Flexible pretreatment technology supports production of biobased co-products at pulp and paper mills

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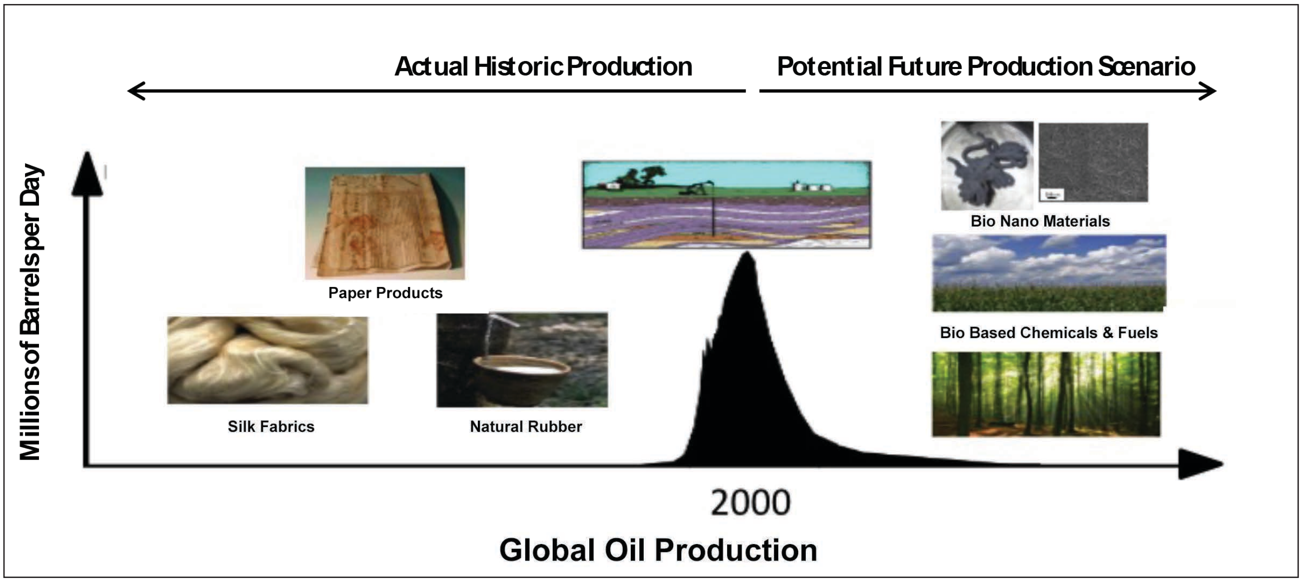
ABSTRACT: The AVAP™ biorefinery technology from American Process Inc. is a flexible, cost-effective process for production of cellulose-, sugar-, and lignin-based products from biomass. The process is currently operating at demonstration scale in the southern United States and supplying products to partners for conversion to fuels, biochemicals, and other advanced biobased materials. Engineering for the first commercial facility is underway.

Application: Forest products companies may be interested in learning more about AVAP biorefinery technology as a way to increase the profitability of biomass conversion to pulp and paper products by adding a variety of coproducts, including fuels, chemicals, and nanocellulose.

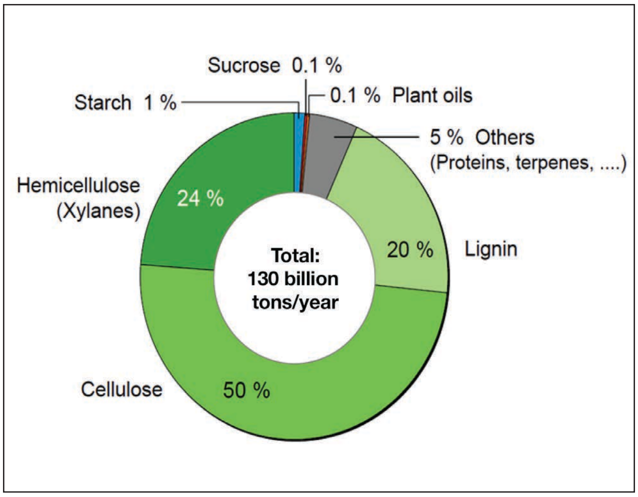
Before the discovery of oil, manufacturing and the economy-at-large were largely based on renewable materials (**Fig. 1**) [1]. Modern biorefinery processes are making it possible to produce advanced renewable materials that can compete on price and performance with traditional fossil fuel-derived materials, and offer environmental and sustainability advantages. Whereas fossil fuel is a finite material, non-edible biomass represents 98% of the organic material on earth, with an availability of 130 billion tons/year. (**Fig. 2**) [1,2].

