

Green chemistry: making wood chemicals profitable

by Patricia GUIRAUDIE

The transformation of the main constituents of wood makes it possible to obtain a large number of products for wide-ranging applications in different fields. In this article, the author presents the Biorafmed project whose objective is to set up a cluster of biorefineries facilitating the profitable use of bioresources in France's Provence-Alpes-Côte d'Azur Region.

Making the most out of wood: a great opportunity

Wood is an abundant resource capable of playing the major role in tackling present-day environmental issues and challenges and in the establishment of a bio-based economy. It is a renewable resource that offers a substitute for increasingly scarce fossil fuels whose prices are bound to rise. Wood can substitute in the fields of energy production, construction, producing chemical molecules —both new or similar to those obtained by the petrochemical industry— and in the production of new composite materials.

Wood is a first-rate choice in all undertakings with an ecological conception whose aim is to develop new products having little negative impact on the environment throughout their life cycle.

A reasoned exploitation of forests enables a country to maintain a carbon sink, thus helping to reduce the greenhouse effect by stocking CO₂.

1 - PIPAME report
« Current market for new
wood-based products and
evolution through to
2020 », 2012.

Wood and its main uses¹

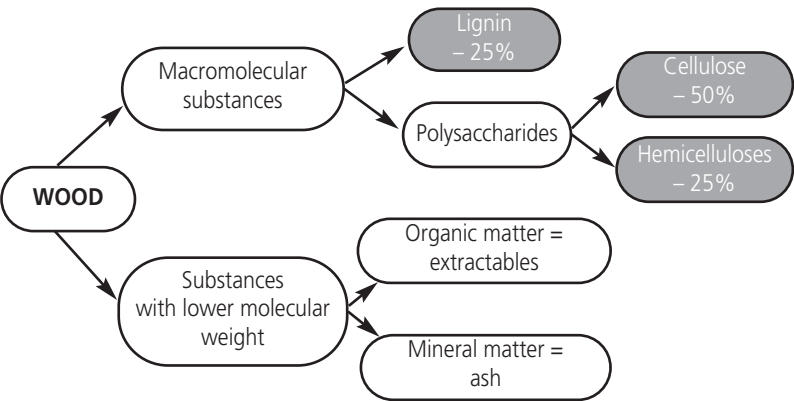
Wood is understood to mean a “tree” with all its constituent elements which include lignin, hemicellulose, resin, bark and leaves and, also, the by-products such as shavings and chips resulting from the transformation of wood.

The main sectors in which wood is used are:

- **saw wood**, including packaging in wood (pallets, light packaging, cooperage, industrial packing), fittings (domestic and professional), construction industry (building structure and roofing, openings and fittings, flooring and wall panels, exterior cladding, outdoor facilities). Also includes here are plywood and chipboard;
- **wood fibre**: this concerns essentially the paper industry. Uses are for printing (newsprint, finer and writing paper), wrapping and packing (corrugated, flexible and flat cardboard), domestic and health-related uses (sheeted sanitary articles, sanitary articles for wearing), industrial applications and special paper (bank notes, special printing, industrial applications). Wood fibre insulation can also be included under this heading;

Fig. 1 (below):
The different constituents
of wood.
Source : Alcimed,
following Laval University.

Fig. 2 (below) :
The various intermediate
products from
transforming wood
and their applications.
Source: Alcimed,
following PNNL-NREL,
2004.



Biomass	Intermediate stage	Building blocks	Secondary chemical substances	Intermediate products	Products/ uses
Cellulose Hemi-celluloses Lignin	Saccharides (glucose, arabinose, fructose...)	Sugars in C3, C4, C5, C6 which give: glycerol, furfural, xylitol, sorbitol...	Intermediate pharmaceutical derivatives	Solvents, resins, nylons, polycarbonates, etc	Transport, textiles, food industries, environment, communications, construction, entertainment, health, industry

- **composite materials** or “plastic wood”: these materials associate wood fibre with plastics;
- **wood chemicals** as raw material in the chemical production of new molecules; this aspect will be considered in detail below;
- **energy**: this is one of the oldest uses for wood. Wood as fuel can be divided into three categories: fuelwood directly from the forest (logs and chippings), products from the industrial use of wood (bark, chips, plaques, pellets) and fuel from waste treatment. Biofuel applications are sometimes classified here but we classify it under chemical wood.

