This activity is supported by
National Science Foundation award #EPS-0554545
to Maine EPSCoR at the University of Maine

Potential Markets for Chemicals and Pharmaceuticals from Woody Biomass in Maine

March 11, 2009

Authors:

Donald G. MacKay[1]
Barbara J.W. Cole
Raymond C. Fort
Amy Mares

---

[1] Correspondence to Donald G. MacKay, Forest Research LLC, 20 Godfrey Drive, Orono, Maine 04473. E-mail: don@forestresearchllc.com. Website: www.forestresearchllc.com.

Barbara Cole and Raymond Fort are at the University of Maine. Amy Mares is a student at Orono High School. The authors would like to thank Michael Bilodeau at the University of Maine and Susan MacKay at Zeomatrix LLC for their assistance with this report. Copyright © 2009 by Forest Research, LLC.

Executive Summary

The production of chemicals and pharmaceuticals from woody biomass is likely to increase substantially. This paper provides a broad overview of some of these potential chemicals and pharmaceuticals, including a food additive, with a focus on activities currently taking place in Maine. It identifies some key chemicals and pharmaceuticals that might be produced, and describes some market characteristics for these chemicals. The chemicals are: acetic acid, furfural, itaconic acid, lactic acid, succinic acid, hydrogen, and methanol. The food additives and pharmaceuticals are: shikimic acid and vanillin. Note that some of these chemicals have multiple uses, and thus we have categorized them by their primary use.

Using wood for chemicals and pharmaceuticals has a long history. However, for more than a half a century the chemical industry has relied primarily on hydrocarbons. Now there is renewed interest in using wood and carbohydrates as a feedstock. Given current factors, it is likely, and perhaps inevitable, that an incremental approach to development of chemicals from wood will occur. Maine is well positioned in this area, in that the state enjoys a large forest product industry and a substantial forest resource.

Interest in chemicals and pharmaceuticals from woody biomass is primarily driven by concerns about oil and gas feedstock prices, carbon emissions, and declining levels of non-renewable resources. However, the viability of the renewable products depends on their cost, as well as the expected prices of oil and natural gas, which are used as the feedstock in traditional chemical plants. A shift from using hydrocarbons to carbohydrates will be difficult. The chemical industry has adapted to using fossil fuels, and oil and natural gas feedstocks still offer economies of scale in processing and distribution.

However, biomass is a very flexible feedstock, and many useful products can be created from it. Also, today chemicals are wasted as the water soluble components of wood are partially lost, perhaps in leachate from wood chip piles, or as they pass into the waste stream from mills. Nonetheless, a substantial amount of research remains on the optimal way to produce chemicals and pharmaceuticals. The market for these materials will be a key component in their viability.

Disclaimer

The information in this report is not guaranteed to be correct or suitable for any particular purpose. The appropriate specialist should be consulted and/or appropriate legal advice should be obtained before any action or decision is taken on the basis of any material in this document. The authors or contributors do not assume liability of any kind whatsoever resulting from any person's or organization's use or reliance upon the content of this document.

Table of Contents

Introduction

Petroleum and other fossil fuels have dominated fuel and chemical production for the last century. This has been largely because oil and natural gas have been relatively cheap and plentiful. However, the dominance of fossil fuels may be reaching its end. The environmental impact of oil and natural gas production has been questioned, with fossil fuels being closely linked to climate change. Additionally, oil and natural gas supplies are finite, and with the exception of the current economic crisis, prices have been rising. As a result, new technologies are being explored and older ones reexamined. Substantial efforts are underway to find new, better ways to provide, fuels, chemicals, and energy. Wood, which has been used for energy since the discovery of fire, is under consideration as a source of fuels and chemicals, too (FAO 2008).

The dominance of fossil fuels has been convenient, but it didn’t necessarily have to be this way. A century ago, inventors and scientists alike were investigating a range of solutions for producing fuels, chemicals, and energy. For instance, a range of fuel types were examined for early motors. Inventors such as Nikolaus August Otto, the inventor of the internal combustion engine, originally used ethanol to fuel one of his engines. Rudolf Diesel, the German inventor of the Diesel engine, designed his engine to use peanut oil. Henry Ford, the creator of the Model T, tested it using a biofuel derived from hemp.

Many chemicals were originally developed using raw materials such as natural plant oils and wood and coal tars (Chemical Industry 2007). Additionally, two chemicals explored in this report, acetic acid and methanol, were produced by wood products firms into the first part of the Twentieth Century. A report by the USDA Forest Service remarks that a hardwood distillation industry once existed in the United States, numbering roughly 50 plants in the mid-1930s (USDA-FS 1956). However, chemical production migrated to using oil and natural gas as feedstocks due to their lower cost in raw materials and processing. The financial economics of the reliance on oil and natural gas worked well for many years. However, this may be changing. Prices for oil and natural gas have been extremely volatile in recent years. In recent years, they have risen substantially, though they declined during the financial crisis of 2008. Faced with rising prices and the knowledge that oil and natural gas resources are finite, the chemical industry has begun to seek new feedstocks, including biomass.

Biomass has some advantages over other feedstocks. Notably, a recent study, *Alternative, renewable and novel feedstocks for producing chemicals* (Chemical Industry 2007) examined a variety of feedstocks, including biomass, coal, petroleum coke, tar sands and oil shale, organic municipal solid waste, and “unconventional” natural gas. Also, it examined five technologies, including coking, fermentation/extraction, gasification, liquefaction, and pyrolysis. The study found that, particularly for near term purposes, the gasification of coal, petcoke, and biomass and the fermentation/extraction of biomass had the highest probabilities of success. This report study examines some of the products that might be produced, using gasification, as well as fermentation and extraction from biomass.

In addition to fuels and chemicals, biomass has a tremendous potential for renewable energy. Notably, while there are other avenues to generating electric power (e.g., solar and wind), biomass is the only renewable source able to create chemicals. Additionally, biomass as a potential feedstock has a variety of potential benefits, including the potential for less contribution to CO_2 emissions, though this is still controversial.

This report examines some potential products that could be produced in Maine, focusing on some key chemicals and pharmaceuticals. We identify and provide preliminary information on potential candidates for production, and discuss some of the issues around producing these products. However, the potential scope of such a study is large, and thus our effort has been to summarize and simplify this complicated subject matter. Note that this report does not address ethanol or similar fuels. These fuels have been the subject of numerous recent, larger studies, and they are outside the scope of this project.

Finally, this report is not a feasibility study. Issues around biorefineries have been explored elsewhere, and the full analysis necessary to analyze the profitability of particular chemicals and pharmaceuticals it outside the scope of this project. A preliminary review of the literature, conducted during this project, does suggest that at current energy prices, a new standalone facility is not cost effective. In Maine, integrated facilities located at an existing mill, most likely a Kraft paper mill, are more likely to be economically viable (Atlantica Bioenergy Task Force 2008) (Dickerson and Rubin 2008) (Mao et al. 2008).

Background

Wood has provided a variety of benefits to society. Conventional products from wood include building materials, paper, resins, adhesives, coatings, road and roofing pitch, to name a few. Additionally, a number of bioproducts are already produced from wood. These chemicals include turpentine oil, rosin, tall oil, and cellulose derivatives, such as esters and acetates. Paster et al. (2003) estimated the production of these various materials at 5.3 million pounds. Primary feedstocks for these chemicals include pines and other softwoods and black liquor.[2]

Rising oil prices and concerns about future energy and chemical supplies have encouraged policy makers and the private sector to examine the potential for additional products from wood. Substantial resources are being brought to bear on the concept of biofuels and bioproducts. As gasoline and oil prices have increased, ethanol has received the bulk of the attention as a biofuel. However, other products, such as chemical and pharmaceuticals, may also be produced in a biorefinery. This idea is not entirely new.