The AVAP™ (American Value Added Pulping) process, developed by American Process Inc., is representative of this new technology. Having achieved low-cost production and efficient fractionation and separation of the principle components of biomass with minimal degradation, the AVAP process has overcome significant barriers to commercialization of 21st century biomaterials.

The AVAP technology offers economy of scale production in a compact design platform using traditional pulping equipment backed by Valmet, a major pulp and paper equipment manufacturer. Unlike traditional chemical pulping processes, the complex recovery cycle has been replaced by simple, low-cost distillation of the volatile pretreatment chemicals, sulfur dioxide, and ethanol.



1. Shift to the 21st century bio-economy.



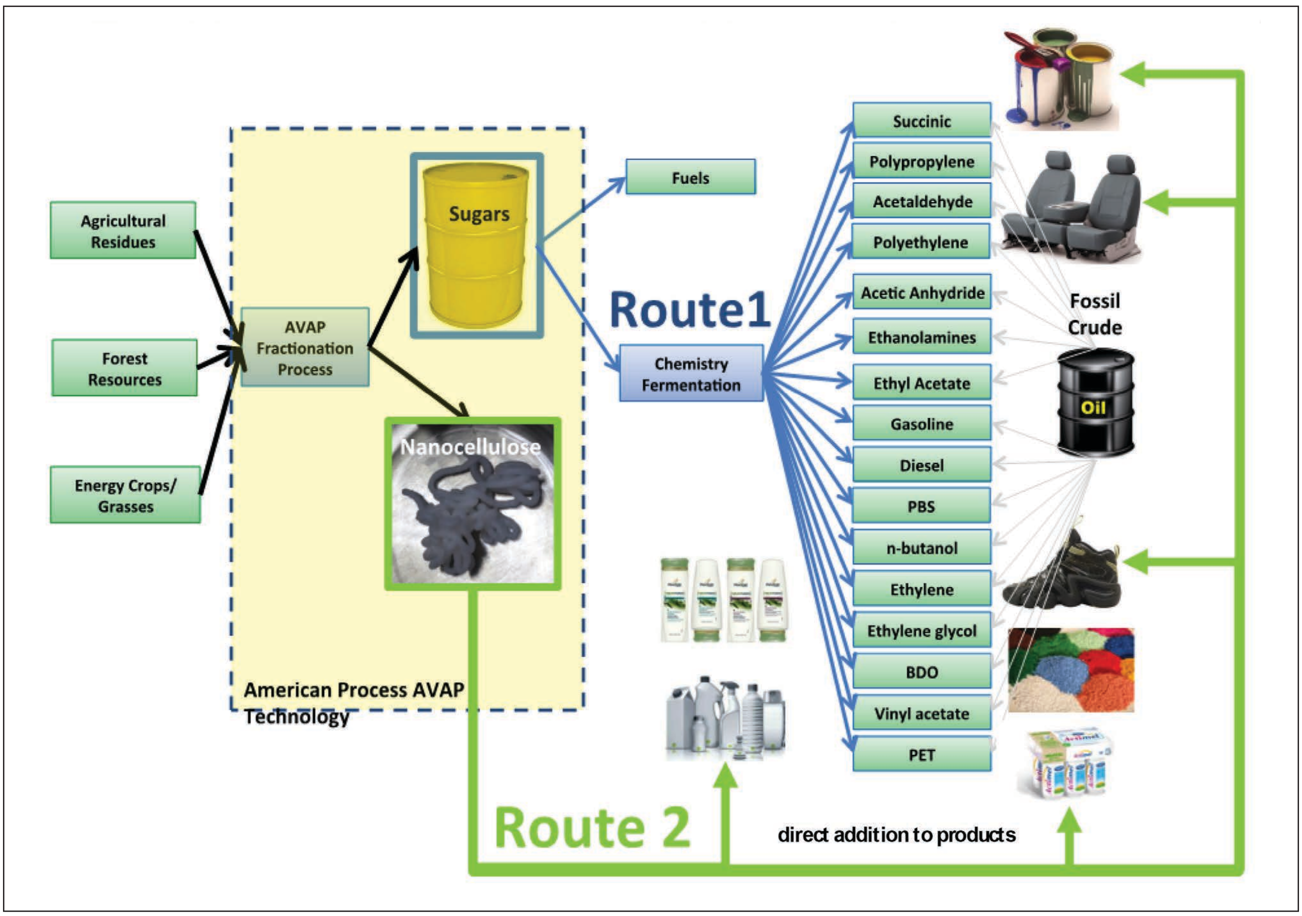
2. Total global availability of biomass.

