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INFLUENCE OF THE CHEMICAL PROPERTIES OF BIOMASS ON THE USE AS BIOFUEL

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Abstract: Currently, the most widespread form of renewable energy is biomass, and its research is continuously increasing due to concerns about the major impacts of fossil fuel consumption, namely global warming, climate change, and the impact they have on people's lives. In the current context, emphasis is placed on the global status of biomass compared to other renewable energies. This paper is a brief introduction to biomass, in particular the chemical properties of lignin, cellulose and hemicellulose and the production of biofuels from them.

Keywords: biofuels, biomass, lignin, cellulose, hemicellulose

1. INTRODUCTION

Our planet stores a large amount of biomass that is available both in forest areas and oceans. After some studies it was concluded that the total terrestrial biomass reserves are about 1.8 trillion tons, and the aquatic ones are about 4 billion tons. Also, from an energy point of view, the total amount of biomass worldwide has a potential production capacity of 33,000 EJ, which corresponds to more than 80 times the world's annual energy consumption. According to Chum, biomass, at the moment, is not exploited to the maximum, it represents only 14% of the primary energy in the world, standing at approximately 56 million TJ/year (Chum et al., 2011).

Kaltschmitt classifies biomass sources as follows (Kaltschmitt, 2013):

- Animal residues;
- Industrial residues;
- Animal residues;
- Municipal solid waste;
- Forestry residues;
- Sewage.

The structure of biomass fuels is related to many physical forms, but for plant species, the main structural components of cell walls are almost always cellulose, hemicellulose and lignin (Jaya Shankar et al., 2010).

The polymer in the largest quantity found on Earth is cellulose, and its abundance makes it the most common organic compound. The annual synthesis of cellulose generated by plants is approximately 10^{12} tons. The cellulose content of plants is approximately 33%, wood contains around 50% cellulose, and cotton contains 90% cellulose. The largest amount of cellulose is used in paper production, more precisely around 10^8 tons of cellulose produced annually, of which only 4 million tons are used annually for subsequent chemical processing (Granström M., 2009).

The composition of wood was first recognized by Anselme Payen (1838) who referred to a carbon-rich substance as the "inlay material" that incorporated cellulose into wood. In 1865, Anselme defined this material as lignin, which he characterized as a three-dimensional network polymer made up of distinctly linked phenylpropane units. After cellulose, lignin is the second most abundant biological material found on Earth, comprising 15–25% of the dry weight of woody plants. Lignin plays an essential role in providing mechanical support for the binding of plant fibres, helps to slow down the process of water penetration through the xylem cell walls, provides the plant with the ability to defend itself against degradation by preventing the penetration of destructive enzymes through the cell wall (http://biorefinery.utk.edu/technical_reviews/Lignin%20Overview.pdf).

Hemicelluloses constitute roughly one-third of the wall biomass and encompass the heteromannans, xyloglucan, heteroxylans, and mixed-linkage glucan. The fine structure of these polysaccharides, particularly their substitution, varies depending on the plant species and tissue type. The hemicelluloses are used in numerous industrial applications such as food additives as well as in medicinal applications. Their abundance in lignocellulosic feed-stocks should not be overlooked, if the utilization of this renewable resource for fuels and other commodity chemicals becomes a reality (Markus P. et al., 2013).

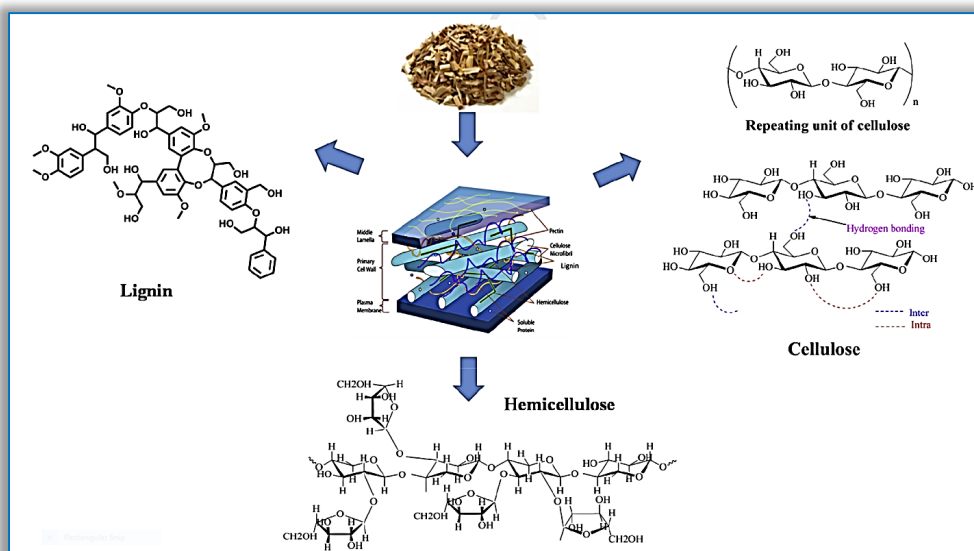


Figure 1 – The distribution and structure of cellulose, hemicellulose, and lignin in biomass (Adarsh Kumar et al., 2019)