---

[2] Black liquor is a byproduct of kraft pulping, also known as the sulfate process. It contains a mix of hemicelluloses, lignin residues, and inorganic chemicals.

Historically, chemicals and pharmaceuticals have come from both conifers and hardwoods. One common use of chemicals from trees was in tanning. Tanning occurs because of a property of chemicals known as tannins, which allows them to combine with the protein of animal skins, known as collagen, to produce leather. The result of this process is a product tougher and more permanent than unprocessed (untanned) skins. This process has been known for many years. For instance, the Romans tanned with the bark from oak trees (FAO 1995). In eastern North America, a historical source of tannins was the bark of the eastern hemlock. The bark of the eastern hemlock has a tannin content of about 10 to 12 percent. Trees were felled and the bark removed in spring when the sap was flowing and the bark was easiest to peel. The product was used to tan sheepskins and heavy leather for shoes (FAO 1995).

Resins are an important product from conifers. Most conifers will seep resin if damaged. Others will give off resin from branches and cones. Resins harvested from various pine species are likely the most ancient and important of non-wood products from conifers. Pine resin products were previously called "naval stores," because the British Royal Navy used to use resin products from pines to waterproof ships. Other conifers also produce resins. Liquid resin from bark blisters of balsam fir was once collected in certain sections of eastern Canada (FAO 1995).

Hardwoods produce chemicals and pharmaceuticals, and even foods. In New England, maple syrup is a well known food product. Additionally, vanillin, a substitute for vanilla flavoring, was originally obtained from oak trees. Chemicals and dyes were another common product. Several native North American oaks were traditional dye sources and used by dyers in the eighteenth and nineteenth centuries. Quercitron is a bright yellow dye that occurs in the bark of black oak. The bark is rich in tannic acid. The bark of northern red oak produces another yellow dye (Ciesla 2002).

While some of these uses are now historical footnotes, it is interesting to note that the idea for extracting chemicals and pharmaceuticals from wood are not new. Indeed, some of the extraction techniques currently under consideration, such as using hot water, have been used for many years, and even centuries. Nonetheless, these ideas are the focus of new interest as scientists and entrepreneurs find new, more efficient way to extract, separate, and produce chemicals from wood.

Renewed interest in woody biomass for chemicals and energy depends on a series of factors (Skog and Rosen 1997). These factors include, but are not limited to:

- Changes in price relationships between current wood uses such as pulpwood and alternative uses such as energy and chemical feedstocks.
- Price and demand for energy and chemicals that can be produced from woody biomass.
- Availability and prices of woody biomass sources and existing sources such as petroleum and natural gas.
- Relative environmental impacts of using woody biomass or fossil fuels as a feedstock.

These factors, identified roughly a decade ago, shed light on our current situation. For instance, price relationships have changed, in that oil and natural gas feedstock prices have been rising, providing an incentive to seek other raw materials. Additionally, chemical prices were high, making their production attractive. At the same time, biomass was identified as being available from the nation's forests, and wood is identified as a renewable resource with potentially lower environmental impacts than oil and gas.

Forest Biorefinery

To address the modern needs for chemicals and pharmaceuticals from wood, researchers and industry experts have developed the concept of a forest biorefinery. In general terms, a forest biorefinery is a facility that combines both a biomass conversion process and a chemical pulp mill to produce products such as fuels, chemicals, and energy, and also traditional pulp products (Goyal et al. undated). Reviewing the literature, it is obvious that there are an abundance of ideas about how to best obtain chemicals from wood, and implement the biorefinery concept. However, many of these ideas are currently theories or are still being tested or explored.

The study, *Alternative, renewable and novel feedstocks for producing chemicals* (Chemical Industry 2007) examined some key ideas and discussed the state of the industry. In examining biomass, the report found that both fermentation and extraction and gasification were favored, but both of these processes require substantial research and development (Chemical Industry 2007). The fermentation and extraction processes will require research and development to make such processes technically and economically feasible. With gasification of biomass, there are a variety of issues that will have a bearing on the success of potential applications in the chemical industry. The literature suggests that the biorefinery concept, which may involve co-production of both biofuels and chemicals, may improve the economic prospects for both processes.

Wood-based feedstocks for biorefineries can come from a variety of sources. Skog and Rosen (1997) identify some major sources:

- Roundwood
- Short rotation woody crops
- Wood residue from primary wood products mills, such as wood and bark
- Wood residue from secondary wood products mills
- Commercial and demolition debris
- Black liquor from pulpmills

While the biorefinery concept is potentially attractive from the perspective of both improving the economics of facilities and developing new sources for chemical and pharmaceutical products, there are potential drawbacks as well. The potential problems have been discussed at length elsewhere, but some key drawbacks with using biomass as a feedstock are:

- New technologies are unproven, technologically and economically
- Biomass is sourced over a wide area
- Moisture content can be high, and may necessitate drying
- Biomass supply is uncertain compared to other sources such as coal, and seasonal as well as other factors may cause variation in supply
- Transportation of biomass and storage may be problematic

Additionally, a matter of contention around using biomass for the production of fuels and chemicals is whether it will result in increased energy consumption and increased CO_2 emissions. Compared to fossil fuels, the plants used for biomass consume CO_2 as they grow (through photosynthesis) and this may offset CO_2 emissions from fuel combustion. Thus, biomass as a raw material has been described as creating less CO_2 and other greenhouse gas emissions compared to conventional fuels. However, the accounting for CO_2 emissions from biomass is complicated, and there are no uniform national or international standards. On its own, biomass is typically considered nearly carbon neutral, making it an attractive raw material for policy makers. However, there are a variety of inputs that tend to increase carbon emissions, such as activities to foster tree growth (fertilizer or herbicides), thinning, harvesting, transporting and possibly drying. "Well-to-wheels" studies measure net CO_2 emissions from the time the plant is grown, through harvesting, processing and vehicle exhaust. More work is necessary to fully understand this issue.

Forest Resources

While forest resources can be converted into biofuels and bioproducts, not all tree species are equal in the types of uses they might have. As noted previously, specific chemicals and pharmaceuticals are more likely to be found in certain tree species. In particular, there may be important differences between hardwoods and softwoods for some uses. These differences in chemical composition are primarily genetic in origin. While trees differ in their chemical constitution, they have some components in common. For instance, woody biomass has four primary components: cellulose, lignin, hemicellulose, and extractives (Amidon et al. undated).

Cellulose

Cellulose is the most abundant structural material used by plants (Allcock and Lampe 1981). Wood is roughly 40 to 45 percent cellulose (Rowell 2005). Cellulose is a homopolymer of glucose, and is a highly crystalline matrix. It is insoluble in water and an excellent material for structural reinforcement. Cellulose is a straight chain polymer. Its strength is important in cell walls. Cellulose can be degraded into its component glucose units by treating it with concentrated acids at high temperature.

Lignin

Lignin is one of the most abundant polymers on Earth, second only to cellulose. It is primarily found in the cell walls and in the middle lamella between the cell walls, and is important in the transport of water. Substantial amounts of lignin in wood tend to make it more durable. Also, lignin is used as a fuel. Lignin yields more energy when burned than cellulose. Lignin is removed as sulfonates from pulp before the pulp is used to make high quality bleached paper. These sulfonates have a range of uses, but most often they are burned for their fuel value, providing more energy to run help run the mill. Other uses for lignin include animal feed additives, vanillin, and road dust suppression (Lignin Institute 2008).

