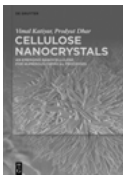


## **Pulp Production and Processing**

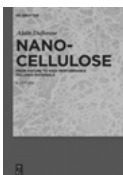
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# **Pulp Production and Processing**



High-Tech Applications

Edited by  
Valentin I. Popa

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## Preface

Pulp and paper mills are ideal sites for integrated biorefinery operations for **four basic reasons**. **First**, they are already set up to receive and process massive amounts of delivered round wood and woods chips, and they have access to at least an equal amount of forest residuals and even a greater amount of waste paper and agriculture wastes and energy crops if needed. **Second**, these mills have basically the same existing infrastructure for warehousing and shipping out finished products around the world. **Third**, they have a well-established in-place administrative infrastructure and related human resources that can be extended to serve a biorefinery business without incurring significant new costs. **Fourth**, pulp and paper mills have operating utility support systems for processing water, electricity, steam, and waste/environmental treatment that can easily be umbrella to support biorefinery operations without major new investment. And possibly, as a strong **fifth** reason, chemical pulp mills already operate as biorefineries of sorts, producing fiber to make paper and paperboard as well as some specialized dissolving pulps to make viscose types of “bio-plastics” and rayon materials. Bioproducts can be made from pulp as cellulose derivatives and as other high-tech value-added products, as well as from spent cooking liquors including ingredients used in making coatings, adhesives, detergents, paint, varnish, ink, lubricants, waxes, polishes, gasoline additives, agricultural products, and so forth. There is also a spectrum of lignin-based products derived from refinement of black liquor. Tall oil along with turpentine could be obtained during the pulping of softwoods with kraft process. Therefore, the integrated biorefinery is a processing facility allowing extraction of polysaccharides, lignin, and other chemicals from biomass (extractives), and convert them into multiple products including materials, fuels, and high-value chemicals.

It is known that the conventional different procedures to obtain pulp and paper include mechanical and chemical treatments of fibrous raw materials. Each variant has both advantages and disadvantages being recommended in function of specific conditions. The resultant pulp yield and quality depend on the applied technology, and the by-products are used to recover chemicals and energy.

At present, deforestation is a vital problem at global level, being one of the main causes of climate change. Volume of wood used as fuel, in construction, furniture, and pulp and paper industries increases year by year. Stopping the decrease of forests surface is of imperative importance from the point of view of sustainability. Pulp and paper industry is confronted with severe lack of pulpwood, and for this reason other raw materials must be taken into consideration. This is why obtaining of chemical pulp from other raw materials is of particular importance. In these conditions some agricultural residues such as wheat straw, rapeseed stalks, and corn stoves were proposed to be used as raw materials in producing papermaking pulp. At the same time, there are many advantages of using of agricultural residues: high availability, low price, favorable chemical composition, and suitable papermaking properties of fibers.

Bleaching is the following step connected with pulp manufacturing. The process to remove the residual lignin and other oxidizable structure can be performed using different oxidants such as oxygen, chlorine dioxide, hydrogen peroxide, ozone, and peracetic acid. The use of enzymes in the bleaching process, particularly of thermostable and alkali-tolerant xylanases, is regarded as a success story of biotechnological approaches in the pulp industry. The reaction mechanism, kinetics, process parameters, and technology details of the different bleaching technology are important for optimization and to obtain good characteristics of the pulp.

On the other hand, the integration of biomass resources in the biorefining has to be associated with the new conversion environmentally friendly technologies. Thus, the application of this novel bio-greening approach in the pulp and paper industry include along with fractionation of lignocellulosics; upgrading of plant extractives and resins; production of biohydrogen; and other “clean” technologies, products, and systems. In these conditions important changes in the field of research and education are expected to be produced.

At present, among the products obtained from biomass, an increased interest was observed for biochar. This product results by hydrothermal treatment of different lignocellulosic wastes existing in the pulp and paper factory (e.g., sawdust, bark, or wastes from waste paper processing) or disposable from agriculture. The interesting properties of the biochar recommend it to be applied in agriculture, bioremediation, and environmental protection.

The rapid depletion of fossil fuels has led to a huge effort to increase the use of renewable biomass. The replacement for fossil fuels comes from lignocellulosics using biorefining procedure. At the same time, some building blocks used for synthesis of biopolymers or other compounds can be obtained from a vast number of feedstocks. Thus, the most promising building blocks are hydroxymethylfurfural (HMF) and levulinic acid (LA), which could be used as intermediates for derivatives with commercial relevance for the future of biorefinery.

The knowledge and understanding of properties of cellulose depends on its basic chemistry, epimolecular, supermolecular, hypermolecular structure, interaction with water, elementary cellulose components (i.e. cellulose crystallites; wet-web strength and wet strength of materials; enthalpiometric observations of interactions in cellulosic fibrous slurries; existence of water inclusions among cellulosic chains; hydrogel structure of cellulose; H-bond ability and hydration bonding and anti-bonding concept; rheosedimentation; thermo-responsive hydrated macro-, micro-, and submicro-reticular systems of cellulose; swelling; recycling; interaction with gases and vapours).

What makes wood and nonwood fibers suitable for papermaking more than other fibers? What happens with fibers during papermaking? Is the hornification process from paper recycling a reversible one or not? Cellulosic fibers are the main constituent of all plant material, and they are a renewable source available abundantly in nature. Cellulosic fibers are made of a multilayer of a very small thread-

like structure called fibrils. These fibrils can be exposed by beating/refining of fibers and provide a very large area for bonding. But the most important feature of cellulosic fibers that makes it suitable for papermaking is that fiber develops physical and chemical bonding with other fibers when it changes from wet to dry state. High tensile strength, flexibility, water-insoluble, hydrophilic character, chemical stability, and relatively colorless (white) are other particularly important features of wood and nonwood fibers, which make it suitable for papermaking. Even if papermaking is one of the most common uses of cellulosic fibers, today's applications such as paper-based microfluidic devices are a particularly attractive topic for research on high-tech applications of fibrous structures. Materials in which cellulosic fibers are used after nanofibrillation processes are also highly appreciated opening new high-tech applications for multifunctional fibrous structures.

Hydrogels represent a family of customizable three-dimensional polymeric networks with unique features, such as to absorb, swell, and release large quantities of water or biological fluids and simulate biological tissue when swollen. Polysaccharides are important candidates for the design and preparation of hydrogels, since they provide a handful of distinctive biological, physical, and chemical characteristics which favor several demanding applications, especially in the medical field. Therefore, cellulose, a key bioresource of the twenty-first century, is a versatile candidate for the construction of biomaterials with tunable network structure, receiving increasing attention in recent years due to an advantageous mixture of proper biocompatibility, hydrophilicity, and mechanical properties.

Nowadays, due to its hydrophilicity, nontoxicity and antimicrobial properties, cellulose is used in medical applications, as wound dressing, tissue engineering, controllable drug delivery system, and so on. The ability to control the material features at the nanoscale brings new and promising properties, such as high mechanical characteristics and low density, which provides the opportunity to develop new applications. The differences between nanomaterials and bulk materials are controlled by two main factors – as the increased relative surface area, so an enhanced reactivity and the quantum effects offered by the changes on mechanical, optical, thermal, and electrical properties. In addition, the combination of nanoparticles with polymers provides a route to a wide variety of old and new applications.

Water insolubility of cellulose, generally is attributed to the existence of extensive intra/intermolecular hydrogen bonds, limiting its applications. This disadvantage can be eliminated by derivatization reactions of cellulose. The introduction of functional groups (derivatization) has an important effect on macroscopic behavior; for example, solubility, stability, and viscometric/rheometric characteristics. In this respect, the synthesis of the ionic derivatives of cellulose presents an important opportunity to develop new applications.

Cellulose ester films are preferably employed in optical functional films because of its good transparency with high glass-transition temperature. Since the main chain of cellulose has low level of optical anisotropy, orientation birefringence of a stretched

film can be easily controlled by chemical modification such as esterification. A small amount of crystallinity also plays an important role on the hot-stretching process. Moreover, good miscibility with various plasticizers widens the material design to control the birefringence. A novel material designs of a multi-band quarter-wave plate, one of the optical retardation films used in advanced display system, has been demonstrated using cellulose esters.

The idea to edit the second edition of this book belongs to Lena Stoll editor in the Industrial Chemistry section of De Gruyter publishing house who allow me to cooperate with Ria Senbusch, Anna Bernhard, and Dipti Dange who were involved in this project, taking the risk to bring out such a book and for ensuring the excellent quality of the publication.

