diagram above, the device is made up of an aero-valve that provides air and fuel to a combustion chamber which exhausts to a resonance tube. Fuel and air are initially ignited by a spark plug or pilot light. Combustion causes expansion and the gases exit the combustion chamber down the resonance tube. Because of a patented geometry within the aerovalve called a fluidic diode, almost none of the gases exit via the intake of the aero-valve and instead exit through the tail pipe. As the exhaust gases expand and exit, a vacuum is created in the combustion chamber which causes air and fuel to enter the combustion chamber via the aero-valve. The vacuum also causes some of the exhaust gases in the tail pipe to reverse direction and return to the combustion chamber. As the exhaust gases return, compression takes place in the combustion chamber. The heat of compression causes ignition and this cycle repeats itself 60 cycles per second. The oscillating exhaust gases in the resonance tubes greatly increase the heat transfer capability of the system (30-40%) compared to other technologies.

COMMERCIAL PROJECT; NORAMPAC, TRENTON, ONTARIO, CANADA

TRI's technology is employed at this paper mill to process spent liquor, a paper mill process stream that contains biomass and valuable chemicals, to recover the chemicals and produce steam for the mill.



The Trenton mill is located on the Trent River, a popular recreation area. The mill, which has been a zero effluent mill since 1996, produces 500 tpd of corrugating medium.

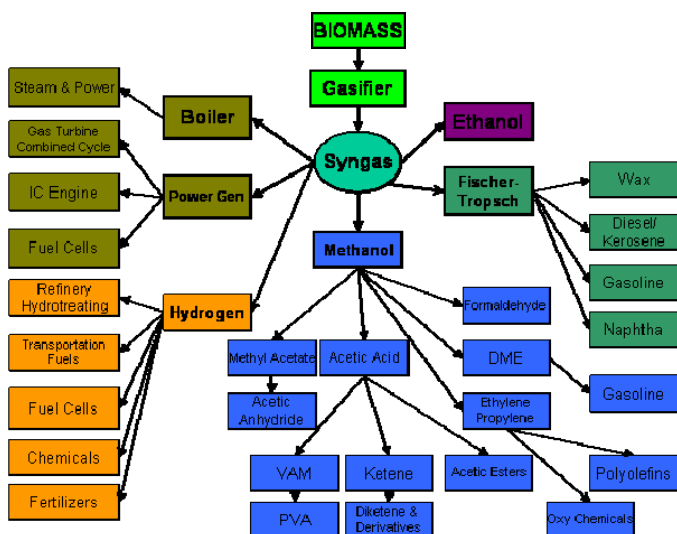
Prior to the start-up of the gasifier the mill had no chemical recovery system. For over forty years the mill's spent liquor was sold to local counties for use as a binder and dust suppressant on gravel roads. The discontinuance of the spreading of spent liquor required Norampac to select, purchase and install a technology to process spent liquor. The TRI black liquor gasification system was selected

The capacity of the spent liquor gasification system is 125 tons per day of black liquor solids (BLS). Our scope of supply included the steam reformer, pulse combustors and fuel train, detailed engineering and start-up support, materials handling equipment, and instrumentation.

The project, which started operations in 2003, is operating day in and day out meeting all of the needs of the mill's chemical recovery requirements. Process optimization is continuing in the area of energy recovery.

BIOREFINERIES

The scalable, indirectly heated, biomass gasification process is ideal for use in a forest products biorefinery as it is uniquely configured for high-performance integration with pulp and paper facilities and is capable of handling a wide variety of cellulosic feedstocks, including woodchips, forest residuals, agricultural wastes and energy crops, as well as mill byproducts (spent liquor). Compared to other biomass gasification technologies that are based on partial oxidation, the steam reforming system converts biomass to syngas more efficiently, producing more syngas per ton of biomass with a higher Btu content. This medium-Btu syngas can be used as a substitute for natural gas and fuel oil, and as a feedstock for the production of value added products. **The Optionality provided by the Thermochemical Biorefinery Platform is shown below**



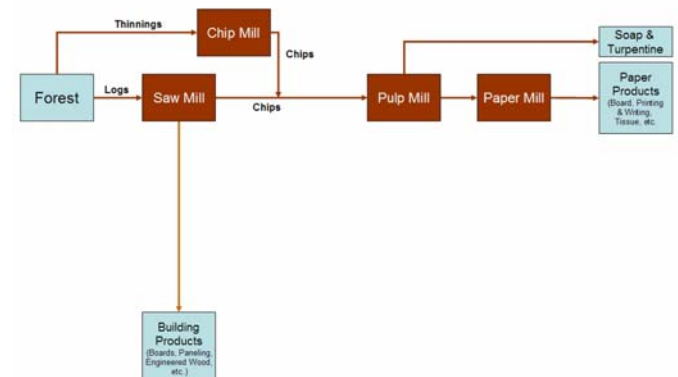
The steam reforming biomass gasification technology can be integrated with a wide variety of catalytic and fermentation technologies to convert the syngas to high-value bio-based fuels and chemicals. For example, syngas generated by TRI's technology can be conditioned and sent to a commercially proven gas-to-liquids ("GTL") facility (i.e., Fischer-Tropsch or other catalytic technologies) inside the biorefinery. The GTL process produces a range of products (naphtha, gasoline, diesel/kerosene, wax, methanol, DME, etc.) that are stabilized for storage and transported off-site to a downstream refinery for conversion to marketable products. The unreacted syngas and light non-condensable gases (tail gas) are utilized in the process to replace fossil fuels. Additionally, the GTL conversion, which is exothermic, provides another source of process heat that is recovered and used. A fully integrated forest products biorefinery utilizing TRI's technology will achieve thermal efficiencies from 70%- 80% depending upon process configuration and biomass feedstock

A PHASED APPROACH TO IMPLEMENTATION OF THE INTEGRATED FOREST BIREFINERY

The following is one proposed path for converting an existing pulp and paper mill to a fully integrated biorefinery - carbon neutral and energy independent - producing a number of value-added products as well as traditional paper products. Process engineering and mass and energy balances developed by our engineers, in concert with a key client and engineering consultants, form the basis for this model.

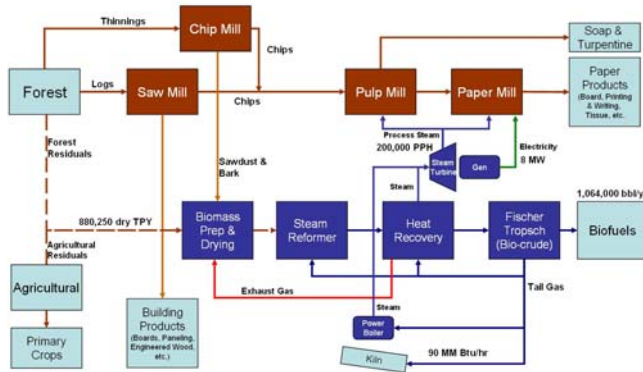
THE CURRENT MILL

Provided below is a simple block flow diagram of a pulp and paper mill. For illustrative purposes we have established an energy and mass balance for a typical integrated paper mill. It is an average mill producing 1,000 TPD of finished product. This mill uses as its fiber feedstock wood chips that are produced at wood products mills and off site chip mills. It uses steam, electricity, and chemicals to convert the wood chips to cellulose and the cellulose to paper products. This mill provides for a portion of energy requirements by burning spent liquor and woody residual biomass, but it also imports both natural gas and electricity. The natural gas is burned in a boiler to produce additional process steam and in a lime kiln as part of its chemical recovery process.



INTEGRATED FOREST BIOREFINERY-PHASE ONE

A Biomass to Syngas to Gas-to-Liquids Plant integrated into the Pulp and Paper Mill



The first phase of biorefinery implementation includes the installation of a biomass to syngas to gas-to-liquids plant at the paper mill which is represented by the dark blue boxes in the block flow diagram shown above. The feedstock for this biorefinery is biomass including both forest and agricultural residuals.

The biomass is dried and sized prior to gasification. The biomass is fed into the fluidized bed steam reformer through a screw feed system and is gasified to produce synthesis gas with the correct hydrogen to carbon ratio required for the gas to liquids plant. The synthesis gas then goes through a conventional heat recovery and gas clean-up train prior to the gas-to-liquids plant.

The gas-to-liquids plant technology we have chosen for this biorefinery is the Fischer-Tropsch (FT) process, a very mature and known technology. The syngas is compressed and fed into the FT process, which is a catalytic process using a slurry bed reactor. In the reactor the hydrogen and the carbon monoxide in the synthesis gas comes into contact, under pressure and temperature, with the catalyst to form straight chain hydrocarbon molecules that range from very light gases to heavy waxes. The hydrocarbons are removed from the reactor vessel, distilled to fractions that include gasoline, naphtha, diesel, and waxes, and stored prior to shipment to a refinery for further processing, distribution and sale.

The biorefinery is exothermic, meaning it gives off energy as it makes the FT hydrocarbon liquids. The exothermic heat from the FT process has to be removed, resulting in the manufacture of process steam and hot water that can be used by the paper mill replacing steam and hot water made through the burning of natural gas. The FT gas-to-liquids process also releases a tail gas that is made up of unreacted synthesis gas and light, non-condensable hydrocarbon gases. In a conventional FT plant this tail gas is flared. When integrated into the paper mill this tail gas is used to replace natural gas and other fuels used to make paper.

This paper mill uses 200,000 pph of steam produced from natural gas and burns natural gas in its lime kiln to calcine

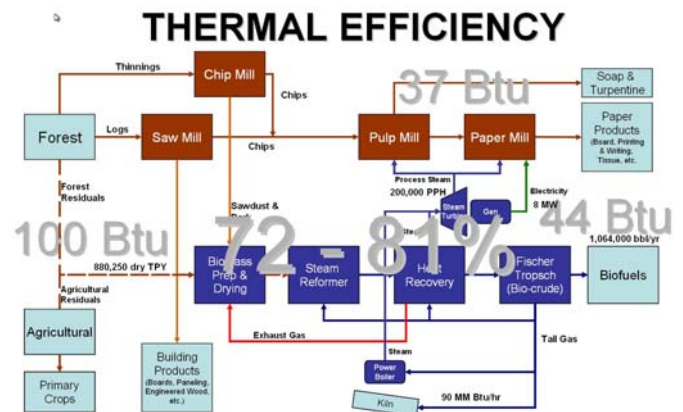
lime. TRI sized the exothermic heat and energy from the biorefinery to match the heat and energy sink provided by the paper mill. In other words, the waste energy from the biorefinery is enough to produce 200,000 pph of steam and replace 90 MMBtu per hour of natural gas with tail gas in the lime kiln.

The input to this phase one biorefinery is about 880,000 dry tons per year of biomass. Its outputs are the 200,000 pph of steam used for paper making and 90 mm Btu per hour of tail gas for the lime kiln. The biorefinery also produces about 1,000,000 barrels per year of FT straight chain hydrocarbon liquids that can be taken by any petroleum refinery for manufacture of petroleum liquids. 1,000,000 barrels per year is 42,000,000 gallons per year. The Btu value of FT liquids is 135,000 Btu's per gallon compared to 76,000 Btu's per gallon for ethanol. So the ethanol equivalent production of the biorefinery is 74,600,000 gallons per year.

The process can make a barrel of FT liquids for under \$25.

INTEGRATED FOREST BIOREFINERY-PHASE ONE

Thermal Efficiency



The historic petroleum industry paradigm regarding the manufacture of FT liquids is the minimum size plant that can be cost effectively built and operated is about 20,000 barrels per day. The petroleum industry design includes a number of reactors in series to maximize the amount of FT liquids made and minimize the amount of tail gas which is flared as wasted energy.

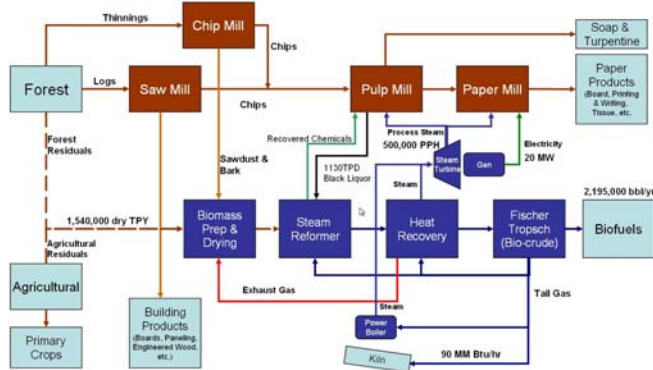
When the thermochemical biomass biorefinery is integrated with the pulp and paper mill the GTL process does not need to have high conversion efficiency because the paper mill will use the exothermic heat and the tail gas provided by the gas-to-liquids process to offset fossil and other fuels needed by the paper mill to make paper.

In the example shown above for every 100 Btus of biomass fed to the biorefinery, 44 Btus of FT liquids are produced. 37 Btus of exothermic heat, tail gas and hot water from the gas-to-liquids plant are used by the paper mill. So very high

thermal efficiencies are possible - as high as 81%. This synergetic integration of a paper mill, a biomass to syngas process, and a gas-to-liquids plant producing carbon neutral transportation fuels is the industry paradigm of the future. The economics of this paradigm are compelling.

INTEGRATED FOREST BIOREFINERY-PHASE TWO

Replacing the Tomlinson Recovery Boiler with Spent Liquor Gasification



The second implementation phase of the integrated forest biorefinery at this mill eliminates the chemical recovery boiler which burns black liquor from the pulp mill to produce steam and electricity, and recover the cooking chemicals for re-use. It is an old, unsafe, inefficient technology.

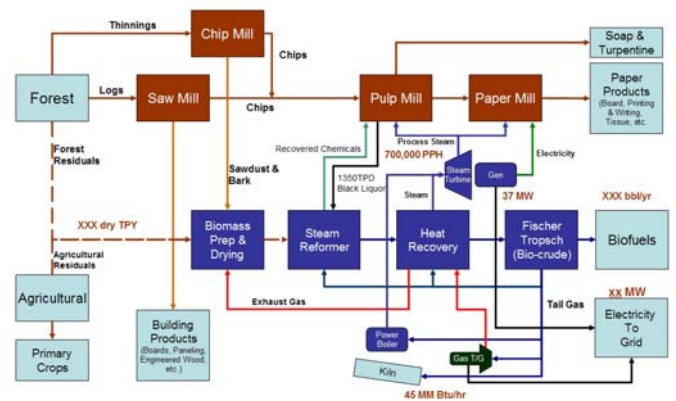
In Phase Two, the biorefinery is increased in size to process the organics in the black liquor to syngas and to recover the cooking chemicals for reuse by the pulp mill. The syngas from the black liquor is cleaned up and fed to the gas-to-liquids plant to produce more transportation fuels.

