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## Use of vegetal biomass for biofuels and bioenergy. Competition with the production of bioproducts and materials?



*L'utilisation de la biomasse végétale pour la production de biocarburants et de bioénergie. En compétition avec la production de bioproducts et de matériaux ?*

Christine Chirat

University of Grenoble Alpes, LGP2, CNRS, Grenoble INP-Pagora, 38000 Grenoble, France

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## ABSTRACT

The total European bioeconomy represents 2.1 trillion euros turnover. It includes the food, feed and beverages sectors that are responsible for about half of the turnover. The bio-based industries – chemicals and plastics, pharmaceuticals, paper and paper products, forest-based industries, textile sector, biofuels, and bioenergy – contribute with 600 billion euros and 3.2 million employees. This paper will first give key figures for fossil fuel versus vegetal biomass stocks and production. The chemical composition of vegetal biomass will be described in a second part, and compared with fossil raw material. The use of vegetal biomass for energy will then be discussed, with a focus on the production of biofuels. The last part will give examples of bioproducts that could be obtained from wood in biorefineries integrated into the cellulose fiber industry.

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## R É S U M É

La bioéconomie européenne représente un chiffre d'affaires de deux mille cent milliards d'euros. Elle inclut les secteurs de l'alimentation humaine et animale. Les industries dites « basées sur le végétal », qui fabriquent des produits chimiques, des plastiques, des produits pharmaceutiques, du papier et ses produits dérivés, l'industrie de la forêt, le secteur des textiles, les biocarburants et la bioénergie y contribuent pour 600 milliards d'euros et 3,2 millions d'emplois. Cet article compare le pétrole et la biomasse végétale en termes d'extraction, de gisement et de composition chimique. L'utilisation de la biomasse végétale pour la production d'énergie est ensuite présentée, en détaillant la production de biocarburants. La dernière partie donne des exemples de bioproducts qui pourraient être

E-mail address: [Christine.Chirat@pagora.grenoble-inp.fr](mailto:Christine.Chirat@pagora.grenoble-inp.fr).

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obtenus dans des bioraffineries lignocellulosiques (à base de bois) intégrées à la production de fibres de cellulose.

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## 1. Introduction

A recent study evaluated the key figures for the bioeconomy in Europe in 2013 [1]. The total European Bioeconomy (the EU-28) amounted to 2.1 trillion euros turnover and 18,3 million employees. It includes the food, feed, and beverages sectors, which are responsible for roughly half of the turnover. The bio-based industries – chemicals and plastics, pharmaceuticals, paper and paper products, forest-based industries, textile sector, biofuels, and bioenergy – contributed with 600 billion euros (28.6% of total turnover in the European bioeconomy) and 3.2 million employees. Bioenergy and biofuels accounted respectively for 4 and 0,6% of the total turnover, and 1 and 0,2% of the total employees. The bio-based industry is thus already an important part of the European economy.

The objectives of this paper are to give key figures for fossil fuels versus vegetal biomass stocks and production. The chemical composition of vegetal biomass will be described in a second part, and compared with fossil raw material. The use of vegetal biomass for energy will then be discussed, with a focus on the production of biofuels. The last part will give examples of bioproducts that could be obtained from wood in an integrated lignocellulosic biorefinery and that are currently under development.

## 2. Key figures. Oil versus vegetal biomass

The consumption of crude oil in 2015 was 4.33 billion tons worldwide, to be compared to 2.98 billion in 1973 [2]. In January 2016, the proven crude oil stocks were 225.95 billion tons, which represents about 52 years of exploitation if one assumes that the annual consumption stays at the 2015 pace. About 10% of crude oil is used for petrochemistry to produce plastics, textiles, detergents, adhesives... Two sectors rely today most exclusively on crude oil: transportation (fuels) and organic products (mainly plastics).

Most of vegetal biomass is forest and it covers about 30% of land. The forest stock in 2015 was 531 billion m<sup>3</sup> spread on 4.00 billion hectares (it was 4.13 in 1990). Wood removals by human activity in 2015 were 2.99 billion m<sup>3</sup> (2.72 in 1990) (60% for energy, 40% for the industry) [3].