We have removed few chapters from the first edition, and we have added new ones having in view new progresses in the field of cellulose as renewable and sustainable raw material.

The publishing of the book was accomplished with the contributions of renowned specialists in the pulp and paper and cellulose derivatives production from all over the world. We are grateful to these scientists for their efforts and dedication to this reference book.

The book is a very useful tool for many scientists, students, and postgraduates working in the field of pulp and paper and cellulose derivatives, aimed at opening a new era of renewable resources processed by refining. It may not only help in research and development, but may also be suitable in the line of teaching.

I hope that you as reader will enjoy the volume.

Valentin I. Popa  
2020



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Valentin I. Popa

## Chapter 1

# Biorefining and the pulp and paper industry

## 1.1 Introduction

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

According to 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 “A biorefinery is a facility that integrates biomass conversion process and equipment to produce fuels, power and chemicals from biomass.” These definitions of biorefinery are analogous to today’s integrated petroleum refinery and petrochemicals industry to produce multitude of fuels and organic chemicals from petroleum [1].

However, we think that we have a priority because we have introduced this concept in the paper [2]:

In our days, the idea that vegetable biomass represents a source of liquid fuel and of different new materials has led to the development of various research programs in this field. Our investigations in this direction are based on the following premises: (1) all kinds of vegetable biomass include almost the same components; (2) the macromolecular compounds existing in the vegetable biomass incorporate biosynthesis energy, and their conversion to useful products seems to be considered; (3) the complex and total processing technology may be modulated depending on the chemical composition of the vegetable source, as well as on the utilization of the obtained chemical compounds. The possibilities of complex processing of soft- and hardwood bark, agricultural wastes, and some energetic cultures of *Helianthus tuberosus* and *Asclepias syriaca* are exemplified.

In order to face the present state of affairs, the manifested tendency is that of adopting the existing classical technologies of carbo- and petrochemical fields in processes of converting biomass into products possessing energetic and/or chemical value. The technology of integral and complex valorization of biomass has been proposed 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.

A plant for the fractionation and refining of biomass and to use of its entire components is a “biorefinery” plant, will have to display a high level of process integration and optimization to be competitive in the near future. Forest products companies may increase revenue by producing biofuels and chemicals in addition to wood, pulp, and paper products in a so-called **integrated forest biorefinery (IFBR)**. The concept of an **IFBR** is being advanced by a number of investigators who envision converting cellulose, hemicelluloses, and lignin from woody biomass, dedicated annual crops, industrial and municipal waste in bioenergy, and basic chemicals [3–5].

A pulp mill has excellent prerequisites to be the base for a biomass-based biorefinery: large flow of raw materials (wood and annual plants), existing process equipment, and good process knowledge. The key strengths of the pulp and paper industry are the wood and biomass sourcing along with the logistic infrastructure, a sustainability existing base of 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.

The current chemical pulp process use approximately 50% of the organic raw material in the production of paper pulp; the remaining 50% is combusted in the recovery boiler to produce steam. A modern energy-optimized pulp mill has a substantial excess of energy/steam. This excess can be utilized in several different ways:

- The first is to produce electrical power.
- The second is to replace the recovery boiler with a black liquor gasification unit to produce syngas.
- The third is to extract some lignin from the black liquor and sell it as a new product to be used as fuel or raw materials for biobased products.
- The fourth is to attract the other external sources of biomass or wastes and to process them with the aim of obtaining fuels and chemicals [6].

In the pulp mill of tomorrow, the hemicelluloses and extractives, dissolved in process streams, could also be extracted and used as chemical raw materials. As a consequence the chemical pulp mill could be transformed into an integrated biomass biorefinery, producing different chemicals besides traditional pulp and papers [2].

At the same time, the utilization of biomass as a renewable raw material may have the following advantages: (1) reduced dependence on imported fossil oil; (2) reduction in greenhouse gas emissions; (3) building on the existing innovation base to support new developments; (4) a bioindustry that is globally competitive; (5) the development of processes that use biotechnology to reduce energy consumption and the use of non-renewable materials; (6) the creation of jobs and wealth; (7) the development of new, renewable materials; (8) new markets for the agriculture and forestry sectors, including access to high-value markets; (9) underpinning a sustainable rural economy and

infrastructure; and (10) sustainable development along the supply chain from feedstocks to products and their end-of-life disposal.

## 1.2 Possibilities of biorefining implementation into the pulp industry

Examples of fractionation technologies are several biomass pulping processes that are common practice in the pulp and paper industry (e.g., kraft pulping, sulfite pulping, soda pulping, organosolv pulping, etc.). Here, the biomass is essentially fractionated into cellulose (for paper) and black liquor, a waste stream that predominantly contains residual carbohydrates and their degradation products (e.g., from the hemicelluloses), partly degraded lignin, and inorganics from the pulping process. The main application to date of this black liquor is combustion for heat. In addition, lignin and lignin-containing residues are large side streams from the pulp and paper industry and from biorefineries that use the carbohydrate fraction of the biomass, for example, for the production of bioethanol. Globally ~ 50 Mt per year of lignin originates from the pulp and paper industry, predominantly from kraft-, soda-, and sulfite-pulping of softwood, hardwood, and agricultural residues such as straw, flax, and grasses. Only 1 Mt is used for commercial purposes including liginosulfonates from sulfite pulping and 0.1 Mt as (chemically modified) kraft lignins from kraft pulping [7].

At present, most of these sulfur-containing lignin streams are combusted for generating power and/or heat, an application with very limited added-value. These sizable amounts of lignin are in principle available for valorization into chemicals and performance products. New developments in soda-pulping technology have resulted in sulfur-free lignins from herbaceous types of biomass such as straw and grass [8, 9].

Furthermore, large amounts of (hydrolytic) lignin will be produced from future bioethanol-based biorefineries by processes such as steam explosion and organosolv pulping. The first is a thermomechanical treatment that uses sulfuric acid for the hydrolysis and steam-explosion for breaking up the fibrous biomass structure. Organosolv pulping of hardwood, grasses, and straw leads to a high-quality lignin that is essentially sulfur free. The biomass is fractionated into lignin, cellulose, and a hemicelluloses containing-side stream. Generally, the hydrolytic lignins are the main fraction in the side stream that originates from the processing of wood and agricultural residues for transportation fuels and chemical building blocks.

Taking into account the utilization of different biomass sources as raw materials in a complex integrated pulp mill producing bioproducts and biomaterials, after our opinion we have to consider the following aspects: (1) all kinds of vegetable biomass contain almost the same main compounds; (2) the macromolecular compounds existing in the biomass incorporate biosynthesis energy, and their conversion to useful products seems to be economical; and (3) the complex and total processing technology may be

modulated depending on the chemical composition of the biomass sources, as well as on the utilization of the obtained chemical compounds [2].

Thus, the specific objectives of this proposal have to be the following:

1. Identification, quantification, and characterization of resources from chemical composition point of view.
2. Separation and establishment of optimal conditions for fractionation using an original scheme that allows isolating chemical compounds as a function of their structure and raw material accessible to be processed (Fig. 1.1). Conventional and nonconventional extraction procedures will be used.
3. Characterization of isolated products; comparative studies of extraction methods will be carried out; correlation of the characteristics with the possibilities of utilizing the obtained products; establishing potential applications.
4. The elaboration of sequential technological procedures to recover separated compounds with the aim of transferring them to the pilot-scale level.
5. Evaluation of the results obtained in technological transfer from the efficiency, economical, and social points of view.
6. Evaluation of the economical feasibility of applications of the proposed technologies; analysis of cost–benefit ratio.

The world distribution of phytomass evidences huge quantities still unexploited by man (about 89%), together with significant forest, agricultural, industrial, and urban wastes [4].

**Wood phytomass** is still being incompletely exploited (important amounts are used as fuel (about 50%) for local energetic requirements and, only to a certain extent, for chemical ones).

**Agricultural phytomass** is now being confronted with a new problem: “limited grounds against an ever increasing number of people,” a situation that could not assure by any means new stocks (wastes excepted); consequently, there is no reason to replace valuable food products as wheat, sugar beet, and sugar cane for conversion into liquid fuels (e.g., ethanol). In such circumstances, mention should be made of the efforts to use soil inadequate for agriculture in order to energetically culture of fast-growing plants, species with high content of biological compounds or hydrocarbons. At the same time, it is known that processing of agricultural products and plants containing biological compounds results in a substantial amount of waste. This can represent a raw material allowing the separation and upgrade of different components with energy and chemical value, using technology proposed by us.