With the chemical recovery boiler gone, the steam it was generating for the paper mill is gone as well, increasing the process steam need by the paper mill from the biorefinery to 500,000 pph. To match this heat sink about 1,500,000 dry tons per year of forest and agricultural residual biomass is fed to the biorefinery, which now produces 2,200,000 barrels per year of carbon neutral transportation fuels. This is 164,000,000 gallons per year on an ethanol equivalent basis.

With the installation of Phase Two of the biorefinery, the mill is fossil fuel and purchase electricity independent. It is a carbon neutral manufacturing site producing paper products and transportation fuels.

INTEGRATED FOREST BIOREFINERY-PHASE THREE

Adding a Combined Cycle Generating Plant to Export Electricity



As discussed earlier, the basis for the design capacity of the biorefinery is based on matching the paper mill heat and energy sink to the waste heat and energy provided by the biorefinery. Following the elimination of the chemical recovery boiler, the only way to increase the output of the biorefinery economically is to increase the size of the paper mill heat and energy sink. In Phase Three a combined cycle gas turbine, HRSG, and steam turbine is added with tail gas as used as the fuel for the gas turbine. We have not run the mass and energy balance for this option. At this level the manufacturing site would be carbon neutral and purchased energy independent. It would be producing pulp and paper products as well as renewable transportation fuels and exporting "green" electricity to the grid.

THE BUILD-OWN-OPERATE BIOREFINERY AT A PULP AND PAPER MILL

We believe there is a significant opportunity now for investors to build, own, and operate biorefineries at existing pulp and paper sites in North America and Europe that will work synergistically and economically for the pulp and paper mill owner and the biorefinery owner.

The pulp and paper industry is the world's largest non-food biomass collection system. In North America there are approximately 200 chemical pulp mills and high-yield pulp mills that could economically host Phase One biorefineries of the size described above. There are also another 100 large, nonintegrated paper mills with heat and energy sinks large enough to support a biorefinery.

Internationally, we conservatively estimate that there are over 450 pulp and paper mills and another 400-500 nonintegrated paper mills that are sound potential sites for biorefineries. In Europe there is high demand for distributed "green" energy where incentive structures for carbon neutral fuels and electricity have been established.

In the United States, forest and agricultural residual-based feedstocks constitute a huge and readily available biomass source for the biorefinery, and the pulp and paper industry is the most qualified industry to take advantage of it.

The pulp and paper industry is a mature industry producing low margin commodity products. But it has the ideal infrastructure, experience and resources to capitalize on the strategic interest in renewable fuels in the United States via the biorefinery. The industry is short of capital which provides an excellent opportunity for investment firms to partner with owners of mill sites to install a biomass-to-syngas-to-transportation fuels biorefinery that dramatically improves the economics of the host paper mill and provides excellent returns to the owners of the biorefinery.

BIOREFINERIES- OUR BIO-FUTURE

Industry leaders, investors, policy-makers and others are now beginning to better understand the vital role to be played by biorefineries as we move from a fossil fuel-based energy economy toward a bio-based one. We believe the potential of an integrated forest biorefinery to be huge: a very attractive and synergistic business opportunity for both the co-located pulp and paper mill and for the biorefinery itself.

As outlined in the paper above, we believe very strongly that

- Biorefineries are a key pathway to our Bio-future, displacing fossil fuels and supplying clean, renewable and carbon neutral energy.
- Biorefineries fit very well at pulp and paper mills because of their inherent ability to gather and process biomass and create energy from biomass.
- The indirectly heated steam reforming of biomass to syngas technology is the best technology for enabling the biorefinery, providing excellent thermal integration with the host site, syngas optionality, and excellent economics.

EVALUATION OF WOOD-BASED BIOREFINERY OPTIONS FOR PULP AND PAPER MILLS

Authors:

Theodora Retsina, Vesa Pylkkanen
American Process Energy Recovery
theodora@americanprocess.com, vpylkkanen@americanprocess.com

ABSTRACT

A large potential opportunity is presented to the pulp and paper industry, in the emerging cellulosic ethanol market.

The pulp and paper industry is a large biomass handler with the know-how and personnel to operate a complex process industry, and therefore are a natural host of cellulosic ethanol production.

The success and profitability of such a venture is first a function of the fundamental economics and second, it also depends on the careful choice of technology and products.

This paper will present an overview of existing and emerging cellulosic ethanol technologies, as well as the fundamental economics behind cellulosic ethanol production.

Finally, this presentation will demonstrate the importance of process integration and energy efficiency in the viability and profitability of cellulosic ethanol production in the pulp and paper industry.

BACKGROUND

What is a Wood-based Biorefinery

It is important to define the way the term will be used in this article. A wood-based biorefinery is a plant that produces multiple value added chemical products from wood. True pulp mill based biorefineries have existed for a hundred years. The two most notable examples are the now closed Georgia Pacific Bellingham mill and the Park Falls Flambeau River Papers existing mill. These facilities produce(d) sulfite pulp, ethanol, xylose, furfural, lignosulfonates and acetic acid. In 1945, 34 Swedish pulp mills produced 27 million gallons of ethanol¹ together with chemical pulp.

Similar to petroleum refineries, biorefineries will produce several products, and likewise, the products with smaller yields will provide the largest profit contribution. A wood-based biorefinery will be a plant providing chemicals, materials and transportation fuels derived from wood.

The opportunity to repurpose existing North American chemical pulp mills as biorefineries has emerged from the convergence of two facts; the large ethanol market and the dire financial performance of the North American pulp and paper mills. Specifically, the emergence of the cellulosic ethanol market presents to pulp and paper mills an opportunity that, at the least, must be investigated.

The Ethanol Market

The U. S. gasoline market was approximately 140 billion gallons in 2006. Ethanol has rapidly replaced the carcinogen MTBE as an oxygenate in 10% blends (E10). Ethanol can be used in 6 million cars today and is proposed for all post-2012 gasoline powered cars up to 85% blends (E85). This will create a potential market that can be satisfied by all the domestically produced all starch and cellulosic ethanol. Indeed, the recent DOE report concludes that there is a billion ton sustainable biomass supply² of which 368 million dry tons is from annual forest derived feedstock. Even at the most optimistic estimation, this can supply only 25% of the 2007 transportation fuel demand in the U.S.

Cellulosic Ethanol

Cellulosic ethanol (or cellulose derived bioethanol) is ethanol produced from cellulosic resources, (plants) that are composed of lignin, cellulose and hemicellulose. Cellulosic ethanol is chemically identical to ethanol from other sources, such as corn starch or sugar, but has the advantage that the raw material is available in a great diversity and does not compete with the food chain agricultural products.

Cellulosic resources are in general very widespread and abundant. Forests comprise about 80% of the world's biomass. Being abundant and outside the human food chain makes cellulosic materials relatively inexpensive feedstocks for ethanol production. Cellulosic materials are comprised of lignin, hemicellulose, and cellulose and are thus sometimes called lignocellulosic

materials. One of the primary functions of lignin is to provide structural support for the plant. The hydrophobic aromatic lignin molecules in between fibers make cellulose and hemicelluloses difficult to reach.

Cellulose molecules consist of long chains of glucose molecules just as starch molecules, but have a different structural configuration. These structural characteristics plus the encapsulation by lignin makes cellulosic materials more difficult to hydrolyze than starch based materials.

Corn Ethanol

Corn ethanol production has become more expensive as the corn feedstock has nearly doubled over the last 14 months in part of demand exerted by new plants. Current corn ethanol production costs range between \$1.85 and \$2.00 per gallon³. On the other hand, the use of wood for making ethanol is not expected to add pressure to the wood costs as the regional competition for this wood from other users is able to pay more for it. The corn futures price has nearly doubled from \$2.50/bushel in June 2006 to peaking over \$4.00/bushel in June 2007 - quite in contrast with the ethanol futures, which have dropped from over \$4.00/USG peak price to \$2.00/USG range at the same time.⁴

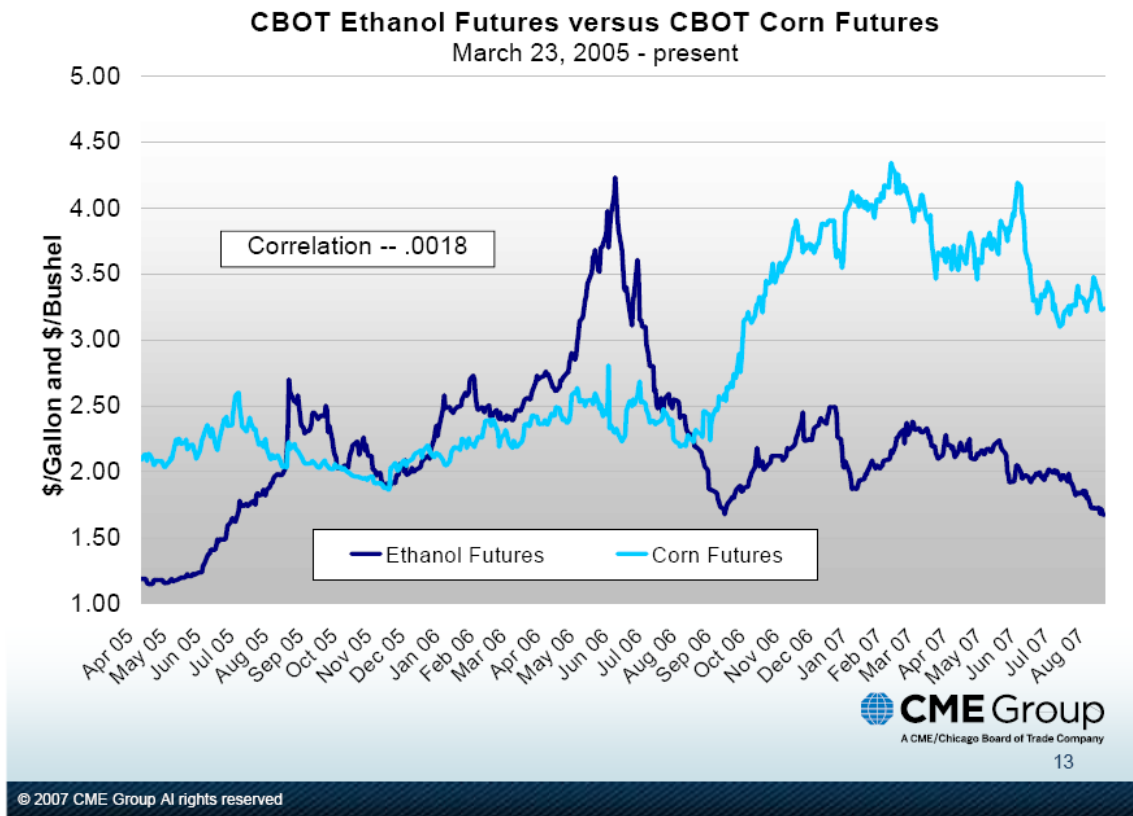


Figure 1. Ethanol and corn futures recent pricing history.⁵

Furthermore, the production of corn-ethanol is limited by the available land space and escalation of competing food product prices. The corn ethanol production is expected to level at ~12 billion gallons per year.

Corn ethanol, often referred to as first generation renewable fuel, has kick started the alternative transportation fuel market. Cellulosic ethanol, referred to as second generation renewable fuel, is chemically identical and will not have to battle over ethanol quality standards.

Today 119 ethanol biorefineries are operating in 26 states with a capacity to produce more than 6.2 billion gallons of ethanol, an increase of almost 1 billion gallons from the beginning of the year⁶. An additional 86 ethanol new biorefineries and expansion projects are set to come online in the next 15 months that will add nearly 6.4 billion gallons of new production capacity.

Ethanol is today blended into more than 45 percent of the nation's gasoline. Some 6 million flex-fuel vehicles (FFV), capable of burning ethanol blends up to 85 percent (E85), are in use today. Over 1000 thousand E85 retail outlets are in operation⁷.

However the construction of new ethanol plants is now slowing down as the high corn prices have decreased or erased the profitability of corn ethanol. Additionally there are many concerns being raised about the "greenness" of corn ethanol, i.e. the life cycle impact on CO2 emissions once the emission, from fuels used in the plant, and the growing and harvesting of the corn are correctly accounted for. Having said all these arguments regarding corn ethanol, it is not in any way in competition with cellulosic ethanol (the one that can be produced from wood in pulp mills), because the future market exceeds the possible domestic agro-based production of ethanol.

The Performance of the Pulp and Paper Sector in USA

The performance of the U.S. pulp and paper sector has been lack luster for the last 10 years. In the last 5 years the closures of pulp mills, and the devastation of the local communities where they are based, has accelerated.

Industry Profitability

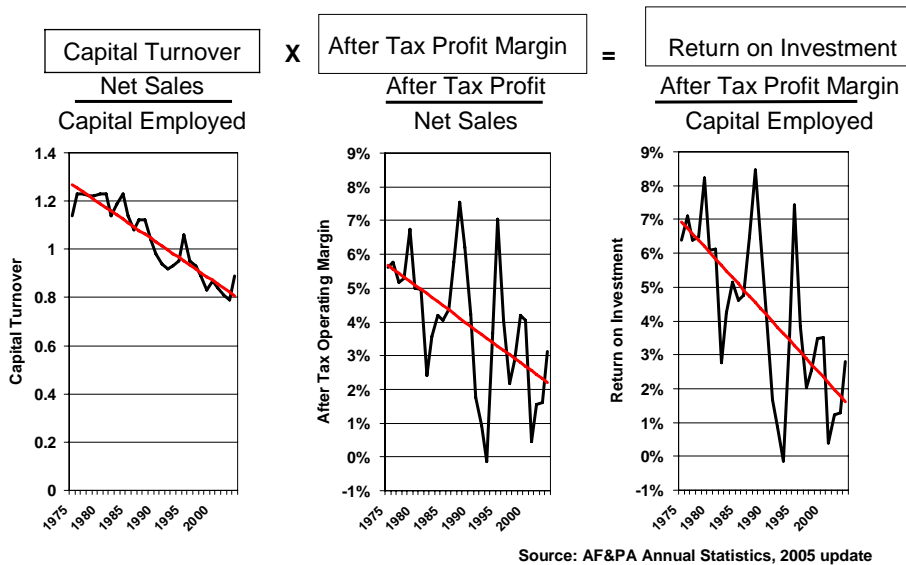


Figure 2. Industry historical profitability⁸.