Hemicellulose

Hemicelluloses are a group of polysaccharide polymers. They primarily contain sugars such as xylose, arabinose, glucose and mannose. In plants, the hemicelluloses interact with lignin and cellulose, strengthening the plant wall. One advantage of hemicellulose is that it is much more easily hydrolyzed than cellulose. In plant materials, some of the hemicellusloses can be solubilized and hydrolyzed to hexose and pentose sugars. Hexose sugars are 6-carbon sugars ($C_6H_{12}O_6$) such as glucose and pentoses are 5-carbon sugars ($C_5H_{10}O_5$) such as xylose. These sugars can be fermented or catalyzed to produce certain chemicals.

Extractives

Wood extractives are primarily non-cell wall components. They are relatively small molecules that typically can be extracted using solvents, including water. Extractives are usually one to five percent of wood. They may be found in wood, bark, or foliage. They vary by tree, and even vary within trees (Cole undated).

Classes of extractives include:

- Terpenoids, which are primarily found in softwood species. Terpenoids have a range of potential uses, including turpentine, fragrance, and flavor chemicals.
- Phenolics, which include:
    - Simple phenolics such as vanillin,
    - Stilbenes, which can be very toxic and are primarily found in conifers,
    - Flavonoids, which provide coloring, flavoring, and may be used for tanning and adhesives
    - Lignans, which can be antioxidants
- Others, including alkanes, proteins, and others

Table 1 shows the chemical composition of various timber species (Amidon et al. undated). Notably, hardwoods and softwoods are different in important ways, including the structure of hemicellulose and the extractive compounds found in wood (Stenius

2000). These differences have implications for the types of chemicals produced from wood.

Table 1. Chemical composition of various tree species found in Maine.

Species	Common Name	Total Extractives	Lignin	Cellulose	Glucomannan[1]	Glucuronoxylan[2]	Other Polysaccharides	Residual Constituents
Hardwoods								
Acer rubrum	red maple	3.2	25.4	42.0	3.1	22.1	3.7	0.5
Acre saccharum	sugar maple	2.5	25.2	40.7	3.7	23.6	3.5	0.8
Populus tremuloides	trembling aspen	3.8	18.1	49.4	3.6	23.0	1.7	0.4
Fagus sylvatica	common beech	1.2	24.8	39.4	1.3	27.8	4.2	1.3
Betula pendula	silver birch	3.2	22.0	41.0	2.3	27.5	2.6	1.4
Betula papyrifera	paper birch	2.6	21.4	39.4	1.4	29.7	3.4	2.1
Softwoods								
Abies balsamea	balsam fir	2.7	29.1	17.4	17.4	8.4	2.7	0.9
Tsuga canadensis	eastern hemlock	3.4	30.5	18.5	18.5	6.5	2.9	0.5
Picea glauca	white spruce	2.1	27.5	17.2	17.2	10.4	3.0	0.3

Source: Amidon et al. undated.

Notes: 1) includes galactose and acetyle in softwood.
2) Includes acetyl in hardwood and arabinose in softwood.

Hardwoods

Hardwoods, which are generally broadleaf, deciduous trees, differ from softwoods in their chemical makeup. An important difference is that hardwoods typically have more hemicellulose than softwoods, and that hemicellulose is superior for producing certain types of chemicals. For instance, the hemicellulose in hardwoods is glucomannan and glucuronoxylan (xylan). Xylan is the largest component of the hemicellulose portion of hardwoods. Xylan, a five carbon sugar polymer, is the most easily separable component of hardwood wood. Three primary components of xylan in hardwoods are xylose, glucuronic acid, and acetic acid (Amidon et al. undated). Extractives also vary by softwood and hardwood. Notably, hardwoods typically lack resin acids and monoterpenes (turpentine). Fatty acids may make up 60 to 90 percent of extractives in hardwoods, with much of the remainder in the form of phenolics. These chemical differences mean that there are some differences in the types of chemicals that may be made from hardwoods. Hardwoods are the only type of raw material that is appropriate for the extraction process currently being developed at the Old Town Fuel and Fiber facility in Old Town, Maine.

Softwoods

Softwoods, which are generally evergreen and needle-leaved, have long been used as a source of chemicals. Softwoods are particularly advantaged in terms of producing resins and products such as turpentine. As previously mentioned, naval stores have typically been obtained from southern softwoods. Resin acids may comprise roughly 40 to 45 percent of extractives, with fatty acids comprising roughly 40 to 60 percent, depending on the tree. Notably, softwoods cannot be used with the extraction processes currently under development in Maine. The hemicelluloses from softwood are primarily galactoglucomannan and arabinoglucuronoxylan, rather than xylan as in hardwoods.

Softwoods generally lack more than a trace of xylan, which is the starting point for a variety of potential biorefinery products (Amidon et al. undated).

Feedstock Processes

A variety of potential processes to obtain chemicals from wood are being examined in Maine. To simplify matters, it is useful to separate the approaches into two general types of processes. The first type we have termed "low energy" processes, because they rely less on high heat to convert wood to chemicals. This includes processes that are typically called extraction, "near-neutral", biochemical conversion, and fermentation. The second type of process we have termed "high energy" because the process consumes the entire biomass by heating it. Also, these approaches are sometimes called thermochemical conversion methods (Winandy et al. 2008). The processes used here are typically called gasification or pyrolysis, a difference being that pyrolysis involves heating the biomass in the absence of oxygen. Notably, some authors have suggested that both types of processes could occur at the same facility (Dickerson and Rubin 2008).

Low Energy Processes

This class of process includes a range of techniques, most of which are in the exploratory phases of development. A review of the literature indicates a variety of techniques are being developed, including fermentation, extraction, and others. Many of the approaches remove the hemicellulose from wood, and use it as a starter for chemical building block chemicals. Potentially extracting the hemicellulose has the advantage of leaving the cellulose and lignin behind to produce pulp and other forest products. This process is sometimes called the "value prior to pulping" pathway (Cowie 2008). A similar but broader concept is Value Prior to Processing. These concepts are sometimes abbreviated VPP (Winandy et al. 2008).

Extraction

An example of this type of process is under construction at the Old Town Fuel and Fiber facility in Old Town, Maine. The Old Town Fuel and Fiber mill was previously Georgia-Pacific's 208,000-mtpy northern bleached hardwood kraft (NBHK) pulp line and 43,000-tpy parent-roll tissue mill. This mill utilized hardwoods and the Kraft process, and thus can make use of hardwood hemicellulose to produce chemicals.

This procedure has been postulated to have a variety of potential benefits, all of which are still being studied. Goyal (undated) notes that these potential benefits include:

- Potentially being able to extract hemicelluloses before pulping would create an additional revenue stream for a mill, with potentially the same pulp mill production as before the extraction.

- Reduction of black liquor solids sent to the recovery boiler, potentially allowing the production of more tonnage.

The process is generally characterized by these steps, as adapted from Amidon et al. (undated):

1. Wood chips and hot water are combined, and various compounds are extracted, including hemicelluloses.
2. The extracted compounds are hydrolyzed to yield xylan and other products.
3. The xylan, a complex polysaccharide, is reacted to yield acetic acid from its acetyl groups.
4. The five carbon sugars are fermented to other products.
5. The wood chips are used for pulping or burned for energy.

Currently, this extraction process can only be accomplished using hardwoods and the Kraft process.

Fermentation

Fermentation is widely used to produce bioproducts. It has been used for many years in agriculture to create a variety of chemicals and food products. For instance, ethanol from biomass is produced from the fermentation of glucose in corn starch. Notably, fermentation is a very general term, and can have a variety of meanings. Typically it means the breakdown and conversion of organic substances, typically carbohydrates, into other substances through the actions of a microorganism. A variety of everyday materials are produced through fermentation. For instance, vinegar (which is approximately 5 percent acetic acid) is a product of fermentation. Other well-known fermentation products include beer and wine.

