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**CHEMISTRY**

# PROFESSOR CRISTOFOR I. SIMIONESCU AND THE CONCEPT OF BIOMASS BIOREFINING

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Settlement of the world crisis of energy and chemical compounds, strongly manifested since 1973, urged the intensification of researches for finding new renewable resources capable of assuring a sustainable development. In this context, phytomass/ biomass was considered a solution, due to its complex composition. It was appreciated that biomass can be converted to produce fuels, power and chemicals based on procedures similar to those used in petrochemistry. Thus, the concept of biorefining was introduced. The same proposal was put forward by professor Cristofor I. Simionescu and his coworkers as "complex phytomass valorization" in a paper published in 1987, which represents the first contribution to biorefining definition. The obtained results, applied and demonstrated at pilot plant level, continued along the years, being published and included in different internal and European programs.

*Keywords:* phytomass, biomass, biorefining, energy, fuels, chemicals

The concept of biorefinery originated in late 1990's, as a result of the scarcity of fossil fuels and increasing trends of biomass use as a renewable feedstock for the production of non-food products. The term of "Green Bioefinery" was first introduced in 1997: "Green biorefineries represent complex (to fully integrated) systems of sustainable, environmentally and resource-friendly technologies for a comprehensive (holistic) material and energetic utilization, as well as exploitation of biological raw materials in the form of green and residue biomass from a targeted sustainable regional land utilization".

According to the US Department of Energy (DOE): "A biorefinery is an overall concept of a processing plant where biomass feedstocks are converted and extracted into a spectrum a valuable products". The American National Renewable Energy Laboratory (NREL) defined biorefinery as follows: "A biorefinery is a facility that integrates biomass conversion process and equipment to produce fuels, power and chemicals from biomass". These definitions are analogous to today's integrated petroleum refinery and petrochemicals industry for producing a multitude of fuels and organic chemicals from petroleum [1].

However, the term *biorefining* was introduced by professor Cristofor I. Simionescu in a paper published together with his coworkers in 1987, defined at that time as "complex phytomass valorification" [2], and further developed with new contributions in a review published in 1992 [3].

The researches concerning biomass use as a raw material to obtain energy and chemical compounds started in 1982 at the "Petru Poni" Institute of Macromolecular Chemistry, Iasi and "Gheorghe Asachi" Polytechnic Institute of Iasi, Romania, against the background of the world crisis of energy strongly manifested since 1973. A research program entitled "**Complex valorization of vegetable resources with high content hydrocarbons**", financed by the National Council for Science and Technology, was supervised by professor Cristofor Simionescu. In a first stage, a latex-bearing plant, *Asclepias syriaca*, was selected and cultivated [4].

The hydrocarbons content of this plant is relatively low (about 8%), so that the efficiency of the process could be improved by taking into account its other characteristics, such as seed fibers, oil from seeds, secondary and main components of the biomass. These aspects led us to a new idea concerning a complex valorization not only of this plant (as energetic culture), but also of other resources, such as forestry, agriculture, industry or urban wastes. Consequently, *Asclepias syriaca*, *Heliantus tuberosus*, barks of spruce, beech, aspen, stems of tomato and potato, and residues from medicinal herbs, were studied and chemically characterized. The conclusions reached at and other literature information showed that:

(i) All categories of vegetal biomass, without taking into account their sources, are composed of the same compounds, arbitrarily divided into three large groups, as follows: (a) primary compounds: cellulose and lignin; (b) secondary compounds: hemicelluloses and polyphenols; (c) specific compounds: pigments, hydrocarbons, simple sugars, alkaloids, oils, proteins, bioactive compounds, etc. Following the selective isolation of the specific and secondary compounds (performed in successive stages), structural heterogeneity gets reduced, the vegetal material becoming a lignocellulose (cellulose/ lignin in variable ratios) characteristic to all higher plants. Consequently, any category of available biomass may constitute a source of raw materials for its complex and integral valorization.