Chemistry of wood

Wood is a mixture of three natural polymers: cellulose (fibres which bestow rigidity and texture to plants generally, including trees), hemicellulose and lignin (which favour the adherence of fibres to each other). Cellulose and hemicellulose are carbohydrate polymers (polysaccharides). Along with these constituents are other extractable mineral substances (small molecules concentrated in different degrees in certain parts of plants). The accompanying chart shows this make-up (see Fig. 1).

By transforming these constituents, chemistry makes it possible to obtain a large number of intermediate products that have applications in a wide range of fields (see Fig. 2).

Several methods of extraction are used to isolate the main constituents:

- **cellulose** is used profitably, essentially for paper and cardboard, while small quantities go into textiles and cosmetics;
- **lignin** is extracted from wood to form a black liquid mainly burnt as fuel to drive the papermaking process. But lignin can be recovered from this black liquid for use in aromas, resins and adhesives. It can also result in methanol, an additive in second-generation biofuels;
- **pharmaceutical industries**;
- **extractable substances** are numerous and varied with uses in several sectors including gemmes for the production of turpentine and colophan essence, tannin for the ageing of wine and for pharmaceuticals, terpenes for use in antiseptics and bactericides, polyphenols as antioxidants.

Other technology facilitates obtaining other products which constitute the principal intermediate stages in the chemical industry:

- **Gasification** enables wood to be transformed into a gas known as “synthetic gas” leading to methanol which is incorporated into biofuels;

- **Fermentation** which transforms polysaccharides into ethanol, also a biofuel constituent.

Some production processes combine these two processes.

Making profitable use of the chemistry of wood through the diversity of processes, either perfected or in the process of development, offers a wide range of opportunities.

The CRITT: Chemistry – Formulation – Materials Association of the Provence-Alpes-Côte d’Azur Region

The scope of this association, now 30 years old, is to contribute to regional economic development by providing back-up to regional companies in the field of chemistry and materials and, to this end, its tools are innovation, setting up networks allying companies and university research teams, the use of information and communications technology, export assistance and fostering social responsibility.

The CRITT has more than 200 member companies and 80 associated academic research groups. It is funded by the French Government, the Provence-Alpes-Côte d’Azur Regional Government Council and by the fees it charges its members. It has the status of a PRIDES –*Pôle Régional d’Innovation et développement économique solidaire*– accorded by the Region, and *Cellule de Diffusion Technologique* by the Ministry of Research and Higher Education.

CRITT and the wood sector

The Provence-Alpes-Côte d’Azur Region ranks second in France for forest resources. The Regional Government Council believes that such resources could be better exploited in order to foster economic development and job creation. It thus encourages all initia-

tives in this direction for the development of new products and markets.

The region’s forests are made up largely of coniferous species, especially Aleppo pine, but also larch. This last is used essentially by a regional pulp and paper plant, with timber only a small though increasing fraction. Projects for centralized heating facilities using wood could lead to its hugely profitable use for energy.

During a symposium organized by the CRITT on the topic of bio-based chemistry, a number of companies in the region showed an interest in bio-based products sourced from the wood sector. The CRITT has thus begun to explore this field, an initiative which has resulted in setting up the *Biorafmed* project

The Biorafmed project

The Biorafmed project (BIORAFfinerie en MEDiterranée, in French) was put together by the CRITT with the help of regional businesses, representatives of the central government, the Regional Government Council, various institutional bodies and academics. The project’s objective is: To set up in the PACA Region a cluster of biorefineries (industrial and/or demonstration facilities) permitting the handling of bioresources, regional whenever possible (specific cultivated crops, gathered plants, domestic waste, cultivated vegetable oil, used vegetable oil), otherwise imported, in order to make bioproducts (biofuel, products identical to those produced by the petrochemical

Picture 1:

Wood is a mixture of three natural polymers. Several methods of extraction are used to isolate the main constituents.

© DA



industry, products for new applications) matching the needs of the clientele (refineries, big chemical and pharmaceutical companies, SM-S businesses in the paint and varnish sector, hygiene and beauty products –detergents, cosmetics, aromas and perfumes, composite materials...).

The bioresources envisaged are not limited to the Aleppo pine but encompass a wide range:

- plants from agriculture and forestry: Aleppo pine, targeted plants (grown or waste/byproducts from other processes), mixed plants (from gathering), all both regional and imported (lively interest by the Marseille Port Authority – GPMM);

- domestic waste;

- vegetable oil (from crops and used oil);

without forgetting:

- dedicated crops such as acanthus, eucalyptus, sorgho;

- the possibility of incorporating biosourced products used in the formulation of polymers destined for the manufacture of composites (option for biorefinery residues);

- the likelihood of crops on landfill sites and solar panel farms.

