

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

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ABSTRACT

A large diversification 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 but 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. This presentation will also demonstrate the importance of process integration and energy efficiency in the viability and profitability of cellulosic ethanol production in the pulp and paper industry.

Keywords: Pulp and Paper, Biorefinery, Process Integration, Pinch Analysis.

1. BACKGROUND

1.1 What is a Wood-based Biorefinery

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 ethanol together with chemical pulp [1].

Similar to petroleum refineries, biorefineries will produce several products, and likewise, the products with smaller yields will sometimes 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 South American chemical pulp mills as biorefineries are driven by the two facts; the large ethanol market and the fast growing fiber source for the South 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.

1.2 The Ethanol Market

The production of Ethanol is usually divided into three categories: fuel ethanol, industrial products application and alcoholic beverages. Ethanol for fuel accounts for 70 percent of world output and it can either be used directly in vehicles built to run on pure ethanol, or mixing dehydrated ethanol with gasoline. Ethanol can also replace chemical additives such as methyl tertiary butyl ether (MTBE) to reduce pollution from additives in unleaded gasoline. Brazil and the United States are the two major fuel ethanol producing and consuming countries, which accounts for 85 percent of the global demand. This illustrates a potential market that can be satisfied by produced corn, cane and cellulosic ethanol. Indeed, the recent DOE report concludes that there is a billion ton sustainable biomass supply of which 368 million dry tons is from annual forest derived feedstock [2]. Even at the most optimistic estimation, this can supply only 25% of the 2007 transportation fuel demand in the U.S. Therefore the market is very large and cannot be saturated by domestic ethanol production, once distribution and blending infrastructure issues have evolved.

1.3 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 cane sucrose, 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 similar to sucrose and corn 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.

1.4 Corn Ethanol

Corn ethanol, often referred to as first generation renewable fuel, is produced from the corn kernels by enzymatic hydrolysis and fermentation of starch. A modern corn ethanol biorefinery produces 2.8 gallons ethanol per bushel of corn. The corn yields also byproduct oils and Dried Distillers Grains (DDGS), but is reliant to external energy to operate the plant.

Today 211 corn ethanol biorefineries are operating in the USA with a capacity to produce 14.7 billion gallons of ethanol according to renewable fuels association [3]. This represents an increase of almost 11 billion gallons from the year 2005, when the first Renewable Fuels Standard (RFS1) was established.

However, the construction of new corn ethanol plants has slowed as the high corn prices above \$5/bushel [4] 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.

1.5 Cane Ethanol

Cane ethanol, also referred to as first generation renewable fuel, is produced from the cane juice by fermentation of sucrose. A modern cane ethanol biorefinery produces 85 liter ethanol per ton of wet cane. Some plants convert the cane juice to sugar and molasses/ethanol, depending on the economic factors. The leftover lignocellulosic bagasse represents 50% of the dry material, and is combusted to provide virtual self-sufficiency in energy.

Cane based biorefineries in Brazil produced 22.7 billion liters of ethanol in 2011/12 harvest according to Unica [5]. The production was the same as 2007/08 harvest. The exports represented 3 billion liters, and most of the cane ethanol can qualify as advanced biofuel under the second Renewable Fuels Standard (RFS2), established in 2007.

1.6 The Opportunity for the Pulp and Paper Industry

The performance of the world pulp and paper industry has been driven by ever larger units in the South America and Asia. In 2009, Brazil was world's fourth largest pulp producer with 13.3 million tons per year [6]. As the expansion in Brazil continues with ever increasing scale, the smaller pulp mills are feeling the pinch for profitability.

These pulp mills have some inherent advantages when investigating possible locations for cellulosic ethanol production. They have extensive wood procurement and handling logistics

and skilled workforce. Pulp mills also have a very large investment in infrastructure that can be leveraged in wood-based biorefineries. The existing infrastructure of power house, water treatment, effluent treatment, control rooms, substations, pipe bridges, air compressors, warehouse, offices, storage tanks etc. can reduce capital cost between 20% and 30%.

2. 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, chemicals etc., are important but do not have a catastrophic effect on the viability of the biorefinery.

2.1 The impact of the cost of wood

Our calculation, as well as those of others, determines that if the entire wood was to be converted to ethanol, (i.e. the cellulose, hemicellulose and lignin), the expected ethanol yield would be ~475 liter/Oven Dry ton (ODt) wood. If the lignin is used for energy the expected ethanol yield from the cellulose and hemicellulose fractions is ~375 l/ODt.