Even though most of vegetal biomass on earth comes from the forest, the estimated global biomass used by man in 2011 (11,4 billion tons of dry material) for food, feed, energy, and material was supplied first by agriculture (harvested agriculture biomass (40%), grazed biomass (31%) and harvest residue (12%)) and then by wood (18%, 2.12 billion dry tons). This biomass was used in the following sectors: feed (58%), bioenergy (16%), plant based food (14%), material use (10%) and biofuels (1%) [4].

A recent study detailed different scenarios of biomass supply and demand in Europe (EU27) and in the world until 2050, compared to the situation in 2011 [4]. The range of worldwide biomass supply in 2050 based on these scenarios would be between 12.4 and 25.2 billion tons of dry matter (wood supply would go from about 2 to about 8 billion tons of dry matter). The “low” scenario would just be able to cover the demand for food and feed, only part of the demand for materials and bioenergy and no demand for biofuels. The “business-as-usual case”, which is intermediate (about 18 billion tons of dry matter including about 5 billion tons of wood), would cover the demand for food, feed, materials, and bioenergy, and could enable an expansion of biofuels of up to 1 billion tons of dry matter of biomass. However, only the “low” supply scenario may be considered to be sustainable when one considers maintaining biodiversity. It is thus not easy to predict how much more vegetal biomass, and particularly wood, will be available in a sustainable way to increase the production of bioenergy, biofuels, biomaterials, and biochemicals. It is doubtful that vegetal biomass will be able to replace all the fossil fuel production.

## 3. Oil versus vegetal biomass chemical composition

Crude oil is mainly composed of hydrocarbon chains containing only carbon and hydrogen atoms (C<sub>n</sub>H<sub>2n+2</sub>), which is distilled to obtain different fractions used mainly as fuels. One fraction, called naphtha, containing molecules bearing between 4 and 8 carbons, is used for petrochemistry. It is cracked at very high temperatures in the presence of steam to obtain smaller molecules and introduce carbon-carbon double bonds. Catalytic reforming can also be applied to obtain aromatic compounds. These processes lead to the main intermediates used in petrochemistry: ethylene (C<sub>2</sub>H<sub>2</sub>), propylene (C<sub>3</sub>H<sub>6</sub>), butadiene (C<sub>4</sub>H<sub>6</sub>), benzene (C<sub>6</sub>H<sub>6</sub>), toluene (C<sub>6</sub>H<sub>5</sub>-CH<sub>3</sub>), styrene (C<sub>8</sub>H<sub>8</sub>), xylenes... The four latter are represented in Fig. 1, they belong to the family of aromatic compounds.

Wood, which is the dominant vegetal biomass on earth, is composed of up to 60–70% of polysaccharides (cellulose and hemicelluloses), and 20–30% of lignin. Cellulose, which represents 40 to 45% of wood (Fig. 2), is a linear polymer of β-glucose, its degree of polymerization (DP) can reach 10000 in wood. Hemicelluloses are heteropolymers of much

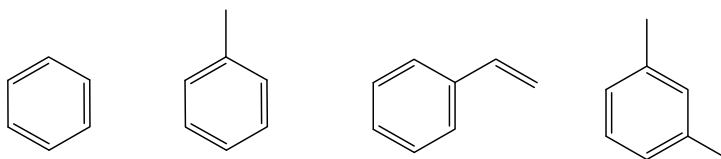


Fig. 1. Examples of aromatic compounds produced from naphtha. From left to right: benzene, toluene, styrene, and meta-xylene.

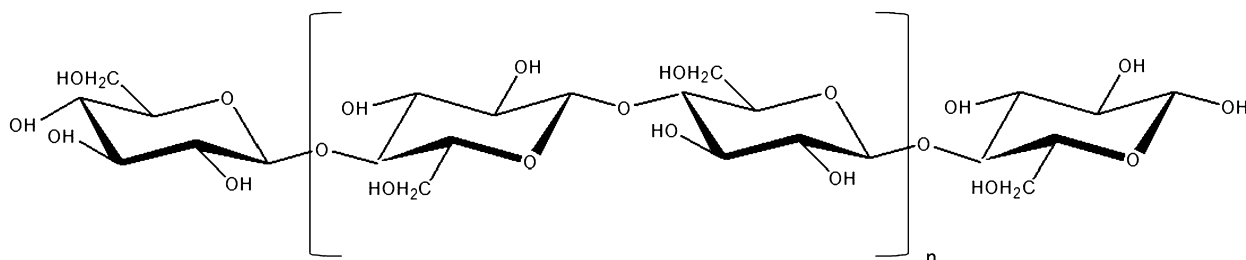


Fig. 2. Cellulose molecule.