Biomass products other than wood have been fermented for many years. Two types of sugars are typically present in biomass: 1) five carbon sugars and 2) six carbon sugars. Five carbon sugars are known as pentoses, and xylose is the most common of these in hardwoods. Six carbon sugars are known as hexoses, and glucose is the most common of these.

Wood has been more difficult to ferment than many other types of biomass. Cellulose is a polymer that is more difficult to breakdown into fermentable glucose than starch-based materials. Additionally, the purity of cellulose is a potential problem. However, hemicellulose can be hydrolyzed relatively easily into 5-carbon mono sugars that can be fermented. Tethys Research LLC is searching for enzymes to break down wood structure into its major components (FBRI 2008). A variety of companies are seeking new fermentation technologies. Certain components of wood have proven difficult to ferment, particularly cellulose. Additionally, certain chemicals in biomass, such as phenolics, may inactivate bacteria and fungi and prevent fermentation (Fort undated).

Separation

A key attribute of these low energy processes is the ability to filter or separate different chemicals (Amidon et al. undated). The lack of appropriate membranes has hampered the ability to commercialize certain chemical production pathways. In particular, energy-efficient technologies are necessary to separate and concentrate desired products (National Research Council 2000). A membrane that can be reused and withstand high temperatures and cleaning would be desirable. In particular, a membrane that would be appropriate for nanofiltration may potentially use substantially less energy than other separation processes. Separation of the breakdown products of woody biomass requires ceramic membranes with pore sizes less than 20 angstroms.

A great advantage of molecular separation by membranes rather than distillation is lower cost, primarily from energy savings. The membranes used to filter the extracts are therefore critical. For instance, current membrane technologies can separate sugars from acetic acid and furfurals. However, a new membrane technology is needed which will separate furfural compounds from acetic acid. Additionally, lactic acid production might be increased with an appropriate membrane. Currently, costs to separate and purify lactic acid are higher than other products, such as ethanol (Paster et al. 2003).

Inorganic membranes such as the one under development by Zeomatrix LLC in Orono, Maine may provide this capability. Zeomatrix is developing a membrane with pores which are uniform in size and oriented perpendicular to the surface of the membrane. The membrane is designed to be without defects, be ultra-thin for high throughput, and be thermally and chemically stable.

High Energy Processes

The high energy route to products is different from the extraction and fermentation processes. A primary difference is that all the biomass is consumed in the process. These are sometimes called “whole wood” processes. It might perhaps be called a high temperature process as well as a high energy process. A high-temperature treatment results in syngas or pyrolysis oil. The two primary processes are generally known as gasification and pyrolysis. A difference between the two processes is that gasification occurs with the presence of some oxygen, while pyrolysis occurs in the absence of oxygen. Additionally, gasification produces a gas as a product, while pyrolysis produces a liquid. This process does not have the limitation of the extraction process that may only use Kraft pulping process and hardwoods. A variety of high-energy processes are being studied at the University of Maine.

Gasification

Gasification has been applied for many years to coal. However, pilot plants using biomass gasification are already in operation in Arkansas (Goyal undated) and Choren Industries has reportedly started a large (2000 tonnes per day) commercial biomass to

Fischer-Trophs liquid fuel via gasification in Germany. (Gasification takes place in a unit called a gasifier). Synthetic gas, or syn gas, is a combination of carbon monoxide, carbon dioxide, hydrogen, with additional gases such as methane and nitrogen.

This route to produce chemicals can result in a variety of products, because syngas has a variety of potential uses. Syngas can be used to develop a range of fuels and chemicals, including acetic acid, methanol, and mixed alcohols. The major synthesis gas derivatives are methanol and ammonia. Hydrogen from syngas can be used to power fuel cells. Also, syngas could be used in the production of Fischer-Tropsch fuels, potential desirable replacement fuels for products such as diesel. Notably, the producers of synthesis gas are often the consumers, and most plants are integrated. Synthesis gas cannot travel over pipelines in excess of one or two miles.

Pyrolysis

Pyrolysis involves heating the organic components in biomass in the absence of oxygen (Babu 2008). It is similar to gasification. However, the mixture produced is mostly liquid with some solids and gas. Depending on conditions, the products may include valuable chemicals and chemical intermediates. Pyrolysis is a complex process that can consume a lot of energy. It occurs at a high temperature, generally in the range of 400 degrees Celsius or higher (Chemical Industry 2007).

Market Trends

The market for chemicals and pharmaceuticals is ever changing. The market is driven by the same forces that impact all markets, in that new processes and products, and sources of demand and supply are entering and leaving the market. This is particularly true today, as there are a series of substantial changes that are impacting the market. Four of these critical trends are:

1) *The Financial Crisis of 2008*. The financial crisis is having a substantial impact on the commodity and specialty chemical market. Prices for feedstock chemicals have declined substantially compare to a year ago (Deutsche Bank 2008) (Brice 2008). The decline in prices is worldwide, as the world economy is increasing tight knit. This decline in prices underscores a difficulty in developing new facilities, in that investment decisions become more difficult and price risk more of a factor in project planning and financing.

2) *Shifts in supply and demand for chemicals.* A major trend has been the shift of chemical production away from the United States, and to other countries, particularly China and the Middle East. China in particular has become a low cost producer of many chemicals and a growing consumer as well. Chemical production as a proportion of world production has declined. Notably, permitting difficulties have been cited as a reason why new capacity has not been developed in the US. While there are still many unknowns, it may be that the use of biomass

as a source of chemicals may be easier to permit than a greenfield project. This may be particularly true in facilities located in concert with an existing pulp mill.

3) *Volatility in the price of traditional feedstocks (primarily oil and natural gas).* The market for oil is a complex factor impacting chemical prices. Oil is a primary raw material, and in recent years the price had increased substantially, with a high of $147 per barrel in July 2008. Oil supply and price has been a source of concern for the chemical industry and government. Increasing prices were joined with an increasing realization that oil supplies are finite in a world with growing energy demand. Underscoring the difficulties in predicting the future, oil prices tumbled to $42 per barrel only 6 months later.

4) *Increasing concern around greenhouse gas emissions*. Government and industry are increasingly concerned about emissions from fossil fuels contributing to climate change. As a result, substantial investment and incentives have been implemented to find alternatives feedstocks that reduce the emission of greenhouse gases.

Summary

The decline in oil and gas prices will have a dampening impact on the potential for using biomass for chemicals. However, while oil prices are currently low, it is likely that demand for oil will recover. Oil supplies are indeed finite, and both governments and industry are seeking alternative energy and chemical feedstock sources. Sources that emit less carbon are preferred. Additionally, it is important to note that while the market for chemicals is likely to be dampened, the market for pharmaceuticals is likely to be less impacted. Prices for pharmaceuticals are generally less well correlated with the economy.

Products

Wood can be converted to a multitude of products. Here we focus primarily on some key chemicals and pharmaceuticals that might be produced in Maine. It is important to note that a vast number of chemicals and pharmaceuticals might be made. Given unlimited time and money, chemists and chemical engineers can eventually produce nearly any chemical from wood. Therefore, we have explored a more limited set of products, and products that are typically identified as being candidates worthy of additional research. Finally, it is important to note that some chemicals are also potentially pharmaceuticals. Many of the chemicals potentially produced from wood will have many uses, though most of those uses will not be economically viable.

Chemicals

We identify seven chemicals that appear to have potential for production from wood. Some of these chemicals, such as acetic acid and furfural, have been classified elsewhere as *common intermediate chemicals* (RIRDC 2006). We have selected the chemicals because they are often cited in the scientific research as potential products, and some have the potential to be platform chemicals. These seven are potentially worthy of additional research. These chemicals come from a range of technologies, many of which are still emerging technologies for biomass. The chemicals are: 1) acetic acid, 2) furfural, 3) itaconic acid, 4) lactic acid, 5) succinic acid, 6) methanol, and 7) hydrogen. The first five would more likely be created through low energy processes, and six and seven though high energy processes.