(ii) The compounds present in the vegetal biomass store an important amount of energy, as a result of their biosynthesis. Thus, the biosynthesized macromolecular structures from phytomass require an equivalent amount of external energy for their scission into energetic or chemical compounds (*e.g.* glucose, phenol). That is way, depending on the available raw material, our investigations have not been restricted exclusively to obtaining ethyl alcohol from cellulose, *via* "glucose", or only to phenol separation from lignin, aiming also at modifying the micro- and macromolecular structures existing in nature, from which usable products should be obtained. Therefore, the main objective was that all specific secondary and primary constituents isolated from phytomass, modified or not, should be functionally substituted by products with new properties

(iii) The technology of integral and complex valorization here proposed (Fig. 1) is to be performed on several stages and modules, depending on the chemical composition of the available vegetal resources and on the corresponding field of application for the obtained products, as well [2,5,6].

Prior to phytomass harvesting, the morphological elements meant at different valorization are isolated. Then, the previously ground vegetal material (with different contents of humidity), was subjected to stepwise processing. The technology we have thus imagined for the complex and integral processing and valorization implies two distinct stages: extraction/ separation and conversion, which be modularly applied, depending on both the species and chemical compounds had in view. The raw material may run through certain sequences of this flow sheet, which may be detached as a single separated technology and may be applied as a function of the available amounts of phytomass.

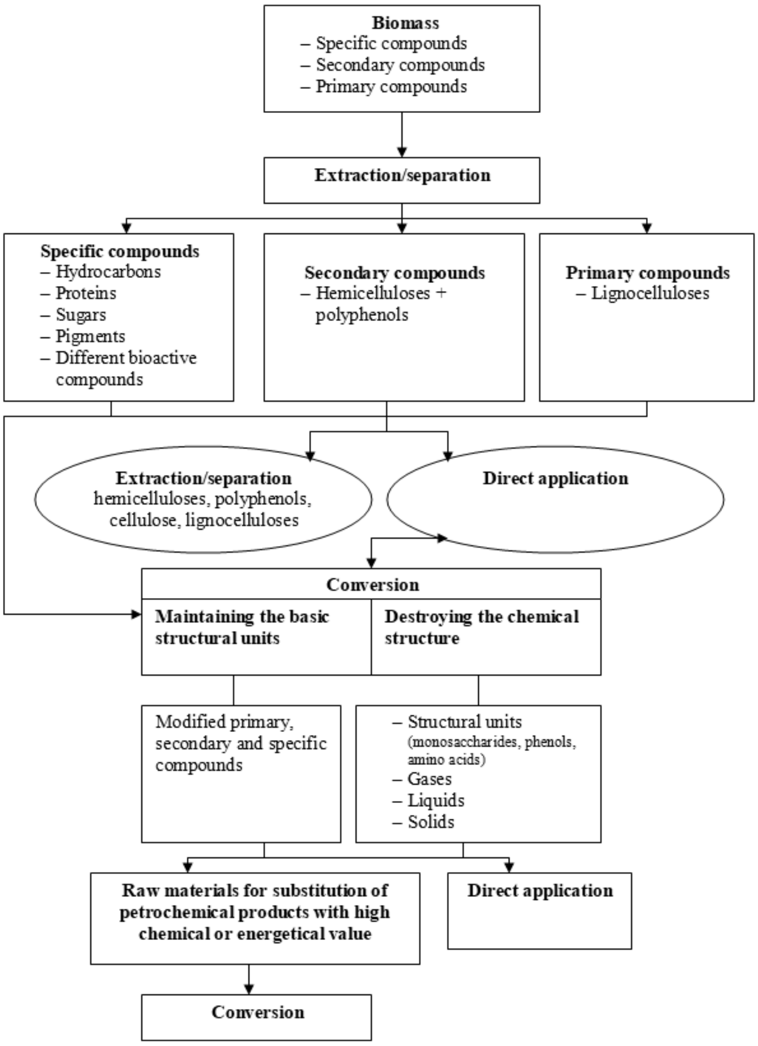


Fig. 1. Flow sheet of integral and complex processing of phytomass.