Thus from a pulp mill biorefinery, the following products can be obtained in addition to pulp and paper: phenols, adhesives, carbon fibers, activated carbon, binders, barriers, antioxidants, pharmaceuticals, nutraceuticals, cosmetics, surfactants, chelants, solvents, descaling agents, specialty polymers, and biofuels (pellets, lignin fuel, methanol, DME, ethanol, etc.). New or increased amounts of traditional products can be made from internal/or external biomass sources (Fig. 1.2).

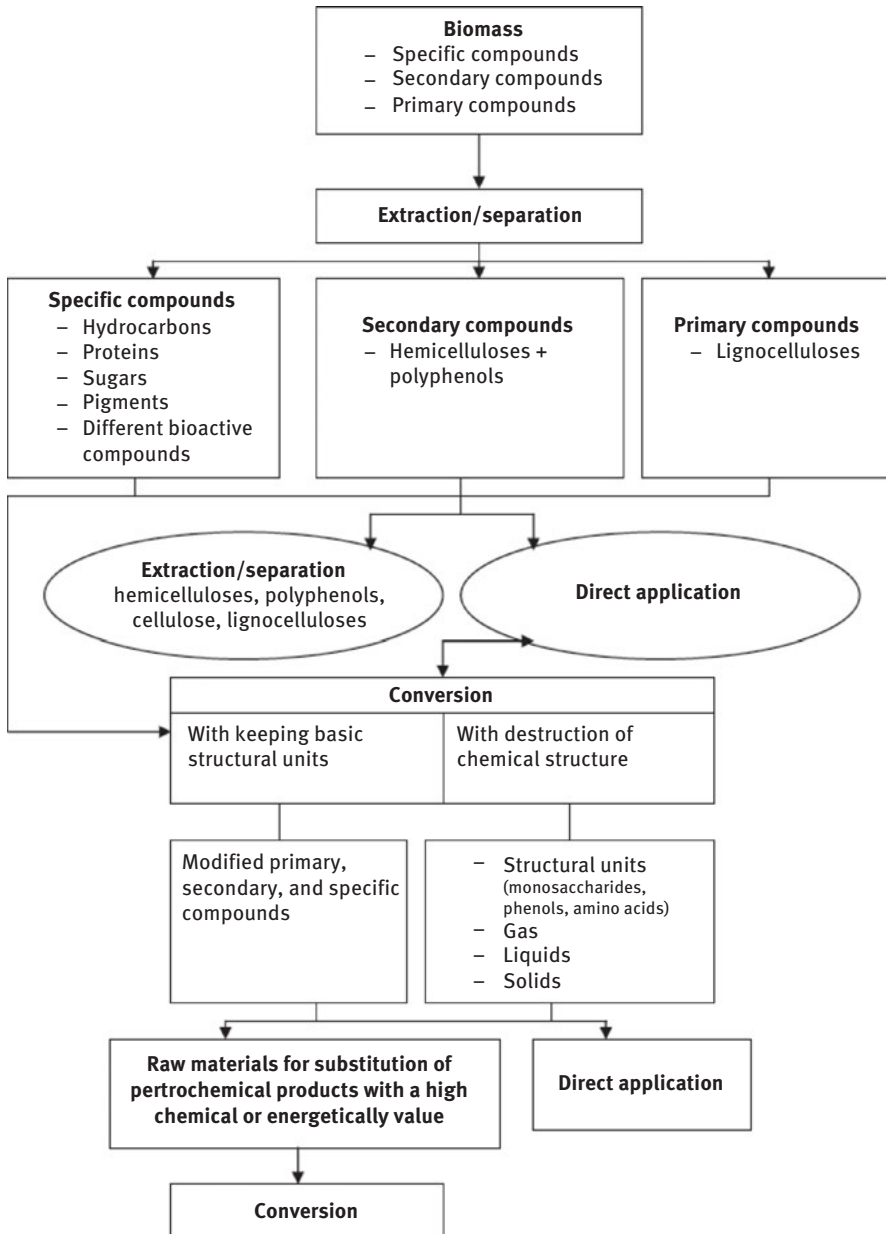
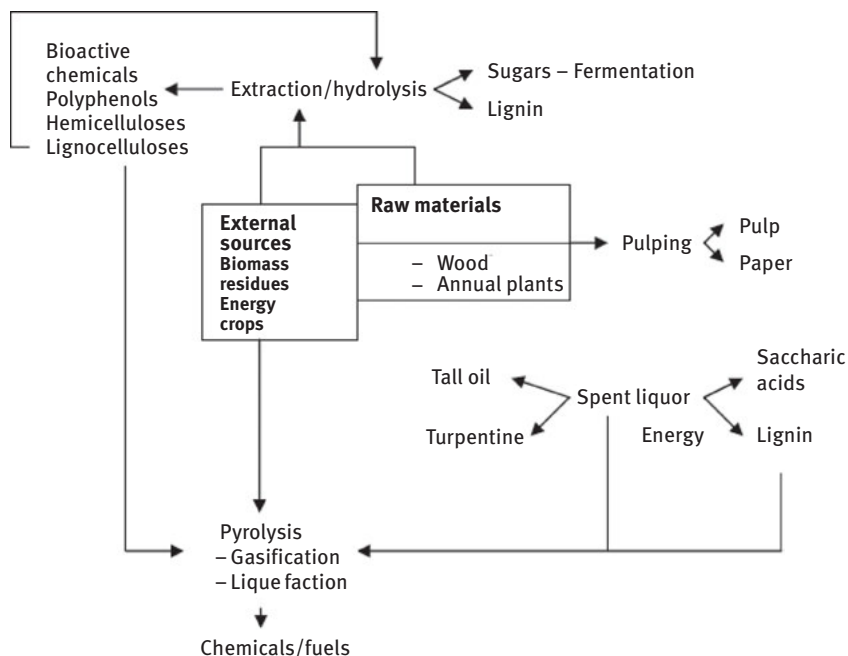


Fig. 1.1: Flow sheet of integral and complex processing of phytomass.

Three different levels can be identified: (1) a high degree of energy saving in future mills, especially chemical pulp mill, will lead to large amount of excess internal biomass, which can be transformed into the products mentioned above; (2) components



**Fig. 1.2:** Flow sheet for biorefining technology application using internal and external biomass sources.

in, for example, the black liquor, forest residues, and bark can be upgraded to more valuable ones and the energy balance of the mill is kept through fuel import, wholly or partly depending on the level of mill energy efficiency. The imported fuels can be biomass or other types; (3) external (imported) biomass (in some cases together with excess internal biomass) can be upgraded using synergy effects of docking this upgrading to a pulp mill.

To develop and apply new technology, we took into account the following considerations also as a result of our previous researches [2, 10, 11].

I. *All categories of phytomass contain the same compounds, arbitrarily divided into three large groups:*

- primary compounds: cellulose and lignin;
- secondary compounds: hemicelluloses and polyphenols; and
- specific compounds: pigments, hydrocarbons simple sugars, alkaloids, polyphenols, other bioactive compounds, oils, proteins, and so on.

After the selective isolation of the specific and secondary compounds (performed in successive stages), the structural heterogeneity is being reduced. Thus, the residual material becomes lignocellulose (cellulose/lignin in variable ratios) characteristic