Cellulose, lignin and hemicellulose are linked together in a heteromatrix with different degrees and different comparative composition, so the structure and quantity of the biomass constituents varies depending on the species, tissues and maturity of the plants (Adarsh Kumar et al., 2019).

Table 1. Cellulose, hemicellulose and lignin content in different biomass (Adarsh Kumar et al., 2019)

Biomass Feedstock	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Hardwoods	40.50–56	24–40	18–25
Softwoods	46–52	25–35	25–35
Grasses	24–41	35–50	10–30
Wheat straw	34–39	20–25	15–20
Switch grass	31–51	10–40	5–20
Sugarcane bagasse	19.60–26	32–48	23–32
Miscanthus	24.50	44.20	17.10
Leaves	15.51–20	80.4–85.3	0–0.50
Bamboo	25–43	15–27	20–31
Jute fiber	43–53	18–22	21–28
Industrial waste paper	60–71	11–20	5.55–10
Banana waste	13.32	14.68	14
Sunflower shell	488.43	33.90	16.99

2. MATERIALS AND METHODS

Different types of bonds are found in cellulose, lignin and hemicellulose. Cellulose fibers are full of hemicellulose and lignin. In principle, a hydrogen bond connects the cellulose and the lignin or hemicellulose molecules. Also, chemical bonds are found between lignin and hemicellulose together with hydrogen bonds. Chemical bonds are usually present between the galactose and arabinose units on the lignin and hemicellulose side chains. In table 2, the links between cellulose, hemicellulose and lignin, chemical composition and structure are listed (Adarsh Kumar et al., 2019).

Table 2. Structure and chemical composition of cellulose, hemicellulose, and lignin in plant cell walls (Xu F. et al., 2005, Chum H. et al., 2011)

Compositional element	Subunits	Subunits bonds	Composition	Polymer
Cellulose	D–Pyranoglucose units	β –1,4–Glycosidic bonds	β –Glucan	Several hundred to tens of thousands
Hemicellulose	D–Xylose, mannose, L–arabinose, galactose, glucuronic acid	β –1,4–Glycosidic bonds in main chains; β –1,2–, β –1,3–, β –1,6– glycosidic bonds in side chains	Polyxylose Galactoglucomannan (Gal–Glu–Man) Glucomannan (Glu–Man)	Less than 200
Hemicellulose	Guaiacylpropane (G), syringylpropane (S), p–hydroxyphenylpropane (H)	Various ether bonds (mainly β –O–4); carbon–carbon bond	G lignin, GS lignin, GSH lignin	4,000

— The chemical properties of cellulose

Cellulose, a linear polymer, is a complex carbohydrate (or polysaccharide) with a high molecular weight and a maximum of 10,000 monomeric units of D–glucose, linked by β –1,4–glycosidic bonds. The molecular formula of cellulose is $(C_6H_{12}O_6)_n$, where n is the degree of polymerization. The alternation of crystalline and

amorphous regions of cellulose could affect the accessibility of its functional groups, which are involved in reactions. In fact, the reactivity of cellulose depends on the reactivity of its primary and secondary hydroxyl groups, which emerge from the glycosidic rings. In particular, primary hydroxyl groups have higher reactivity than secondary ones due to lower steric hindrance. X-ray diffraction studies have shown that cellulose macromolecules in their crystal structure have a regular and ordered arrangement, resulting in a dense of 1.588 g/cm³. In contrast, in the amorphous regions, there are larger distances between the molecular chains due to the wide and irregular arrangement of the macromolecules, and as a result, the density of cellulose in the amorphous regions is lower, i.e. 1.5 g/cm³. Most of the time, the percentage of crystalline structure in cellulose varies between 30–80% (Antonio Tursi, 2019).

Cellulose also has the following chemical properties:

- usually, cellulose is a macromolecule with a very variable degree of polymerization;
- cellulose macromolecules are filiform in some parallel oriented regions (crystallite regions); in other regions they are interlaced, with gaps between them (amorphous regions).