Based on the results obtained in our researches we designed and built up a pilot plant at the "Petru Poni" Institute of Macromolecular Chemistry of Iasi, which allowed us to demonstrate each technological step proposed for different types of raw materials.

*Stage I. Extraction/ separation*

*Phase I. Extraction/ separation of the specific compounds* implies isolation of hydrocarbons (Fig. 2), proteins, pigments and alkaloides (Fig. 3), of simple sugars and of other bioactive compounds, as well.

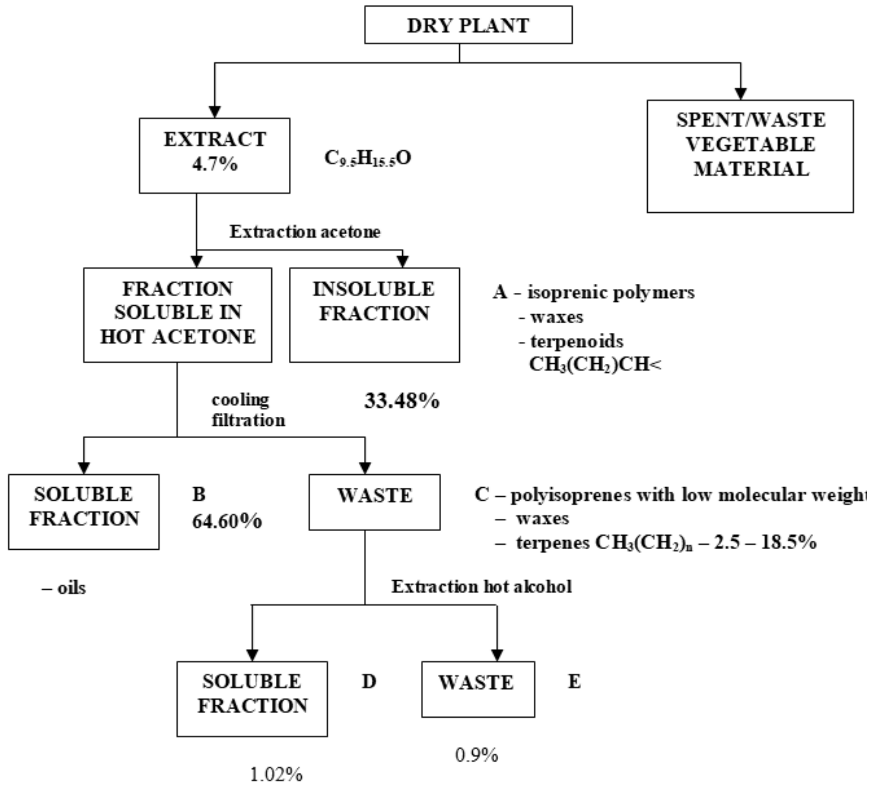


Fig. 2. Extraction and separation of specific compounds (isolation of hydrocarbons from *Asclepias syriaca*).