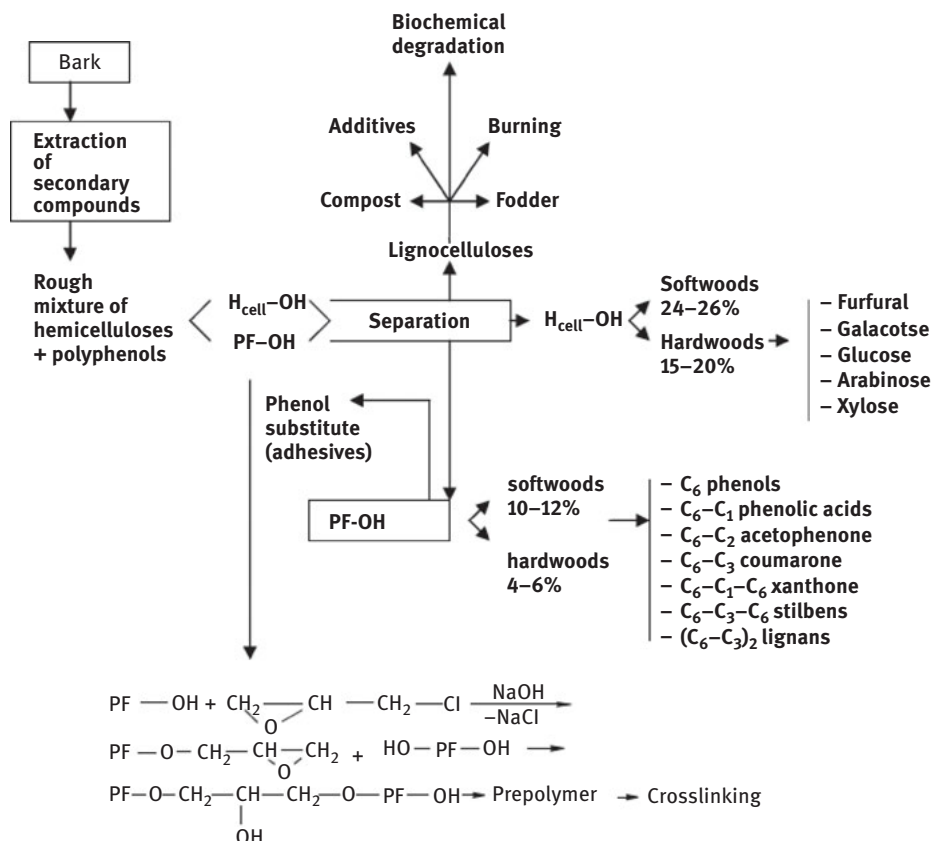


of all higher plants. Consequently, *any category of available vegetal biomass may constitute a source of raw materials in its complex and integral valorification.*

- II. *Compounds existing in phytomass store an important amount of energy as a result of their biosynthesis.* Thus, the biosynthesized macromolecular structures in phytomass require an amount of equivalent external energy for their cleavage into energy or chemical compounds (e.g., glucose from cellulose and phenol from lignin). That is why, depending on the available raw materials, the investigations have not been restricted exclusively to the obtaining ethanol from cellulose, via “glucose” or only to phenol separation from lignin, aiming also at the modification of the micro- and macromolecular structures existing in nature, from which valuable products can be obtained. Thus, the main objective is that all specific, secondary, and primary constituents isolated from phytomass, modified or not, should functionally substitute the classical chemical products or can represent materials with new properties.
- III. *The technology of integral and complex valorization that has been proposed is to be performed on several stages and modules, depending on the chemical composition of the available resources and on the corresponding field of application for the obtained products.*

Prior to biomass harvesting, morphological elements destined for different valorifications are isolated. Then, the biomass that has been ground (containing a different content of humidity) is subjected to a stepwise processing. The technology we have thus imagined for the complex and integral processing and valorification implies two distinct stages: *extraction/separation (extraction of the specific compounds, extraction of the secondary compounds) and conversion (with or without maintaining the structural integrity of the initial compounds)*, which may be modularly applied, depending both on the species and on the chemical compounds utilized. The raw material may run through certain sequences of this flow sheet (see Figs. 1.1 and 1.2), which may be detached as single separated technology and may be applied depending on the available *amount and composition* of phytomass. After the separation of the specific compounds from phytomass, we can apply an **alkaline extraction**, which allows the isolation of complex consisting of polyphenols and hemicelluloses (Fig. 1.3). The idea of separating phenolic products from plants, especially from wood bark, is not new. It was proposed many years ago, yet its development has been prevented due to phenol accessibility in petrochemistry. Lately, as a consequence of the newly created economic conditions, the problem of extracting and utilizing phenolic compounds has been overcome.

The European pulp mills produce large amounts of bark as by-products, about 5.5 Mt/y. Additional amounts of bark are produced in sawmills. To date the major use of bark is a fuel, although alternative use has been sought for a long time. Thus, the bark can be used for extraction of useful chemicals and the process can be integrated in the production cycle, allowing them to be implemented industrially



**Fig. 1.3:** Examples of extraction and separation of secondary compounds (isolation of hemicelluloses and polyphenols from wood bark).

(instead of being only a matter of academic interest) [5]. The alkaline extracts were tested as phenol substituent in the synthesis of phenolformaldehyde resins, a bisphenol substituent in the synthesis of polyphenol epoxy resins, or as a phenolformaldehyde resin substituent [12].

Further conversion of resulted lignocelluloses could be performed by synthesis, using chemical or biochemical procedures that offer the possibilities of transforming the specific, secondary, and primary compounds while maintaining their basic structural units, or processing them by procedures presented in Fig. 1.4.

IV. *Products obtained by phytomass chemical processing, using above-mentioned methods, may structurally and/or functionally substitute certain raw materials of carbo- and petrochemical origin.*

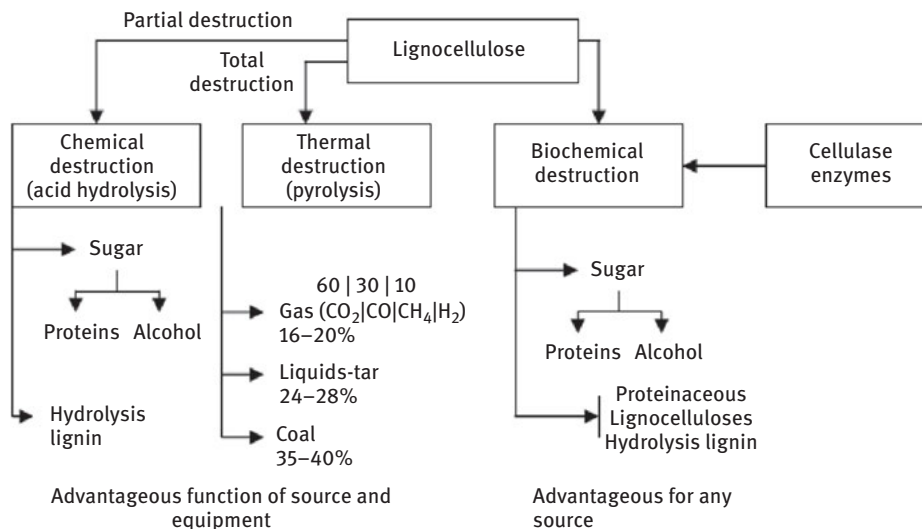


Fig. 1.4: Possibilities of lignocellulose complex valorification.

All these considerations will determine the approach to new directions of research:

- separation and direct utilization of chemical compounds isolated from biosystems;
- chemical processing of biomass and or wastes in their components by destruction, thus assuring raw materials for synthesis of polymers and chemical energy sources;
- chemical or biochemical transformation of both components and integral biomass (functionalization or functionality) for specific uses;
- elucidation of structures and functions of natural compounds in biosystems aiming at their utilization in structures with advanced properties and improving their behavior against physical, chemical and biological agents; and
- in vitro and in vivo simulation the synthesis of natural chemical compounds.

Using our proposed classification, cellulose and lignin can be considered as primary compounds in the pulp and paper industry.

### 1.2.1 Cellulose

The main utilization of pulp is to obtain paper and dissolving pulp (for cellulose derivatives, fibers, sponges, and films). At the same time, many chemicals can be produced from lignocelluloses, but recently there has been a new preoccupation to find special uses for cellulose. Thus, the cellulose would appear to have a great potential as nano-material. To fully exploit cellulose nanotechnology, research and development investment must be made in science and engineering that will determine the properties and

characteristics of cellulose at the nanoscale, developing the technologies to manipulate cellulose self-assembly and multifunctionality within plants, and develop these new technologies to the point where industry can produce much more advanced and cost-competitive cellulose-based products. The properties of nanocellulose makes it an interesting material for many applications such as composites, paper and board, food, hygiene and absorbent products, emulsion and dispersion, oil recovery, medical, cosmetics and pharmaceuticals, and so on.

An expert survey with 150 respondents from 21 countries, together with other inputs, predicted biorefining to be most profitable investment over the coming 10 years. Nanotechnology will generate most attention in research, followed closely by biorefining and niche products. Nanocellulose can be produced by biorefining [13–15].

## 1.2.2 Lignin

Today, wood is converted into pulp, and in chemical pulp mills, steam and electricity are generated in the recovery boiler. In the pulp mill of tomorrow, lignin, hemicelluloses, and extractives dissolved in process streams will be extracted and used as chemical raw materials.