Two types of biorefinery are possible:

- an industrial plant owned by a company which already runs an industrial process elsewhere and would like a regional base to benefit from location in the region and access to certain resources;

- a “show plant”, i.e. a semi-industrial pilot plant set up at the industrial hub (see below) to take advantage of local positives (qualified staff, energy, logistics, Seveso classification...) and the availability of competent academic research teams.

Possible set-ups include:

- an industrial hub consisting of a geographic network of a number of companies grouped within a legal framework enabling them to pool resources with the following key factors for success: competitive energy supply, competitive supply of raw materials with low-cost logistics, competitive fixed costs, basic chemistry integrated with specialised chemistry, proximity of R&D centres for process enhancement and development of new products. The legal framework permits the admission of new companies. Several hubs of this type already exist in the region. Industrial site developers are stakeholders in the project;

- a facility built at the site of a company

already using a considerable quantity of wood: pulp and paper mill, central heating unit.

Several university research teams in the region specialise in making the most out of bioresources.

A further bonus point is the existence of the major international port of Marseille which is well connected to road and rail networks, facilitating the importation of supplementary resources. The port authorities are particularly interested in this project.

We have studied with special attention the Aleppo pine in its regional context since, in our view, it is the resource offering the largest quantities.

The Aleppo pine in the region²

The biological growth of the Aleppo pine in the region is more than 500,000 m³/year but only 130,000 m³ are harvested annually. It is thus a resource that is vastly under-exploited.

Availability, in the light of accessible stands, is in the range of 270,000 m³/yr and could reach 450,000 m³ if a rational forestry operation was set up.

However, there are a number of obstacles to such an initiative:

- 80% of the forested area is privately owned and a third of all individual holdings are each less than 4 hectares;

- many abandoned plots near the coast and in the low hill country carry self-seeded Aleppo pine with the result that the landholders find themselves owners of woodland and forest without any such intention. Some owners would like to eradicate the species and introduce, for example, evergreen oak;

- Mediterranean forests, occupying land freed by the abandonment of agriculture, can be considered as young forests whose owners absolutely do not have a forester's turn of mind;

- the dominant mindset revolves around heritage and often results in keeping the land as it is with a view to passing it down in good state to the next generation: doing nothing appears as the best solution;

- in the Mediterranean context, the threat of wildfire provides additional grounds for refusing to fell any trees: after felling, the

2 - « *Le pin d'Alep en France* » Bernard Prévosto, publisher Quae, 2013.

residual branches and litter on the plots are seen as so much inflammable material which irrationally cause a mental, but very real, block to any thought of harvesting;

- various legislation –forestry, environmental and linked to urban development—must be taken into account;

- elected officers at the head of forest municipalities are often faced with conflicting demands by their residents and, more generally, by those frequenting the forests:

- * hunters of woodcock want to stalk in adult stands with low undergrowth;

- * walkers want shade and prefer cleared ground underfoot;

- * naturalists want an interwoven mix of open and closed habitats favourable to biodiversity or, otherwise, would like to see forests left to age naturally with no intervention by man;

- * local residents, used to the surrounding landscape, don't want to see it modified;

- * mushroom gatherers take a dim view of disturbance of the soil by forestry vehicles;

- little by little, traditional forestry has given up on timber production and turned to providing areas for leisure pursuits;

- low profits at present from wood: actual income, on the basis of current rates between €6 and €8/m³, is between €20 and 25€/hectare/year. Some forest owners with a forestry background deplore the failure to make profit from “noble” timber products: most saw wood goes to the pulp mill.

Land managers and owners complain about the damage to tracks and to unculled trees as well as about payment and the difficulty of finding out exactly what has been sold.

To sum up, many owners consider that the income is too low to compensate for the bother it brings.

Even so, there are possible solutions to overcome the obstacles; they are beginning to make their impact:

- informing and educating owners and, indeed, the general public: felling can be compatible with maintaining biodiversity; the resource is renewable within the framework of sustainable management; forestry management has a positive impact on the prevention of wildfire;

- approach landowners via themes that motivate them: initially not felling trees but, indirectly, this can subsequently ensue;



- obtain a better understanding of the territory involved by setting up massif-wide development plans and a strategy for tackling the issues and challenges;

- foster concertation whenever improvement plans are drawn up for municipal forests;

- set up umbrella associations to regroup private landowners with scattered holdings and ensure their management without circumscribing property rights. To this end, design measures to foster owner interest and provide back-up to their umbrella organisations;

- simplify paperwork;

- improve the quality of subcontractor work and train their staff;

- enhance the profitable use of forest products: wood chemicals is one line to pursue, particularly because it involves multiple processes and can fit in with various other kinds of profitable use by using the by-products of already-existing operations.