Product Summary: Acetic acid

Acetic acid has been historically produced from wood, and continues to be cited as a potential product. Notably, in the early 20th Century, acetic acid was one of the most important products of the wood distillation industry, and wood was the primary source of acetic acid (Kirkpatrick 1933). It can be isolated from wood via a variety of processes. Two commonly cited processes to derive acetic acid are: 1) extracting it from wood directly and 2) deriving it from syngas. Here we focus on the extraction of acetic acid from the wood directly using low energy processes. Low energy methods proposed to obtain acetic acid include hot water extraction and fermentation. Fermentation research has focused on certain microorganisms, such as *Clostridium thermoaceticum*. Bacteria reportedly may ferment a range of sugars, including glucose, xylose, and some other pentoses to acetate (National Research Council 2000).

Acetic acid is an important industrial, intermediate chemical. Its structural formula is CH_3COOH. The National Research Council identified acetic acid as a potential target chemical for biobased industry in its report *Biobased industrial products* (NRC 2000). A variety of products can be manufactured from acetic acid, including: vinyl acetate monomer (VAM), acetic anhydride and terephthalic acid. Additional products include latex emulsion resins for paints, adhesives, paper coatings, and textile finishing agents are made from vinyl acetate. Acetic anhydride is used in making cellulose acetate fibers and cellulosic plastics. Acetic acid is also used as a fungicide and as a solvent for many organic compounds. Finally, acetic acid is used in the preparation of pharmaceuticals. Aspirin (acetylsalicylic acid) is formed by the reaction between acetic acid and salicylic acid.

The market for acetic acid declined during the Financial Crisis of 2008. VAM, which is used in paints and coatings and is the largest acetic acid derivative, declined along with the US housing and construction sectors. The price of acetic acid in the US was in the range of $0.57 to $0.61 per pound in the fourth quarter of 2008 (Deutsche Bank 2008). Total world production capacity exceeded 7.8 million metric tons, of which 37 percent was located in North America. The price of acetic acid is indirectly linked to the price of methanol, which is a precursor chemical. Roughly 50 to 75 percent of worldwide acetic acid production comes from methanol, and perhaps one-third from acetaldehyde oxidation (Spath and Dayton 2003). Methanol prices are forecast to be flat or have only a slight real increase through 2009 (Scotia Capital 2008).

Roughly 33 percent of global acetic acid consumption is for VAM production. VAM capacity is expected to increase significantly in the next few years, with acetic acid growth tied largely to vinyl acetate monomer manufacture in Asia. An additional 20 percent of acetic acid is used for terephthalic acid (TPA) production. TPA is used primarily for the manufacture of polyethylene terephthalate (PET) solid-state resins, fibers, and films. Acetate esters production using acetic acid accounts for roughly 15 percent of total global acetic acid demand. Acetate esters are used primarily as solvents for inks, paints and coatings. Finally, acetic anhydride production also accounts for approximately 15 percent of total global acetic acid consumption. Acetic anhydride is used mainly for cellulose acetate flake production (SRI Consulting 2007).

Acetic acid is growing at about industrial production growth rates plus 1 percent, and much faster in China. China is projected to account for 32 percent of global acetic acid consumption by 2011. In the coming years, Asia is expected to account for more than 57 percent of acetic acid consumption in 2011. The US is expected to account for an estimated 19 percent of demand in 2011 (SRI Consulting 2007).

Product Summary: Furfural

Furfural is an aromatic aldehyde with the chemical formula $C_5H_4O_2$. It is a clear, yellowish liquid with a smell suggestive of almonds. Furfural production from biomass feedstocks has occurred for roughly 75 years or more. For instance, Quaker Oats made furfural from oat hulls, rice hulls, and sugar cane bagasse for many years until the late 1990s. However, any agricultural product with high pentose-containing hemicelluloses could be used, as existing sources have been chosen because they are available in larger qualities and within economic hauling distances (Natural Research Council 2000). Furfural could be produced from wood wastes (RIRDC 2006).

Furfural is usually hydrolyzed from the pentosans, such as xylans, in hemicellulose. Pentose is produced, which is then dehydradated (acid solutions are used to break down polysaccharides into sugars). New technologies are being developed to improve furfural yields. Furfural can be produced from both softwoods and hardwoods (RIRDC 2006). However, hardwood hemicelluloses appear to be more appropriate (Mamman 2007). One particular attraction of furfural is that its production retains all of the carbon to carbon bonds of pentose, retaining more energy than other processes such as the production of ethanol (Unpublished document 2005).

Furfural is an intermediate commodity chemical that can be used to synthesize a range of specialty chemicals. Notably, there is no synthetic pathway for the production of furfural (Mamman et al. 2008). Furfural has a variety of uses, including resin production, as a solvent in the petroleum production of lubricants, nylons, and other uses. Resins are reported to account for roughly 70 percent of the market (RIRDC 2006). A new use for furfural is for soil fumigation to control nematodes.

Furfural is reportedly "one of the few renewable carbohydrate biomass products that can compete with hydrocarbon chemicals and without recourse to subsidies" (RIRDC 2006). Roughly a quarter of a million tons of furfural is produced worldwide each year. U.S. consumption of furfural is roughly about one-tenth of worldwide production. The price of furfural has been volatile, with reported prices in the range of $1,000 to $1,750 per metric ton (Paster et al. 2003, RIRDC 2006). Prices have increased toward the higher end of this range, though current data reflecting the Financial Crisis of 2008 is not available.

The majority of furfural consumed in the United States is imported from China, the Dominican Republic, and South Africa. China is the dominant producer using corncob materials. There are roughly 200 furfural producers in China, with an average per company production of 1,000 metric tons per year (RIRDC 2006). Costs of production are low in China. However, the yields are low compared to newer technologies. In the US, the last major producer of furfural has closed. However, with improved pretreatment and research into pentose-utilizing organisms, furfural production in the US might become competitive with imported furfural (Paster et al. 2003). One study concluded that a reasonable minimum size furfural plant would need to produce 5,000 metric tons per year (RIRDC 2006).

Product Summary: Itaconic Acid

Itaconic acid, also known as methyl succinic acid, is an unsaturated dicarboxylic organic acid (Willke and Vorlop 2001). It is a five carbon sugar with the formula $C_5O_4H_4$. Use of itaconic acid in industry has been limited by the high cost of its production from petroleum (Paster et al. 2003). However, there is potential to produce itaconic acid from wood through aerobic fungal fermentation of xylose (US DOE 2004). Biosynthesis of itaconic acid by fungi has been reported as far back as 1932 (Willke and Vorlop 2001). The chief fungus used is *Aspergillus terreus*. With a glucose substrate (six-carbon sugars), yields are in the range of 40 to 60 percent. Yields from five carbon sugars are in the range of 15 to 30 percent (Fort undated).

The Department of Energy identified itaconic acid as among the top twelve candidates for chemical production from biomass. Itaconic acid is primarily produced using fermentation and used as a specialty monomer (US DOE 2004). Itaconic acid has potential for use in the manufacture of acrylic fibers, detergents, adhesives, thickeners, and binders, and a range of other products. In particular, itaconic acid can be incorporated into polymers. It has a potential to be used as a substitute for acrylic or methyl methacrylate, both of which are derived from petrochemicals.

Costs associated with current fermentation processes are a major barrier to the production of itaconic acid. Current processes need to be improved in terms of increased fermentation rate and yield. Increased yield will improve the economics of separation and concentration (US DOE 2004). Notable suppliers in the United States include Cargill, which produces itaconic acid using a corn-based feedstock.

