

BIOREFINERY IN A KRAFT PULP MILL: FROM BIOETHANOL TO CELLULOSE NANOCRYSTALS

CHRISTINE CHIRAT, DOMINIQUE LACHENAL and ALAIN DUFRESNE

*Laboratoire de Génie des Procédés Papetiers (LGP2), UMR CNRS 5518,
Grenoble INP-Pagora, France*

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Wood, composed of cellulose, lignin and hemicelluloses, is the main raw material used to produce cellulosic fibres. Mills producing cellulosic fibres, also called kraft mills, look very much like a “biorefinery” plant: isolated cellulose is almost pure, and then exploited today mainly as paper; hemicelluloses and lignin are degraded and solubilised during the process as a very complex mixture, called “black liquor”, which is burnt in a recovery boiler. The heat thus produced covers largely the energy needs of the kraft mill, which may then become a net producer of electricity. The aim of this paper is to present two examples of research pathways aiming at enlarging the products portfolio a pulp mill could offer. The first example deals with the definition of hemicelluloses extraction from softwood, prior to its transformation into cellulosic paper pulp by the kraft process. The hemicelluloses fraction (in the case of softwood species, mainly composed of C6 sugars) should be extracted in a relatively pure form, whereas the cellulose fraction would continue to be obtained as fibres for papermaking. Thus, lignin becomes the main component of the “black liquor” and might continue to be used as fuel for the energy needs of the mill. The extracted hemicelluloses are hydrolysed into hexoses and then fermented into bio-ethanol. This type of second generation bio-ethanol should eventually substitute the first bio-ethanol generation produced today from food raw materials. In the study, softwood chips were submitted to various hydrolysis treatments. Temperature, time and pH were varied so as to optimise the hemicelluloses extraction primarily under the form of sugar monomers. The prehydrolysis liquors were analysed for their total sugar content and submitted to fermentation tests for bio-ethanol production. Very satisfactory results were obtained in terms of bio-ethanol production, which indicated that no active fermentation inhibitors were present in the selected liquor.

The second research pathway deals with cellulose nanocrystals which, in recent years, have attracted the attention of both scientific and industrial communities. It was shown that cellulose nanocrystals reinforced polymer nanocomposites display outstanding mechanical properties and can be used for processing high-modulus thin films.

Keywords: biorefinery, kraft, hemicelluloses, bioethanol, cellulose nanocrystals

INTRODUCTION

The biorefinery concept is quite old in the pulp and paper industry, as kraft and sulfite mills have always been working as biorefineries (Fig. 1), producing material (fibres), chemicals (*e.g.* tall oil and turpentine), the energy needed for the process, and even ethanol – in the case of the sulfite process. In modern kraft mills, extra electricity is also produced and sold to the market. Large-scale fermentation of the sugars from the sulfite waste liquor into ethanol started in 1909 in Skutskär, Sweden.¹ The utilization of wood and wood components for producing chemicals and energy by other ways than sulfite and kraft

processes has been an area of interest for quite a long time, as summarized by Fengel and Wegener.²

In recent years, the need for sustainable energy sources, the strong rise and fluctuation of oil price and the political incentives to work on bioenergies led^{3,4} to a renewed interest in biorefineries and to the emergence of new studies devoted to such topics. Some researchers devoted their efforts to wood and black liquor gasification,^{2,5,6} other teams worked on the production of ethanol from the entire wood or plant, or focused on the simultaneous production of fibres and sugars in a single

mill, as well as on processes that would hydrolyse hemicelluloses from wood chips prior to kraft cooking.^{2,7-10} (Fig. 2). Hexoses can be fermented quite easily to ethanol, whereas work on viable fermentation of pentoses into ethanol is still ongoing.¹¹ Exploitations other than for ethanol could be envisaged for pentoses and hexoses, if ethanol production is not sought, as in the production of surface-active agents. Our group started a project on the simultaneous