### 1.2.2.1 Separation of lignin

Black liquor from cooking process in kraft mills contains cooking chemicals and dissolved and degraded wood substances, with about half of the wood organic material is dissolved into the black liquor. The liquor is incinerated with recovery of inorganic cooking chemicals and production of steam. The modern chemical pulp mill produces an excess of energy in relation to its own needs, but the surplus steam often has no use and is a waste product. The export of biofuels (bark, lignin and so on) from mill would very often be more efficient than onsite incineration of all internally fuels. The production of kraft black liquor lignin amounts to about 16 Mt/y in Europe [16].

The dissolved organics consisted primarily of lignin, hemicelluloses, and degradation products of cellulose and hemicelluloses. Valuable chemical properties and fractions of highly polymeric lignin and hemicelluloses compounds are not used when the black liquor is simply burnt at the mill site for energy recovery. Many other options exist for energy production, whereas the chemical properties of the renewable lignin and hemicelluloses material are unique. The spectrum of potentially interesting products from hemicelluloses and lignin is wide, ranging from upgraded biofuels to high-value specialty chemicals. Furthermore, withdrawal of lignin and/or hemicelluloses would allow the production capacity of

the pulp mill to be profitably increased if the recovery boiler is, as is often the case, the bottle-neck of the mill.

One way of utilizing the energy surplus in a modern pulp mill is to extract **lignin** from black liquor. The extraction of lignin is very flexible; lignin is energy rich (26–27 Mj/kg) and can be used as fuel to replace coal or oil in combustion and/or gasification plants; lignin may be also used as an internal fuel in the pulp mill (e.g., in the lime kiln) or sold either as fuel or raw material to be used for the production of various biobased materials/products (dispersants, various phenols, carbon fibers, etc.). Many of these components have a high market value, implying that lignin demands a high market value. It should also be kept in mind that if lignin is used as raw material, the end product will have a heat value, which, of course, should be utilized after the material has been used. Consequently, the extraction of lignin is not only a very flexible alternative, but it is also sustainable especially if the lignin is used as material before it is used as fuel. Extracting lignin is not, however, a new idea; it was proposed more than 50 years ago and a process for doing so has already been used in a few pulp mills for many years. In this process, the pH of this black liquor is lowered to about 10 and the lignin precipitates. The precipitated lignin is thereafter separated by means of filtration and a simple wash on the filter. Lignin produced using the older process was not very pure; the ash content could vary between 3 and 6%, which limited its use. Furthermore, some of the lignin was partly dissolved during the washing stage, which meant the remaining lignin was very difficult to dewater. This dissolution implies that total yield was reduced. A novel process known as the “LignoBoost” process was proposed few years ago and is a result of scientific investigation. This process has now been tested on pilot as well as demonstration scale and found to work very well: it is possible to produce lignin with a low ash content using the LignoBoost process. Although it lowers the pH of the black liquor to about 10, the separation stage is, however, quite different from the old process. The novel process starts with separation without washing. The filter cake from this stage is resuspended in low pH liquor and the lignin is filtered off and washed on a second filter. This particular procedure ensures that no noticeable amount of lignin amount will be dissolved and reprecipitated during the washing stage; as a result, the filtration resistance will be low throughout the process. The yield loss during washing will also be low. Despite the fact that there are two filters, the total filter area is normally much smaller than of the older process [17, 18].

Lignin does not possess a true repeating unit that can be selectively produced by degradation of the polymer, either chemically or enzymatically. Therefore, the future use of lignin (except as fuel) will depend on the possibilities of either its *degrading* or as *multifunctional macromolecule* [19].

Degradation of lignin can be obtained by *pyrolysis* under reductive conditions. Such methods have been tried for the production of phenols or aromatic hydrocarbons,

respectively. In the latter case, substituted benzene structures can be obtained with properties suitable for *biodiesel ingredients*. Since very harsh conditions are employed in the degradation reaction, the structure of lignin seems to play a minor role, whereas the choice of reaction conditions must be done such that tar formation is minimized [20, 21].

### 1.2.3 Degradation products of polysaccharides

Various saccharinic acids and other monocarboxylic acids are formed from polysaccharides during alkaline pulping of wood and nonwood raw materials. Their formation depends on the cooking conditions and composition of raw materials, but typically up to 10% of the charged raw materials are converted to these acids. In addition, varying amounts of volatile acids (formic and acetic acids) and different dicarboxylic acids are formed [22].

Although dozens of compounds have been identified so far, usually a few major compounds can be recognized. Among these, the most interesting compounds for the potential applications include glycolic, lactic, 2-hydroxybutanoic, 2,5-dihydroxypentanoic (3,4-dideoxypentonic), xyloisosaccharinic, and glucoisosaccharinic acids. The isolated hydroxyl acids or acid mixtures can find applications in many different fields. The simple hydroxyl acids, glycolic, and lactic acids are currently used as industrial chemicals with several applications. The higher homolog, 2-hydroxybutanoic (which is one of the main hydroxyl acid in hardwood black liquors), could find uses in the manufacture of resins and polymers; for example, after conversion to crotonic or isocrotonic acids. It should also be noticed that lactic and 2-hydroxybutanoic acids in the black liquors are of a racemic nature. The studies carried out have demonstrated the strong complexing capabilities of saccharinic acids, especially for many radionuclides and other materials. They have also been used for the preparation of various fine chemicals and as energy sources for aerobic and anaerobic bacteria [23, 24].

### 1.2.4 Black liquor as a feedstock for synthesis gas

An opportunity for biobased synthesis gas processes is integration of biofuel production with pulp and paper manufacture. For many of today's mills, this would enable the high-grade by-product energy of the biofuel plant to be fully exploited in the paper mill. The biofuel plant would also benefit from the existing infrastructure of the paper mill, in particular from that pertaining to feedstock procurement and handling.

Black liquor is a by-product from pulping, which is used today for steam and power production in the pulp mills. The black liquor is pumpable liquid, which is a significant advantage when the goal is to produce a clean syngas for use in catalytic

processing. The challenge with black liquor as a fuel is that it is highly corrosive and that the cooking chemicals in the black liquor must be recovered in a form that is compatible with the pulping process. Black liquor, the spent liquor of kraft mill pulping, is a major potential biofeedstock for synthesis-gas production. However, gasifiers developed for solid biomass cannot be applied, as such, to black liquor. Significant efforts are currently being made to develop the required specialized technology. Synthesis-gas production from black liquor has the potential of being somewhat more economical than synthesis-gas production from solid biomass residues. On the other hand, the latter technology has a greater market potential, poses a smaller availability risk for a pulp mill, and is technically more certain at the present time [25].

In the gasification process, black liquor is atomized by a gas-assisted nozzle and sprayed into the reactor where it is directly gasified. Gasification of lignin offers a smart option also for other biomass sources use that can be included in pulp mill allowing as a broad range of different feedstocks to be converted into one homogeneous synthesis gas. This product can be used for electricity generation (combined power and heat gas engine, gas turbine) as well as for chemical synthesis (production of hydrogen, ammonia, methanol, methane from remethanization, hydrocarbon formation using Fischer–Tropsch reactions, etc.) by conventional technologies.

Wood biomass can be also transformed into a liquid product through pyrolysis. Other products from this process are a solid biomass residue called *char* and *noncondensable gases* mainly CO, CO<sub>2</sub>, and light hydrocarbons. The liquid product, which is highly oxygenated, can be upgraded by removing oxygen. Application of zeolites during the upgrading removes the oxygen as water at low temperatures and as CO and CO<sub>2</sub> at higher temperatures, changing the yield of the produced phases. The major products in the resultant bio-oil, besides water, were 1-hydroxy-2-propanone, 2-methoxy-4-(1-propenyl)-phenol, 2-methoxy-4-methyl-phenol, and acetic acid. The phenolic products are formed in the pyrolysis of lignin, while the two other are formed of the wood carbohydrates [26, 27].

### 1.2.5 Biochar

Through pyrolysis of lignin along with other wastes from pulp and paper industry, carried out at temperatures that range from 250 °C to >900 °C and under limited oxygen availability, it is possible to obtain biochar. This char could be used as a solid fuel to generate process heat. It has also been demonstrated that biochar can reduce bioavailability of some heavy metals and that it has a high adsorption capacity to persistent organic pollutants and can be used for environmental protection [28, 29].

## Secondary compounds: hemicelluloses and polyphenols

### 1.2.6 Separation of hemicelluloses

The flow of kraft black liquor carbohydrates derived by-products (including degraded sugar acids) amounts to about 12 Mt/y in Europe. In spite of the large amounts available, hemicelluloses have not yet been utilized commercially to any longer extent. The main obstacle is the difficulty of extracting them in their native form, since they are intimately associated with cellulose and lignin in the wood structure [30].