PATH TO COMMERCIALIZATION

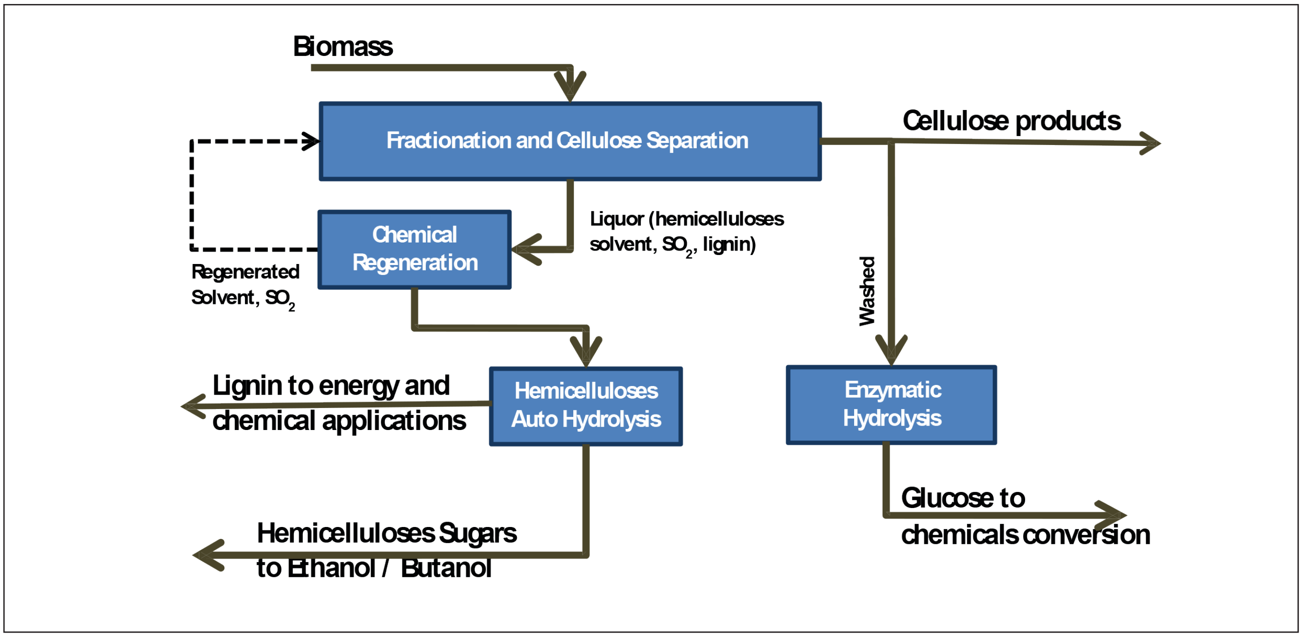
Traditional chemical pulping dissolves and combusts for energy approximately half of the biomass feedstock. This is in stark contrast to an oil refinery, where 95% of the crude is sold. American Process observed that application of the results of their process integration studies to reduce energy use in mills made excess dissolved biomass components available, which were typically burned for sale of electricity.