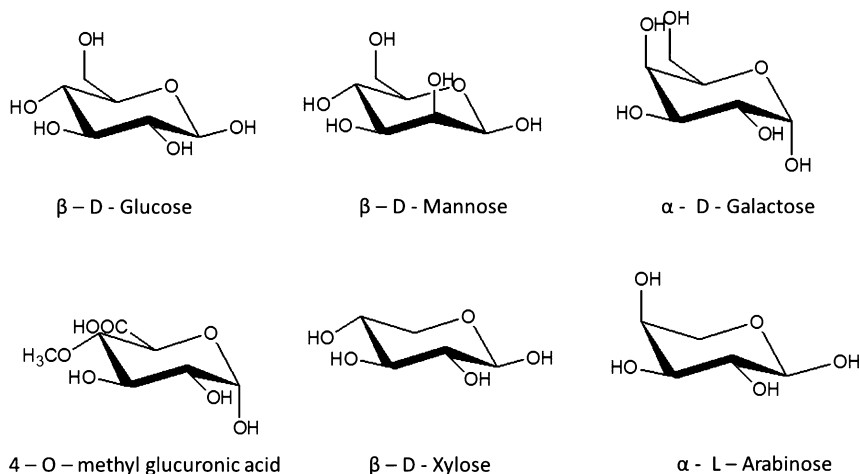


Fig. 3. Main sugars constituting hemicelluloses in wood.

smaller sizes (DP of about 100–200 in wood) composed of hexoses (mannose, glucose, galactose) and pentoses (xylose and arabinose). They can be partly acetylated and contain lateral groups such as 4-O-methyl glucuronic acid groups. Their nature and quantities are specific to the species: for example, softwood species hemicelluloses are mainly galactoglucomannans, whereas hardwood species contain mainly xylans. The main sugars constituting wood hemicelluloses are represented in Fig. 3.

Lignin is the second component of wood, accounting for 20 to 30% of wood dry weight. It is a complex polymer composed of phenyl propane units linked together by ether or by carbon–carbon bonds (Fig. 4). It is the only polymer available in big quantities in nature that could provide aromatic compounds to replace those produced by petrochemistry, provided that efficient ways to hydrolyze the different bonds in lignin are found.

Extractives represent the third family of components: they account for only a few percents of wood weight, but are composed of hundreds of different molecules. Among them can be found hydrolysable and condensed tannins, terpenes, resinic acids, fats, and waxes.

To conclude, the major difference between oil and vegetal biomass is that only carbon and hydrogen atoms are found in petrol, whereas vegetal biomass is mostly composed of molecules containing carbon, hydrogen, and oxygen atoms. The cracking of vegetal biomass will thus yield different and higher number of molecules than those obtained from petrol. The second difference is the high diversity of molecules, mainly polymers, which are constituting wood. Their separation will be rather difficult, as they are all intimately mixed within the wood cells.