During the chemical pulping using kraft method, most of the hemicelluloses are degraded and dissolved as monomeric and oligomer sugars or sugar acids, in the black liquor. However, xylans – the main constituent of hemicelluloses in, for example, birch and eucalyptus – are preserved in a more native form to a certain extent. When isolated, the hemicelluloses have many potentially valuable properties. They could be used as paper additives, thickeners, food additives, emulsifiers, gelling agents, adhesives, and adsorbents. Some hemicelluloses have shown cholesterol-lowering effects and even antitumor effects [31].

The *hemicelluloses* that normally end up in the black liquor of a hardwood kraft mill can be extracted prior to kraft pulping and used for the production of ethanol and acetic acid. The extracted liquor undergoes evaporation, hydrolysis, separation, fermentation, and distillation for the production of acetic acid and ethanol. During extraction process acetyl groups, which are side chains on the xylan hemicelluloses, are cleaved to give dissolved sodium acetate, which will be converted to acetic acid in the hydrolysis stage of the plant.

The hardwood biorefining uses green liquor in addition to AQ for wood extraction prior to modified kraft cooking to preserve both pulp yield and quality. During extraction, about 10% of the wood goes into solution. The extract mostly contains hemicelluloses derived organic compounds and has a near-neutral pH. The extracted chips require a 3% lower white liquor (as Na<sub>2</sub>O on original oven dry wood) and a lower H factor in the subsequent kraft cook.

*Galactoglucomannan* (GGM) dominates the softwood hemicellulose. During refining of mechanical pulp, a part of the GGM is dissolved in the process water, which can be recovered from the water by ultrafiltration. The molar mass of GGM depends on the filtration methods, but is typically 20–30 kDa. GGM has been found to stabilize colloidal pitch by forming a hydrophobic layer on the surface of the pitch particles, thus reducing the risk for deposit formation during papermaking. Other possible uses of GGM can be also found, as their sorption property can be utilized together with fillers, cellulosic, and mechanical fibers. GGM can be modified by grafting it with other types of functional groups than hydroxyl groups. It is also an interesting polysaccharide as food additive, as it may be used as the so-called dietary fibers. GGM has also been studied also as film-forming constituents [32].



**Specific compounds: pigments, hydrocarbons simple sugars, alkaloids, polyphenols, other bioactive compounds, oils, proteins, and so on**

### 1.2.7 Fine and specialty chemicals

Black liquor contains compounds of potential value. Roughly half of the dissolved organic material is lignin and the rest is mainly sugar acids, other organic acids, and methanol.

Tall oil and turpentine products from kraft pulping were developed in the beginning of last century and have been produced ever since. Distillation technology has been improved during the last decades, and today, very pure rosin and fatty acids products can be manufactured. Tall oil fatty acids and tall oil rosin have found a wide variety of applications. The fragrance industry largely utilizes turpentines both sulfate turpentines and sulfite turpentines distilled from tapped oleoresin. A new use of tall oil fatty acids could be production of conjugated linoleic acids (CLAs). Nordic tall oil fatty acids are rich in linoleic acid (9,12–18:2), typically containing 40–50% linoleic acid. It is possible to make CLAs with the aid of heterogeneous catalysts and in the absence of solvents. Various antioxidant and antitumor properties have been attributed to CLAs and such preparations are marketed as dietary supplements [33].

In addition to naturally occurring constituents, chemical modification of isolated wood compounds provides new options. For example, new physiologically active compounds can be derived from wood using heterogeneous catalysis; *sitostanol* can be produced by catalytic hydrogenation from *sitosterol*, conjugated *linoleic acids* can be synthesized via isomerization of *linoleic acid*, and other lignans can be obtained from hydroxymatairesinol hydrogenolysis [34].

### 1.2.8 Bioactive compounds

Some ideas concern new high-added value applications in the medical field, where these raw materials have not been used before, the driving force being to replace polymers/materials obtained from nonrenewable feedstocks. Xylitol and sitosterol/sitostanol are health-promoting products from wood, both of which have found their own special niche; xylitol promotes hygiene of mouth and sitosterol/sitostanol exerts a lowering effect on the cholesterol level in the human coronary flow. However, wood constituents still offer additional new opportunities for health-promoting products, as well as being a raw material of chemicals. For example, knots in spruce, that is, inner parts of the branches, have been found to contain extremely high concentration of polyphenols compared to the stem. Generally, these polyphenols are strong antioxidants. The dominating lignan, *hydroxymatairesinol* (HMR), has been documented to carry favorable properties in the fight against cancer and also coronary heart diseases.

The HMR lignan is extracted from spruce knots that are separated from chips of spruce trees grown in Northern part of Finland. After purification and formulation of HMR lignan product, it has been marketed as a health-promoting food supplement since 2006.

Stilbenes are also interesting bioactive constituents in trees; these can be found in the bark of spruce, up to the level of 10%. *Piceatannol*, which is the main spruce bark stilbene, is an efficient antioxidant. The same group of antioxidants is also found in grapes and in red wine [35].

In our study lignins and polyphenols extracted from different sources of biomass using biorefining [36] have been used in model experiments to follow their actions as allelochemicals [37].

Polyphenols extracted from spruce wood bark have been tested as plant growth regulators and the results showed that the isolated compounds exhibited similar effects to the endogenous hormones cytokinin and auxine [38]. Based on the obtained results, lignin and polyphenols were used in seeds germination, plants tissue culture, plants cultivation [38, 39], bioremediation [40] or as substrate for microorganisms development [41].

## 1.3 Conclusions

Plant cell wall biomass is composed of cellulose, hemicelluloses, lignin, protein, lipids, and several small molecular weight components with different ratios depending on the raw materials.

The key issue for a successful valorization of biomass to chemicals is efficient fractionation into hemicelluloses, cellulose, lignin, and the other compounds.

Thus, a plant for the fractionation and refining of biomass, and for the utilization of all its components, a “biorefinery” plant will have to display a high level of process *integration* and *optimization* to be competitive in the near future. A biorefinery is an installation that can process biomass into multiple products using an array of processing technologies. By integrating *forest biorefinery (FBR)* activities in an existing plant, pulp and paper mills have the opportunity to generate significant amounts of bioenergy and bioproducts and to drastically increase their revenues while continuing to produce wood, pulp, and paper products. A new generation of technologies based on thermochemical, biochemical, and chemical pathways is likely to enable the development FBR. Manufacturing new value-added by-products (e.g., fuels, bulk and specialty chemicals, pharmaceuticals, etc.) from biomass could represent for some forestry companies an unprecedented opportunity for revenue diversification. At the same time, biorefineries in the pulp and paper sector will integrate several biomass raw materials.

In addition to process technology development, product development will be essential for identifying successful new markets for biorefining products and their supply chain management. Therefore, incorporating new products, in addition to

existing pulp and paper product portfolio, is a complex problem and perhaps the key to a company's successful diversification.

Biorefinery technology development will typically be implemented in retrofit and must be accompanied by careful process systems analysis in order to understand the impact on existing processes.

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## Chapter 2

# Pulping fundamentals and processing

## 2.1 Introduction to pulping

Pulping is a process by which plant material (wood, straw, grass, etc.) is reduced to a fibrous mass. Pulp refers to a suspension of cellulose fibers in water and represents the raw material for producing paper and board and obtaining cellulose derivatives. There are two major pulp grades: paper-grade pulp and dissolving pulp. The properties of paper-grade pulp refer to pulp yield, pulp brightness, and strength properties. The properties of dissolving grade pulp refer to high cellulose content and to a high reactivity toward derivatization chemicals.

According to the Confederation of European Paper Industries [1], the global production of pulp was 180.6 million tons in 2016 and the main pulp producers are North America, Europe, and Asia. The pulp and paper capacity survey (2016–2021) of the Food and Agriculture Organization of the United Nations [2] shows that in North America and Europe pulp production in the next few years will remain at relatively constant level, while pulp production in Latin America will increase due to wood abundance and low cost of labor.

A study of Haley [3] affirms that, in 2008, China overtook the United States to become the world's largest producer of paper due to the fact that this country has been rapidly expanding its paper-producing capacity. A forecast of domestic paper consumption in China shows that paper demand is projected to grow to 143 million tons in 2021 [3]. The demand for pulp in China increased at a rate of 10.3% between 2007 and 2017, and in 2017 China consumed 35% of the world produced pulp [4].