To maximize the conversion yield of biomass for further use, the process must efficiently fractionate the components, with limited degradation. Furthermore, the process chemicals should be separated from the individual products and recovered with low energy and capital requirements. The present AVAP process achieves these goals with overall product yields approaching 95%. Unlike the early organosolv processes, whose economic viability was hampered by not fully recovering the solvent from the pulp, the AVAP process efficiently recovers the sulfur dioxide and ethanol pretreatment chemicals. In addition, the omnivorous nature of the process allows users to optimize the feedstock mix to local availability, including hardwood, softwood, forest residues, agricultural residues, grasses, energy cane, bamboo, and kenaf. This is important in achieving low-cost positioning in commodity markets, such as sugar or ethanol. Alternatively, producing small quantities of high-end co-products, such as nanocellulose, can enhance the economics of an AVAP facility.

Figure 3 highlights the two process routes from biomass to biofuels, biochemicals, and biomaterials. In Route 1, exceptionally pure sugars produced with the process are converted to fuels and chemicals such as butanediol polymer precursors,



3. AVAP's two biomass routes to renewable materials.



4. A simplified process flow diagram of the AVAP process.

butanol, and acrylic acid using chemical or fermentation methods. The cellulosic sugars are fermented and catalytically converted to major building block chemicals with performance equivalent to corn-based dextrose. In Route 2, AVAP nanocellulose is converted directly into biomaterials such as foams and plastic-like packaging materials. AVAP nanocellulose is anticipated to be cost competitive with petroleum-based polymers and polymer additives. This breakthrough technology can help achieve the U.S. Department of Agriculture's future global market size estimate for nanocellulose of 34 million tons/year [3].

AVAP PROCESS OVERVIEW

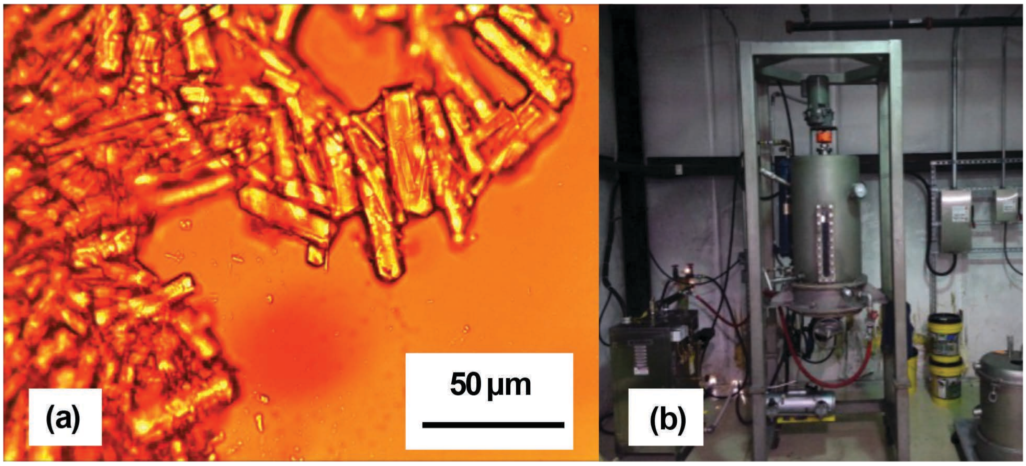
Figure 4 shows a simplified flowsheet for the AVAP process. The chemical pretreatment step uses sulfur dioxide (SO_2) and ethanol to remove from biomass the hemicelluloses, lignin, and if required for nanocellulose grades, the amorphous regions of cellulose. Sulfur dioxide acts as a delignifying agent, effectively freeing cellulose and hemicelluloses from lignin. Ethanol acts as a solvent, aiding penetration of sulfur dioxide into the biomass, dissolving resins, and extractives, and preserving crystalline cellulose. After pretreatment, the cellulose is washed to remove the dissolved lignin and sugars. The dissolved hemicellulosic sugars extracted during pretreatment can be fermented into cellulosic ethanol or other biochemical co-products. Lignin is removed from the process and burned, making the process self-sufficient in energy use or a net energy (power) exporter, depending on the biomass feedstock. The pretreatment chemicals are recycled with high recovery rates in an energy efficient manner for reuse. Depending on the pretreatment conditions used (time and temperature), the cellulose can be used to make tissue, papermaking, or dissolving pulp; enzymatically hydrolyzed to glucose; or converted to nanocellulose with minimal mechanical energy requirements.