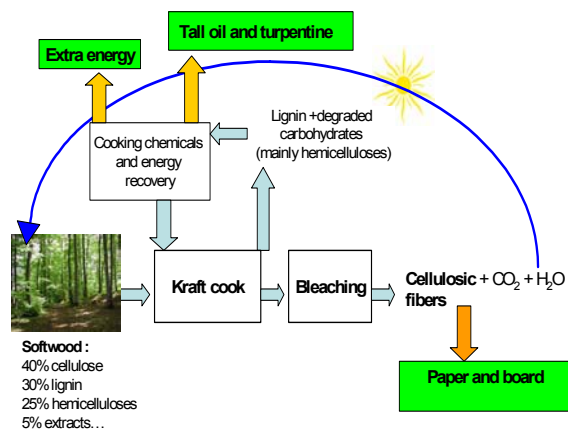


Figure 1: Today's kraft pulp mill

Another area of interest in wood chemistry is that of cellulose nanocrystals. Nanoscience and nanotechnology correspond to science and technology that focus on the sizes from about 100 nm down to atomic orders of magnitude of around 0.2 nm, and on the physical phenomena and material properties observed when operating over this size range. Conceptually, nanocomposites refer to multiphase materials where at least one of the constituent phases has one dimension less than 100 nm. Among the biologically inspired nanocomposites, polysaccharides are probably among the most promising sources for the production of nanoparticles. Some of these carbohydrates, like cellulose, can be used for the preparation of crystalline nanoparticles with different geometrical characteristics, as depending on both plant and preparation treatment, providing a wide range of potential nanoparticles properties. Huge quantities of these nanoparticles are potentially available and can be prepared by acid hydrolysis. Chemical pulp would be an ideal substrate. Throughout the published papers, different descriptors of the resulting colloidal

production of sugars and cellulosic fibres, for both hardwood and softwood species, with the aim to optimise the hydrolysis of wood chips prior to kraft cooking with regard to cooking ability, bleaching ability, strength properties and ethanol production – in the case of softwoods, and specialty chemicals – in the case of hardwoods. The results presented in this paper discuss softwood hydrolysis prior to kraft pulping.

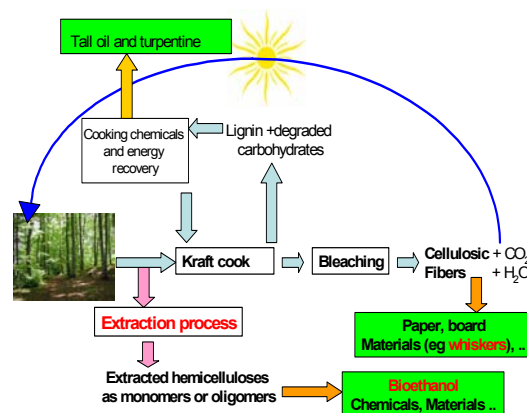


Figure 2: A possibility of tomorrow's kraft biorefinery mill

suspended particles will be used, including whiskers, monocrystals and nanocrystals. The word “whiskers” is often preferred to the name “elongated rod-like nanoparticles”. These crystallites have also often been referred to in the literature as “microfibrils”, “microcrystals” or “microcrystallites”, despite their nanoscale dimensions. Most of the studies reported in the literature refer to cellulose. A recent review reported the properties and application of cellulosic whiskers,¹² especially for nanocomposite production.

EXPERIMENTAL

Part 1

Wood samples: The softwood sample, representing the current raw material in one of the French kraft mills, is a mixture of several softwood species (35% Sylvestre Pine, 24% Black Pine, 18% Alep Pine, 16% Spruce, 7% Douglas fir). The average hemicellulose content was of 28%.

Prehydrolysis: The prehydrolysis step was performed in autoclaves, then placed in an oil bath to adjust the desired temperature. The system was rotating. Autohydrolysis consisted of acidic hydrolysis, without addition of any

external acid. For acid hydrolysis, sulfuric acid was added. The operating conditions were the following: liquor-on-wood ratio – 7, no acid (autohydrolysis) or acid charges of 0.7 to 3.5% H₂SO₄ on wood for acid hydrolysis, time to T - 50 min, time and temperature were varied (values given in the Figures).