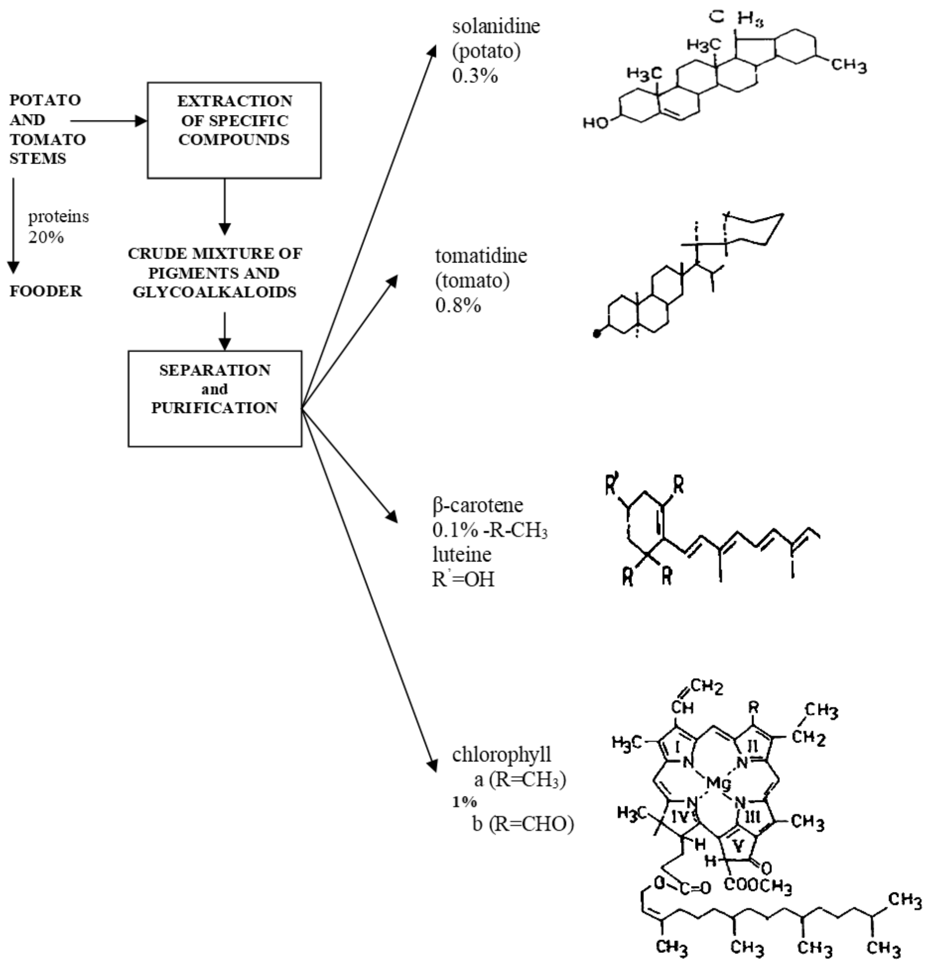


Fig. 3. Extraction and separation of specific compounds
(isolation of pigments and alkaloids from tomato and potato stems).

*Phase 2. Extraction/ separation of secondary compounds* leads to obtaining hemicelluloses and polyphenols/ low molecular fractions of lignin (Fig. 4), followed by isolation of the lignocellulose residue. These compounds may be used either as such [7,8], purified, or subsequently transformed by conversion.