If all the wood would be used in the ethanol production, energy would have to be supplied from other sources (possibly also biomass) for the distillation and other process needs of the plant.

The capital cost required for the construction of cellulosic ethanol plants is estimated herein to be ~\$2.5/liter/a. It is likely that the capital cost will reduce to ~\$2/liter/a capacity in the collocated facilities.

In the Table 1, the size of the plant was assumed to be 300 million liters per year. This size is in line with modern cane ethanol plants and would require the same order of magnitude of wood as a 1000 ADMt/d Kraft pulp mill. In this Table 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/ODt, or the capital cost will have to be much smaller than \$2.5/l/a. Other factors, such as technology risk and plant size, will also have an effect, but the latter will be of secondary importance.

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 \$0.50/liter. However, if the ethanol market price climbs back to \$1.00/liter, then there will be competition for pulp wood from ethanol producers. And for those skeptics of this possibility, the recent history of oil price in combination with a resilient demand from rapidly developing Asian countries should be a sign.

As will be demonstrated in the next section, 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.

Table 1. Sensitivity of the wood based biorefineries to capital investment and wood cost.

Plant size	Liter/a	320,000,000	320,000,000	320,000,000	320,000,000
Investment	\$/Liter/a	\$2.50	\$2.50	\$2.50	\$2.50
Wood cost	\$/BDt	\$30.00	\$80.00	\$80.00	\$80.00
Yield	Liter/BDt	475	475	375	375
Cost contributions					
	Wood \$/Liter	\$0.07	\$0.18	\$0.22	\$0.22
	Capital Cost \$/Liter	\$0.14	\$0.14	\$0.14	\$0.07
	Energy \$/Liter		\$0.06		
	Labor \$/Liter	\$0.01	\$0.01	\$0.01	\$0.01
	Other Raw Materials \$/Liter	\$0.06	\$0.06	\$0.06	\$0.06
	Maintenance \$/Liter	\$0.03	\$0.03	\$0.03	\$0.03
	Overheads \$/Liter	\$0.04	\$0.04	\$0.04	\$0.04
	\$/Liter	\$0.34	\$0.51	\$0.50	\$0.43

3. 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.

3.1 Thermal 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 or mixed alcohols. Fischer Tropsch process has been proven commercially starting from coal and natural gas. The 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 faction 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).

3.2 Hydrolysis Technologies

Enzymatic hydrolysis

The cellulose enzymes have advanced steadily to hydrolyze recalcitrant cellulosic material such as wood fibers. Thermochemical pretreatment plays still a great importance to reduce dosage and hydrolysis time. Alternatively, wood can be milled to fine powder prior to enzymatic hydrolysis. The latter would require large amount of electrical energy - which could approach the energy that will be contained in the generated products. Enzymatic hydrolysis breaks down the biomass into monomer sugars which 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 of water soluble hemicelluloses has been successfully practiced in forest industry (in DPI hardboard plant in Alpena). The pre-extraction of hemicelluloses uses only a portion of the wood, thereby leaving the remaining portion to produce pulp product. The AFPA sponsored study shows that no yield loss was observed for up to 10% extraction levels [7].

A major concern is the fact that the extract is dilute and, therefore a large amount of energy must be used to concentrate it. A recent plant was build by American Process inc. in Alpena to demonstrate energy efficient concentration of the extract and its conversion to Ethanol and Potassium Acetate. Pre-extraction will play a role in the pulp mill based biorefinery technologies, where producing the pulp is the main focus and transportation fuels and chemicals can increase the revenue gained from wood.

Complete dilute or strong acid hydrolysis

Acid hydrolysis can dissolve 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, and the ethanol yield can be negatively affected.

Selective hydrolysis of hemicelluloses

Fractionation breaks wood 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 patented process and technology was designed and is being demonstrated by American Process Inc. in Thomaston, Georgia. The technical and economic analysis for the full scale plant shows high profitability as well as high flexibility to adapt to market conditions.

In the AVAP® process as shown in Figure 1, wood chips are pulped in the presence of alcohol and sulfur dioxide. The cooking conditions as well as the pre-processing and post digestion treatments are proprietary and tailored to match the desired properties of the cellulose and the yield of co-products.