Sugar analysis: The analysis of sugar monomers was performed by ionic chromatography (*Dionex DX500*) with a *Carbopac PA-1* column and guard column, and an electrochemical detector ED40 with a gold electrode.

Fermentation: Fermentation was done with *Saccharomyces cerevisiae*, at a temperature of 30 °C, for 24 h.

Ethanol analysis: Ethanol analysis was performed by GC-FID, using a Trace GC (*Thermo Finnigan*) and a *J&W Scientific DB-MS 5* column (30 m x 0.32 mm, 1 micron phase width).

Pulp characterisation: After kraft cooking, the pulp samples were characterised as to their lignin content (as kappa number, which is proportional to the lignin content: % lignin = 0.15 x kappa number), and also for their resistance properties (tear and tensile indexes), according to the conventional ISO standards.

Part 2

Polysaccharide nanocrystals: The procedure for the preparation of colloidal aqueous suspensions of cellulose nanocrystals is described in detail in the literature.^{13,14} Generally, the biomass is first submitted to a bleaching treatment with NaOH, in order to purify it by removing other constituents. The bleached material is then disintegrated in water and the resulting suspension is submitted to a hydrolysis treatment with acid. The amorphous regions of cellulose act as structural defects and are responsible for the transverse cleavage of the microfibrils into short nanocrystals, under acid hydrolysis. Under controlled conditions, this transformation consists in the disruption of the amorphous regions surrounding and embedded within cellulose microfibrils, while leaving the microcrystalline segments intact, which is ascribed to the faster hydrolysis kinetics of the amorphous domains – compared to the crystalline ones. The resulting suspension is subsequently diluted with water and washed by successive centrifugations. Dialysis against distilled water is then performed, to remove the free acid in the dispersion. Complete dispersion of the whiskers is obtained by a sonication step. After filtration, the dispersions are stored in the refrigerator to remove the residual aggregates and several drops of chloroform are added. Determination of the whisker content can be done by weighing aliquots of the solution before and after drying.

RESULTS AND DISCUSSION

Prehydrolysis of softwood chips for ethanol production

As shown in a previous study,¹⁵ when autohydrolysis is applied on softwood chips, it mainly leads to the dissolution of oligomers. Autohydrolysis means that no extra acid is added for the hydrolysis of sugars, while the acidity necessary to hydrolyse the carbohydrates arises naturally: indeed, the hemicelluloses contain acetyl groups readily hydrolysed into acetic acid, when the wood is heated. If the intention is to produce ethanol directly on the hydrolysate, hydrolysis should be conducted under stronger conditions, to yield several monomers (Fig. 3).

Prehydrolysis of mixed softwood was thus carried out using 0.7 to 3.5% sulphuric acid on wood, under various time and temperature conditions. The objective was to solubilise at least 50% of the hemicelluloses present in wood in the form of monomers, by varying the hydrolysis time and the amount of acid; about 160 kg monomers/ton of wood could be thus obtained (Fig. 4).

The hydrolysates were fermented into ethanol (Fig. 5). The production of about 89 L ethanol/ton wood could be obtained for the highest acid charge. The lowest charges led to a maximum of about 77 L/ton. Fermentation yields close to the theoretical value were obtained, indicating that the amount of fermentation inhibitors, if any, was not significant.

Polysaccharide nanocrystals

The general procedure described in the experimental part to produce stable aqueous suspensions of polysaccharide nanocrystals has to be adapted according to the nature of the cellulosic substrate. The constitutive nanocrystals occur as elongated rod-like particles or whiskers. The precise physical dimensions of the crystallites depend on several factors, including the source of cellulose, the exact hydrolysis conditions and ionic strength. The typical geometrical characteristics for crystallites derived from different species and reported in the literature are listed in Table 1. Length is generally of the order of a few hundred nanometers, and width is of the order of a few nanometers. The aspect ratio of these whiskers is defined as the length-to-width ratio.