Product Summary: Lactic Acid

Lactic acid is a carboxylic acid and has the chemical formula $C_3H_6O_3$. It is primarily produced through the fermentation of glucose. The primary potential from wood is through fermentation from six carbon sugars (glucose) (Paster et al. 2003). Currently, much of the production is from six carbon sugars from corn grain. Research is being conducted to find ways to produce lactic acid from both five and six carbon sugars, including hemicellulose from wood.

Lactic acid is primarily used in foods and beverages, but it is also used as an electroplating bath additive and in the production of biodegradable polymers. Notably, lactic acid is used to produce polylactide (PLA). In Maine, PLA could potential be produced from other forms of biomass, including waste potatoes. Additionally, ethyl lactate, an environmentally-benign solvent is derived from lactic acid. A range of other minor uses are reported.

While substantial progress has been made in fermentation technology, costs to separate and purify lactic acid are higher than some other fermentation products, such as ethanol. Lactic acid production costs were reportedly in the range of $0.50 or less per pound, with the potential for decreases to $0.25 per pound in the future (Paster et al. 2003). The market price was in the range of $0.70 to $0.85 per pound, during the same time period. Additionally, in 2006, the price was reported to be in the range of $0.79 per pound (van Haveren et al. 2008). Per pound prices can vary considerably by product quality. Additionally, subsequent to the Paster (2003) study, prices have increased substantially, as oil prices have increased processing and transport costs.

Product Summary: Succinic Acid

Succinic acid is a dicarboxylic acid with the chemical formula $C_4H_6O_4$. It is produced by most microbes, plants, and animals. Industrial succinic acid is produced from petroleum, through butane, with maleic anhydride as an intermediate. Food grade succinic acid is primarily produced through older fermentation and separation technology (Paster et al. 2003). Older data on the size of the market suggests total worldwide production is in the range of 20,000 to 30,000 tonnes per year (Cukalovic and Stevens 2008).

The US Department of Energy (DOE) listed succinic acid as one of the top twelve chemical building blocks from biomass (US DOE 2004). Research has been conducted with both fungal and bacterial fermentation. The primary source material is the six carbon sugar glucose, but some strains will utilize xylose, too (Fort undated). Succinic acid has in the past been produced by a specially engineered organism, *A. succiniciproducens*. Recently, research has been conducted to encourage overexpression of succinate in E. coli. This strain of E. coli was developed by DOE laboratories and subsequently licensed to Bioamber. The DOE technology consumes CO_2 and is reportedly available for further licensing.

Succinic acid is a platform chemical, from which a variety of derivatives may be created. Potential uses include green solvents, surfactants/detergents, runway deicer, and a range of other potential food and pharmaceutical uses (Paster et al. 2003). There is little published information about the price of succinic acid. One estimate is that there is a potential 250,000 ton per year market at a price of roughly $1.25 per pound (Rova undated).

Product Summary: Hydrogen

Hydrogen is the simplest and lightest element on earth -- an atom of hydrogen has only one electron and one proton. Hydrogen exists in nature in its molecular form, which contains two atoms of hydrogen, and thus pure hydrogen is commonly expressed as H_2. It combines easily with other elements and is generally found as part of some other substance, such as water. It is also found in biomass. Hydrogen can store and deliver energy, but it usually doesn't exist by itself in nature. It must be produced from compounds that contain it.

Hydrogen has been extensively studied as a potential product of biomass. Currently, hydrogen is primarily made from natural gas, where hydrogen is separated from carbon dioxide. Hydrogen has been judged a clean, attractive fuel, because it does not release CO_2 when it is consumed at its end use. Hydrogen can be produced from biomass using many routes, particularly via various forms of gasification, but with potential for production via fermentation. Notably, hydrogen has been considered for use primarily at the location where it is produced, primarily due to transportation issues.

When gasification of biomass occurs, the biomass is converted into a gaseous mixture of hydrogen, carbon monoxide, carbon dioxide, and other compounds by applying heat under pressure in the presence of steam and a controlled amount of oxygen. The biomass is chemically broken apart by the gasifier's heat, steam, and oxygen, setting into motion chemical reactions that produce a synthesis gas, or "syngas"—a mixture of primarily hydrogen, carbon monoxide, and carbon dioxide. The carbon monoxide is then reacted with water to form carbon dioxide and more hydrogen. Absorbers or special membranes can separate the hydrogen from the gas stream. New membrane technologies are needed to separate and purify hydrogen from the gas stream produced (US DOE 2007).

The DOE estimates that one kilogram of hydrogen contains about the same energy as a gallon of gasoline. The term gasoline gallon equivalent (or gge) is sometimes used to describe the cost of hydrogen. In 2005, DOE set a hydrogen cost goal for the year 2015.

The cost was set in the range of \$2.00-\$3.00/gge. This goal assumed the hydrogen was delivered, without sales taxes, and in 2005 dollars. While researchers have hailed the promise of hydrogen, there are still a variety of technological barriers to overcome. Hydrogen from biomass has been termed "biohydrogen." Analyses have shown that, in part due to the immature technology associated with using hydrogen, and the transportation costs, other uses of biomass are currently superior. In particular, the costs of transportation and lack of transportation infrastructure have been identified as potential problems. Notably, the delivered price for hydrogen can be significantly higher than the gate price (Spath and Dayton 2003).

Product Summary: Methanol

As with acetic acid, methanol was historically produced from wood. In the early 20th Century, wood distillation was the only source of methanol. This continued until 1927, when DuPont developed process to produce methanol as a byproduct of ammonia production. By 1930, the more efficient DuPont process produced more than 50 percent of total methanol production, and a year later, more than 80 percent (Kirkpatrick 1933). Eventually, as fossil fuel-based sources were less expensive, wood was nearly completely replaced as a source (USDA-FS 1956). Most methanol is currently produced by chemically oxidizing natural gas (Natural Research Council 2000). Recently, researchers have developed new processes to produce methanol via gasification of biomass.

Methanol is an important industrial chemical, and one that can be used to produce a wide range of other chemicals. Roughly 35 to 40 percent of methanol is used to create formaldehyde as a feedstock for phenolic resins, much of which ultimately is used as an adhesive in plywood. An additional roughly 20 percent is used in gasoline, either directly or as methyl tertiary butyl ether (MTBE). The remaining production is used to create substances such as acetic acid (Scotia Capital 2008). Methanol and hydrogen have been rated the best near-term prospects for biobased syngas products, because other products have been found to require additional development and are not currently economically viable

The methanol market is mature. However, methanol prices have fallen due to the economic slowdown. The primary uses of methanol are both impacted by the slowdown. For instance, the housing market represents roughly half of formaldehyde demand in North America (Scotia Capital 2008). The housing market has weakened and the particle board, fiber-board, and similar industries in North America are under stress due to international competition. Additionally, MTBE has been under pressure in many countries due to mandates to use renewable ethanol-based ETBE or ethanol in fuels (Scotia Capital 2008).

As of November 2008, spot prices for methanol in the United States were in the range of US\$0.74 to US\$0.78 per gallon. A possible long-term base price is \$0.70 per gallon (Scotia Capital 2008). Notably, since 2000, China has represented roughly 79 percent of demand growth. High cost methanol producers are closing down, with Middle East exports generally filling any gap in supply. Coal gasification plants are likely to be a future source of methanol. However, production of methanol from biomass is relatively advanced, with several companies seeking to develop renewable methanol. A range of methodologies are being developed to more efficiently produce methanol from biomass. The overall shifts in the industry may double methanol capacity between 2006 and 2010.

