AVAP™, A Novel Biorefinery Concept

By Theodora Retsina and Vesa Pylkkanen

The current state of the North American pulp and paper industry

Not very uplifting! Production of commodity products, which cannot be clearly differentiated by quality, in a market place where competition from South American, Asia and Russia, (coming), is fierce.

Let's look at oil refineries. Oil refineries differentiate by accepting inferior raw material and producing value added chemicals from the last fractions of oil.

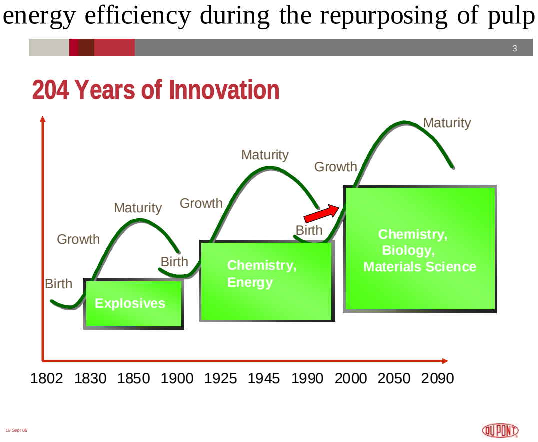
Biorefineries can differentiate by producing multiple products from heterogeneous raw materials. Furthermore, the product mix may vary depending on the market conditions.

Rethinking of our practices

All businesses have to reinvent themselves to survive mature markets. A good example is the figure below, showing how Dupont has survived and thrived by rethinking their strategies as the markets mature. Pulp and Paper in North America is challenged to do the same.

- Pulp and Paper manufacturing is an increasingly capital intensive business; are there alternatives processes that lower capital costs?

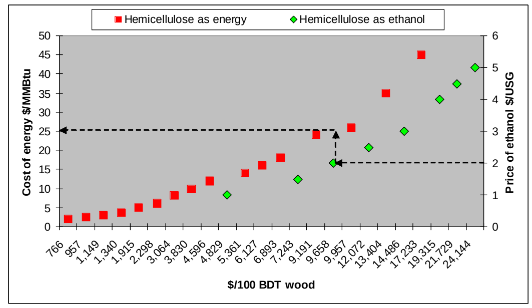
- The North American pulp and paper mills tend to use energy inefficiently for historical reasons; is there an opportunity to increase energy efficiency during the repurposing of pulp



mill to biorefineries?

- Pulp and paper are becoming commodity products; is there an opportunity to produce value added products from the wood, without putting additional pressure on the forests and the wood cost?

Current pulp mills produce pulp and energy. Almost 60% of the raw materials are sacrificed to produce energy for the process. The majority of the



hemicellulose contained in the dry wood, ends up in the recovery boiler where it is burned to generate energy. Much of this energy is consumed within the recovery cycle itself.

The Value of hemicellulose – an untapped resource

To put it in relative terms the equivalency graph below compares the value of cellulosic ethanol and energy as two alternative products from hemicellulose. Even allowing for different assumptions on yields, efficiency etc. the graph clearly demonstrates that hemicellulose is worth 3 to 4.5 times more as ethanol rather than as energy.

To put this in economic terms; if a 1000 ADMT bleached pulp mill converted its hemicellulose to ethanol (without affecting the pulp production), the additional net revenue stream (even if the energy shortfall was replaced with $6/MMBtu fuel) is between $30 to $40 million USD per year, with net income increase between $20 to $35 million USD per year[1].

This example shows that there is a fundamental basis for biorefineries and for the proposed pulp mills repurposing as biorefineries.

Furthermore, tax incentives – particularly for cellulosic ethanol, government grants, an enormous ethanol market and the gradual banning of MTBE, all reinforce the current opportunity. If all the U.S, pulp mills upgraded their hemicelluloses to produce ethanol, it would still amount to less than 2% of the U.S. gasoline consumption.

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[1] *This calculation was based on a market price of $2.00 per USG ethanol*

Market penetration is therefore primarily dependent on costs of production. Leveraging the infrastructure of the pulp and paper industry and choosing the most appropriate technology or, combination thereof, for each location can ensure ethanol production at low cost.

Repurposing the mill as a biorefinery

An efficient biorefinery fractionates the feedstock and uses each faction for the most profitable product. API analysis suggest that given the current markets and technology status, the best matching of wood fractions to final products is as follows:

Cellulose ------> Pulp and Paper products
Hemicellulose-> Ethanol & bio chemicals
Lignin---------->Energy now, bio chemicals later
Bark, Residues->Future energy supply

No matter what technology is used in the biorefinery conversion one thing is clear: the energy efficiency and process integration of the new biorefinery / pulp mill, is key to its success. This is intuitive, since the hemicellulose (which provides much of today's energy) will be used to make value added products.

Biorefinery platforms

Besides the Tembec and Borregaard plants[2], today there is no other industrial application of cellulosic ethanol production. There are several emerging technologies some of which are more developed and proven than others.