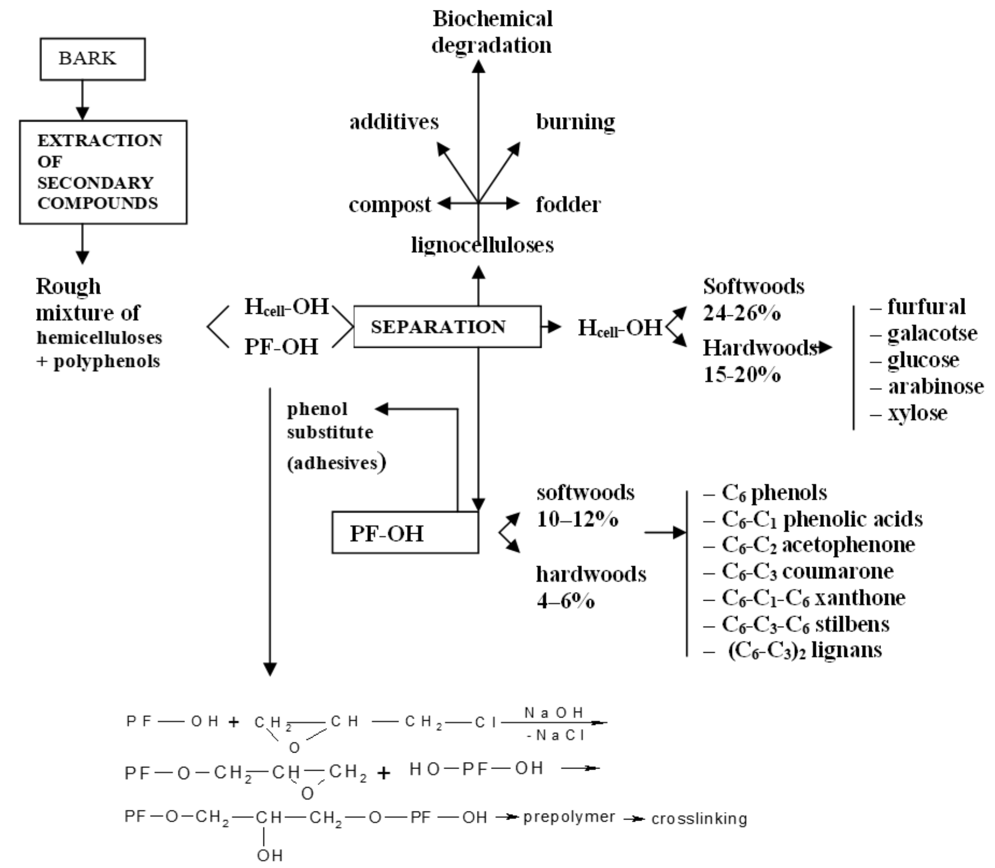


Fig. 4. Extraction and separation of secondary compounds
(isolation of hemicelluloses and polyphenls from wood bark).

The extracts containing hemicelluloses and polyphenols were used for obtaining fiber wood- or plywood-based composites, to synthesize phenol-formaldehyde resins, to substitute phenol, or for polyphenol-epoxij resins [7,8].

In our studies, the lignins and polyphenols extracted from different sources of biomass through biorefining [2] have been used in model experiments, to observe their action as allelochemicals [9].

Polyphenols extracted from spruce wood bark and other sources have been isolated, characterized [10] and tested as plant growth regulators, the results obtained evidencing that the isolated compounds exhibited similar effects to those of the endogenous hormones cytokinin and auxine [11].

Based on these results, lignin and polyphenols were used in seeds germination, plants tissue culture, plants cultivation [12,13], bioremediation [14,15], or as substrates for microorganisms development [16].

*Stage II. Conversion is performed with or without* maintaining the structural integrity of the initial compounds.

In the former case, conversion occurs through *synthesis*, using chemical or biochemical procedures (Fig. 1), which induces the possibility of transforming the specific, secondary and primary compounds and of maintaining the basic structural elements of the product subjected to these transformation, such as polyphenolepoxy (Fig. 4), or through *destruction* of lignocelluloses (Fig. 5) [3].

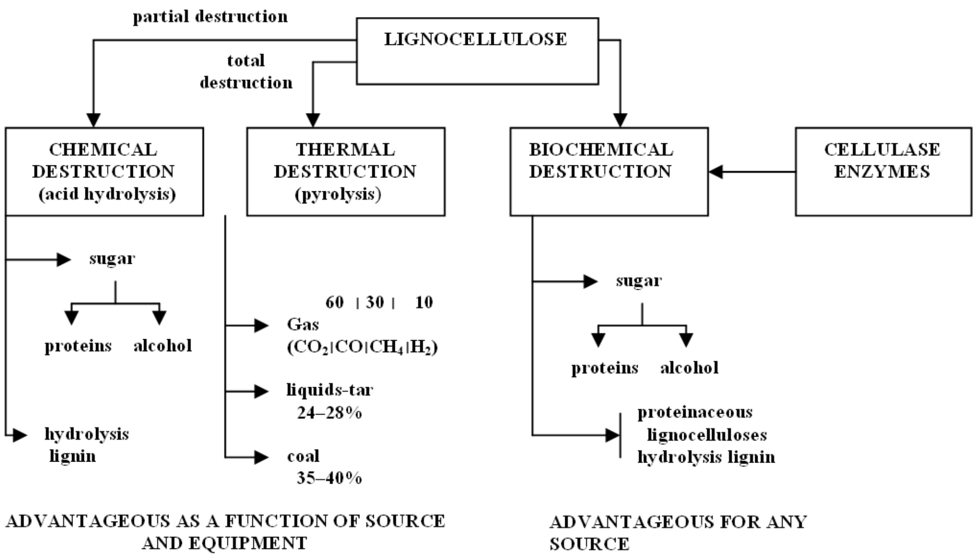


Fig. 5. Possible lignocelluloses valorization.