This explains the high resistance of the cellulose threads, as well as the much lower joining power than in the case of starch, which is in the form of granules.

- by heating, cellulose decomposes, especially in the presence of oxygen;
- cellulose is insoluble in water – due to the numerous hydrogen bonds between macromolecules, water cannot penetrate inside the crystallites to produce an imbibition and a distance of the molecules from each other.
- diluted mineral acids and organic solvents also do not dissolve cellulose;
- cellulose is soluble in concentrated mineral acids, such as sulfuric acid, hydrochloric acid, phosphoric acid.

The dissolution is preceded by soaking, the cellulose solutions being viscous.

- the action of acids on the cellulose leads to a decrease in the degree of polymerization, resulting in hydrocellulose. Depending on the strength of the acid and the duration of action, hydrocelluloses with different properties are obtained.
- the characteristic solvent of cellulose is the ammoniacal solution containing copper hydroxide [Cu(NH₃)₄].(OH)₂ – the Schweitzer reagent. From such solutions, cellulose can be precipitated by adding mineral acids.
- the hygroscopicity of cellulose (the ability of cellulose to absorb moisture from the air) is due to the fixation of water molecules only in the outer regions of the crystallites or in the amorphous regions of the macromolecules. For this reason, the amount of water retained by the cellulose fibers is small.
- through enzymatic hydrolysis – produced by cellulase
- cellulose is converted into cellobiose.

The enzyme is not contained in the digestive juice of humans and higher animals, for this reason cellulose cannot constitute food for these animals (<https://www.scribd.com/doc/38639633/Chimie-organica-celuloza>).

— The chemical properties of lignin:

The term lignin designates a three-dimensional complex amorphous aromatic polymer composed of phenylpropane units linked together. The monomeric units are held together in various ways: by oxygen bridges between two propyl and phenyl groups, between a phenyl and a propyl group, or by bonds carbon-carbon between the same groups. In particular, this macromolecule is formed by the radical oxidative polymerization of three hydroxycinnamyl alcohols representing the basic structural monomers: p phenyl monomer (type H), guaiacyl monomer (type G) and syringyl monomer (type S), coming from coumarin alcohol, respectively coniferyl and sinapilic. These compounds differ from each other due to different degrees of methoxylation. In addition, in the structure of lignin, there are many polar groups and hydroxyl groups allowing the establishment of strong intramolecular and intermolecular hydrogen bonds. These in turn make lignin insoluble in any solvent except alkaline solutions. Through condensation reactions, lignin is divided into soluble and insoluble lignin, the latter forming a precipitate. The softening temperature of dry lignin varies between 127 and 129°C, however, as the molecular weight of lignin increases, the softening temperature increases as well. In addition, the water contained in the molecules acts as a plasticizer, leading to a decrease in the softening temperature with an increase in water content. The modification of the cell wall by the infiltration of lignin is called lignification, a phenomenon that leads to a high mechanical strength of the structure.

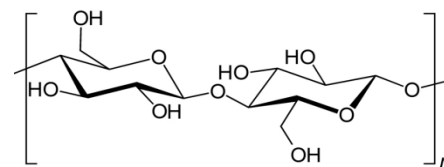


Figure 2 – The structural formula of cellulose
(Antonio Tursi, 2019)

Besides possessing greater mechanical resistance, lignified membranes become less swollen than cellulosic membranes, because the dipole $-OH-$ cellulose groups are largely saturated with lignin (Antonio Tursi, 2019).

Lignin is mainly aromatic, as can be seen from its chemical structure. Its basic molecular units are mainly connected by ether bonds, but carbon-carbon bonds also exist. Different functional pendant groups such as hydroxy, methoxy and carbonyl can be distinguished. Covalent bonds are present in hemicellulose and cellulose and can increase the mechanical strength of plants. Lignin has multiple functions in plant biomass. In addition to helping improve mechanical strength, it also protects plants from attacks such as bacteria, as it is not normally digested by animal enzymes. In addition, it stimulates water circulation in the plant's vascular system. Finally, it is the most resistant part of the dead plant, the most important component of the humus, and has a calorific value (HHV). Lignin is produced in large quantities as a by-product of the pulp and paper industry, requiring cellulose fibers with low lignin content, mainly used as heating fuel. It can also be used as the base material for the manufacture of high value-added products such as vanillin, phenol and derivatized phenolic resins).