The AVAP process uses low-cost raw biomass and pretreatment chemicals, a small number of process steps, and standard unit operations, which lead to low operating and capital cost requirements. In addition, the unique pretreatment chemicals (sulfur dioxide delignifying agent and ethanol penetrating solvent) make the process suitable for all biomass feedstocks.

SUGAR TECHNOLOGY

The AVAP process generates separate hemicellulose-based and cellulose-based sugar streams. Depolymerization of the pure, washed cellulose using enzymes at low charge has proven to produce an exceptionally high-purity glucose stream at high consistency. This glucose solution can be evaporated to 650 g/L molasses syrup with low energy input. As such, the cellulose-based molasses can be used as a direct replacement for dextrose (D-glucose, corn sugar) for conversion to chemicals and materials. Because dextrose is a well-known feedstock for fermentation and catalytic conversion to end-use products, the process eliminates downstream conversion risk. The hemicellulose sugars are a mixture of pentose and hexose sugars. The dominant sugar is xylose for the nonwood and hardwood biomass and mannose for softwood. The hemicelluloses stream has been fermented at high yield to ethanol.

In pilot-scale tests, cellulose-based D-glucose from the process has been crystallized (**Fig. 5**), which suggests potential use as a sweetener for human and animal consumption. Thus, cellulose, the most abundant organic material on earth, may soon be used to supplement edible sugars in the human diet and grow protein through animal feed.



5. (a) D-glucose sugar crystals from AVAP and (b) pilot crystallizer used for production of the crystals.

LIGNIN TECHNOLOGY

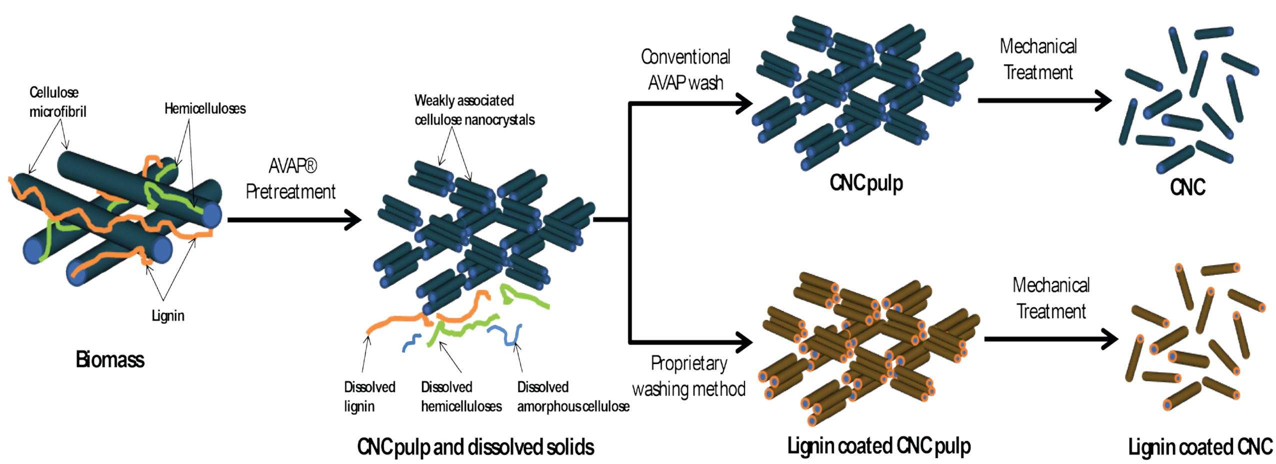
The AVAP process generates two forms of lignin: "native" lignin with very low levels of sulfonation (~0.1 S/C9) and sulfonated lignin (~0.3 S/C9) or lignosulfonate. The native lignin has minimal levels of chemical modification and is highly reactive, showing promise in the chemical industry for the production of carbon fiber, lignin-formaldehyde resins, etc. It is separated from the dissolved sugars stream using a proprietary separation process. The lignosulfonate is soluble in water and is separated by precipitation (e.g., overliming) or after removal of sugar fermentation products (e.g., distillation of ethanol).