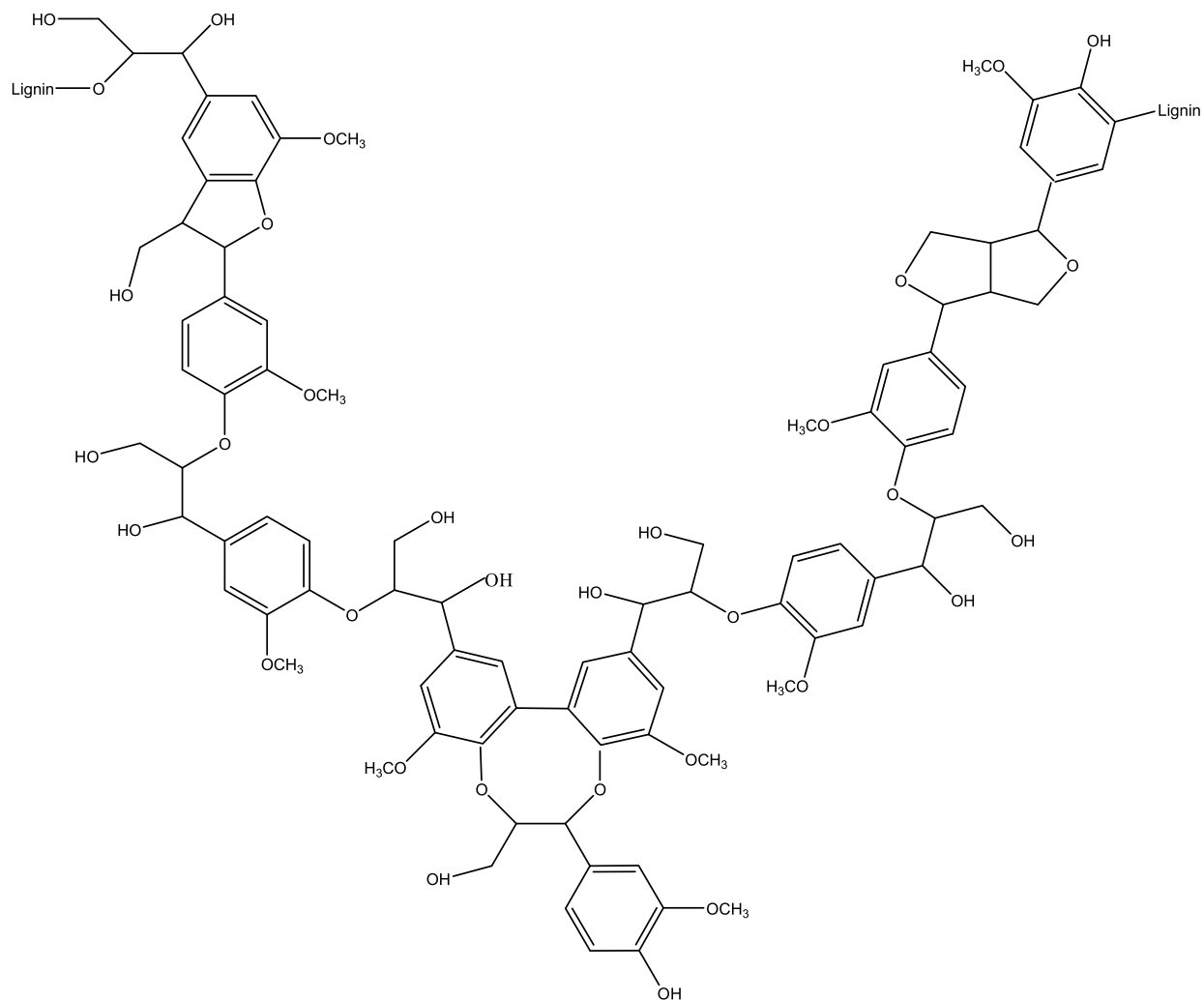


Fig. 4. Proposed structure of softwood lignin, adapted from [9].

#### 4. Use of vegetal biomass for energy – example of biofuels

In 2014, the world's Total Primary Energy Supply (TPES) was 13,700 Mtoe (tons of oil equivalent), of which 13.8%, or 1,894 Mtoe, was produced from renewable energy sources. The major part comes from biomass, representing 72.8% of renewable energy sources: solid biofuels/charcoal is by far the largest renewable energy (66.2% of global renewables supply), then liquid biofuels (4.1%), biogases (1.6%), and renewable municipal wastes (0.8%). The other renewable sources are hydro (17.7%), geothermal (3.8%), wind (3.3%) and solar/tide (2.5%) energies [5].

Fig. 5 presents different ways that can be used to produce energy from biomass. As far as liquid biofuels are concerned, they are mainly first-generation biofuels, which means that they use edible part of plants [6]. In the case of bioethanol, saccharose (from sugar beet or sugar cane) or starch (from maize and wheat) are used as raw material. Saccharose (which is a dimer composed of glucose and fructose) can be fermented directly to ethanol using the common baker's yeast (*Saccharomyces cerevisiae*), whereas starch, which is a polymer of  $\alpha$ -glucose, first needs to be depolymerized into glucose using an enzymatic treatment, and then glucose is fermented into ethanol.

Biodiesel is the second type of biofuel, produced from vegetal oil (e.g. rapeseed, sunflower): fatty acid methyl esters are produced by reacting vegetal oil with methanol, glycerol being the by-product of the reaction. Hydrogenation of vegetal oil is another process that can be used to produce biodiesel [7].