However, pulp mills have some inherent advantages when investigating possible locations for cellulosic ethanol production. They have extensive and well tested wood procurement and handling logistics. They have a highly skilled workforce. Pulp mills also have a very large investment in infrastructure that can be redeployed to be used in wood-based biorefineries. Even if no process equipment were redeployed, the existing infrastructure of power house, water treatment, effluent treatment, MCC and control rooms, substations, pipe bridges, air compressors, warehouse, offices, storage tanks etc. would convert a greenfield site to a brown field site with a capital cost estimated to be between 30 and 50% lower.

FUNDAMENTAL BIOREFINERY ECONOMICS

The economics of biorefineries are very strongly influenced by:

- 1) The cost of wood and
- 2) The capital investment required

Other factors, like labor cost and intensity, size, other additives etc., are important but do not have a catastrophic effect on the viability of the biorefinery.

The impact of the cost of wood

Our calculation, as well as those of others, determine that if the entire wood was to be converted to ethanol, (i.e. the cellulose, hemicellulose and lignin), the expected yield would be ~114 USG/BDT wood. If the lignin is used for energy the expected yield from the cellulose and hemicellulose fractions is ~90 USG/BDT.

Given that all the wood would be used in the ethanol production, energy would have to be supplied from other sources (possibly also biomass) for the fermentation and distillation needs of the plant. In this paper it is assumed that 50,000 Btu is required per USG of ethanol. This is nearly equivalent of lignin fraction heat value in the wood to be converted to ethanol.

The capital cost required for the construction of cellulosic ethanol plants is estimated herein to be ~\$10/USG/y. On February 28, 2007, the US Dept of Energy announced \$385 million in grant funding to 6 cellulosic ethanol plants with projected capacity of 140 million gallons annually. This grant funding accounts for up to 40% of the investment costs, while the remaining 60% comes from the matching funds. It is likely that the original capital cost estimates of \$7/Gal/y capacity will be exceeded in these demonstration facilities.

In the table below the figures above were used together with some assumptions regarding labor and additional raw materials. The size of the plant was assumed to be 80 million USG per year. This size is in line with modern corn ethanol plants and would require the same order of magnitude of wood as a 1000 ADMT/d Kraft pulp mill.

In the table below it can be seen that in order for the biorefinery to have acceptable economics, either the wood cost will have to be well below \$80/BDT, or the capital cost will have to be much smaller than \$10/USG/y.

Other factors, such as technology risk and plant size, will also have an effect but it can be seen clearly that the latter effects will be of secondary importance.

Table I. Sensitivity of the wood based biorefineries to capital investment and wood cost.

Plant size	USG/y	80,000,000	80,000,000	80,000,000	80,000,000
Investment	\$/USG/y	\$ 10.00	\$ 10.00	\$ 10.00	\$ 5.00
Wood cost	\$/BDT	\$ 30.00	\$ 80.00	\$ 80.00	\$ 80.00
Yield	USG/BDT	114	114	90	90
Cost Contributions					
Wood	\$/USG	\$ 0.26	\$ 0.70	\$ 0.89	\$ 0.89
Capital cost	\$/USG	\$ 0.54	\$ 0.54	\$ 0.54	\$ 0.27
Energy	\$/USG	\$ -	\$ 0.25	\$ -	\$ -
Labor	\$/USG	\$ 0.05	\$ 0.05	\$ 0.05	\$ 0.05
Other raw materials	\$/USG	\$ 0.25	\$ 0.25	\$ 0.25	\$ 0.25
Maintenance	\$/USG	\$ 0.10	\$ 0.10	\$ 0.10	\$ 0.10
Overheads	\$/USG	\$ 0.15	\$ 0.15	\$ 0.15	\$ 0.15
	\$/USG	\$ 1.35	\$ 2.04	\$ 1.98	\$ 1.71

So is this good news or not? In one sense it is good news because it demonstrates that pulp wood will not be sought after for cellulosic ethanol production at least not in today's market of expected ethanol sale price at \$2/USG. However, if the ethanol market price climbs back to \$4/USG as seen in June 2006, then there will be competition for pulp wood from ethanol producers. And for those skeptics of this possibility, the recent history of gas prices and oil prices in combination with a resilient demand from rapidly developing Asian countries should be a sign.

As will be demonstrated in the next session, pulp mills are in an advantageous position to take care of the emerging ethanol market and increase their profitability. At today's ethanol and pulpwood prices, pulp mills are the only industrial players that can produce ethanol profitably. Starting today, this will place existing pulp mills in a position to be first and most competitive as/if the ethanol prices climb and as pressure is put on the price of biomass.

BIOREFINERY TECHNOLOGIES

The technologies that exist or are under development for the production of ethanol from wood can be categorized in thermal and hydrolysis based technologies.

Thermochemical Technologies

These methods do not fractionate the wood into its three basic components, i.e. cellulose hemicelluloses and lignin. Instead, the whole wood is converted (in the case of gasification) into an intermediary synthesis gas (a mixture of H₂, CO, CO₂ and CH₄), which is then the feedstock for downstream chemicals or transportation fuels. Furthermore, the gasification process emits large amounts of lower grade energy. Sometimes this energy can be successfully sold to another operation (displacing fossil fuel there) or converted to power (directly or indirectly). Therefore, the economics of gasification, hinge on two things; First the cost of the biomass and second, the ability to sell surplus energy at a good price.

The conversion of the synthesis gas to transportation fuels can be done by the Fischer Tropsch method, or by the use of catalysts to ethanol or by the use of micro-organisms to ethanol. Fischer Tropsch process has been proven commercially starting from coal and natural gas. FT process requires both a large scale (because of the high capital intensity) as well as an end utilization of a wide range of side products. Smaller wood based FT plants would require proximity to a petrochemical refinery – for the final product refining.

On the other hand, the biotic and catalytic processes for converting the synthesis gas to ethanol or mixed alcohols are still not well documented, but progress is being done daily. Our economic analysis shows, that using expensive biomass costs, such as wood, it is essential to make the highest value added products from each wood fraction as well as achieve the highest yield from each conversion. Thermal processes are therefore not suitable economically for biomass such as wood that has high cost, i.e. higher than ~ \$40/BDt. These technologies do have a role to play in the mix of biorefinery technologies when biomass is cheap (grasses or crop residue) or has a negative cost (urban forests, or infested wood).

Hydrolysis Technologies

Enzymatic hydrolysis

The enzymatic hydrolysis has not been proven for recalcitrant material such as wood chips without chemical pretreatment, as it would take a very long time. Alternatively, wood can be milled to fine powder prior to enzymatic hydrolysis. The latter would require about 1,500 kWh/ton of amount of electrical energy - which would be between 50% and 100% of the energy that will be contained in the generated products. Still progress in enzymatic methods will no doubt decrease the time required. However, these methods break down the biomass into monomers that must undergo secondary processing to be converted into higher value-added chemicals products.

Pre-extraction of hemicelluloses, from wood via alkaline, acid or steam solvents, VPP

Pre-extraction has been successfully demonstrated in hardwoods. To date there is no confirmation of a successful trial on softwood (which is the supply proposed in this project). Furthermore, pre-extraction of hemicelluloses uses only a portion of the hemicelluloses, (~1/4), thereby it could distort the capital cost required to the revenue of the transportation fuels derived.

Another major concern is the fact that the extract is very dilute and, therefore a large amount of energy must be used to concentrate it. A recent patent pending development, the Red Shield Ethanol process, has overcome this problem, by using process integration at the design stage. Pre-extraction will most likely have a role in the biorefinery technologies, but it will probably be producing a mix of transportation fuels and higher value added chemicals, which increase the revenue gained from the required capital expenditure

Complete dilute or strong acid hydrolysis.

Hydrolysis dissolves both hemicelluloses and cellulose, thereby degrading the cellulose to a lower economic value product. Because of the severe acid treatment, some of the sugars get converted to degradation products such as aldonic acids, and therefore the ethanol yield is negatively affected.

Selective hydrolysis of hemicelluloses.

Wood is fractionated into its three main components. Only the hemicellulose is hydrolyzed and used for the production of ethanol. The cellulose is preserved and used for the production of value added products such as fluff pulp, dissolving pulp or high value added cellulose derivatives. The lignin can be either sold or burned depending on the path that yields the highest income.

American Value Added Pulping, AVAP™.

This patent-pending process and technology was designed and tested by American Process based on the technical and economic analysis above so that it provides high profitability as well as low risk and high flexibility to adapt to market conditions.

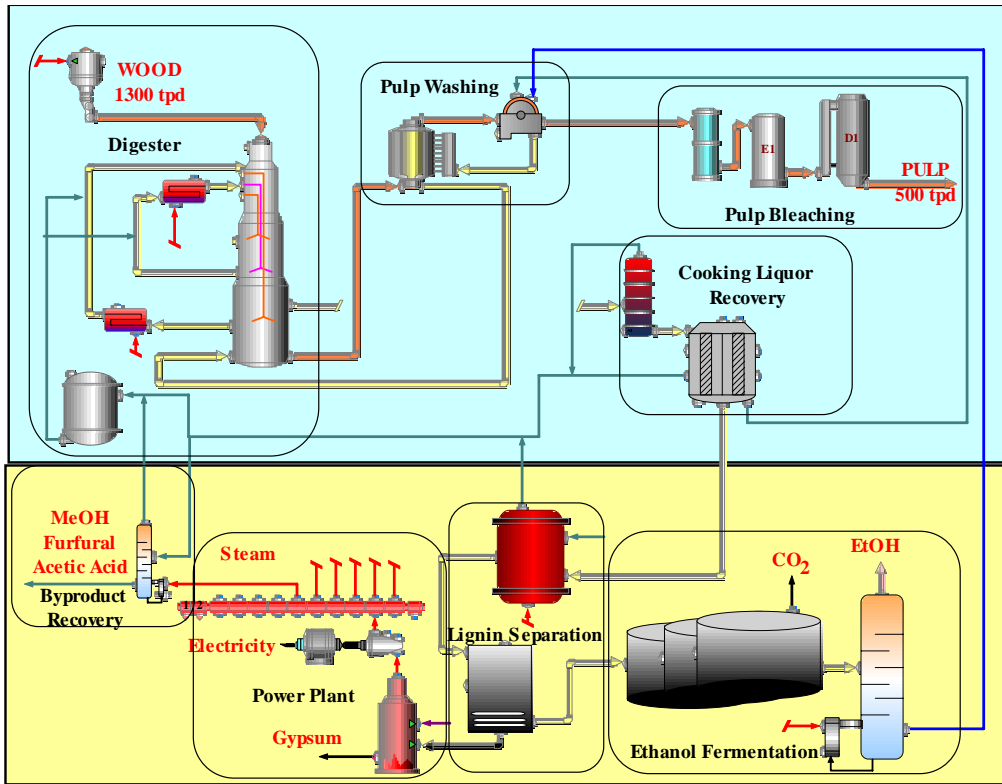
In this process, wood chips are pulped in the presence of alcohol and sulfur dioxide. The cooking conditions as well as the pre-processing and post digestion treatment are proprietary and tailored to match the desired properties of the pulp and the yield of co-products.

Pulping in aqueous alcohol facilitates penetration of wood chips and avoids lignin condensation reactions to allow rapid solubilization of lignin and hemicelluloses. Spent liquor is subjected to a secondary treatment in a reactor to ensure maximum monomeric sugar yield and fermentation inhibitor removal.

Separation of the lignin is achieved by reduction in solubility and subsequent precipitation. The lignin can be sold, burned or even gasified depending on the route that is most appropriate in each application.

The absence of sodium eliminates the expensive Kraft recovery cycle and enables a simpler, highly integrated and unique recovery system. Energy to this recovery cycle is provided, to a large extent, by use of vapor compression in a patent pending process that concentrates the liquor. The integrated stripper column regenerates the processing ethanol and isolates the condensate for by-product recovery and process reuse.

The recovery cycle is designed for recovery of chemicals and high conversion rates. The process is effective for softwoods, in which the majority of sugars are fermentable by baker's yeast, *Saccharomyces cerevisiae*. Proprietary 3rd party pentose converting microorganisms can be used to ferment the remaining pentoses or in the case of hardwood sugars.



AMERICAN VALUE ADDED PULPING™
(C) AMERICAN PROCESS INC., 2007

Figure 3. Continuous process for AVAP™ biorefinery process.

Competitive Advantage of Cellulose Preserving Technologies

Having reviewed the known technologies, American Process Inc. has summarized its findings in the table below. This table clearly shows that at today's market conditions and technical knowledge, the most economically stable technologies are those that fractionate the wood and

produce from each fraction the highest value added product. In the table below, it can be seen that of these technologies, those that co-produce ethanol with pulp bring the highest revenue per ton of wood used.

Of these, it can also be seen that the economic value is further increased when the yield from hemicelluloses is maximized.

Table II. Comparison of wood based biorefinery technologies.

		Gasification/ Catalysts	Gasification/ Enzymes	AVAP™ Phase I	AVAP™ Phase II	VPP	Strong Acid Hydrolysis
Practical Yield	USG/BDT	113	85	45	96	18	55
Price of Ethanol	\$/USG	\$2.00	\$2.00	\$2.00	\$2.00	\$2.00	\$2.00
Price of Pulp	\$/BDT			\$550	NA	\$550	NA
Fuel Income	\$/BDT of wood	\$226	\$170	\$90	\$192	\$37	\$110
Pulp Income	\$/BDT of wood			\$226	NA	\$237	NA
Total Product Income	\$/BDT of wood	\$226	\$170	\$316	\$192	\$274	\$110
Technology Risk		High	High	Low	Low	Medium	Medium
Labor		Yes	Yes	Shared	No	Shared	Yes
Energy		Extra	Extra	Included	Included	Included	Included
Infrastructure		No	No	Exists	Exists	Exists	No
Capital Cost		High	High	Modest	Low	Low	Modest
Major Issue		Technology Status	Technology Status	Pulp Quality	None Known	Scale	ROI

Technology Progress

During the last 18 months the process has been investigated in the lab and the preliminary engineering is completed. Several of the original possible showstoppers have been eliminated.

A wide range of cellulose grades has been produced by modifying cooking conditions. The capital cost of the digesting equipment has been halved in very rapid cooks. The properties and bleachability of the produced cellulose has been found to be suitable for commercial grade pulp specifications.

The pulping to low hemicellulose content to low Kappa yields an initial alpha cellulose content of over 90% of the holocellulose. The bleaching conditions have been adjusted to match properties of commercial grade dissolving pulps. Dissolving pulps have a bright future as feedstock to replace cotton and polyester based fibers in textile manufacturing.

Fluff pulp is another grade that benefits from low hemicellulose content. Absorbent grades have large and growing markets.

Higher yield pulps and high strength pulps can be produced with the same process to maximize pulp production. The yields higher than Kraft pulping are achieved because of high selectivity for lignin removal.