The aim of all pulping processes is to separate the fibers from the lignocellulosic materials to obtain pulp grades that must be suitable for papermaking. Cellulosic fibers can be separated from each other by mechanical, chemical, or by a combination of both treatments. According to Biermann [5], there are three main categories of pulping processes: mechanical, semichemical, and chemical.

Mechanical pulping uses mechanical energy to separate fibers from the wood matrix. There are several variants of mechanical pulping depending on the process parameters and equipment. Wood is processed either in the form of logs treated in grinders or in the form of wood chips that are converted to pulp in a refiner. Lignin or other wood components are not intentionally removed in mechanical pulping. Höglund [6] shows that in order to weaken the strength of the fiber–fiber bonds,

steaming or/and a gentle chemical treatment of wood is performed. Classification of mechanical pulping comprises four processes:

- Groundwood pulping includes stone groundwood (SGW) and pressure groundwood (PGW) methods. Atmospheric grinding and pressure grinding of logs using a pulp stone are the main alternatives of the groundwood pulping.
- Refiner mechanical pulping (RMP) consists of atmospheric refining of wood chips using a dedicated disc refiner.
- Thermomechanical pulping (TMP) consists of refining of steamed chips under pressure and elevated temperature using a disc refiner.
- Chemithermomechanical pulping (CTMP) involves refining of steamed and chemically pretreated chips under pressure and elevated temperature using a disc refiner.

The yield of mechanical pulp grades is high and depends on the process involved, as is presented by Sundholm [7]: groundwood pulp and RMP (96–98%); TMP (94–96%); and CTMP (90–95%). Besides the high yield, mechanical pulps exhibit a high light-scattering power, a high bulk, and a fairly high brightness. These pulps are used in producing papers with good opacity and printability at low basis weight (newsprint and magazine paper). Sundholm [7] also stated that the drawbacks of mechanical pulps refer to their high electrical energy consumption (up to 3.5 MWh/t of pulp) and to the fact that high-quality wood is required.

Semichemical pulping is performed in two steps: a mild chemical treatment of wood chips followed by a moderate mechanical refining. A partial removal of both of lignin and hemicelluloses takes place, so that the yield of pulp ranges between 60 and 80%. The chips are chemically treated at elevated temperature where about 50% of the initial lignin content of wood is removed. The softened chips are then processed in a defibrator enabling fiber separation.

According to von Koeppen [8], the most frequently employed process is neutral sulfite semichemical (NSSC) pulping, which uses cooking liquor containing  $\text{Na}_2\text{SO}_3$  and  $\text{Na}_2\text{CO}_3$ . Sodium sulfite is the reagent for lignin sulfonation while sodium carbonate acts as a liquor pH buffer. A high cooking temperature (160–180 °C) is necessary both for both lignin sulfonation and dissolution. Hardwood is usually the best fiber source for NSSC pulp. The high lignin content makes the fibers very stiff, with the NSSC pulp being found to be the best raw material for a corrugated medium [9]. NSSC pulping generates spent liquor (usually named as red liquor) that contains dissolved lignin and hemicelluloses as well as inorganic substances. Ingruber [10] showed that the red liquor must be processed to recover the process chemicals.

Chemical pulping uses chemicals for lignin degradation and dissolving. Due to the fact that lignin is extensively removed, the fibers can be separated with little or no mechanical treatment. The process requires high temperature and pressure. Pulping chemicals are not selective regarding lignin degradation, the carbohydrates

being also affected during the process. Almost half of the wood material is removed during chemical pulping and the pulp yield ranges from 45 to 55% depending on the pulping technique [11].

According to Sixta and coworkers [12] it is impossible to remove all lignin in any pulping process; hence, the cooking is intentionally stopped at a certain lignin content of the pulp. The residual lignin content represents the most important parameter that characterizes the pulp grade. The properties of chemical pulps must be compared at the same residual lignin content. In a chemical pulp mill, further delignification is achieved by bleaching of pulp.

Gullichsen [13] stated that pulping methods are classified according to the composition of cooking liquor and delignification can be performed in alkaline or acidic domain. Chemical pulping can also be performed in one or two stages.

Kraft pulping strongly dominates the world pulp production due to the following advantages:

- Kraft cooking is able to produce pulp from any kind of raw materials (wood species and nonwood plants).
- Kraft pulp exhibits very good strength properties.
- Cooking chemicals are produced via processing of the spent liquor in a recovery plant. Both steam and electrical energy are generated, so that the process is self-sufficient with respect of energy.
- The large capacity of kraft pulp mills reduces the specific consumption of materials and energy and enhances the profitability of pulp making.

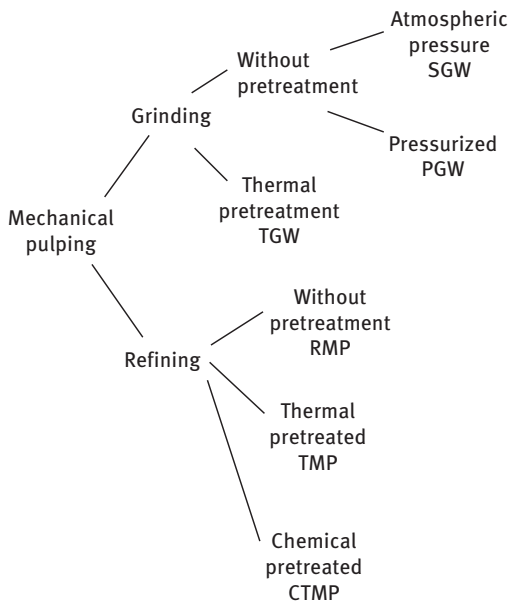
Drawbacks of kraft pulping are as follows:

- Pulp yield is lower when compared with other pulping processes.
- The kraft pulp mill represents a source of polluting materials that are very different regarding their quantities and characteristics.

## 2.2 Mechanical pulping

During mechanical pulping, forces of various magnitude and duration are applied on wood matrix to separate the fibers. Wood is a viscoelastic material so that its behavior to mechanical forces is influenced by its moisture, temperature, load intensity, and time under load. Water plays a key role in mechanical pulping due to the fact that the softening temperature of wood main components depends on wood moisture. Salmen and coworkers [14] showed that for water-saturated lignin, the softening takes place at 80–90 °C. Mechanical energy is partially converted into heat as a result of friction between wood and pulpstone or refining plates. The fibers are removed from the wood matrix once the lignin from middle lamella has been heated to the temperature that exceeds its glass transition point.

Mechanical pulp is manufactured by mechanical defibration using two procedures: grinding of wood logs using a pulpstone (grinding process) and refining of wood chips in a dedicated disc refiner (refining process). Figure 2.1 shows the mechanical pulping techniques.



**Fig. 2.1:** Mechanical pulping processes.

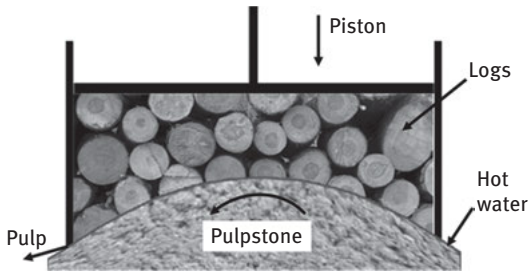
As is shown in Fig. 2.1, the commercial grinding processes are SGW, PGW, and thermogroundwood (TGW). The refiner processes are represented by RMP, TMP, and CTMP.

A mechanical pulp mill includes the following stages: logs debarking and chipping, grinding of logs or refining of wood chips, and the screening and bleaching of mechanical pulp.

The grinding process consists of pressing the wood logs against a rotating pulpstone in the presence of water. According to Karnis [15], the process is divided into two consecutive stages: (i) softening of the wood and breakdown of the wood matrix and (ii) peeling and successive refining of the fibers. The pulpstone contains grits that pass over the wood surface at very high frequencies, yielding a compression/decompression process. The grinding principle is shown in Fig. 2.2.

The wood structure is loosened due to the fatigue work performed by the grits. At the same time, temperature increases rapidly in the grinding zone, causing the lignin to soften. The presence of water reduces the softening temperature of lignin.





**Fig. 2.2:** Grinding process.

The high-frequency pressure pulsations determine deformation of the fibers and breakdown of bonds between the fibers. The fibers are peeled from the wood surface and then successively refined in the fibrous layer generated between the wood surface and pulpstone.

There are many parameters influencing the defibration of wood by grinding. Liimatainen and coworkers [16] showed that the most important are wood moisture, logs feeding speed (grinding pressure), pulpstone peripheral speed, water temperature in the grinder pit, surface shape of the pulpstone, and specific energy consumption.