In the past fifteen past years, a great deal of interest was focused on investigating the use of polysaccharide nanocrystals, especially cellulose whiskers, as a reinforcing phase in a polymeric matrix, for evaluating the mechanical properties of the resulting composites and for elucidating the origin of the mechanical reinforcing effect.

The first demonstration of the reinforcing effect of cellulose whiskers was reported for poly(S-co-BuA) reinforced with tunicin whiskers.²⁴ The authors measured a spectacular improvement in the storage modulus after filler addition, even at low contents, into the host polymer. This increase

was especially significant above the glass-rubber transition temperature of the thermoplastic matrix, because of its poor mechanical properties within this temperature range. For instance, the rubbery modulus of the composite reinforced with 6 wt% tunicin whiskers was more than 2 orders of magnitude higher than the one of the unfilled matrix. Moreover, the introduction of 3 wt% or more cellulosic whiskers provides an outstanding thermal stability of the matrix modulus, up to the temperature at which cellulose starts to degrade (500 K).

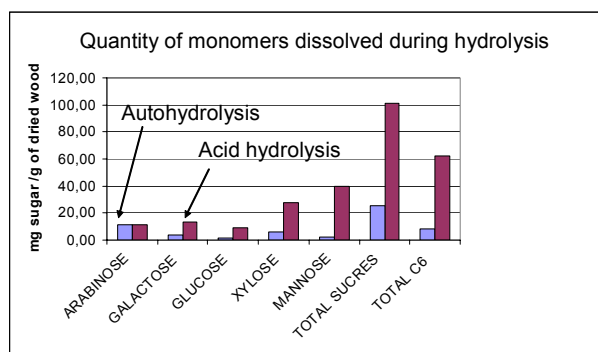


Figure 3: Solubilisation of monomers of softwood chips during autohydrolysis and acid hydrolysis (autohydrolysis conditions: 160 °C, 2 h at T; acid hydrolysis conditions: 160 °C, 0.7% H₂SO₄, 1 h at T)

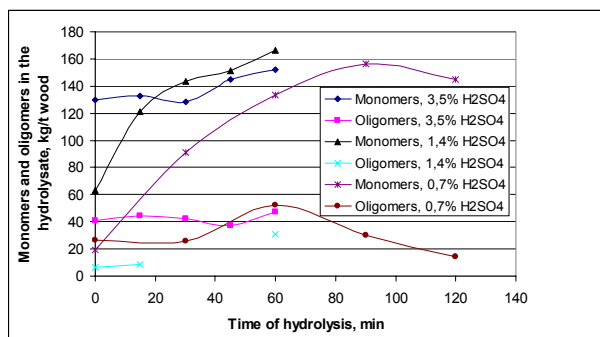


Figure 4: Formation of monomers and oligomers during acid hydrolysis at 160 °C with 0.7, 1.4 and 3.5% H₂SO₄

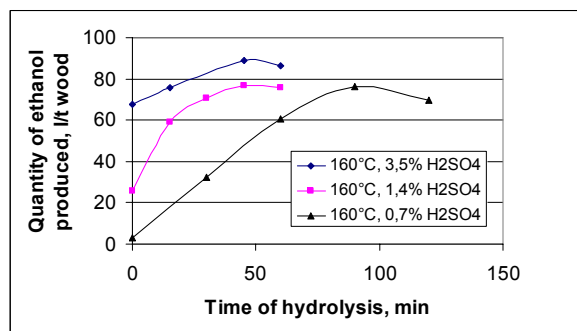


Figure 5: Fermentation of hydrolysates into ethanol

Table 1
Geometrical characteristics of polysaccharide nanocrystals from various sources: length (L) and diameter (D) of rod-like particles obtained from cellulose