Foods and Pharmaceuticals

Many pharmaceuticals and food additives were originally extracted from trees, but now come from a variety of other sources, including petroleum. On familiar example is vanillin, the base for the synthetic flavoring vanilla. Historically, vanilla flavoring was extracted from oak trees, but is now synthesized from petroleum. Also, pharmaceuticals have a long history of being obtained from trees. Three important examples are:

- Salicylic acid was originally isolated from the bark of white willow. Salicylic acid was a precursor to aspirin, and was used in teas as a pain reliever and fever reducer, among other uses. It is now used to treat acne and warts. It can be derived from shikimic acid and is a phenol.

- Quinine was found in the bark of Cinchona succirubra. The native Indians of South America had known of the bark as a cure for malaria, and the Spanish and Portugese brought the knowledge to Europe.

- Taxol was found in the bark of the Pacific yew. Taxol has value as an anticancer drug.

Foods and pharmaceuticals might come from both the foliage and bole of the tree. Estimates suggest that up to 10 percent of the dry weight of wood and foliage is composed of hydrophilic substances. Some of these hydrophilic substances include: shikimic acid, stilbenes such as pinosylvin, and flavanoids.

Knots are another potential source of chemicals (Pietarinen et al 2006). Notably, softwood knots are a negative in both pulping and papermaking. However, they can be removed prior to pulping. Knotwood occurs where branches meet the bole of a tree. Knots have been noted to be a source of natural antioxidants. The type of chemical varies by tree species, with larger amounts of pinosylvans being found in some softwoods and flavanoids in some hardwoods. Pinosylvins have been noted as fungicides and bactericides. They are believed to be found in greater quantities in knots because tree wounds are more likely when a branch is broken near the bole. Thus, knot areas are more susceptible to attack by fungi. Notably, pinosylvins have been found to predominate in white pine knots. Additionally, antioxidants may be useful because some fungi use radicals to disrupt cell walls (Pietarinen et al 2006).

While there are many chemicals from plant that are of interest to researchers, two particularly interesting classes of compounds are 1) shikimic acid and its derivatives, including vanillin, and 2) polyphenols, which include pinosylvins and flavanoids. In Maine, some unpublished research is being conducted around both shikimic acid, and its derivatives, and polyphenols. However, this research is currently proprietary, and thus we focus on two better known examples, shikimic acid and vanillin.

Product Summary: Shikimic acid

Shikimic acid was first extracted from the star anis flower, which is native to China. It is found also in the foliage of trees. Shikimic acid is present in every plant in small amounts. Researchers have been trying to find were it may be more plentiful. Studies have found that shikimic acid is present both in Christmas trees and pine trees, and particularly in pine needles. Recent research has examined ways to separate shikimic acid from pine needles (Sui 2008).

A use of shikimic acid is in the production of Tamiflu®. Shikimic acid is used to make oseltamivir phosphate (trade name Tamiflu®), used to fight bird flu and influenza. Prices reported for shikimic acid are volatile, but recently have been reported in the range of \$250 to \$500 per kilogram, with mention of higher prices in the \$700 per kilogram range. In recent years, buyers have purchased Tamiflu® in order to avoid or address potential outbreaks of bird virus and influenza. The World Health Organization indicated Tamiflu® was a primary recommended antiviral of choice in managing patients infected with the bird flu virus. That prompted a number of governments to stockpile the drug.

Product Summary: Vanillin

Vanillin is an organic compound with the molecular formula $C_8H_80_3$. It is an organic compound, with functional groups that include aldehyde, ether and phenol. It is the primary component of the extract of the vanilla bean. Artificial vanillin is made from either petrochemicals, guaiacol or from lignin, which is a natural constitute of wood and byproduct of the paper industry. Roughly one ton of wood produces four kilos of lignin.

Vanillin from lignin is said to have a richer flavor than the oil based flavoring, due to the presence of acetovanillone in the lignin derived product. Due to the rising oil prices, the demand for lignin based vanillin has grown. By early 2008, demand had exceeded production (Borregaard Ingredients 2009).

Vanillin has many uses, but most importantly it is the primary component in vanilla extract. It is also used in chemical intermediates for pharmaceuticals, cleaning products, perfumes, ice cream and chocolate. Vanillin was first made into a pure substance in 1858 by Nicolas-Theodore Gobley. He obtained it by evaporating vanilla extract and then recrystalizing the resulting solids from hot water. In the 1930's, synthetic vanillin became more available because they had begun to extract vanillin from lignin that came from the pulp and paper industry. In 1981, 60% of the worlds market for vanillin was being produced from one single pulp mill in Ontario. However changes in the pulp and paper industry have caused buyers to turn to the petrochemical and guaiacol process. Soft drinks reportedly consume approximately 75% of the vanillin market in the world, and they apparently use petrochemical vanillin. However, with the rising oil prices, the petrochemical process has become generally less attractive, and the market for lignin based vanillin is again increasing (Borregaard Ingredients 2009).

The most likely commercial uses of vanillin today and in the future are vanilla extract. Vanillin will be used in the production of a large range of food and beverages. Vanillin may also be sought by pharmaceutical companies. Demand for vanillin is quite high due to the fact that the demand for vanilla flavoring has typically exceeded the supply of vanilla beans. In 2001, the annual demand for vanillin was 12,000 tons, but only 1,800 tons of natural vanillin was produced. Much of the remainder was produced through chemical synthesis.

Biocomposites

Composites are composed of load-bearing materials and reinforced, weaker materials. The reinforced weaker materials add rigidity and strength, and help support the structural load. Engineered biocomposites are increasingly important in the wood products industry, and the potential for growth is large. The primary markets for biocomposites are in the construction and transportation markets (Fowler et al. 2006). Wood-based composite comprise roughly 40 percent of total residential construction materials used in North America (Winandy et al. 2008). Applications include decking, siding, and roofing. Advanced products continue to be developed in biocomposites, particularly in the realm of nanotechnology. One example of this is nanocrystalline cellulose. While not as strong as other structures, such as carbon nanotubes, it may be substantially less costly to produce (Winandy et al. 2008).

Conclusions

The development of chemicals and pharmaceuticals from biomass is likely to grow. There are a variety of reasons why this shift will continue. A major impetus will be increasing cost of petroleum and natural gas feedstocks, as the world economy improves. Long-term, the supplies of these fossil fuel feedstocks are limited, and will eventually be depleted. Another major reason is that such a shift may have a positive impact on the environment. Policy-makers will favor using biomass, because it may reduce environmental impacts, partly through decreasing greenhouse gases. Other reasons are more subtle. Biomass is a very flexible feedstock – many products can be created. Also, some chemicals are simply lost today as the water soluble components of wood are partially lost in leachate from wood chip piles, and pass into the waste stream from mills.

This potential shift from using hydrocarbons to carbohydrates will be difficult. It will be some time before the price of carbohydrate feedstocks are tracked alongside fossil fuels. Industry has adapted to using fossil fuels, and oil and natural gas feedstocks still offer economies of scale in processing and distribution. Even with rising prices, some fossil fuel-based feedstocks are relatively inexpensive. In addition, the new technologies require substantial capital investment, and there are significant technical problems that must be overcome. For instance, the bacteria and fungi used in fermentation are fragile can be difficult to use in commercial applications. Also, testing for chemical content of woody biomass is not simple. For instance, it is not easy to examine certain biomass components, such as pine needles, with current detection equipment. Other potential barriers are that competing uses for biomass, including using biomass for fuel, energy, and papermaking, may inhibit use for chemicals. Finally, woody biomass feedstocks aren’t pure or homogeneous and thus can be difficult to utilize.