The evaporation of cooking alcohol precipitates a non-sticky native lignin suspension. This lignin has been easily co-precipitated along with lignosulfonate when treated with the conditions of the process. Both lignins exhibit purity and reactivity which are under investigation for potential valuable uses as a chemical feedstock, beyond the sale price as lignosulfonates assumed herein.

The preliminary engineering has confirmed that with the selected process steps, the process will be energy self sufficient with its own lignin and lignosulfonate streams, (if the choice were to burn these). Utilization of bark and wood residues enable the sale of the lignin without use of fossil fuel in the process.

Ethanol losses have not completely been verified, but the possibility has been mitigated by process design. Since ethanol is both part of the “cooking” chemicals, as well as the end product, it is important not to lose ethanol with the cellulose, the lignin and lignosulfonate products. The latter two have proven not to be issues, because they would leave the process at 60+% solids and, therefore, contain very little ethanol and other solutions constituents.

Ethanol losses with the cellulose stream are mitigated the current process design with 4-stage high consistency cellulose washers – to minimize the ethanol loss. Furthermore, any ethanol that would leave with the condensate from the sugar stream concentration or with the distillation bottoms, is captured and recycled in the process, therefore maximizing ethanol recapturing through internal recycle.

Still there is a danger of some of the ethanol covalent bonding with the cellulose and trapping inside of the lumen. Also, further research is needed to evaluate chemical reactions of ethanol, such as reversible esterification. Even so, this esterification reaction is reversible, and such chemistry would have to be employed. For current project design, without continuous experimentation, it has been assumed that 6.5% of the ethanol produced will be used as makeup into the process. This is considered to be conservative assumption.

Beyond Ethanol

It is important to note herein that the ethanol market has spurred the biomass biorefinery. Although most discussion today is focused on the production of ethanol, research is already under way for the third generation biorefineries that would produce other chemicals in, or not in, combination with ethanol, such as levulinic acid, butanol, acetic acid, acetone and others.

The Importance of Process Integration in Design

Our review of the wood-based biorefinery technology has made one thing abundantly clear: the importance of process integration in the design phase. Here we must stress that process integration is not just the application of few heat exchangers to recover and reuse heat. In its true form, the process integration ensures that the fundamental process reactions are carried out in such conditions so as to minimize the energy usage. Therefore, choices such as concentration of extracts, operating pressures and temperatures of columns and digestion vessels, sequence of

process units, recycle of streams and choice of makeups are specified upfront, prior to any equipment design.

If we look at a typical Kraft mill, the process operating today has grown organically over 90 years, mostly dictated by equipment vendors whose emphasis was the performance of a piece of equipment within its limited boundaries.

Only in the last 15 years has the pulp and paper industry employed process integration as an energy conservation analysis method. Although this has produced very good results, the complete success was hampered by the large capital investment that had been anchored into inefficient processes and equipment.

This historical route of patch work design, to correct deficient process, must be avoided in the design of biorefineries.

CONCLUSIONS

Today, incremental improvements in pulp mills are no longer enough. Future success requires technology leaps, departing from traditional practices, and better use of wood fractions.

The existing ethanol market presents an opportunity to pulp mills to be reborn as full fledged biorefineries.

The perceived risks are often the result of refusal to do a paradigm shift and testament to perhaps the only industry that has not changed its fundamental process for 100 years.

The least we must do as an industry is to investigate the biorefinery opportunity seriously before dismissing it.

¹ Sune Wännström, presentation

² R. Perlack, L. Wright, A. Turhollow, R. Graham, B. Stokes, D. Erbach, "Biomass As Feedstock For A Bioenergy And Bioproducts Industry: The Technical Feasibility Of A Billion-Ton Annual Supply", DOE/GO Report 102005-2135, April, 2005

³ Phil Flynn, a senior market analyst at Alaron Trading, Chicago

⁴ Chicago Board of Trade, July 2007 Chartbook, 08.08.2007

⁵ Jeffry Kuijpers, "Ethanol Derivatives, Key Charts & Data, updated through August 2007", reproduced with permission

⁶ Ethanol Industry Overview. Renewable Fuels Association, September 2007

⁷ Department of Energy, Biomass program, <http://www1.eere.energy.gov/biomass/>, September, 2007

⁸ Richard Phillips, 2006, reproduced with permission

A Biorefinery Process Suitable for Non-Wood Fibers.

E. Kendall Pye, Michael Rushton and Alex Berlin

Lignol Innovations Ltd., 3650 Wesbrook Mall, Vancouver, BC, V6S 2L2, Canada

ABSTRACT

The large-scale production of fuel ethanol from lignocellulosic materials is now a major commercial objective worldwide. Agricultural residues and deliberately grown annual crops are receiving the most attention as feedstocks mostly because of their widespread availability and relative ease of processing when compared to wood. Non-wood fibers are generally easier to process partly because of their more open structure, whereas wood, with its dense and compact cellular morphology, requires significant pretreatment. Because of these and other factors, many developing biorefinery technologies are designed to preferentially utilize non-wood fibers. Lignol Innovations Ltd. has developed a modified organosolv biorefinery process that includes enzymatic saccharification and fermentation of cellulose and other polysaccharides. This biorefinery technology produces not only fuel ethanol but also other valuable industrial chemical co-products from non-wood fibers and other types of woody biomass. With the higher revenues generated from these co-products this technology can be economically-attractive even when built at a significantly smaller scale than is required by many other developing biorefinery processes. This is advantageous for non-wood fiber feedstocks, such as agricultural residues, since it reduces the cost of feedstock storage and transportation to the biorefinery.

KEY WORDS

Biorefining, non-wood fibers, organosolv, ethanol

INTRODUCTION

There is now a worldwide interest in the production of fuels and chemicals from renewable materials resulting from the convergence of significant problems and concerns that include climate change associated with greenhouse gas emission from fossil carbon sources; escalating crude oil prices and the anticipated large increases in oil demand from the developing economies of China and India, coupled with a shrinking supply of easily produced oil; energy security; and the economic impacts of higher oil prices on the economies of oil importing nations [1,2].

Recent studies by various government agencies have concluded that liquid transportation fuels and many petrochemicals can now be produced competitively from renewable resources that include agricultural residues such as corn stover and bagasse, wood and forestry residuals from lumber and pulp mills and woodland clearing and deliberately grown crops [3,4]. In fact woody biomass represents the only renewable resource with sufficient potential to significantly impact the current demand for these products. While fuel ethanol production from cane sugar, corn and other cereals is now a major and rapidly developing industry, it is generally recognized that these sources cannot supply sufficient ethanol fuel and chemical products for those industries without causing a major disruption of the food and feed markets [5]. Therefore, technologies for the conversion of the vast amounts of available lignocellulosic biomass must now be developed to supplement or even totally displace sugar and cereal grains as sources of these products. In the US it has been determined that over one billion tons of lignocellulosic feedstock a year could be made available for such a use without impacting on the nation's ability to produce food and feed [6]. Much of this would come from annual fibers, either as residues or as deliberately grown crops.

Major economic and social advantages can also be anticipated from the development of industries that use renewable lignocellulosic materials for production of liquid transportation fuels and chemicals. These include higher incomes and economic improvement for the forest industries and the domestic agricultural economy; reductions in trade imbalances of oil importing nations; and a reduction in the need for agricultural subsidies from certain governments for set-aside programs and crop surpluses. As a result of these considerations, governments, venture capitalists, large corporations, including many of the major oil companies, are now providing enormous budgets to stimulate research, technology development and the commercial introduction of bio-based fuels, chemicals and

materials [7]. As a result, there has been a major development of technologies, mostly by relatively new start-up companies, designed to convert lignocellulosic biomass into fuel ethanol and other transportation fuels, industrial chemicals and materials. Surprisingly, very little of this activity has been undertaken by the traditional forest products companies, which to a great extent control the forest biomass resource and also have most experience in operating large industrial facilities using woody biomass.

Developing Technologies for Biomass-Derived Fuels and Chemicals Production

Thermo-chemical conversion of the entire biomass into highly degraded organic compounds by pyrolysis, or into synthesis gas by gasification technologies is one approach to the production of fuels, chemicals and materials from plant biomass. These types of processes destroy most of the fine chemical structures present in biomass and yield gaseous or liquid mixtures of lower molecular weight products that must be further processed to create the desired products, either by fractionation or, in the case of synthesis gas by using Fischer-Tropsch catalysts, for example [8].

A second approach is the extraction, purification and possible further chemical modification of biomass components used directly in commerce. Within this class is the production of biodiesel obtained from vegetable oils and the production of ethanol from the sucrose in sugar cane [9]. In these processes much of the original chemical structure and value of the biomass is retained in the final product.

A third approach is the processing of plant materials to produce sugars from the plant polysaccharides for use in microbial fermentations from which the products of fermentation are recovered. Examples of these are motor fuel ethanol from corn by yeast fermentations, polylactic acid from *Lactobacillus* fermentations [10] and 1,3-propanediol from the Dupont engineered microorganism [11]. This approach generally requires that the polysaccharide component of the plant material be exposed to facilitate either acid-catalyzed or enzyme-catalyzed hydrolysis. In the case of the utilization of starch in cereal grains little more than physical disruption by grinding and then relatively gentle heating with water is required.

However, where the target is the cellulose and hemicellulose of the fibrous portion of plants, much more aggressive pretreatment processes are required in order to make these polysaccharide materials accessible to enzymatic attack. This is because they are intimately associated with and protected by a third polymer, lignin, in the fibrous structure of the woody material. Various pretreatment options are now under investigation for the disruption of the lignocellulosic feedstock to expose the cellulose and hemicellulose to enzymatic attack. These include ammonia fiber explosion (AFEX), ARP, steam explosion, SO₂-catalyzed steam explosion, lime treatment, dilute acid pretreatment, and others [12].

Organosolv Biorefinery Processes

Another form of pretreatment of lignocellulosic biomass is organosolv treatment in which the biomass is “cooked” with an aqueous organic solvent such as a short chain aliphatic alcohol, short chain carboxylic acids (Formacell, Acetosolv, etc.) or an aromatic solvent such as phenol [13]. Generally, these types of processes operate at elevated temperatures and consequently higher pressures, but some are able to operate at atmospheric pressures, depending on the nature of the solvent being used. The economic key to most of these types of processes are the complexity and cost of recovering and recycling of the process solvent, together with the avoidance of solvent loss in the process.

EXPERIMENTAL

The alcohol-based modified organosolv biorefinery technology described in this paper aims to retain and maximize the value of the chemical structures that exist in lignocellulosic biomass [14, 15]. In this process the biomass is cooked in an aqueous alcohol liquor at elevated temperatures for a specified time that is dependent on the nature of the biomass feedstock. Generally, annual fibers require lower temperatures and shorter cook times than do either hardwoods or softwoods. There is little need for physical preprocessing of the feedstock other than to create a reasonably uniform-sized material for feeding into the extraction vessel, which can either be of batch or continuous design. The typical size of the feedstock is a function of the type of feeder employed, but can range from wood chips, short billets of stover or straw and sawdust.

The function of the modified organosolv pretreatment step, the detailed conditions for which are proprietary, is the hydrolytic cleavage of the lignin into smaller molecular weight fragments, which then dissolve into the hot solvent liquor. At the same time various other cleavage reactions occur, especially involving the hemicellulose, in which acetic acid is formed from acetyl groups, monosaccharides and oligosaccharides are created and some pentose sugars are converted to furfural. At the same time various lipophylic extractives dissolve into the hot organic liquor and are thus removed from the cellulose-rich solid residue and can be later recovered. By careful choice of the process conditions, some reduction in the degree of polymerization but very little actual degradation of the cellulose can be achieved. The result of the modified organosolv cooking is the formation of a “black liquor” containing dissolved lignin fragments, monosaccharides and oligosaccharides derived from the hemicellulose, acetic acid, furfural and extractives. Remaining as a solids fraction is a cellulose-rich fiber, or “pulp”, from which most of the lignin, hemicellulose, extractives and minerals have been removed.

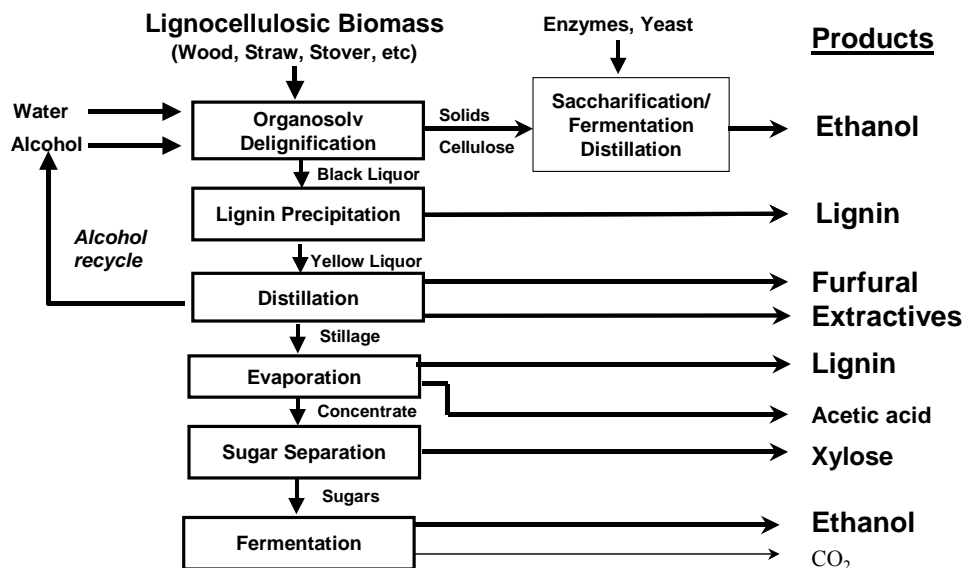
The Cellulosic Fraction

This cellulose-rich pulp is readily and easily saccharified to glucose using suitable cellulase enzyme complexes and further converted to fermentation products. The removal of lignin from the pulp, and possibly also the removal of lipophylic extractives, is a major advantage in the economic conversion of this material to fermentation products because there is less opportunity for enzyme inactivation through non-specific binding to these materials [16].

The Black Liquor

The black liquor from the modified organosolv pretreatment is processed through a series of steps to recover multiple, commercially valuable co-products that include organosolv lignin of extremely high degree of purity, extractives, process alcohol for recycle, furfural, and possibly acetic acid, xylose and a second lignin stream, depending on the composition of the feedstock. The general process stages are illustrated in Figure 1, although there are significant variants to this scheme that have been employed successfully.