In 2015, the production of bioethanol was 115.6 billion liters [6]. About 53% of it came from maize, 26% from sugar plants (sugar cane and sugar beet), 7.5% from molasses, only a few percent from wheat, and less than 1% from lignocellulosic biomass (wood, agriculture residues). The forecast is 128.4 billion liters by 2025, 51% coming from maize, 28% from sugar plants, 8% from molasses and still less than 1% from lignocellulosic plants. Biodiesel production was 31.1 billion liters in 2015 and should increase by 33% since 2025 to 41.4 billion liters. A little more than 80% of biodiesel is produced from vegetal

### Several ways to produce energy/biofuels from biomass

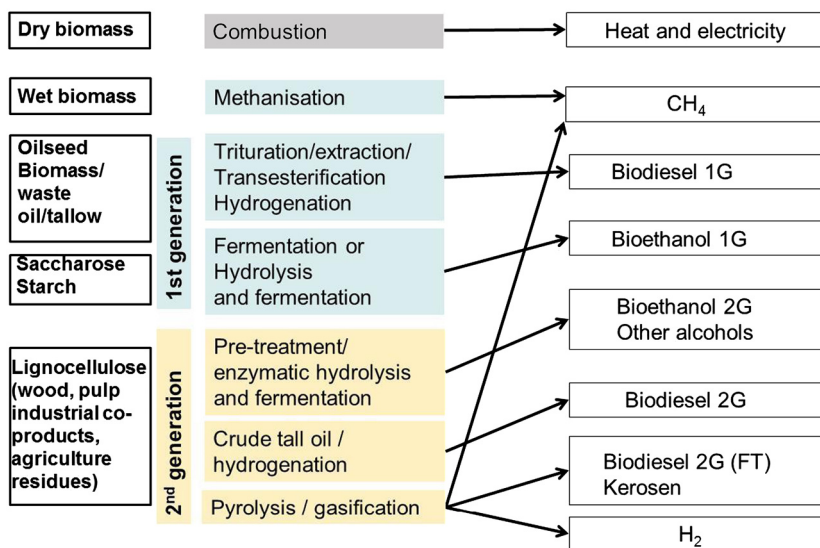


Fig. 5. Different current ways to produce energy and biofuels from biomass.

oil, this percentage will be about 72% in 2025. The use of other sources like waste oil and tallow to produce biodiesel will increase from 15% in 2015 to almost 25% in 2025. The % coming from lignocellulosic biomass is very small today and will be less than 0.5% in 2025 [6].

Wood contains a few percent extractives, among which fats (ester between glycerol and fatty acid) and waxes (esters between fatty alcohols and fatty acids). Part of these extractives are recovered in pulp mills that are treating wood with a chemical process, the kraft process, to extract cellulose fibers for paper and board production. These recovered fatty acids and fatty alcohols are contained in crude tall oil (CTO). This CTO has started to be used to produce biodiesel of second generation in 2011 in Sweden (SunPine company) and in 2015 in Finland by the UPM company. Its production process requires a final refinery process step including a hydrogenation treatment that converts the CTO to biodiesel by removing oxygen. Then a fractionation unit removes hydrogen sulfide and incondensable gases. The remaining liquid fraction is distilled to separate biodiesel. About 230 000 tons of CTO is used to produce biofuels [7,8]. This is an illustration of the competition of usage of biomass: indeed, CTO has been used for decades by the chemical industry for the production of chemical compounds (fatty acids, fatty alcohols, sterols...), and now it is also used for the production of second-generation biodiesel. The competition is not necessarily fair, as the production of biofuels is subsidized in some countries, which is not the case when bioproducts are produced.

Even though second-generation biofuels start to be produced, they still represent only a very small part of biofuels. There will certainly be a strong competition of usage of wood and other lignocellulosic raw material (agriculture residue) to produce material and bioproducts versus the production of biofuels.

### 5. Bioproducts and biomaterials that can be obtained from wood in an integrated lignocellulosic biorefinery

IEA (International Energy Agency) Bioenergy Task 42 “Biorefining” has formulated the following definition for a biorefinery: “Biorefining is the sustainable processing of biomass into a spectrum of bio-based products (food, feed, chemicals, materials) and bioenergy (biofuels, power and/or heat)” [10].