Nature	Source	L (nm)	D (nm)	Ref.
Cellulose	Algal (<i>Valonia</i>)	> 1000	10-20	[16]
	Bacterial	100-several 1000	5-10 × 30-50	[17]
	<i>Cladophora</i>	-	20 × 20	[18]
	Cotton	100-300	5-10	[19]
	Cottonseed linter	170-490	40-60	[20]
	MCC	150-300	3-7	[21]
	Sisal	100-500	3-5	[22]

Sugar beet pulp	210	5	[23]
Tunicin	100-several 1000	10-20	[24]
Wheat straw	150-300	5	[25]
Wood	100-300	3-5	[26]

The outstanding properties observed for these systems were ascribed to a mechanical percolation phenomenon.²⁴ It was suspected that the whole stiffness of the material was due to infinite aggregates of cellulose whiskers. Above the percolation threshold, the cellulosic nanoparticles can connect and form a tri-dimensional continuous pathway through the nanocomposite film. The formation of this cellulose network was assumed to result from the strong interactions between whiskers, such as the hydrogen bonds.²⁷ This phenomenon is similar to the high mechanical properties observed for a paper sheet, resulting from the hydrogen-bonding forces that hold the percolating network of fibres. This mechanical percolation effect allows explaining both the high reinforcing effect and the thermal stabilization of the composite modulus for evaporated films.

Any factor that affects the formation of the percolating whiskers network or interferes with it changes the mechanical performances of the composite.²⁸ Three main parameters were reported to affect the mechanical properties of such materials, namely the morphology and dimensions of nanoparticles, the processing method and the microstructure of the matrix and matrix/filler interactions.

Cellulose nanocrystals occur as rod-like nanoparticles. For rod-like particles, the geometrical aspect ratio is an important factor, since it determines the percolation threshold value. This factor is linked to the source of cellulose and to the preparation conditions of the whiskers, as illustrated in Table 2. Fillers with a high aspect ratio induce the best reinforcing effect. It can be seen that the cellulose from softwood or hardwood species gives an interesting result.

Table 2
Aspect ratios and percolation threshold for cellulose whiskers prepared from different sources

Sources	Whiskers			
	L (nm)	D (nm)	L/D	Percolation threshold (vol%)
Cotton	170	15	10	7
Flax	300	20	15	4.6
Sisal	250	4	60	1.1
Luffa	183	5	37	1.8
Sugar beet Pulp	210	5	42	1.3
Palm tree rachis	260	6	43	1.3
Palm tree foliol	180	6	30	2.3
Wheat straw	220	5	45	1.6
Hardwood	200	4	50	1.4
Softwood	200	4	50	1.4

CONCLUSIONS

At present, many developments are performed, for transforming the pulp mills into more complete biorefineries, aiming at producing a larger portfolio of bioproducts and bioenergies than what can be currently obtained in traditional mills. Among the different possibilities, our group focuses on extracting hemicelluloses prior to the process, to better exploit them. In the case of softwood species, the aim is to produce bio-ethanol; extracting hemicelluloses by acid hydrolysis yields mainly monomers and it was shown that the resulting hydrolysate can

be readily fermented into ethanol. The cooking ability of the resulting wood chips and the bleaching ability are under investigation.

One of the ways pursued is to develop the knowledge and applications on cellulose nanocrystals available from a variety of natural sources, such as wood or pulp, where they occur in various shapes and sizes. It was shown that polysaccharide nanocrystals reinforced polymer nanocomposites display outstanding mechanical properties, which recommends them for high-modulus thin films processing. The rich literature devoted

to polysaccharides, mainly cellulose, and to nanocrystals, is a clear indication of the interest in such applications.

To exploit their potential, research and development investments should be made in science and engineering that will fully determine the properties and characteristics of polysaccharides at nanoscale, to establish the technologies to manipulate self-assembly and multifunctionality, and to develop these new technologies up to the point in which industry can produce advanced and cost-competitive polysaccharide nanoscale products. Significant scientific and technological challenges are still to be taken up.

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