In general they can be subdivided into two types; **hydrolysis based or gasification based,** also referred as the sugar platform and the thermal platform**.** Alternatively, they can also be characterized as processes which **co-produce pulp and biofuels and biochemicals** or processes which **only produce biofuels and biochemicals**.

Hydrolysis technologies

Hydrolysis technologies separate the hemicellulose from the lignin and cellulose, break hemicelluloses to simple sugars, and then convert them to ethanol and other chemicals through fermentation and fractionation. These technologies allow the continuation of the production of pulp, (cellulose), while maximizing the value of the byproducts. However they can be extended to complete hydrolysis, where the cellulose is also hydrolyzed to biofuels and biochemicals.

The present processes include AVAP™, VPP[3], the Arkenol Process [4] and traditional sulfite liquor treatment. Plants are being designed or operate at pilot scale by Iogen[5], XEthanol, Flambeau River Biorefinery, JGC, BlueFire Ethanol and possibly others. Hydrolysis can be enzymatic or acidic in nature. Enzymes are used for starch (corn) hydrolysis, but are not yet proven economic in breaking down highly recalcitrant feedstock such as wood, and corn stalks. Acid hydrolysis can utilize wood, straw, municipal waste, seasonal agricultural residues etc.

Gasification technologies

The gasification technologies, (also referred as "thermal route"), use the entire wood, or, the separated lignin, and convert this to a gaseous mixture of CO, H2, CH4 and CO2. This synthesis gas provides the feedstock for further processing to ethanol, methanol and other chemicals.

Depending of the process conditions, the thermal route produces various amounts of tail gas and low grade energy. The economics are most advantageous, when a suitable sink for the low grade energy and tail gases are available, and where these replace a high cost fuel. Therefore, integrating gasification technology adjacent to a biorefinery or a paper mill is a suitable placement.

The initial focus on gasifying black liquor already existing commercial operations appear shifting towards producing value from biomass directly. In a recent white paper[6], 17 wood biomass gasifiers were tracked as being some implementation stage. In all of them, the gasification product, (synthesis gas), is used as combustion fuel for energy or power or cogeneration.

Technology exists to create methanol from natural gas or Fischer-Tropsch liquids from coal synthesis gas. The synthesis gas from biomass is becoming

[2] http://www.chemcell.com/: Ethanol from Borregaard is used for chemical-technical applications

[3] VPP, Value Prior to Pulping, Extraction of hemicellulose prior to pulping
[4] Concentrated acid hydrolysis
[5] Iogen's cellulose ethanol process uses advanced new technology to make ethanol from biomass. The process combines innovations in pre-treatment, state-of-the-art enzyme technology, and advanced fermentation technology. Pre-treated fibre is converted to sugars using enzymes; sugars are subsequently fermented to ethanol; and ethanol is purified to fuel. www.iogen.ca
[6] Ben Thorpe, GLB White Paper

more attractive, as the cost of fossil fuels increase. This is especially true in Europe, where biodiesel has gained support.

There are North American initiatives, which focus on ethanol production from synthesis gas. Syntec of Canada is presently working on a catalytic method of converting synthesis gas to ethanol, while Mississippi Ethanol is working on a biotic method for the same. Both technologies are planned for pilot plant demonstration in 2007.

Novel pulp mill biorefinery process (used for the DOE application of Flambeau River Biorefinery)

American Process Inc. of Atlanta provided its proprietary American Value Added Pulping, AVAP™ (patent pending) pulp mill based biorefinery technology and process design for the consortium of several members at the Flambeau River Biorefinery LLC. An application for DOE biorefinery demonstration solicitation was submitted based on this process.

The AVAP™ process

Wood chips are pulped in the presence of ethanol and sulfur dioxide. The cooking temperature and duration as well as the pre-processing and post digestion treatment are tailored to match the desired properties of the pulp and yield of co-products.

Pulping in aqueous ethanol facilitates penetration of woodchips without fear from condensation reactions, while acid aids in rapid solubilization of lignin and hemicelluloses. Spent liquor sugars are subjected to a secondary treatment in the AVAP™ reactor to ensure their hydrolysis to monomers sugars. Separation of the lignin is achieved by reduction in solubility and subsequent precipitation. Co-product lignin sales compete with energy production from bark and forest residues. Lignin and biomass gasification produces synthesis gas, which can today be used for energy production, and tomorrow as a feedstock for additional biochemical production