— The chemical properties of hemicellulose:

Hemicellulose is one of the major constituents of plant cell walls and consists of heterogeneous branched polysaccharides. Hemicellulose thermally decomposes between 180°C and 350°C , producing non-condensable gas, charcoal and a variety of ketones, aldehydes, acids and furans. In nature, hemicellulose is amorphous and has adhesive properties with a high tendency to harden when dehydrated. While cellulose is composed of glucose units linked by β -1,4-glycosidic bonds, hemicellulose consists almost entirely of sugars with five carbon atoms (xylose and arabinose) and six carbon atoms (glucose, galactose, mannose and rhamnose) with an average molecular weight $<30,000$. The different groups of molecules that make up hemicellulose include xylans, mannans, galactans, and arabinogalactans (Antonio Tursi, 2019).

Hemicellulose is made up of relatively small molecules that contain 50–200 monosaccharide residues and that have bonds distinct from those of cellulose, such as the side groups (branches) of oligosaccharides attached to the polysaccharide backbone and acetyl groups. Hemicelluloses are classified depending on the type of main monosaccharide in their structure. The distribution of hemicellulose in plant tissue varies depending on the type of plant material. Figure 4 shows an example of the hemicellulose structure composed of different sugars. Hemicellulose decomposes more easily than cellulose, both from a thermochemical point of view, but also biochemically, due to intramolecular bonds that are less stable (Wiebren de Jong, 2015).

3. RESULTS

Fuels obtained from biomass in their natural, unprocessed state include wood, plant matter, straw, agricultural waste, animal dung, while processed biomass includes coal, sawdust, methane, but also alcohol produced as a result of fermentation processes.

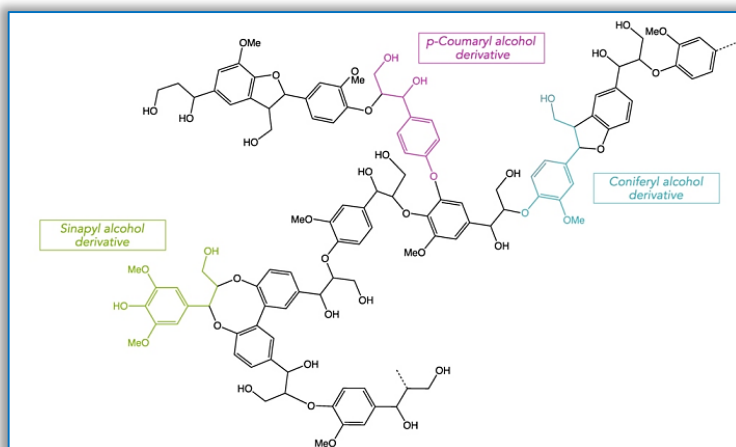


Figure 3 – The structural formula of lignin and its precursors (Antonio Tursi, 2019)

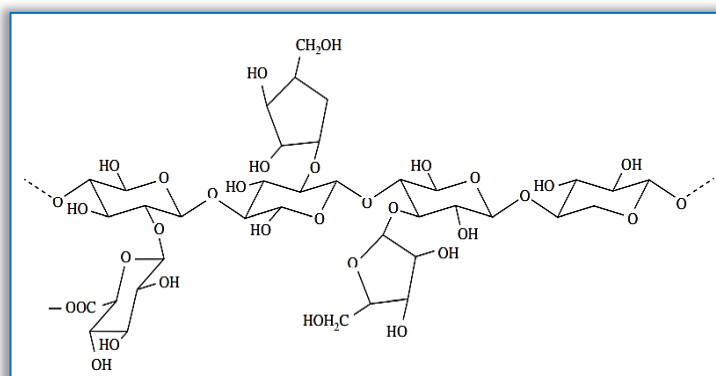


Figure 4 – Hemicellulose example structure. Depicted is glucuronoarabinoxylan β -(1,4)-D-xylan substituted by glucuronic acid at the O-2 and by arabinose at the O-2 and O-3 position (Wiebren de Jong, 2015).

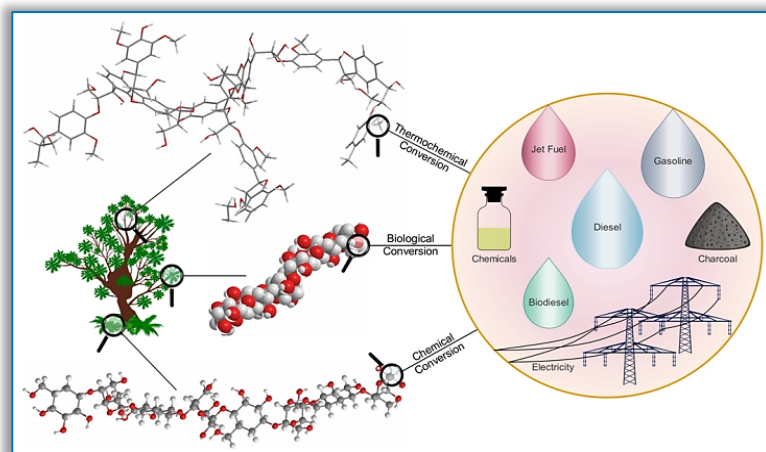


Figure 5 – Obtaining biofuels from biomass through thermochemical, chemical and biological processes (Antonio Tursi, 2019)