Figure 1. The Lignol Modified Organosolv Biorefinery Process



RESULTS AND DISCUSSION

Processing of Annual Fibers

This modified organosolv technology has been successfully employed using an engineering scale pilot plant to process softwood chips and lumber mill or pulp mill residues, hardwood chips and residues, and a wide variety of

annual fibers. A list of the annual fibers that have been processed successfully is given in Table I. In every case a combination of valuable co-products has been produced, the yields of which are naturally a function of the particular feedstock and the processing conditions employed. For example, since furfural is a reaction product of pentose sugars degradation, mostly arabinose and xylose in biomass, conditions that favor furfural formation will reduce the recovery of xylose and *vice versa*.

While the actual results for specific feedstocks are proprietary it can be noted that when using this technology the yields of ethanol from cellulose have at times been higher than 92% of the theoretical yield. These yields are achieved with typical fermentation times of around 48 hours and high final ethanol beer concentrations ($\geq 6\%$ w/w). The total yield of all lignin fractions is generally close to the lignin content of the original feedstock. The yields of the other co-products depend to a great extent on the process conditions employed and the feedstock composition and characteristics. However, for pentose-rich feedstocks such as annual fibers, the yield of furfural can represent an amount in the range of 20% to 25% of the pentosan content of the original feedstock. When considering this yield, however, it must be recognized that the theoretical weight yield of furfural from pentose sugar is only 64% because of the reaction stoichiometry which involves the loss of three moles of water during the conversion of pentose sugar to furfural.

Table I. Some Examples of Lignocellulosic Biomass Successfully Treated with the Modified Organosolv Biorefinery Process.

Lignocellulosic Biomass	Source
Sugar Cane	Whole cane, Barbados
	Bagasse, South Africa
	Bagasse, Jamaica
High Fiber Cane	Rind Chips, Ecuador
	Whole cane, Barbados
Corn Stover	Tennessee, USA
Wheat Straw	Nova Scotia, Canada
	Saskatchewan, Canada
Jute	India
Flax	Manitoba, Canada
Switchgrass	Tennessee, USA
Kenaf	US South
Softwood	Bark beetle-killed pine, BC, Canada
	Alpine fir, BC, Canada
	White Spruce, BC, Canada
Hardwood	Aspen, Alberta, Canada
	Birch, New Brunswick, Canada

Economic Advantages

The benefits of producing multiple salable co-products in a biorefinery cannot be over-stated. These benefits include considerably higher total revenue from the feedstock entering the process. It should be noted here that many other developing biorefinery processes contemplate burning much of the non-cellulosic components, especially lignin, in boilers simply as solid fuel to create process steam and power. The value of lignin as a chemical feedstock is expected to be at least 10 times the fuel value. It should also be noted that other biorefinery processes do not allow the simple recovery of a pure, sodium-free and sulfur-free, non-derivatized form of lignin that would have substantial value in the chemicals market, whereas this is a key feature of the process described here. Table II lists various applications that have been identified for the pure lignin created in this process.

The production of multiple co-products in this biorefinery process contrasts to the thermo-chemical processes that, although able to utilize most forms of biomass, do not preserve the exquisite and valuable chemical structures that nature created. Lignocellulosic biomass, the structural components of plants such as tree trunks and cereal straw, is now the primary focus of the developing biorefining industry because it represents the lowest cost and largest potential volume of any plant material on the planet. Vast quantities of woody agricultural residues, such as bagasse, cereal straw and corn stover, are presently either left in the field or incinerated for no or little value. A recent study forecast that over one billion tons of lignocellulosic material could be recovered or produced in the US alone each year, without impacting on the ability of the country to produce food and feed [6].

Table II. Some Demonstrated Commercial Applications of High Purity Lignin from the Modified Organosolv Biorefinery Process

1. PF and isocyanate resin and wood adhesive substitute
2. Printed circuit board encapsulating resins
3. Foundry resins and molding compounds
4. Degradable plastic films and coatings
5. Friction materials, green strength binders and organic particles
6. Antioxidants in rubber, lubricants, feed additives
7. Rubber tackifiers
8. Renewable surfactants; concrete admixtures, air-entrainers, superplasticizers
9. Carbon fiber and activated carbon production
10. Physiologically-active animal feed additives

CONCLUSIONS

The modified organosolv biorefinery process described in this paper has proven to be a versatile technology that can process and fractionate most forms of lignocellulosic biomass, including non-wood fibers, as well as hardwood and softwood chips or lumber and pulp mill residues. It creates a range of high value products from low value biomass feedstocks, such as agricultural residues, by producing multiple industrial chemicals together with high yields of fermentable sugars that are readily converted into fuel ethanol, or other “sugar platform” chemicals. This value is achieved to a great extent by preserving much of the chemical structure of the components of the original biomass and then recovering these chemicals for direct application in commerce, or for further processing into fermentation products. This provides economic advantages for the utilization of bulky, low density, non-wood biomass, such as an agricultural residue or product that is generally not produced year-round and therefore must be stored for long periods and often needs to be transported considerable distances to the site of the biorefinery. This primary advantage creates greater revenues from the same quantity of lignocellulosic biomass, which in turn allows biorefineries to be economically-attractive even when built on a relatively small scale. Smaller scale biorefineries utilizing non-wood fiber feedstocks should have a lower delivered cost of feedstock because of lower transportation and storage costs and they will also require a smaller total capital investment than large scale biorefineries. A further advantage is the less obtrusive nature of a smaller scale biorefinery together with its environmentally-benign process technology which should accelerate and simplify permitting.

References

1. Ragauskas, A. J., Williams, C. K., Davison, B. H., Britovsek, G., Cairney, J., Eckert, C. A., Frederick Jr., W. J., Hallett, J. P., Leak, D. J., Liotta, C. L., Mielenz, J. R., Murphy, R., Templer, R., and Tschaplinski, T., “The Path Forward for Biofuels and Biomaterials”, *Science*, 311, 484-489, (2006).
2. Towers, M., Browne, T., Kerekes, R., Paris, J., and Tran, H., “Biorefinery Opportunities for the Canadian Pulp and Paper Industry”, *Pulp & Paper Canada*, 108, pp.26-29, (2007)
3. Irwin, L., “Forecasting the Future”, *Ethanol Producer Magazine*, 12, pp.114-119, (2006).
4. Pye, E. K., “Biorefining; a Major Opportunity for the Sugar Cane Industry”. *Intl. Sugar Journal*, 107, 222-227, (2005).
5. McElroy, A. K., “Quest Beyond Corn and Sugarcane”, *Ethanol Producer Magazine*, 12, pp.121-129 (2006).
6. Somerville, C., “The Billion-Ton Biofuels Vision”, *Science*, 312, p.1277 (2006).
7. Jessen, H., “First to be First”, *Ethanol Producer Magazine*, 13, pp. 84-91, (2007).

8. Smoker, N., "Biofuels – A Growing Field of Energy", *Cogenerative Power & Biorenewables*, pp. 40-45, Feb. 2006
9. Ramos, L. P. and Wilhelm, H. M., "Current Status of Biodiesel Development in Brazil", *Appl. Biochem. Biotechnol.*, 121-124, pp. 807-819, (2005).
10. Vink, E. T. H., Glassner, D. A., Kolstad, J. J., Wooley, R. J., and O'Connor, R. P., "The Eco-Profiles for Current and Near-Future NatureWorks Polylactide (PLA) Production", *Industrial Biotechnology*, 3, 58-81, (2007).
11. DuPont web site, http://www2.dupont.com/Sorona/en_US/index.html
12. Laureano-Perez, L., Teymouri, F., Alizadeh, H., and Dale, B.E., "Understanding Factors that Limit Enzymatic Hydrolysis of Biomass", *Appl. Biochem. Biotechnol.*, 121-124, pp. 1081-1099, (2005).
13. Sakai, K., "Organosolv Delignification", *J. Soc. Paper and Pulp Technology*, (Shipa Gikyo Shi, Japan), 48, pp.11-20, (1994).
14. Arato, C., Pye, E. K., and Gjemnestad, G., "The Lignol Approach to Biorefining of Woody Biomass to Produce Ethanol and Chemicals", *Applied Biochem. and Biotechnol.*, 121-124, pp.871-882, (2005).
15. Lignol Innovations Ltd., web site, <http://www.lignol.ca>.
16. Berlin, A., Balakshin, M., Gilkes, N., Kadla, J., Maximenko, V., Kubo, S., and Saddler, J., "Inhibition of Cellulase, Xylanase and β -glucosidase Activities by Softwood Lignin Preparations", *J. Biotechnol.*, 125, pp.198-209 (2006).

A Biorefinery Process Suitable for Non-Wood Fibers

E. Kendall Pye, Michael Rushton and Alex Berlin

Lignol Innovations Ltd.
Vancouver,
British Columbia,
Canada

October 22, 2007

Tappi EPE Conf, Jacksonville, FL

1

The New Industry of Biorefining

- Numerous concerns are now stimulating the need for fuels and chemicals from renewable lignocellulosic materials

- Cost of crude oil

- The peak oil scenario

- Climate change from fossil carbon greenhouse gases

- Energy security for oil consuming nations

- Balance of trade problems for oil importing countries

Advantages of Fuels and Chemicals from Renewable Resources

- Alternative and additional markets for the forest products and agricultural industries
- Opportunities for revenues from wastes and residues
- Less need for government support for agriculture
- Improved rural and forest-related economies

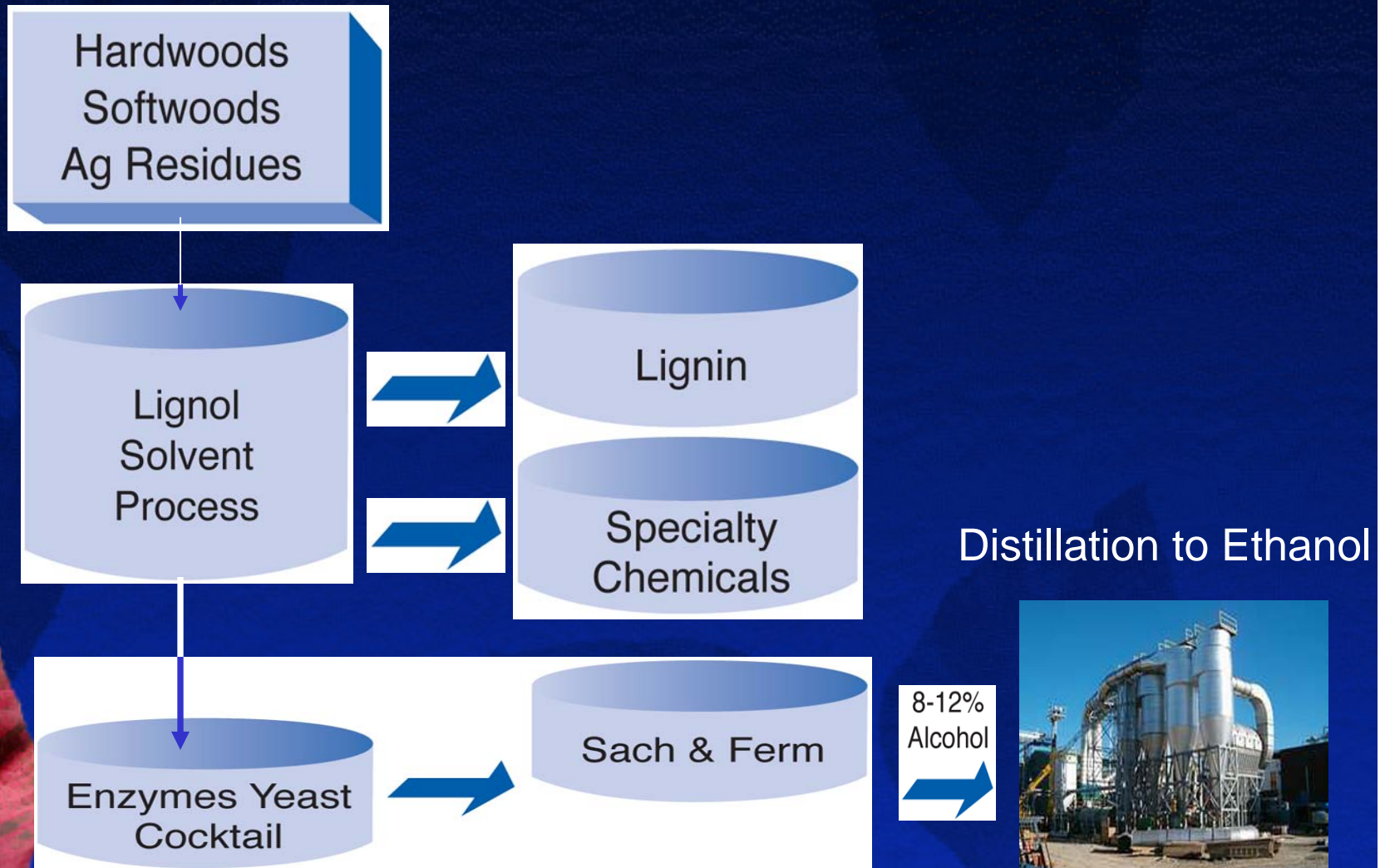
Technologies for the Production of Fuels and Chemicals from Lignocellulosic Materials

- Thermochemical
 - Pyrolysis
 - Gasification
- Biological
 - Anaerobic digestion
- Biorefining
 - Pretreatment followed by saccharification and fermentation of the carbohydrates

Advantages of Biorefining

- Preservation of the value of the chemical structures in the lignocellulosic material
- Environmentally-benign
- Flexible and relatively simple production of multiple co-products