The industry of cellulose production from wood has been working as a biorefinery for more than 100 years. It is today the main industrial actor in wood chemistry, as it produces about 140 million tons per year of cellulose fibers from wood worldwide (1.5 million tons per year in France). Wood is converted into paper pulp (cellulose fibers) by the Kraft process for about 95% of the production (Fig. 6). The kraft process is using caustic soda (NaOH) and sodium sulfide (Na<sub>2</sub>S) at a pH close to 14 at 160 °C for 2 h to fractionate wood. Cellulose fibers are the main product and most of the hemicelluloses end up with lignin in the effluent of the Kraft process, called the black liquor, which is burnt, ensuring the energy autonomy of the mill. Most mills even have an excess of energy and sell green electricity. In some mills, part of the extractives is recovered and sold to the chemical industry or are used to produce biofuel as described in the previous part: volatile compounds like terpenes end up as turpentine and tall oil contains resinic acids, fatty alcohols, fatty acids, and sterols.

Cellulose has many applications: traditional applications in paper and board, production of textile (viscose and lyocell fibers), which is a market that is currently growing because of the stagnation of cotton production, cellulose derivatives (cellulose esters and ethers), and new applications in the area of nanocellulose [11].

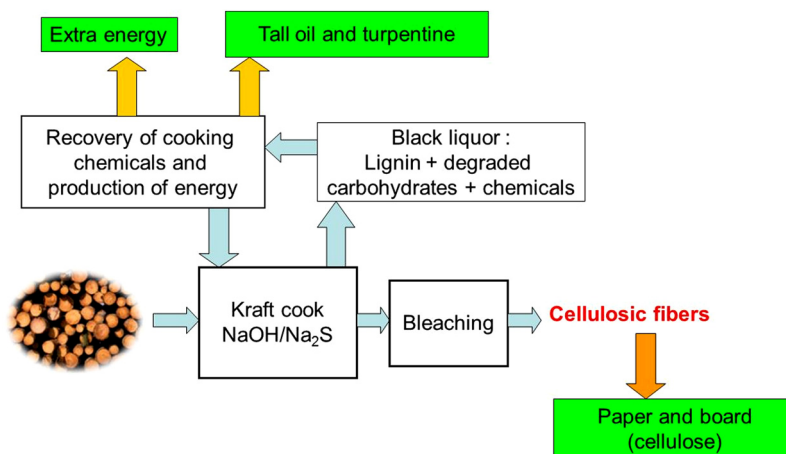


Fig. 6. Current pulp mill: cellulose is extracted and valorized as paper. Hemicelluloses and lignin are burnt to produce energy.

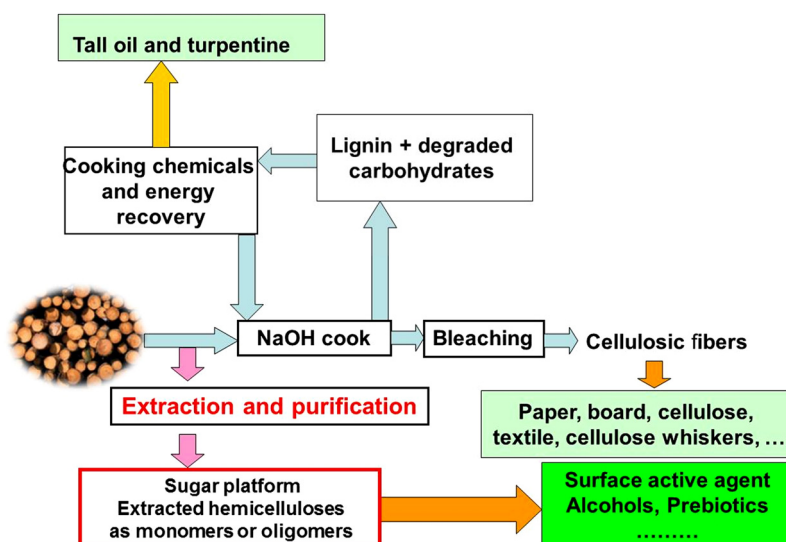
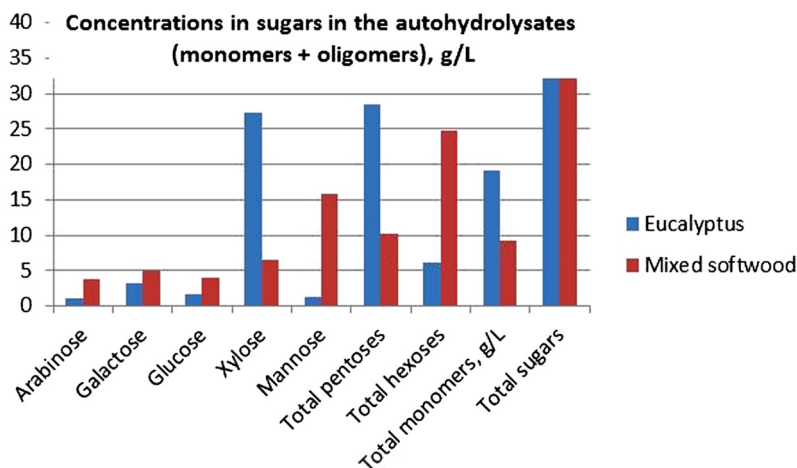