In the latter case, conversion occurs through *degradation*, using the chemical, thermochemical and biochemical procedures applied for specific, secondary, primary, and main compounds, respectively, up to structural units or gaseous hydrocarbons liquid and solids products, used either as such or subsequently forming the raw material for a new synthesis or conversion (Figs. 6–8).

*Stage III. Products obtained by phyotmass processing may structurally and/ or functionally substitute certain raw materials of carbo- or petrochemical origin.*

Hemicelluloses, accessible from wood and annual plants, represent the main component of biomass, with a complex structure including different units (pentoses and hexoses); therefore, they may be considered a valuable raw material for obtaining monosaccharides, intermediaries for chemical synthesis or for various uses in pharmacy and medicine [17–21].

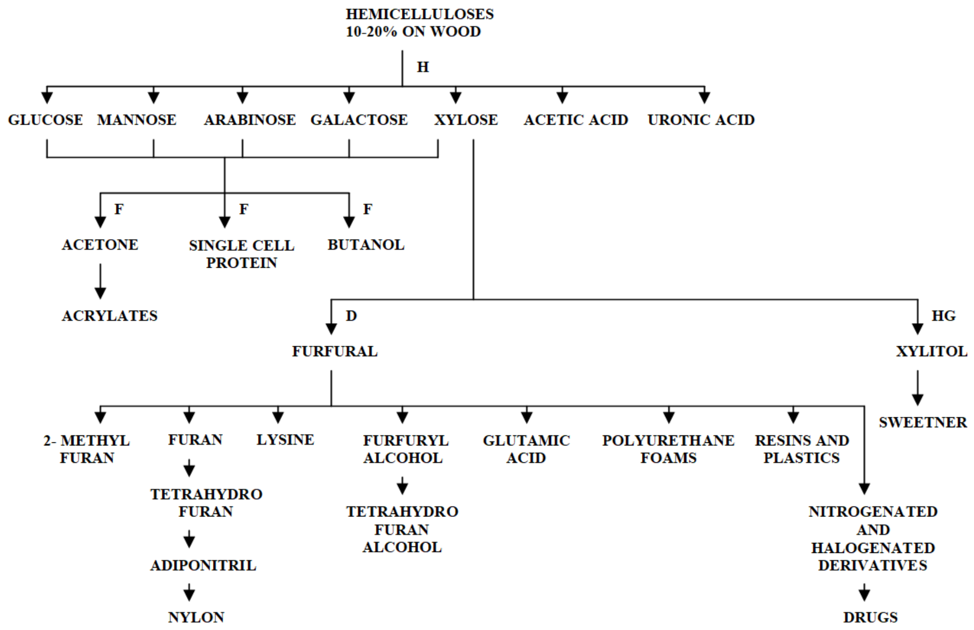


Fig. 6. Hemicelluloses valorization.