The Lignol Modified Organosolv Biorefinery Process



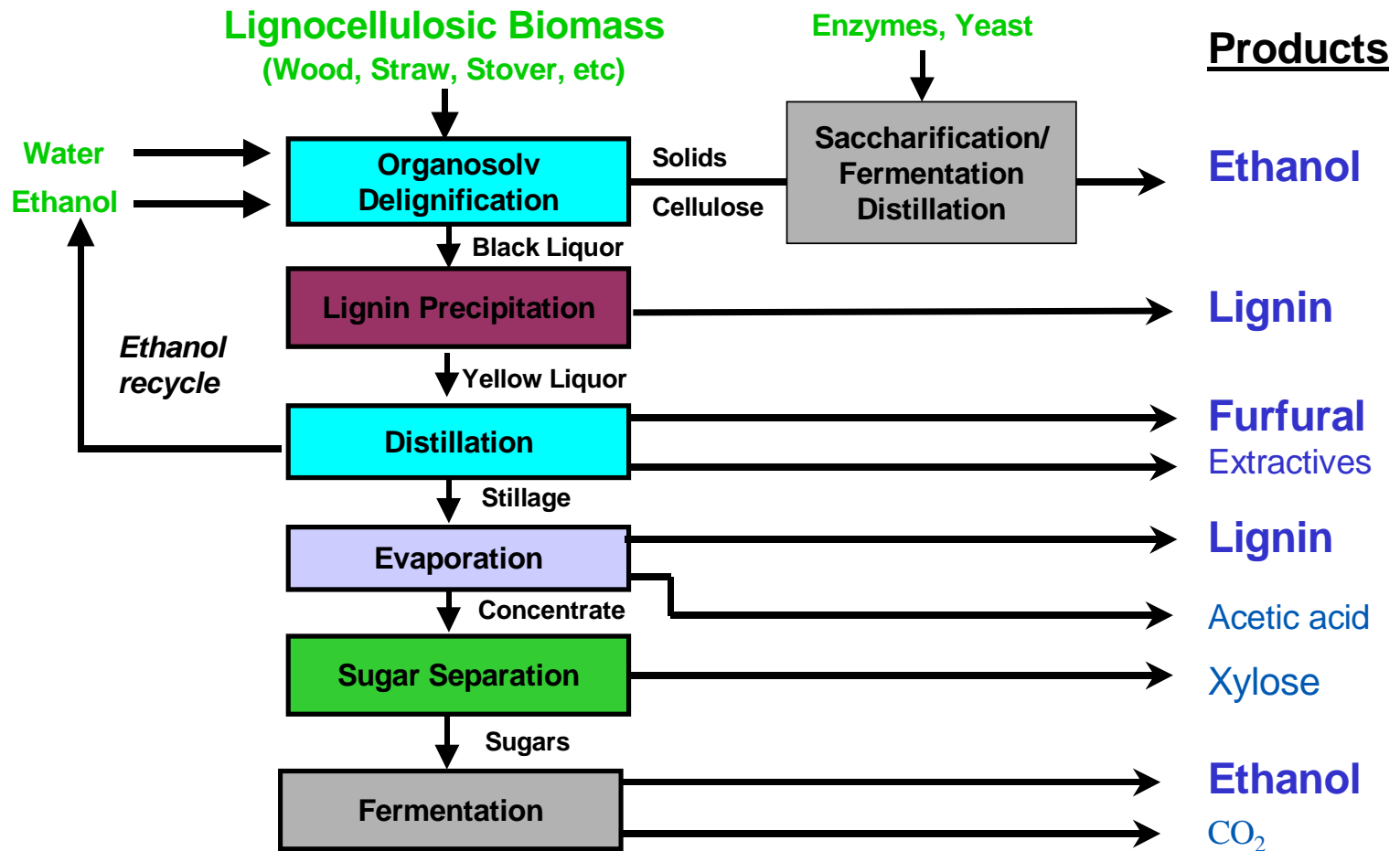
October 22, 2007

Tappi EPE Conf, Jacksonville, FL

New Lignin from Biorefineries

- **Until now commercial quantities of lignin have been available only from chemical pulp mills operated to produce good pulp quality**
 - **Thiolignin**
 - **Lignosulfonates**
 - **Soda lignin**
- **The future introduction of lignocellulosic biorefineries creates potential for new, more consistent types of lignin in vast quantities**
 - **Ethanol and other chemicals from cellulose and hemicellulose, as well as lignin, and extractives**

Modified Organosolv Biorefinery Process



The Modified Organosolv Biorefinery Process is an Improved and Enhanced Version of the Alcell Pulping Process



October 22, 2007

Tappi EPE Conf, Jacksonville, FL

9

Some Lignocellulosic Biomass Successfully Treated with the Modified Organosolv Biorefinery Process

Sugar Cane

- whole cane,
- bagasse
- high fiber cane,
- rind chips

Corn stover

Wheat straw

Flax

Jute

Switchgrass

Kenaf

Softwood

Hardwood

The Fate of Lignin in Biorefineries

- **In most leading biorefinery processes, the lignin remains with the cellulose and hemicellulose fiber**
- **Competing pre-treatments (dilute acid, AFEX, steam explosion, etc.) the lignin is not removed from the fiber**
 - Lignin inhibits the activity of cellulase enzymes
 - Large amounts of enzymes required for saccharification
 - Lignin fraction after saccharification remains as an impure residue, with little value other than as a boiler fuel
- **In the modified organosolv pre-treatment**
 - Lignin is mostly removed from the cellulose and recovered as a pure and valuable co-product

Comparison of Properties of High Purity Lignin from a Biorefinery and Other Commercial Lignins

High Purity Lignin

- <0.5% ash
- <1% carbohydrate
- <0.5 ppm sulfur
- ~3% moisture
- Water solubility, pH7, <0.5%
- Solubility in strong alkali ~100%

Kraft

3%
Low
~1.6%
Low

Sulfite

~2.5%
Up to 50%
>6%
~100%

Some Commercial Applications of High Purity Lignin



Chemical value is ten times greater than fuel value

Some Industrial Applications of High Purity Lignin, HP-L

- PF resin and wood adhesive substitute
- Printed circuit board encapsulating resins
- Foundry resins and molding compounds
- Degradable plastic films, coatings
- Friction materials, green strength binders, organic particles
- Antioxidants in rubber, lubricants, feed additives
- Rubber tackifiers
- Renewable surfactants; concrete admixtures, air-entrainers, superplasticizers
- Carbon fiber and activated carbon production
- Animal feed applications

Conclusions

- **A modified organosolv biorefinery process can produce fuel ethanol, industrial chemicals and a “pure” lignin with physical and chemical properties suitable for various commercial applications**
- **This technology is able to utilize annual fibers, agricultural residues, softwoods and hardwoods**
- **It promises high value creation and new markets for the forest products and agricultural industries.**

A Biorefinery Approach: Non-Sulfur Pulping with Partial Lignin Recovery and Conversion

T. S. Bolton, R. C. Francis and T. E. Amidon
Faculty of Paper & Bioprocess Engineering/Empire State Paper Research Institute
SUNY College of Environmental Science & Forestry
1 Forestry Drive
Syracuse, New York 13210

ABSTRACT

Modifications to Soda/Anthraquinone (SAQ) pulping that produces a hardwood pulp comparable or superior to Kraft will be described. After a mild acid (A) and carbonate (C) pretreatment of hardwood chips an H-factor of only ~700 is required in the SAQ stage to produce a pulp with low rejects. Following an A-stage (20 min at 140°C) and a C-stage (20 min at 160°C), the alkali requirement in SAQ can be as low as 8.0% Na₂O on chips. The green liquor from SAQ pulping would consist of Na₂CO₃ but no Na₂S. Part of the carbonate would go to the C-stage with the amount going to re-causticizing being less than for the kraft process. The use of kraft green liquor would be tedious due to H₂S formation at the later stages of the C-stage when the liquor pH<8.5.

Some of the non-sulfur lignin could be precipitated and results will be presented on the possible oxidation of such a lignin to syringaldehyde and vanillin. The phenolic hydroxyl groups on these monomers could be etherified with a wide range of substituents. These benzaldehydes may be valuable as commodity or fine chemicals. While this paper/presentation will present results on carbonate pretreatment and lignin monomer production, its primary focus will be on the critical A-stage or prehydrolysis.

Introduction

The acid hydrolysis (pre-hydrolysis) of hardwood chips presents itself as a method for improving the delignification during subsequent alkaline pulping. Relatively mild treatments can be employed to achieve above satisfactory results in alkaline pulping. The delignification improvement is found to be more significant for SAQ cooking as compared to kraft.

Acid hydrolysis of hardwood has the largest effect on the hemicelluloses found within the wood structure as compared to the remaining fractions. The effect is seen in both a physical and chemical alterations that benefit subsequent alkaline delignification reactions. This paper will report on investigations into both the chemical and physical aspects.

At lower severities the xylan portion of the wood can be hydrolyzed without significant mass removal. This has the propensity to decrease H-factor in subsequent alkaline pulping by approximately 37.5% while maintaining equal or higher yields after SAQ

pulping. However, little or no sugars are removed, which could be used for the production of transportation fuels and other petroleum replacement products.

At higher severities, most of the hemicelluloses can be removed without affecting the intrinsic strength of the cellulosic fraction. At these extraction parameters, the H-factor in alkaline pulping can be reduced by as much as 77%. However, yield is lower than industrial standards for hardwoods. This is because under conventional conditions, approximately 25% of the hemicelluloses are retained with the fibrous mass adding to yield. The almost complete removal of hemicelluloses may allow for its use in the ethanol transportation fuel sector.

The fibers were also more easily bleached, which would move a mill toward a lower consumption of bleaching chemicals. This combined with an elimination of sulfur from the pulping processes could lead to a mill that is more energy efficient and benign to the environment. After mild pre-hydrolysis the SAQ pulp do require a modest increase in refining energy to achieve the strength values of conventional Kraft and SAQ pulps.

Methods and Materials

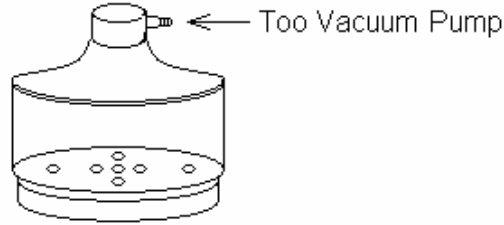
Acid Pre-hydrolysis Effect on Chip Structure

The acid hydrolysis was done in a bank of M&K 4L chemical digesters with liquor re-circulation. The heating elements warm the liquor in the re-circulation line by non-direct electrical resistance. The chips are placed in a basket within the reactors to protect the system against particulates making their way into the pump and indirect heating elements.

The wood of choice for this analysis was *Acer saccharum* (sugar maple), and its hydrolysis at different reaction times at constant temperatures was investigated. The time to temperature was 30 minutes for temperatures $\leq 160^{\circ}\text{C}$, and 45 minutes for 180°C . For the cases that were held at temperature for 15 minutes or less, 1.5% acetic acid was added based on OD chip mass to facilitate acid hydrolysis.

A sample of chips was removed after some pre-hydrolyses for void volume measurement after the hydrolysis step. The chips were never allowed to dry to completion, thereby aspirating the pores, which would deter a complete adsorption of water that is needed for this test. The samples of chips were placed into a sealed glass contained partially filled with water under vacuum, Figure 1.

Figure 1: Sealed Glass Container (Laboratory Descicator)



The samples were saturated for a period of approximately 120 minutes. After the allotted amount of time they were removed. Complete saturation of the chips was indicated when they no longer floated nor were air bubbles present in the water. The surfaces of the removed chips were dried of any external moisture and weighed immediately. After weighing, they were placed into an oven at 105°C for 48 hours to insure complete moisture removal. Once dried, the samples were weighed again.

The difference of weight is attributed to the amount of water that was held within the chip structure. This weight difference can be associated to a volume by the known density of water. Since the chips were completely saturated, the volume of water removed is equal to the volume within the chips.

Two pre-hydrolysis conditions used for void volume determinations were repeated and the chips cooked using conventional alkali treatments. The two hydrolysis conditions were chosen based on a high and low severity treatment, which were 15 minute at 160°C and 15 minutes at 150°C.

Acid treated and untreated sugar maple chips were cooked by the kraft process in the M&K digesters. An AA of 16% with a sulfidity of 25% based on Na₂O and a liquor to wood ratio of 4:1 was used. The cooking parameters are seen in Table 1. A1 & A2 represent the two pulping conditions used for the low and high severity cases respectively.

Table 1: Cooking Parameters

Process	Controls	A1-Stage	A2-Stage
kraft	90 min → 165°C 120 min @ 165°C	60 min → 165°C 90 min @ 165°C	60 min → 165°C 60 min @ 165°C

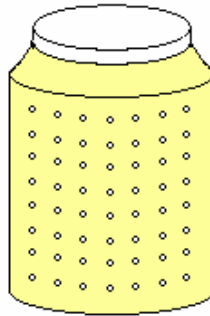
Acid Hydrolysis Effect on Lignin Leachability

The ability of lignin to be dissociated into alkali pulping liquor is dependent on not only physical diffusivity properties of the media, but possibly more due to its ability to be depolymerized chemically. This was determined by submerging both acid hydrolyzed and untreated sugar maple chips in a weak alkali solution.

The treated chips were measured for lignin leachability over three different severity conditions. The M&K digesters were used for the hydrolysis of these chips at the temperatures of 140, 150, and 160°C. For each temperature a time of 120 minutes was employed with no added acetic acid.

The treated and untreated samples were placed into a half gallon “Wiffle” reactor, Figure 2. These reactors were submerged into 4L plastic beakers containing a weak alkali solution comprised of 0.1N sodium hydroxide. A 20:1 liquor to wood ratio was used, which was sufficient to completely submerge the samples within the “Wiffle” reactors.

Figure 2: Wiffle Reactor



Ten milliliter samples of sodium hydroxide solution were removed over a period of one week. The plastic beakers were agitated daily to ensure an even distribution of concentration throughout the solution. The removed samples were measured with an UV/Vis spectrophotometer for the absorbance by lignin at both peaks of 205 and 278 nm. This was similar to TAPPI standard method UM 250.

Improved AQ Catalytic Cycle

Acid treated sugar maple and a hardwood mix were pulped with two conventional alkaline processes, kraft and SAQ. This was done to see if the efficiency of SAQ could approach that of kraft after the acidic pretreatment. For these cooks, the M&K digesters were used. The lower severity case was used for this analysis, because it would allow for a mill to maintain respectable yields.

The SAQ cooks were carried out on the acid treated hardwood using a standard practice. NaOH for the Soda AQ was added at a 16% AA as Na₂O with a 4:1 liquor to wood ratio. The amount of AQ added was 0.1% with 0.25% Na₂SO₃ as an oxygen scavenger based on OD chip mass. The cooking parameters are seen in Table 2.

Table 2: Cooking Parameters

Process	Controls	A1-Stage	A2-Stage
Kraft	90 min → 165oC 120 min @ 165oC	60 min → 165oC 90 min @ 165oC	60 min → 165oC 60 min @ 165oC
Soda AQ	90 min → 165oC 150 min @ 165oC	60 min → 165oC 90 min @ 165oC	60 min → 165oC 60 min @ 165oC

An improvement in SAQ delignification was observed and followed up by an investigation of the effect of reducing end groups entering the SAQ stage. Mild pre-hydrolyses were repeated with the addition of oxygen prior to SAQ pulping, Table 4. Oxygen was added at 85 psig to the reaction vessels during hydrolysis with 50 ppm of a metal catalyst of either Mn(II), Cu(II), or Fe(II). The 6 L bank of the M&Ks was used for this, because they are equipped with a bubble cap facilitating gas diffusion into the liquid phase.