Biogas can represent a source of renewable energy that is easy to control and at the same time clean, obtained from organic waste, replacing fossil fuels or firewood. Over the years, biogas production has increased, thus in 1990 it was approximately 5,000 GWh and in 2001 it reached 13,617 GWh. When biogas began to be produced, the largest production was obtained by the USA, but now the largest production is in Europe OECD (Organization for Economic Cooperation and Development) which contributes 58.1% of the

electricity based on biogas. In recent decades, liquid biofuels have gained importance in Latin America, and more recently in Europe and other countries of the Organization for Economic Cooperation and Development. Currently, biomass is the only renewable energy source available that can produce competitive fuels for transportation in larger quantities. The biomass resources considered and their classification based on fuel quality and conversion technology are presented in Table 5. Liquid biofuels cover biogasoline and biodiesel:

- Biogasoline, includes bioethanol (ethanol produced from biomass and/or the biodegradable fraction of waste), biomethanol (methanol produced from biomass and/or the biodegradable fraction of waste), bioETBE (ethyl tertio-butyl ether produced on the basis of bioethanol: the percentage by volume of bioETBE that is calculated as biofuel is 47%) and bioMTBE (methyl- tert-butyl-ether produced on the basis of biomethanol: the percentage by volume of bioMTBE that is calculated as biofuel is 36%.
- Biodiesel: this category includes biodiesel (a methyl ester produced from vegetable or animal oil, of diesel quality), biodimethylether (dimethylether produced from biomass), Fischer Tropsch (Fischer Tropsch produced from biomass), cold-pressed bio-oil (oil produced from oleaginous seeds ai by mechanical processing) and all other liquid biofuels that are added to, blended with, or used directly as transportation diesel (Maria Gavrilescu, 2008).

Table 3. Classification of the biomass fuel resources under study (Maria Gavrilescu, 2008).

Sector	Resource	Fuel category	Fuel quality (indicative)		Conversion technology
			Moisture content (% wet basis)	Ash content (% dry basis)	
Agriculture	Agricultural residues	Dry lignocellulosic (e.g. straw, pruning)	Sugar/starch crops for ethanol	2.2–17	Combustion, gasification, liquefaction
	Livestock waste	Wet cellulosic	74–92.1	27.1–35.4	Digestion
		Dry lignocellulosic (e.g. poultry litter)	75	17.5–28	Combustion, gasification, liquefaction
	Energy crops	Dry lignocellulosic	12.5–50	0.3–8.4	Combustion, gasification,
		Oil seeds for methylesters.	Na	<0.2	Liquefaction, Extraction
Sugar/starch crops for ethanol.		Na	<0.2	Fermentation	
Forestry	Wood fuel	Dry lignocellulosic	46.7	0.4–5	Combustion, gasification, liquefaction
	Forest residues	Dry lignocellulosic	46.7	3.2	Combustion, gasification, liquefaction
Industry	Industrial residues	Dry lignocellulosic	10–30	0.71–18.34	Combustion, gasification, liquefaction
		Wet cellulosic	80–99	3.8–5.9	digestion
		Black liquor	90	36.4	combustion
Waste	Regulated waste	Municipal waste	30	36	combustion
		Demolition wood	30–40	0.58	combustion
	Non-regulated waste	Landfill waste	30	36	Digestion
		Sewage sludge	72.8	26.4	Digestion
Parks and gardens	Urban wood	Dry lignocellulosic	35	39.4	Combustion, gasification, liquefaction
	Cut grass	Wet cellulosic	75–80	8.4	digestion

4. CONCLUSIONS

Biomass is the right option for obtaining biofuels due to its renewability and the neutral carbon cycle. Biomass sources that are currently unused or that have been less used represent cheap and useful raw material to satisfy the entire demand for biofuel production. Biofuels from biomass have already been sold on the world market in pure form or mixed with gasoline and diesel and have proven their potential for energy independence and reduction of greenhouse gas emissions in the environment. However, the high cost and limited supply represent a problem for them to replace fossil fuels.

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