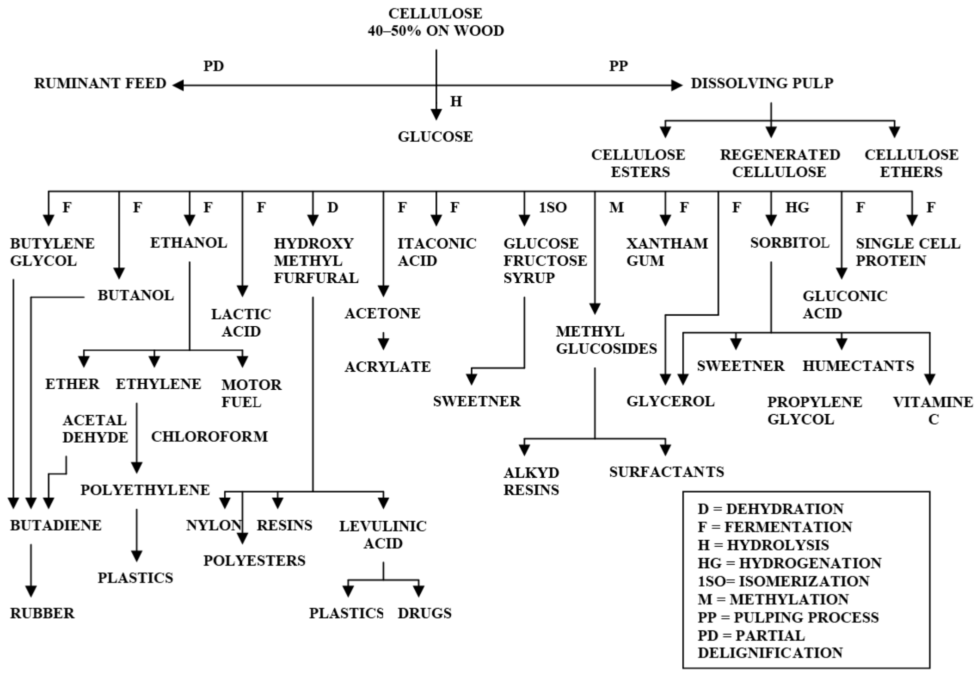


Fig. 7. Cellulose valorization.

At present, cellulose is attracting the attention of researchers to develop new fields for its application not only for fuels (ethanol, butanol, syngas) but equally for new derivatives, composites, high-tech products (*e.g.* nanocelluloses), and bioactive celluloses [22–24] .

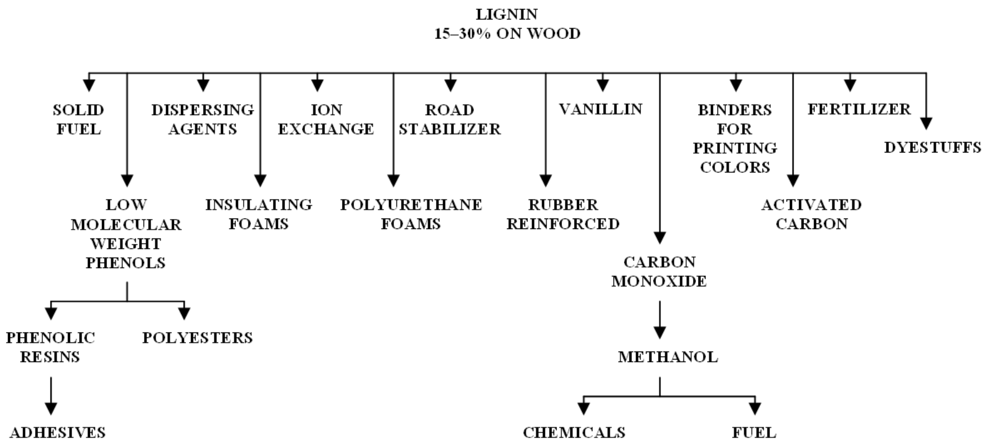


Fig. 8. Lignin valorization.

Lignins can be recovered by applying a biorefining procedure and used in a modified form through oxyammonolysis (as fertilizers with retard action), condensation and substitution reactions, epoxydation (adhesives, composites, bioremediation agents), carbon fibers, biochemical modifications. The nanoparticles and the bioactive products are interesting fields for lignin and its derivatives [25,26].

Based on the concept of valorizing the components of phytomass, our researches were developed for their recovery and investigation by both PhD programs and internal and European projects (*e.g.*, Sciex-IMMOPHENOL cooperation Switzerland-Romania, Wood-Net Implementation of Research Potential of the Latvian State Institute of Wood Chemistry in the European Research Area (FP 7), European Polysaccharides Network of Excellence, ECOBINDERS-Furan and lignin-based resin as eco-friendly and durable solutions for wood preservation, panel, board and design products (FP 6), EUROLIGNIN- Thematic Network: Coordination network for lignin OE standardization, production and application adapted to market requirements (FP 6), SPONGE-GROWTH (FP 6). To this end, a laboratory for complex and integrated processing of biomass resources was created.

At the same time, we demonstrated that a pulp mill has excellent prerequisites as a base for biomass-based biorefinery: large flow of raw materials (wood and annual plants), available process equipment and good process knowledge.