Pulping in aqueous alcohol facilitates penetration of wood chips, avoids lignin condensation reactions and promotes rapid solubilization of lignin and hemicelluloses. Spent liquor is subjected to a secondary treatment in the AVAP® reactor to ensure maximum monomeric sugar yield and minimal fermentation inhibitors.

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 patented process and equipment that concentrates the liquor. The integrated stripper column regenerates the processing ethanol and isolates the condensate for by-product recovery and process reuse.

The AVAP® recovery cycle is designed for recovery of chemicals and high conversion rates. The high alpha-cellulose content in pulp hydrolyses easily pure glucose fraction, which can be in replacement of dextrose in chemical manufacture. Proprietary 3rd party pentose converting microorganisms can be used to ferment the hemicellulosic pentose in the ethanol.

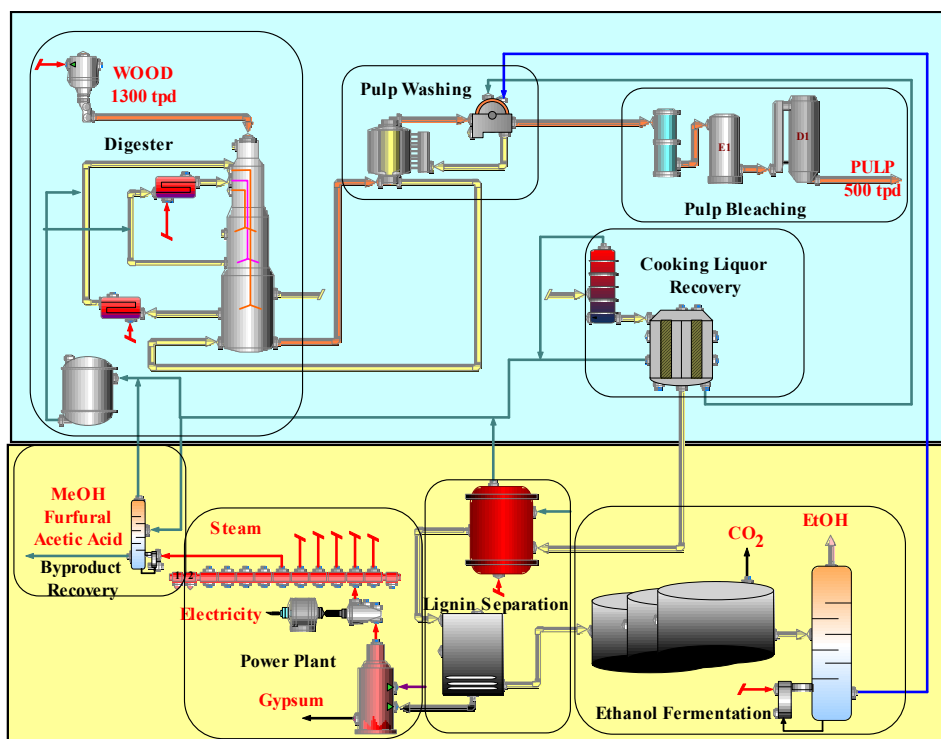


Figure 1: Continuous process for AVAP® biorefinery process.

Competitive Advantage of Cellulose Preserving Technologies

Having reviewed the known technologies, American Process Inc. has summarized its findings in the Table 2. 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, AVAP® and VPP, (Pre-extraction in a Kraft environment), 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, such as in the case of the AVAP® technology.

Table 2. Comparison of wood based biorefinery technologies.

		Gasification /Catalysts	Gasification /Enzymes	AVAP Phase I	AVAP Phase II	VPP	Strong Acid Hydrolysis
Practical Yield	Liter/BDT	452	340	180	384	72	220
Price of Ethanol	\$/Liter	\$0.50	\$0.50	\$0.50	\$0.50	\$0.50	\$0.50
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 Incon	\$/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	Oincluded
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

AVAP® Technology Progress

During the last 6 years the AVAP® process has been transferred from the lab to 3 BDt/d integrated demonstration plant in Thomaston. A wide range of cellulose grades can be produced by modifying cooking conditions. The capital cost of the digesting equipment has been halved by the use of rapid cooks. The properties and bleachability of the produced cellulose has

been found to be suitable, even superior, to those required for commercial grade pulp specifications.