Acid Hydrolysis Effect on Bleaching

Screened pulp from acid treated and untreated sugar maple was bleached using a standard sequence. The sequence chosen was OD_oE_pD₁, and the starting material was at a kappa number of approximately 18.

The oxygen bleaching sequence was done in a Quantum Mark IV reactor. This reactor is equipped with a high shear mixer for medium consistency materials. The pulp was bleached at an approximate consistency of 12.0% with 2 % NaOH and 0.5 % MgSO₄·7H₂O added based on OD mass. The reactor was pre-heated so when loaded it was at a temperature of 90°C which was maintained through out the oxygen bleaching stage. 90 psig of oxygen was added, and ran for an hour. At the completion the pulp was washed and de-fibered to a solids content near 30%.

The remaining stages were done in a hot water bath. The initial chlorine dioxide sequence was done at a consistency of 4 % with a kappa factor of 0.20 for determining charge. Sulfuric acid was added to help maintain a proper pH.

An alkali extraction followed the initial chlorine dioxide step. The pulp was adjusted to a consistency of 12% with the addition of 2% NaOH, 0.1% MgSO₄·7H₂O, and 0.25% H₂O₂ based on OD mass. This was reacted for 120 minutes at 80°C, at the end of which the pulp was washed and de-watered to a solids content of approximately 30%.

The final bleaching stage was another chlorine dioxide step. The pulp was adjusted to a 10% consistency with 0.5% chlorine dioxide added. This was reacted for 120 minutes at 70°C, and at completion the pulp was washed and de-fibered to a solids content near 30%.

The bleached pulp was made into pads and TAPPI standard sheets for the testing of optical properties.

Acid Hydrolysis Affect on Pulp Strength

TAPPI Standard Methods were adhered to for the analysis of the physical properties of fiber from both treated and untreated hardwood chips. The methods used were:

- TAPPI Standard Method T 248 sp-00 Laboratory Beating of Pulp (PFI mill method)
- TAPPI Standard Method T 227 Freeness of Pulp
- TAPPI Standard Method T 205 Forming Hand sheets for Physical Testing of Pulp
- TAPPI Standard Method T 404 Tensile Testing of Hand sheets
- TAPPI Standard Method T 496 Tear Testing of Hand sheets

Results and Discussion

The severity of a hydrolysis is determined through its kinetics. Severity is assumed to be independent of $[H^+]$ (when mineral acids are avoided) and strongly dependent on temperature and time. The P-factor as it is also called becomes a rearrangement of the kinetic expression, equation (i). The omega term (ii), incorporates the activation energy of the hydrolysable component, which is usually determined through graphical analysis of the specific reaction rate constant. The severity, R_o , is sometimes presented as $\log_{10}(R_o)$, because the term can become quite large.

$$R_o = t \times e^{(T-T_{ref})/\omega} \quad (i)$$

$$\omega = (R \times T_{ref}^2)/Ea \quad (ii)$$

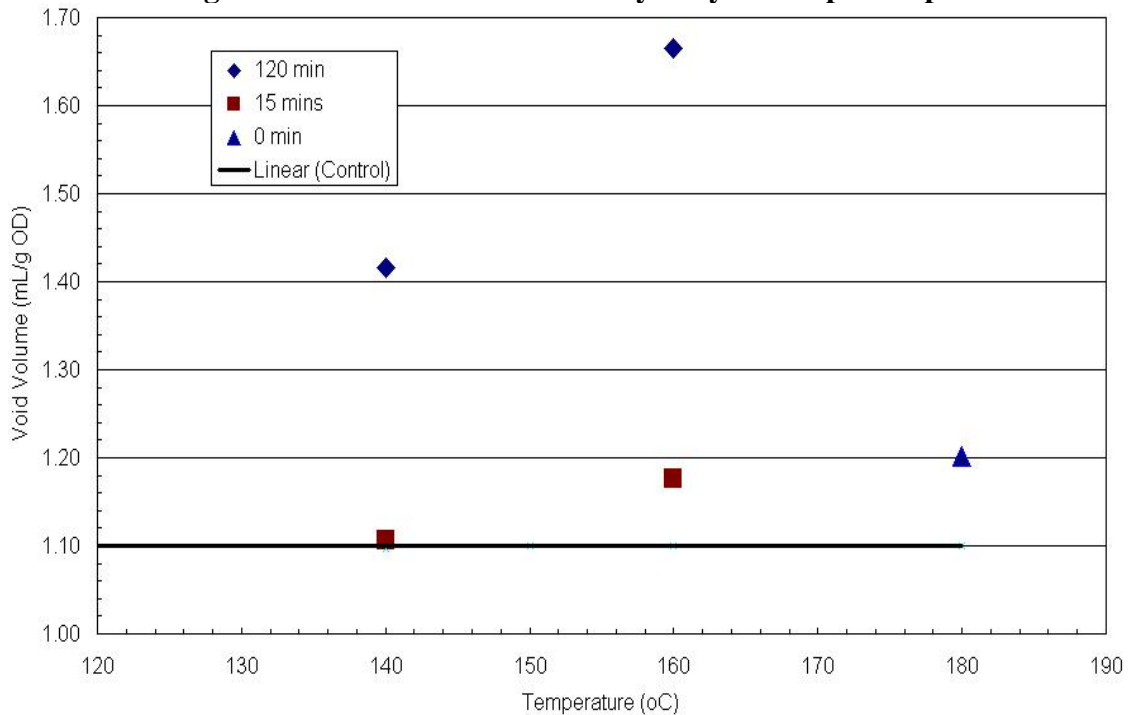
The alteration to the chip structure by acid hydrolysis was determined by measuring void volume. This was done by a water saturation and exclusion method. A series of wood chips were hydrolyzed at different temperatures and times.

Acid Hydrolysis Effect on Chip Structure

The diffusivity of wood is based on its tortuosity, void volume, and hydrophobicity. All three are affected with an acid hydrolysis treatment. The diffusion of cooking liquors into chips is a driving factor for pulping processes and is evident in the initial delignification stage. By improving diffusion, it should be possible to improve mass transfer in subsequent pulping.

The measured total void volumes (including lumens) of sugar maple chips after various hydrolysis treatments are presented in Figure 3. An untreated sample is also present demonstrating the validity of this test. The untreated sample has a void volume of 1.10 mL/g, which was determined both by measurement and calculation using known densities of sugar maple.

Figure 3: Void Volume of Acid Hydrolyzed Maple Chips



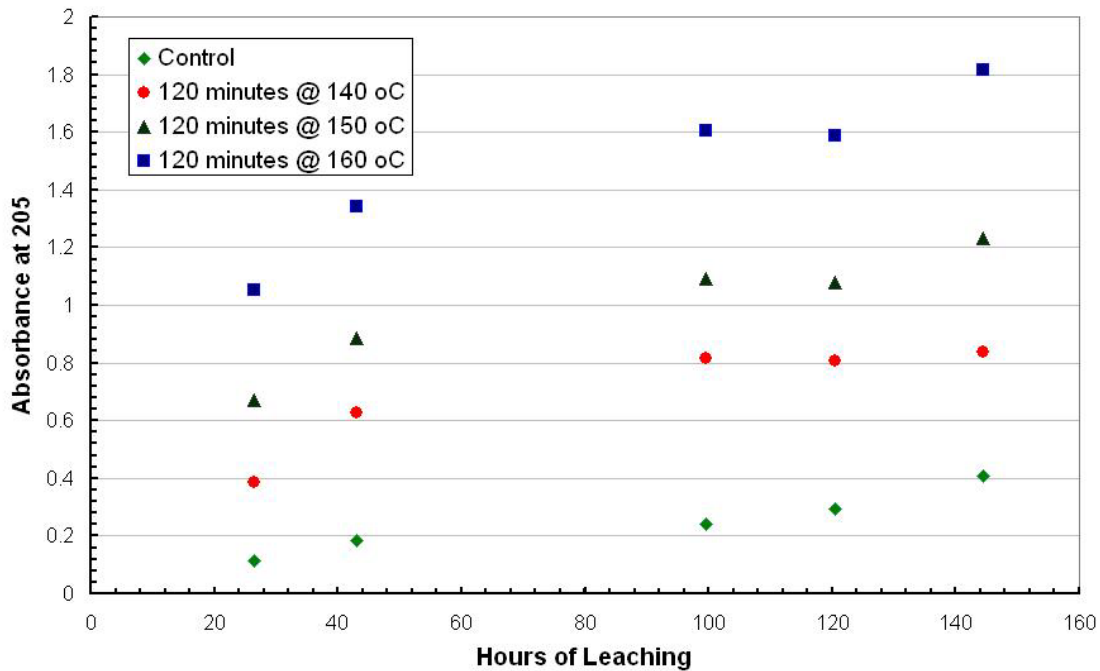
Pre-hydrolysis at 150°C for 15 minutes increased void volume from 1.10 mL/g to approximately 1.15 mL/g and it is likely that this increase enhanced mass transfer rates for higher molecular weight cell wall material. The porosity of the cell wall would be expected to increase significantly and mass transfer accelerated after a harsher pre-hydrolysis.

Acid Hydrolysis Effect on Lignin Leachability

Leachates of the alkali extracted hardwood chips were measured at both 205 and 278 absorbencies, which both demonstrated similar trends. The absorbencies can be directly correlated to soluble lignin.

The treatment of hardwood by acid hydrolysis improves lignin's ability to be solubilized into an alkali solution. This is evident in Figure 4 at the lowest severity case used in this part of the analysis. At 140°C for 2 hours, the amount of soluble lignin extracted from the wood media was approximately three times as much when compared to the untreated chips. With every ten degree increment of temperature, greater amounts of lignin were removed.

Figure 4: Absorbance of Lignin Leachates at 205 nm



This enhancement in lignin removal under alkaline conditions is an indication of improved chemical cleaving. One of the possibilities is the hydrolysis of LCC (Lignin Carbohydrate Complexes) prior to the alkali treatment. This would diminish the entrapment effect that these types of bonds have on local alkali dissociable linkages. Also an increase in void volume would add synergistically permitting for the removal of larger lignin fragments, hastening the process of delignification.

Improved AQ Catalytic Cycle

An improvement is seen in delignification more so with SAQ alkaline pulping as compared to Kraft. AQ is only an activate delignification catalyst when reduced to AHQ (Anthrahydroquinone dianion). This occurs in the presence of aldehyde reducing end groups found on the carbohydrates, mostly with the hemicellulose fraction.

The H-factor for alkaline pulping can be significantly reduced with an acid hydrolysis prior to pulping. The control H-factors for Kraft and Soda AQ are 1294 and 1599 respectively. After the mild treatment, the results in Table 3 where achieved at an H-factor of 997 for both pulping processes. This is a reduction of approximately 23.0 % for Kraft and 37.5% for SAQ. Using a mixed hardwood furnish, the results between Kraft and Soda AQ treated chips are even more pronounced.

Table 3: Kappa and Yields for Alkaline Pulping

Screened Yields (%) & Kappa Number for Sugar Maple HW Pulp			
Cook Type	Controls	A1-Stage @ 150 °C	A2-Stage @160 °C
Kraft	51.8 ¹ [17.4] ²	51.1 ¹ [16.8] ²	47.7 ¹ [17.0] ²
Soda - AQ	52.8 ¹ [19.3] ²	52.4 ¹ [17.9] ²	48.9 ¹ [17.4] ²
Screened Yields (%) & Kappa Number for Mixed HW³ Pulp			
Cook Type	Controls	A1-Stage @ 150 °C	
Kraft	53.2 ¹ [16.7] ²	51.1 ¹ [17.1] ²	
Soda - AQ	53.0 ¹ [16.6] ²	52.7 ¹ [15.9] ²	

¹Screened Yield ²Kappa number

³ Sugar Maple, White birch, Cottonwood (1:1:3)

Acid hydrolysis of wood cleaves the hemicelluloses fraction more dramatically than the remainder fractions. More specifically xylan is randomly hydrolytically cleaved, which form more end groups capable of reducing AQ to AHQ. The mild hydrolysis case retained much of its original mass, so these reducing groups are held within the chip structure.

Oxygen was added to subsequent A stages to see if it would negatively affects subsequent SAQ pulping. Oxygen would be expected to oxidize reducing end groups (REG) in the chips. It was added under three different conditions, Table 4, each of which demonstrated a negative effect on SAQ pulping. This may be because the reducing end groups are oxidized, rendering them ineffective at reducing AQ to AHQ in the catalytic cycle Figure 5.

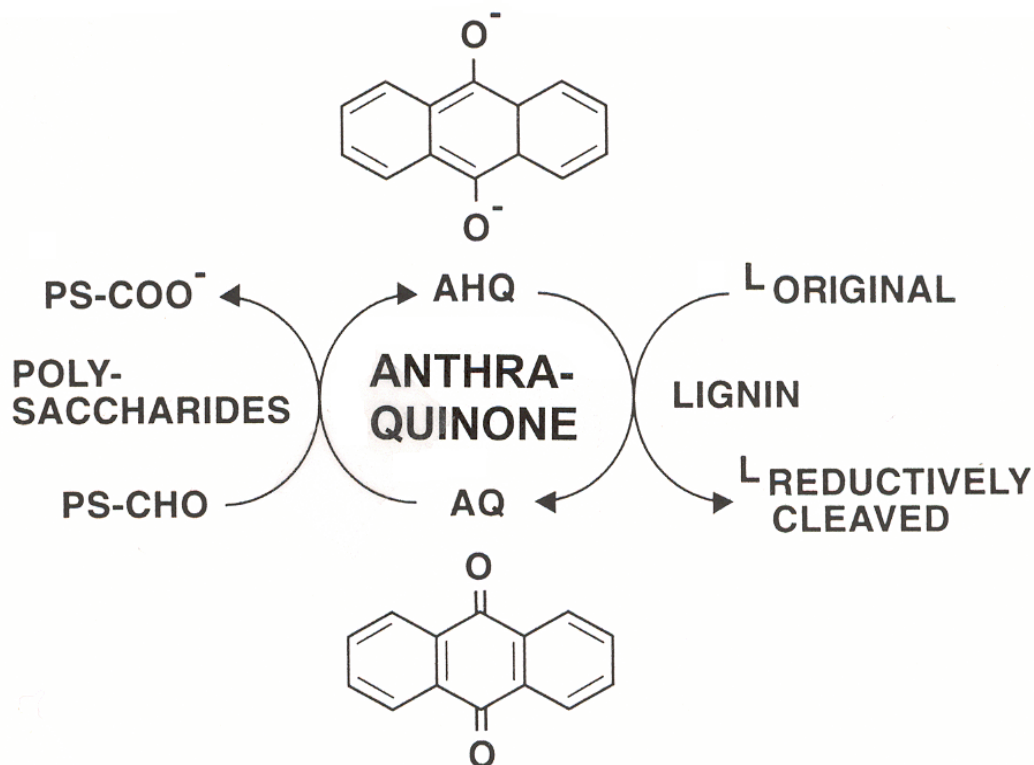
Table 4: Comparison of Oxygen Treated Acid Hydrolysis Screened Yields (%) & Kappa Number for Mixed HW³ Pulp

HWP-E Parameters	A1-Stage Soda AQ
50 ppm Mn, 1.5 % Acetic Acid on chips, 85 psig O ₂ , 15mins @ 150°C	51.3 ¹ [20.0] ²
50 ppm Fe, 1.5 % Acetic Acid on chips, 85 psig O ₂ , 15mins @ 150°C	49.4 ¹ [16.4] ²
50 ppm Cu, 1.5 % Acetic Acid on chips, 85 psig O ₂ , 15mins @ 150°C	48.9 ¹ [16.9] ²
1.5 % Acetic Acid on chips, 15mins @ 150°C	52.7 ¹ [15.9] ²

¹Screened Yield ²Kappa number

³ Sugar Maple, White birch, Cottonwood (1:1:3)

Figure 5: AQ Catalysis Cycle with Carbohydrates and Lignin



In a simple experiment we added Birchwood xylan purchased from Sigma-Aldrich to SAQ pulping and the results in Table 5 were obtained. It can be seen that the SAQ delignification rate was enhanced by the added xylan. Also, at such low kappa number values a 1.0-1.3% decrease on chips yield would be expected when the kappa number is lowered from 14.9 to 12.3. The yield for the 12.3 kappa number xylan-assisted pulp was only 0.2% on chips lower than for the conventional pulp. This appears to indicate that the reducing end groups in the added xylan (and from its hydrolysis) enhanced the delignification rate and also improved pulp yield.