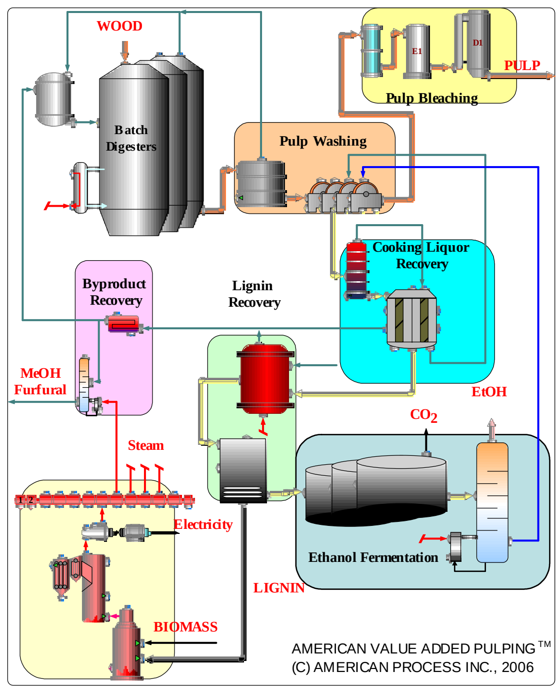
The absence of sodium eliminates expensive Kraft recovery cycle and enables a simpler recovery cycle. Energy to this recovery cycle is provided to a large extent by use of vapor compression in a patent pending process equipment, LEESS™, which concentrates the liquor, regenerates the processing ethanol and isolates the condensate for by-product recovery and process reuse.

High product yield is the ultimate goal in any bioconversion process. The process configuration of this recovery cycle is specifically designed for recovery of chemicals and high conversion rates.

Majority of the sugars are fermentable by Baker's yeast, *Saccharomyces cerevisiae*. Proprietary 3rd party pentose converting micro-organism boosts the ethanol yield. A schematic of the process can be seen below.

Oxygen delignification and two-stage bleaching of the AVAP™ pulp produce brightness to paper grades.

Preliminary engineering for the gasification and ethanol islands were provided by ThemoChem Recovery International (TRI) and XEthanol respectively.



Economy of scale

Preliminary investigation shows that a stand-alone biorefinery reaches economy of scale with a pulp production of 500 T/d and an ethanol production of ~ 20million USG per year. For such a biorefinery, capital costs of the retrofit range between $50 to $200 million USD. The biorefinery with high degree of process integration does not put additional strain on the forest basket.

What pulp will be made?

The research indicates that the AVAP™ pulps have low hemicelluloses content, and they are easier to bleach and refine than Kraft pulps. High alpha cellulose content indicates good retention of the original cellulose, typical of sulfite pulping. The absence of hemicelluloses for bonding strength can be compensated through new furnish mix in the papermaking operations.

The sulfite pulps are softer and more opaque. This furnish is historically preferred for tissue paper, dissolving pulps, fluff pulp and as a part of furnish for printing papers.

The capacity of the above markets in USA for AVAP™ to replace Kraft pulp is estimated to be ~ 6 million tons per year.

The research indicates that customizing the cooking steps and process can improve the properties of the pulp for other grades where this is desired.

AVAP™ process compared to traditional sulfite cooking

The sulfite pulping revived several times in the past century with introduction of soluble bases in an improved chemical recovery. The small scale sulfite pulping of selected species has receded rapidly to larger Kraft mill, which produces good pulp from most trees.

Reinventing the sulfite pulping in the 21st century may necessitate a novel approach such as the process described herein; stand alone or in combination with other processes.

Many aspects of this process are developing in the fast paced biorefinery R&D, but at this point we can say that the AVAP™ process offers:

- Co-production of pulp and ethanol from common raw material
- Paper grade pulp, easy to bleach and refine
- Low energy process, integrating of pulp and ethanol production
- Ability to utilize green softwoods and hardwoods chips.
- Clean byproduct recovery as value-added products
- Closed process, one vapor and one liquid emission point
- Low green field plant capital cost (compared with Kraft and or sulfite alone)
- Low operating costs
- Flexibility of synthesis gas – ability to produce more ethanol / chemicals later

Risks associated with the AVAP™ process

Good engineering practices start with realizing the weaknesses and risks of any process so as to design to minimize them. In the AVAP™ process, the risks are associated with the use of ethanol both as a cooking agent and a product. Engineering and operating practices must i) reinforce safe practices, similar to those when handling of flammable chemicals and ii)ensure low ethanol losses. The engineering of a closed system and the selective removal of some fractions and recirculation of others minimize losses and maximize product yield.

Labor requirements

The labor requirements are reduced (compared to the sum of a traditional Kraft + ethanol plants), due to fewer unit operations. However a skilled workforce is essential for the success of any novel process industry.

Conclusion

There are several emerging technologies that can be used to repurpose the traditional pulp mill into biorefinery. One of them, AVAP™ is covered here in some detail. No matter what technology is chosen or combination thereof, the overwhelming fact is that pulp mills must face the reality where incremental improvements are no longer enough. Future success requires technology leaps, departing from traditional practices, and necessitating better use of the wood fractions.

Tom Browne of Paprican put it best when he quoted in December's issue "Simply put, the status quo is a step toward irrelevance at best or extinction at worst."

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