Dissolving grades

Pulping to a low hemicellulose content and a low Kappa number 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 grades

Fluff pulp is another grade that benefits from low hemicellulose content. Absorbent grades, which have large and growing markets, have been successfully produced using the AVAP[®] process.

Other pulps

Higher yield pulps and high strength pulps can also be produced with the AVAP[®] process, in many cases yields higher than those possible with Kraft pulping are achieved because of highly efficient lignin removal and cellulose preservation.

Recovery process

The evaporation of cooking alcohol precipitates a native lignin suspension. Further liquor treatment using the AVAP[®] process co-precipitates more lignin along with lignosulfonate. Both lignins exhibit purity and reactivity which are under investigation for potential valuable uses as a chemical feedstock.

Energy needs

The engineering has confirmed that with the selected process steps, the AVAP[®] 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 would enable the sale of the lignin without necessitating the use of fossil fuel in the process.

Chemical Losses

Sulfur dioxide is partially bound in the lignin to form lignosulfonate. Lignosulfonate can be sold as product, or sulfur dioxide and energy can be recovered by burning process. Since ethanol is both parts 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. A proper washing and stripping has proven to recover ethanol at very high recovery rates.

3.3 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.

4. PROCESS INTEGRATION

4.1 Background

In the context of the Biorefinery, process integration is based on the examination and improvement of the impact of any departmental action to the process and economics of the entire site. There are many tools used in the application of process integration, i.g. process flow diagrams, simulation modeling, supply chain management, economic analysis, life cycle assessment and pinch analysis. In this paper pinch analysis is presented in more details.

Pinch Analysis [8] is based on identifying the hot streams (i.e. those that must be cooled or are available to be cooled) and cold streams (those that must be heated). Having identified these streams, and using specialized methods for appropriate data extraction, these data are combined so that the whole process, plotted on a Temperature (T) vs. Heat flow (H) diagram, looks like a heat exchanger as shown in Figure 2. These curves are called the composite curves, or the hot and cold composites and they are an amalgamation of the cooling and

heating duties respectively. Just as for a single heat exchanger, the ΔT_{MIN} or approach temperature must be optimized.

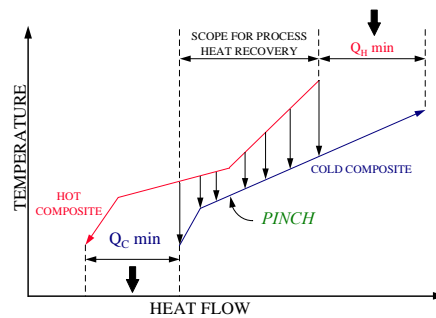


Figure 2: Typical Composite Curves.

Pinch analysis uses two key concepts: the target and the pinch temperature.

- The target is the minimum necessary thermal energy that the mill needs to operate at a steady state. The minimum hot utility, QH_{MIN} , representing the minimum external thermal energy that the process requires assuming that perfect heat recovery has been installed. The minimum cold utility, QC_{MIN} , representing the minimum external cooling duty that the process requires assuming that perfect heat recovery has been installed. By comparing the actual thermal energy consumption with the target, the maximum potential for heat savings is revealed.
- The pinch temperature, unique for every site, is the temperature above which there is a shortage of thermal energy and below which there is a surplus. The practical meaning of this is that no steam should be used below that temperature and no heat should be thrown away to the environment above that temperature. Furthermore, any heat transferred across that temperature between process streams reduces the amount of heat that can be recovered. These three statements are called “Pinch Golden Ryles”

The second depiction often used is the grand composite curve as shown in Figure 3. This is constructed by combining the two composites curves in the appropriate temperature ranges. The pinch, QH_{MIN} and QC_{MIN} can also be seen here. This curve can be used for a proper utility level placement and heat pump opportunity identification.

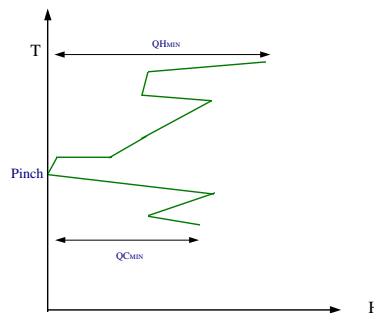


Figure 3: The Grand Composite Curve.

4.2 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.

5. CONCLUSIONS

Technology leaps, departing from traditional practices, and achieving better use of wood fractions are required for future success. 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.

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