Fig. 7. Lignocellulosic biorefinery integrated in a pulp mill: sugar platform integrated in a pulp mill to produce surface active agents, alcohols, prebiotics...

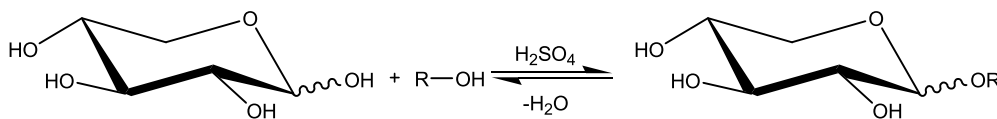
The heating value of hemicelluloses is much lower than that of lignin (13.6 MJ/kg compared to 27.0 MJ/kg, [12]), therefore higher added-value products should be developed from hemicelluloses to ensure additional revenues to this industry, without affecting the energetic balance of the mill.

The approach studied is to extract hemicellulose from wood, prior to kraft pulping, by an autohydrolysis process (Fig. 7) [13]. This is a very green process: wood is heated with water to 150–170 °C, leading to the hydrolysis of the acetyl groups present in hemicelluloses, which decreases the pH and leads to subsequent hydrolysis and solubilization of hemicelluloses. The resulting hydrolysate is composed of sugar monomers, sugar oligomers, organic acids, sugar degradation products (like furfural and hydroxymethylfurfural), and a little amount of solubilized lignin. Depending on the wood source, the hydrolysate is richer in pentoses (case of hardwood species) or in hexoses (case of softwood species), as illustrated by the results given in Fig. 8. The quantities of sugar and the proportion of monomers to oligomers vary with the parameters of autohydrolysis [13]. Not only wood could provide huge amounts of sugars that are currently not, or scarcely, available on the market (xylose, mannose, arabinose), but most importantly, these sugars would be of “non-food” origin.

Several research projects have been done and are on-going to valorize the hemicelluloses sugars extracted with an autohydrolysis. If the wood species is a softwood, the autohydrolysate is rich in hexoses and can be easily fermented into ethanol or other alcohols [14]. Another study has shown that hardwood autohydrolysate rich in pentoses monomers and oligomers can be used to produce a new family of green surfactants (alkylpolyxylosides, Fig. 9) from wood hemicelluloses, which could represent an interesting alternative to the alkylpolyglucosides currently produced from glucose originating from starch (and thus from food origin) [15]. Another application, i.e. the use of wood hemicelluloses as prebiotics, is currently evaluated [16].



**Fig. 8.** Concentration in different sugars of hydrolysates produced from *Eucalyptus globulus* and mixed softwood species. Autohydrolysis conditions: 160 °C, 2 h, liquor/wood ratio = 4.



**Fig. 9.** Alkylpolyxyloside produced from xylose.

## 6. Conclusions

Wood can provide very interesting molecules and polymers (cellulose and the sugar platform from hemicelluloses) that should first be used for their unique properties, before considering burning them or transforming them into biofuels. Once the interesting molecules and polymers are extracted, the residues could then be used to produce energy and biofuels, which would fit very well with the definition of a biorefinery. It is especially the case for lignin, for which no real high-added-value application has been found so far, and which represents up to 30% of wood.

## Acknowledgements

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