The worldwide market for lignosulfonates has decreased to 400,000 tons/year because of limited supply. The widest commercial application of lignosulfonates is in concrete and cement admixtures.

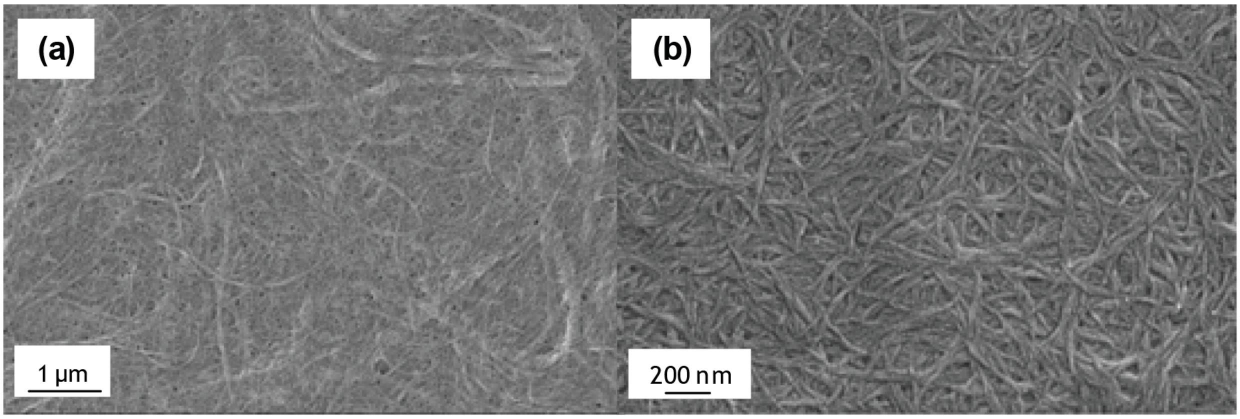
PULP TECHNOLOGY

AVAP offers many advantages for producing dissolving pulp, a relatively pure reactive cellulose used for production of regenerated fibers and cellulose derivatives. At present, dissolving pulp is produced from wood-derived acid sulfite (~50% of total world production), prehydrolysis kraft (~35%) pulps, and cotton linters (~15%) [4]. The global production of textile fibers is predicted to increase from 72.5 million tons in 2010 to 133.5 million tons in 2030 in response to increases in per capita consumption and population [5,6]. This corresponds to the increase in the demand for wood-derived dissolving pulps from the present 4.2 million tons to 19.0 million tons in 2030 [7].

The present commercial processes (acid sulfite and prehydrolysis kraft) are not optimal. The drawbacks of the acid sulfite process include partial loss of dissolved hemicellulose sugars through oxidation to aldonic acids; inefficient chemi-



6. AVAP process routes for traditional cellulose nanocrystals and hydrophobic, lignin-coated cellulose nanocrystals.



7. (a) AVAP cellulose nanofibrils and (b) cellulose nanocrystals from eucalyptus.

cals recovery because of the presence of base; long cooking durations because of the required impregnation stage; and high sensitivity to feedstock. In the prehydrolysis kraft process, most of the hemicelluloses and part of cellulose are degraded to hydroxycarboxylic acids. Decisive disadvantages of the kraft process are the high capital cost of the complicated recovery cycle and extensive bleaching sequences required to reach high alpha cellulose content.

The AVAP process is free from these drawbacks [5,8]. Similar to acid sulfite pulps, AVAP pulps are characterized by near-full cellulose retention, high brightness, and bleachability. The fully bleached AVAP pulps exhibit properties (chemical and macromolecular) very similar to those of viscose-grade acid sulfite dissolving pulps, which is explained by the similar chemistry of the two processes. However, AVAP has advantages over sulfite pulping in preserving the hemicelluloses, having much shorter cooking times, and in producing both lignosulfonates and nonsulfonated lignin. The suitability of the process for production of dissolving pulps has also been confirmed by very good filterability of viscose prepared from these pulps [8-10].