The profitable use of wood chemicals, by virtue of its modular nature, its adaptability and, also, the added value from the products, guarantees a reasoned, economically viable use of the forests' resources.

Such an economic model must rely on a well-structured wood sector that acts as the driving force in its development. Now is the time to seize the main chance

Picture 2:

Felling an Aleppo pine stand (Bouches-du-Rhône area, France).

« Wood for chemicals can combine numerous processes and fit in with diverse types of profitable exploitation through the use of the by-products from existing activities ».

© DA

Patricia GUIRAUDIE,
Director, Regional
Centre for Innovation
and Technology
Transfer in the
Chemistry of
Composite Materials,
Provence-Alpes-Côte
d'Azur Region (France)
CRITT

Immeuble CMCI
2 rue Henri Barbusse
13241 Marseille
cedex 1
FRANCE
Email :
patricia.guiraudie@
critchimie.fr

P.G.

Summary

Wood is a renewable resource in big quantities which can provide a response to the issues and challenges involved in sustainable chemistry and, more generally, in sustainable development. It has a wide range of uses: as timber and saw wood, fibre products, composite materials, a source of chemicals, energy. By transforming its three main constituents, cellulose, hemicellulose and lignin, numerous other products become available for application in many important fields. In addition, certain minor constituents can be extracted for various uses. The CRITT – Chimie – Formulation – Matériaux is an association which provides development support and backup to regional businesses in the chemicals and materials sector. The Provence-Alpes-Côte d'Azur region (S.-E. France) is very interested in the wood resource of which it has big quantities. The CRITT has launched the Biorafmed project whose objective is setting up a cluster of biorefineries to make profitable use of biological resources. Such biorefineries can be built on the numerous industrial sites in the region. The Aleppo pine is the region's main silvicultural resource. Big quantities are available but its management is hindered by numerous obstacles. Even so, solutions do exist and action is under way to remedy the situation.

Résumé

Le bois est une ressource renouvelable importante en volume qui peut répondre aux enjeux d'une chimie durable et plus largement du développement durable. Ses utilisations sont très variées : le bois massif, le bois fibre, les matériaux composites, le bois chimie et le bois énergie

Par la transformation de ses trois composants principaux : la cellulose, les hémicelluloses et la lignine, on peut accéder à de nombreux produits qui trouvent leurs applications dans un nombre important de domaines. En outre, certains composants minoritaires peuvent être extraits pour des usages divers.

Le CRITT Chimie-Formulation-Matériaux est une association qui accompagne les entreprises régionales de la filière chimie et matériaux dans leur développement économique. La région Provence-Alpes-Côte d'Azur s'intéresse de près à la ressource régionale bois qui est importante.

Le CRITT a lancé le projet Biorafmed dont l'objectif est de mettre en place un cluster de bioraffineries permettant de valoriser des bioressources. Ces bioraffineries pourraient être accueillies sur de nombreux sites industriels régionaux.

Le pin d'Alep est la principale ressource sylvicole régionale. Sa disponibilité est importante mais sa gestion se heurte à de nombreux obstacles. Toutefois, des solutions existent et des actions sont en cours pour remédier à cette situation.

Resumen

Química verde: hacia una valoración química de la madera

La madera es un recurso renovable importante en volumen, que puede afrontar los retos de una química sostenible y, de modo más general, de un desarrollo sostenible. Sus usos son muy variados: madera maciza, fibra de madera, materiales compuestos, química de la madera, y biomasa.

Por la transformación de sus tres componentes principales: celulosa, hemicelulosa y lignina, se puede acceder a muchos productos que tienen aplicaciones en un gran número de ámbitos. Además, ciertos componentes minoritarios pueden ser extraídos para distintos usos.

La CRITT Chimie-Formulation-Matériaux es una asociación que acompaña a las empresas regionales del área de la química y los materiales en su desarrollo económico. La región Provenza-Alpes-Costa Azul está muy interesada en los recursos de madera regionales, que son muy importantes.

La CRITT puso en marcha el proyecto Biorafmed, que tiene por objetivo la creación de un grupo de biorrefinerías que permiten valorizar los recursos biológicos. Estas bio-refinerías podrían situarse en numerosos lugares industriales regionales.

El pino carrasco es el principal recurso silvícola regional. Su disponibilidad es importante, pero su gestión se enfrenta a muchos obstáculos. Sin embargo, existen soluciones y se están llevando a cabo acciones para remediar esta situación.