Nonetheless, using wood for chemicals and pharmaceuticals has a long history. It is likely, and perhaps inevitable, that an incremental approach to development of markets for chemicals and pharmaceuticals from woody biomass will occur. Maine is well positioned in this area, in that the state enjoys a large forest product industry and a substantial forest resource. For instance, it has a large hardwood timber resource, an input needed for several processes for obtaining useful chemicals. The production processes that are successful in Maine and elsewhere will be processes that are economically desirable, in terms of the market for the product and the cost to produce it. Finally, we note that the number of chemicals and pharmaceuticals potentially produced from biomass is large, but much research remains on the optimal way to produce these chemicals and pharmaceuticals. The market for these materials will be a key component in their viability.

Literature Cited

Allcock H.R. and F.W. Lampe. 1981. *Contemporary polymer chemistry*. Prentice-Hall, Inc. Englewood Cliffs, New Jersey. 599 pp.

Amidon, T.E., C.W. Wood, and S. Liu. Undated. *Membrane separation: an essential component for a wood-based biorefinery.* SUNY College of Environmental Science and Forestry. 11 pp.

Atlantica Bioenergy Task Force. 2008. *Summary report*. 31 pp.

Babu, B.V. 2008. *Biomass pyrolysis: a state-of-the-art review*. Biofuels, Bioprod. Bioref. 2:393-414.

Borregaard Ingredients. Web address http://www.borregaard.com/eway/default.aspx?pid=227&trg=Column1_8737&MainPage_5913=8737:0:&Column1_8737=3004:25809::0:8738:10:::0:0 Website accessed March 11, 2009.

Brice, A. 2008. *Prices spiral downward*. ICIS Chemical Business. March 17-30, 2008.

Chemical industry vision2020 technology partnership. 2007. *Alternative, renewable and novel feedstocks for producing chemicals.* 2007. 51 pp.

Ciesla, W.M. 2002. *Non-wood forest products from temperate broad-leaved trees*. Non-Wood Forest Products 15. Food and Agriculture Organization of the United Nations. Rome.

Cole, B. Undated. *Extractive components of wood*. Unpublished presentation. University of Maine.

Cowie, J.G. 2008. *The value prior to pulping (VPP) platform for biomass utilization.* Presentation to the American Association for the Advancement of Science. February 18, 2008.

Cukalovic, A. and C.V. Stevens. 2008. *Feasibility of production methods for succinic acid derivatives: a marriage of renewable resources and chemical technology.* Biofuels, Bioprod. Bioref. 2:505-529.

Deutsche Bank. 2008. *Trends for chems: Financial crisis disrupts petchem market*. November 9, 2008.

Dickerson, C. & Rubin, J. (2008). *Maine Bioproducts Business Pathways*. Margaret Chase Smith Policy Center and Forest Bioproducts Research Initiative, School of Economics, University of Maine, Orono.

FAO. 1995. *Non-wood forest products from conifers.* Non-wood forest products 12. Rome.

FAO. 2008. *Forests and energy*. FAO Forestry Paper 154. Rome. 56 pp.

Forest Bioproducts Research Initiative. 2008. Website http://www.forestbioproducts.umaine.edu/Tethy_Technology.php. Accessed December 16, 2008.

Fort, R. Undated. *Value added chemicals from sugar feedstocks.* Unpublished presentation.

Fowler, P.A., J. M Hughes and R. M. Elias. 2006. *Biocomposites: technology, environmental credentials and market forces.* Journal of the Science of Food and Agriculture. 86:1781-1789.

Goyal, G.C., Z. Tan, C. Yin, N. Marsolan, and T. Amidon. Undated. *Biorefinery – an overview*.

Kirkpatrick, S (editor). 1933. *Twenty-five years of chemical engineering progress: 1908-1933*. George S. Ferguson Company. Philadelphia. 373 pp.

Lignin Institute. 2008. Website http://www.lignin.org/whatis.html. Accessed December 5, 2008.

Mao, H., J.M. Genco, A. van Heiningen, and H. Pendse. 2008. *Technical economic evaluation of a hardwood biorefinery using the "near-neutral" hemicelluslose pre-extraction process.*

Mamman, Ajit.Singh., Jong-Min Lee, Yeong-Cheol Kim, In Taek Hwang, No-Joong Park, Young Kyu Hwang, Jong-San Chang, Jin-Soo Hwang. 2008. *Furfural: hemicellulose/xylose-derived biochemical.* Biofuels, Bioprod. Bioref. 2:438-454.

National Research Council. 2000. *Biobased industrial products.* National academy press. Washington, D.C. 147 pp.

Paster, M., J.L. Pellegrino, and T.M. Carole. 2003. *Industrial bioproducts: today and tomorrow*. Energetic, Incorporated. 86 pp.

Pietarinen, S.P., S.M. Willfor, M.O. Ahotupa, J. E. Heming, and B.R. Homlbom. 2006. Knotwood and bark extracts: strong antixidants from waste materials. *J. Wood Sci* 52: 436-444.

Pietarinen, S.P., S.M. Willfor, F.A. Vikstrom, and B.R. Holmbom. 2006. Aspen knots, a rich source of flavonoids. *Journal of Wood Chemistry and Technology*. 26: 245-258.

Rova, U. Undated. *Current research and development: Succinic acid production.* Unpublished presentation. Luleå University of Technology.

Rowell, R.M. editor. 2005. *Handbook of wood chemistry and wood composites*. CRC Press. 487 pp.

Rural Industries Research and Development Corporation. 2006. *Furfural chemicals and biofuels from agriculture.* RIRDC Publication No. 06/127. 28 pp.

Scotia Capital. 2008. *Canadian chemicals and fertilizers outlook*. Equity Research Industry Report. July 2008. 128+ pp.

Skog, K.E. and H.N. Rosen. 1997. *United States wood biomass for energy and chemicals: possible changes in supply, end uses, and environmental impacts.* Forest Products Journal. 47(2):63-69.

Spath, P.L. and D.C. Dayton. 2003. *Preliminary screening – technical and economic assessment of synthesis gas to fuels and chemicals with emphasis on the potential for biomass-derived syngas.* National Renewable Energy Laboratory. NREL/TP-510-34929. Golden, CO. 142 pp.

SRI Consulting. 2007. Web page: http://www.sriconsulting.com/CEH/Public/Reports/602.5000/. Accessed March 11, 2009.

Stenius, P. editor. 2000. *Forest products chemistry*. Fapet Oy, Helsinki, Finland. 350 pp.

Sui, R. 2008. *Separation of shikimic acid from pine needles*. Chemical Engineering & Technology. Vol. 31, Issue 3, 469-473 pp.

Unpublished document. 2005. Accessed January 8, 2009 at http://www.seas.upenn.edu/~seider/2005-2006%20Projects.pdf.

US Department of Agriculture, Forest Service. 1956. *Hardwood-distillation industry*. Forest Products Laboratory, Madison, Wisconsin. No. 738. Revised February 1956.

US Department of Energy. 2004. *Top value added chemicals from biomass. Volume 1 – results from screening for potential candidates from sugars and synthesis gas.* 67+ pp.

US Department of Energy. 2007. *Hydrogen production*. http://www1.eere.energy.gov/ hydrogenandfuelcells/production/biomass_gasification.html. Web page accessed 11/25/2008.

Van Haveren, J., E. L. Scott, and J. Sanders. 2008. *Bulk chemicals from biomass*. Biofuels, Bioprod. Bioref. 2:41-57.

Willke T. and K.D. Vorlop. 2001. *Biotechnological production of itaconic acid*. Appl Microbiol Biotechnol 56:289-295.

Winandy, J.E., A.W. Rudie, R.S. Williams, and T.H. Wegner. 2008. *Integrated biomass technologies: A future vision for optimally using wood and biomass.* Forest Products Journal. Vol. 58, No. 6. P. 6-16.