AVAP pulp is also promising for specialty papers and tissue production. In addition to the process cost advantage of efficient and low-cost chemical recovery, key advantages compared to kraft pulp include high brightness and bleachability and lower refining energy consumption. These advantages result in substantially lower investments in refining and bleaching equipment and lower bleaching chemicals consumption. Overall, AVAP pulp is similar to acid sulfite pulp, so it is highly suitable for low-strength paper grades, such as tissue. The high sheet density of AVAP pulp is an advantage in certain specialty papers, such as greaseproof and release papers [11].

NANOCELLULOSE TECHNOLOGY

The AVAP process produces cellulose nanocrystals (CNC) and cellulose nanofibrils (CNF), and novel, hydrophobic, lignin-coated versions of each, directly from biomass (**Fig. 6**). The AVAP nanocellulose process is based on the "tunability" of the pretreatment step. For each feedstock, the pretreatment conditions (time and temperature) can be selected that give the desired levels of fibrillation and removal of amorphous cellulose, as indicated by the cellulose degree of polymerization.

The unique kinetics of the AVAP pretreatment step are also important for nanocellulose production. In the acidic AVAP process, the amorphous regions of cellulose are more fully hydrolyzed and dissolved. The crystalline cellulose is less accessible because of the non-swelling nature of the ethanolic cooking liquor compared to that of the alkaline kraft process, for example. As a result, the crystallinity of AVAP CNF and CNC are higher than the crystallinity produced by alternate methods. AVAP CNFs from eucalyptus have a high aspect ratio (**Fig. 7**) (5-200 nm wide, 500 nm to several microns in length) and a crystallinity of 88%. AVAP CNCs from eucalyptus are rod-shaped (4-5 nm wide, 50-500 nm in length) with a crystallinity of 93% [12].

AVAP DEMONSTRATION PLANT

The AVAP process and products are covered by several patents, and others are pending [13-16]. The process is currently being used for production of cellulose, cellulosic sugars, lignin, and lignosulfonate at the integrated AVAP biorefinery demonstration plant in Thomaston, GA, USA (**Fig. 8**). The biorefinery, rated at 3.5 b.d. tons/day biomass,

8. American Process Inc.'s AVAP biorefinery in Thomaston, GA, USA.

started up in March 2013. It serves as the site of supply chain-integrated alliances with downstream sugar and cellulose converters into chemicals, fuels, and other biobased materials. The facility is situated on 8 acres. It includes 41000 ft^2 of manufacturing space and API's corporate research and development laboratory. A demonstration line for production of the full range of AVAP nanocellulose products is planned to begin operation at the biorefinery during 2015. **TJ**

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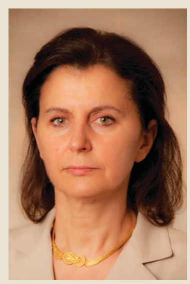

Retsina

The traditional pulp and paper industry (our customers) faced decreasing demand for their products and increasing competition from Southern Hemisphere mills, forcing shutdown of their assets. We envisioned repurposing these mills to add new revenue or transform them to a new business model by converting them to biorefineries.

Our research supports production of sugar, lignin, and nanocellulose to replace or complement traditional forest products. Our project has been highly interdisciplinary. We have benefited from diverse backgrounds from different fields, such as forest, sugar, petrochemical, and polymers.

What was surprising about our findings has been how little different industries know about each other's processes. The combination of different technologies results in new products to the marketplace that can replace incumbent products.

Industries that are seeking new, renewable feedstock from non-food sources might benefit from this technology.

As a next step, we plan to scale-up the production from various lignocellulosic sources.

Pylkkanen is CTO, Nelson is vice president, Nanocellulose Technology, Iakovlev is AVAP R&D group leader, and Retsina is founder and CEO, American Process Inc., Atlanta, GA, USA. Email Nelson at knelson@americanprocess.com.