The key strengths of the pulp and paper industry are wood and biomass sourcing, alongwith the logistic infrastructure, the existing sustainable base for integrated production and the high efficiency and experience in combined heat and power generation. The industry has unique capabilities in handling very large volumes of biomass and the synergies in logistics and energy integration are significant. Therefore, biorefining and bioenergy fit well into the integrated business model of forest products companies (Fig. 9).

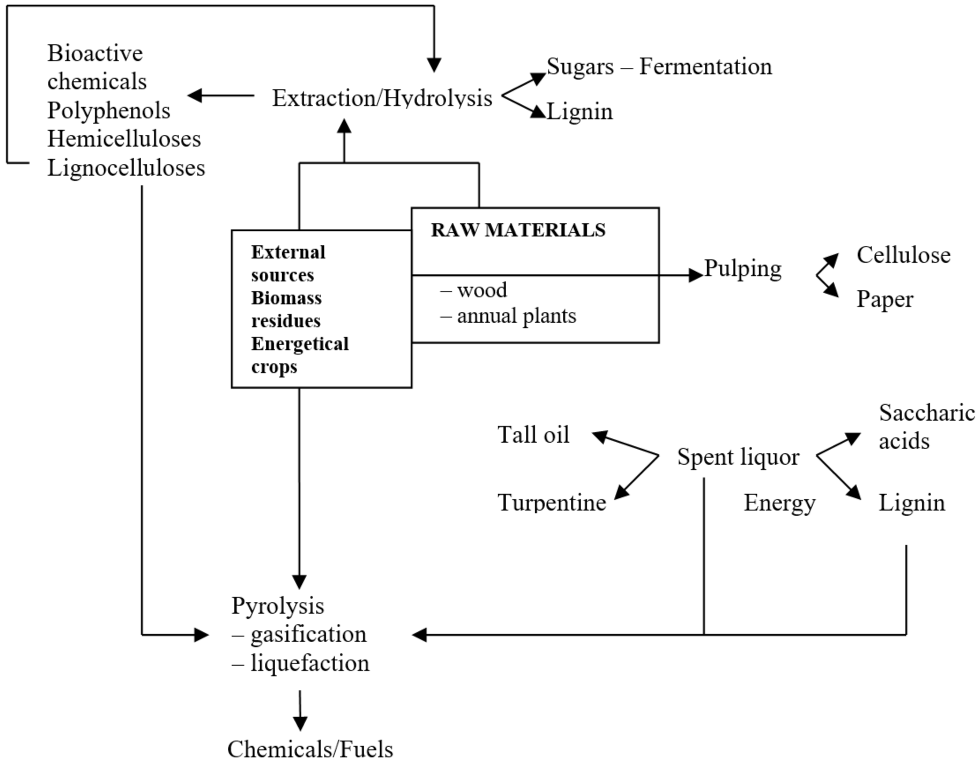


Fig. 9. Integration of biorefining in pulp and paper industry.

## CONCLUSIONS

The world crisis of energy strongly manifested since 1973 urged intiation of research projects for the utilization of biomass/ phytomass as a renewable raw material, to obtain energy and chemical compounds. In Romania, a research program entitled "**Complex valorization of vegetable resources with high content of hydrocarbons**", financed by the National Council for Science and Technology and supervised by professor Cristofor I. Simionescu, started in 1982. In the first stage, a latex-bearing plant, *Asclepias syriaca*, was selected and cultivated, other sources, such as forestry and agricultural wastes, being further added. The obtained results determined the introduction (in a paper published in 1987) of the term **"complex**

**valorization of phytomass"** similar with **"biorefining"**, proposed after 1990. Based on the information provided by the researches performed, a pilot plant was designed and built up, which allowed demonstration of all stages of the proposed technology for all biomass components. The results were published in numerous papers, books, PhD theses, and used in internal and European programs. Therefore, we entitedly claim that the term *biorefining* was proposed by professor Cristofor Simionescu and his coworkers since 1987.

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