Table 5: Effect of xylan addition (containing 0.09 mmole reducing end groups per gram) on SAQ pulping. Time to and time at 165°C were both 90 minutes, 4:1 L to W ratio and 16% Na₂O on chips.

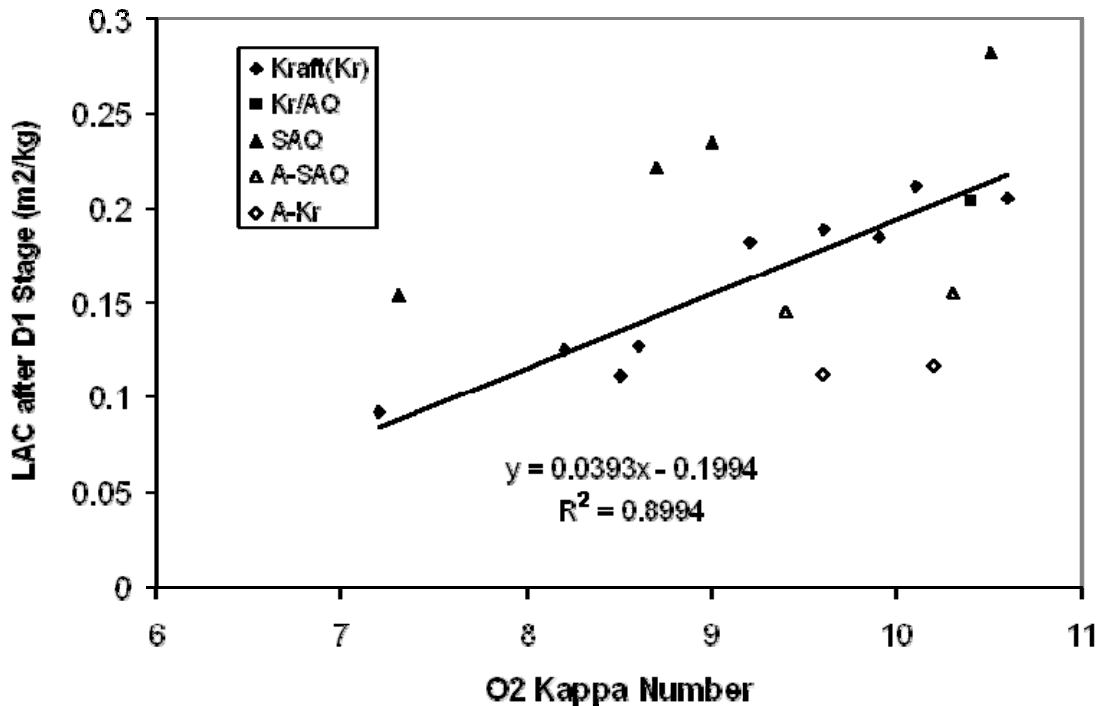
	Control	Xylan-assisted
Xylan, % on chips	0	2.5
Kappa Number	14.9	12.3
Screened Yield ¹	51.5	51.3
Rejects ¹	0.2	0.2

¹ Percent on chips

Acid Hydrolysis Effect on Bleaching

Pulp from acid hydrolyzed treated wood bleaches easier than that of untreated wood. This is observed in the LAC values of treated wood bleached pulp as compared to untreated in Figure 6.

Figure 6: Light Absorption Coefficients for Various Hardwood Pulps



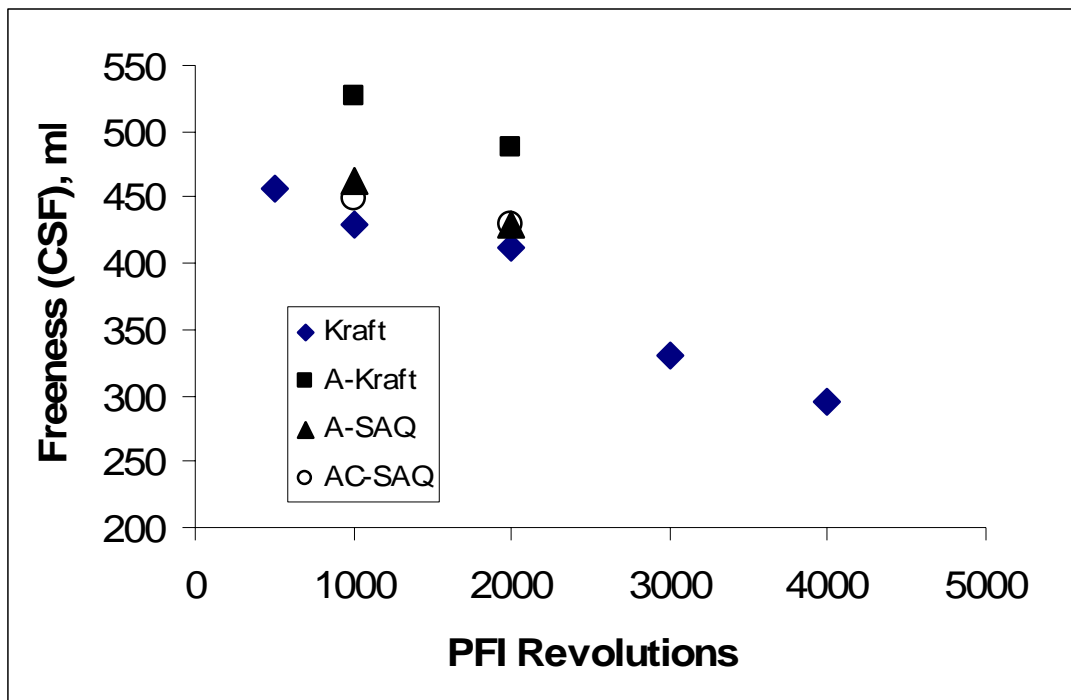
The trend line represents conventional cooked bleached pulp. The higher the LAC value, the more light is adsorbed by the pads, which corresponds to a less bright pulp. Both kraft and soda AQ bleached pulp from acid treated wood chips indicate a lower LAC value at similar oxygen kappa numbers as compared to conventional bleached pulp.

Acid Hydrolysis Effect on Pulp Strength

Treated and untreated hardwood pulp was analyzed for its ability to be refined and its intrinsic strength properties. All of the pulps tested were after a standard O₂ delignification stage.

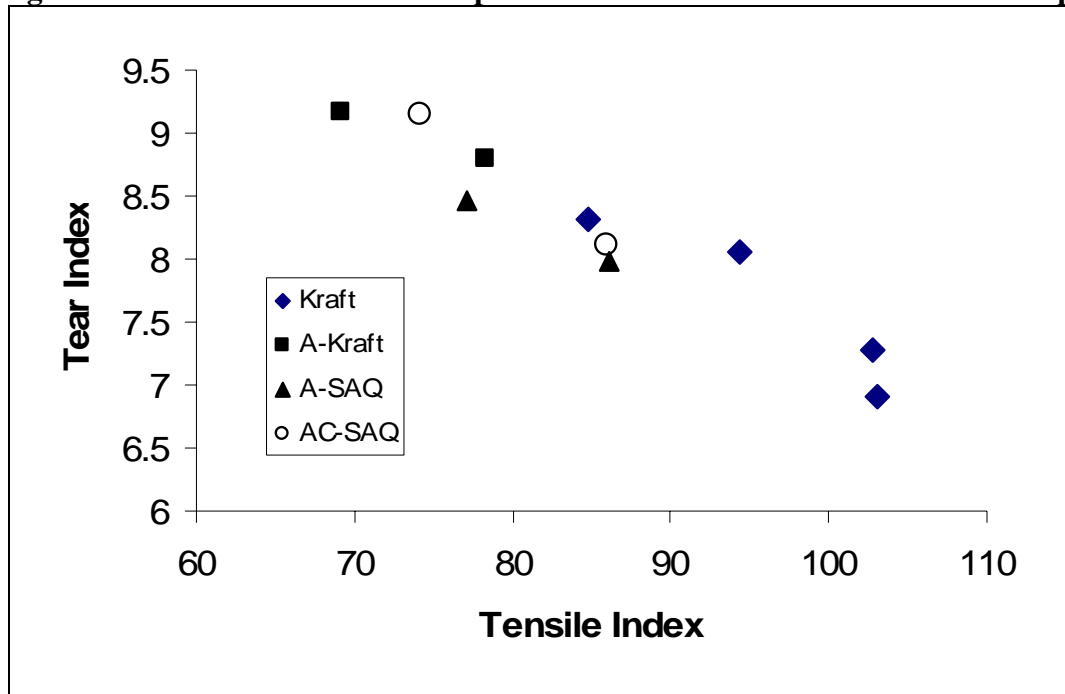
The pulp from acid treated chips does not refine as easily as that of conventional, Figure 7. Acid treated Kraft has a higher freeness at a similar refining as compared to acid treated SAQ and conventional Kraft. This indicates a bulkier fiber, which can be an advantage or disadvantage depending upon its application. For refining purposes the acid treated SAQ had only a slightly higher freeness as compared to that of the treated Kraft case. Carbonate neutralization after the A-stage (AC-SAQ) had no effect on drainage.

Figure 7: Refining Characteristics of Treated and Untreated Hardwood Pulp



Tensile-tear relationships are presented in Figure 8 and there are no significant differences. However, lower tensile indices were obtained for the A-treated pulps.

Figure 8: Tensile Tear Relationship of Treated and Untreated Hardwood Pulps



Conclusions

Hardwood chips are more easily delignified using conventional alkaline pulping processes after an acid hydrolysis. This is most likely due to both a physical and chemical alteration of the hemicellulosic fraction of the wood. The evidence of improved delignification is seen in shorter cook times at similar and sometimes improved yield and kappa numbers.

The mass removed during the pre-hydrolysis would be expected to improve diffusion, but to a less extent as compared to the chemical enhancement factor. SAQ is particularly favored with this process, due to the increase in reducing end groups after the acidic pretreatment. These reducing end groups are oxidized by AQ, which becomes reduced to the AHQ dianion, a nucleophile capable of de-polymerizing lignin.

Pulp from pre-hydrolyzed wood would be beneficial as a bleached fiber source. It is more easily bleached allowing for either a higher quality fiber, or the use of less bleaching chemicals.

An increase in delignification allows for pulping to lower kappa numbers which would save bleaching chemicals and the costs associated with the treatment of the effluents. An elimination of sulfur allows the use of gasification technology and/or lignin precipitation for bio-product synthesis.

References

- (1) Amidon, T. E. "The Biorefinery in New York: "Woody Biomass into Commercial Ethanol." Pulp and Paper Canada. V 107. No 6. p 47-50. 2006
- (2) Ballerini, D.; Desmarquest, J. P.; Pourquoi, J. "Ethanol Production from Lignocellulosics: Large Scale Experimentation and Economics." Bioresource Technology. V 50. p 17-23. 1994
- (3) Fleming, B. I.; Kubes, G. J.; MacLeod, J. M.; Bolker, H. I. "Soda Pulping with Anthraquinone." Tappi Journal. V 61. No 6. p 43-6. 1978.
- (4) Francis, R. C.; Shin, S.-J.; Omori, S.; and Amidon, T. E. "Soda Pulping of Hardwoods Catalyzed by Anthraquinone and Methyl Substituted Anthraquinones." Journal of Wood Chemistry and Technology. V 26. p 141-152. 2006.
- (5) Heitz, M.; Carrasco, F.; Rubio, M.; Brown, A.; Chornet, E. "Physico-chemical Characterization of Lignocellulosic Substrates Pretreated via Autohydrolysis: An Application to Tropical Woods." Biomass. V 13. p 255-73. 1987.
- (6) Keenan, T. M.; Tanenbaum, S. W.; Stipanovic, A. J.; Nakas, J. P. "Production and Characterization of Poly- β -hydroxyalkanoate Copolymers from *Burkholderia cepacia* Utilizing Xylose and Levulinic Acid." Biotechnol. Prog. V 20. p 1679-1704. 2005.
- (7) Lin, S. Y. Ultraviolet Spectrophotometry. In: Methods in Lignin Chemistry. (S.Y. Lin and C.W. Dence, Eds.), Springer-Verlag, Berlin, p. 217-232 (1992).
- (8) Isenberg, I. H. Pulpwoods of the United States and Canada, 3rd Ed; (Revised by M.L Harder and L.Louden), Institute of Paper Chemistry, 1981.
- (9) Simard, G. L.; Genco, J. M.; Henriksson, K. E. Jr. "The Effect of Reducing Agents on Anthraquinone Pulping." Tappi Journal. V 62. No 5. p 91. 1979.
- (10) Whiting, P. and Goring, D. A. I. "Chemical Characterization of Tissue Fractions from the Middle Lamella and Secondary Wall of Black Spruce Tracheids." Wood Sci. Technol. V 16. p 261-267. 1982.