The refining process uses wood chips that are fed in a dedicated disc refiner, where these are defibrated by passing through the refining zone. McDonald and coworkers [17] showed that in order to soften the wood matrix before refining, the chips are steamed and/or they undergo a mild chemical treatment. A mechanical, thermal, or chemical softening of lignin takes place.

The common refining processes are TMP and CTMP. In a TMP process, wood chips are steamed and fed into the refiner, which is pressurized, and the steam pressure corresponds to the temperature of the saturated steam. Berg [18] showed that the friction process between the fibers, and between the fibers and bar edges, causes fibers shortening and fibrillation to take place. The refining process consumes considerable energy that is partially converted into heat that increases the temperature in the refining zone between the plates, as presented by Muhic and coworkers [19]. The additional heating positively influences the chip defibration and fiber fibrillation and has an important influence on the final pulp quality. According to Miles and Karnis [20], the electrical energy demanded using refining to produce TMP pulp for magazine paper grades is 1,800 to 3,000 kWh/t, newsprint grades demand 1,800 to 2,200 kWh/t, and paperboard grades 1,000 to 1,400 kWh/t.

TMP is currently the most important mechanical pulping process and displaced older grinding processes, because similar paper properties could be achieved using a lesser amount of expensive chemical pulp, as shown by Illikainen [21] and Fernando and coworkers [22]. TMP is mostly used for producing printing papers such as newsprints, and uncoated and coated magazine papers.

Figure 2.3 presents the flowsheet of a TMP fiberline with two-stage chips refining. The chips are washed to remove sand and are steamed. The steamed chips are fed into the first refining stage where the wood material is broken into small fragments and shives. After the first refining stage, the semirefined chips feed in the second refiner for fibers separation. After refining, the pulp is screened and it enters the bleaching stage. Rejected material is processed in a two-stage refining line and after screening is combined with screened pulp. Bleached TMP pulp is sent to the paper machine.

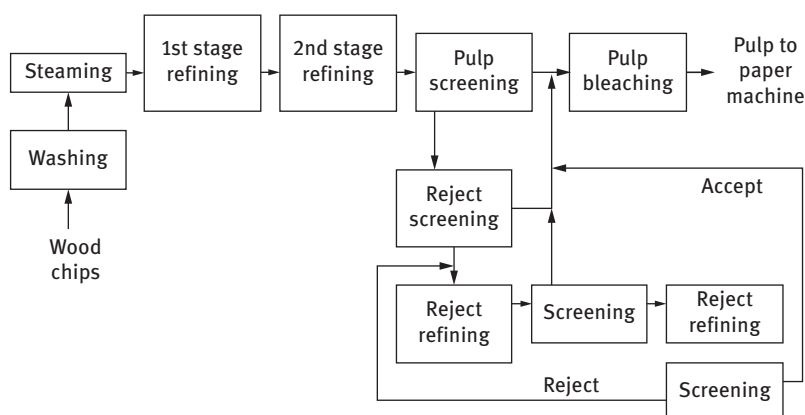


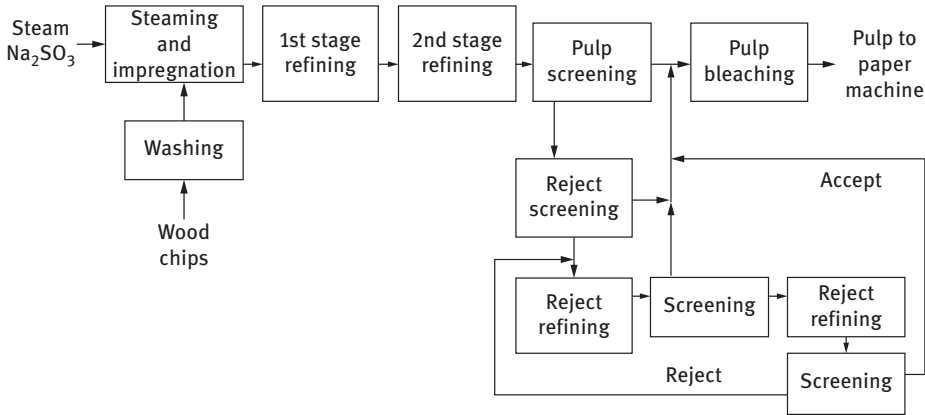
Fig. 2.3: Flowsheet of a TMP fiberline.

CTMP uses both steaming and chemical treatment for lignin softening. Chemical softening exhibits a major influence on the properties of fibers liberated from the wood matrix during the refining of chips. When wood chips are impregnated with chemicals, the softening due to swelling of the reactive middle lamellae and the primary wall regions is predominant, and this is where the defibration fracture zones are located, as was stated by Gorski [23].

During CTMP operations, the chemical treatment is carried out by the impregnation of wood chips. Sodium sulfite is the dominating reagent both in hardwood and softwood pulping. Johansson and coworkers [24] showed that the softening temperature of lignin depends on the sulfonate content of the wood, which is influenced by the sulfite dose and the temperature and duration of chemical treatment of the chips.

According to Lindholm and Kurdin [25], during the production of softwood pulp using CTMP, the parameters of the chemical treatment of the chips are sodium sulfite charge 2–4% on wood; temperature 120–135 °C; and retention time 2–15 min. The sulfonate content of the lignin ranges between 0.25 and 0.75% on pulp.

Figure 2.4 presents a typical flowsheet of a CTMP plant. The major difference between TMP and CTMP processes is the chemical impregnation stage; in this stage, chips are damped and compressed and then are expanded in a sodium sulfite solution. The expansion and condensation effects cause the absorption of the liquid phase into the wood structure.



**Fig. 2.4:** Flowsheet of a CTMP fiberline.

The chips are refined in two stages and the obtained pulp is screened and bleached. The benefits of CTMP refer to the reduction of specific energy consumption and to an increase level of long fibers in the pulp.

The properties of the mechanical pulp depend on the pulping technique. Blechschmidt and coworkers [26] showed that the strength properties increase in the range SGW, RMP, TMP, and CTMP. Regarding the light-scattering coefficient, SGW shows the highest values, followed by RPM, TMP, and CTMP. These pulps are the raw material for the production of some of the most significant paper grades. Both softwood and hardwood species are used in mechanical pulping, and Tab. 2.1 lists the main end products.

**Tab. 2.1:** Paper grades achieved from the mechanical pulp of softwoods and hardwoods.

Wood species	Mechanical process	Paper grade
Softwoods	SGW, TMP CTMP	Newsprint, supercalendered, low-weight-coated (LWC) Tissue Liquid packaging boards
Hardwoods	PGW, CTMP CTMP	Tissues, printing Tissue, fluting

## 2.3 Semichemical pulping

The term semichemical pulping suggests that pulp is produced by a chemical treatment of chips, followed by a mechanical treatment, and both treatments exhibit a fairly equal contribution to the separation of fibers from wood matrix. During semichemical pulping, the partial remove of lignin and hemicelluloses takes place, so that the yield of pulp is 60–80%.

NSSC is the most important semichemical pulping process. The wood chips undergo partial chemical pulping using sodium sulfite liquor, followed by a treatment in a disc refiner to achieve the fibers separation. The sulfonation of the middle lamella lignin causes its partial dissolution so that the fiber–fiber bonds are weakened before the subsequent mechanical treatment. NSSC cooking liquor contains both  $\text{Na}_2\text{SO}_3$  and  $\text{Na}_2\text{CO}_3$ , as presented by Obrocea and Gavrilescu [27]. Sodium sulfite represents the lignin sulfonation agent, while sodium carbonate acts as a buffer of liquor pH. The  $\text{Na}_2\text{SO}_3$  consumption ranges between 6 and 9% on wood and the ratio of  $\text{Na}_2\text{SO}_3/\text{Na}_2\text{CO}_3$  varies between 3:1 and 4:1. The pH of the liquor is 10–11 and cooking time is 0.5–2 h at 160–185 °C.

Hardwoods (beech, poplar, adler) are the best fiber source for NSSC pulp, as found by Nemati and coworkers [28]. Nonwood plants residues (straws especially) are also used, as studied by Ahmadi and coworkers [29] and by Leponiemi [30]. NSSC pulp is used for the production of papers where stiffness is mostly essential, such as a corrugating medium. These papers show the best value for the flat crush of corrugated medium (Concora flat crush), as was found by Gavrilescu and Toth [31].

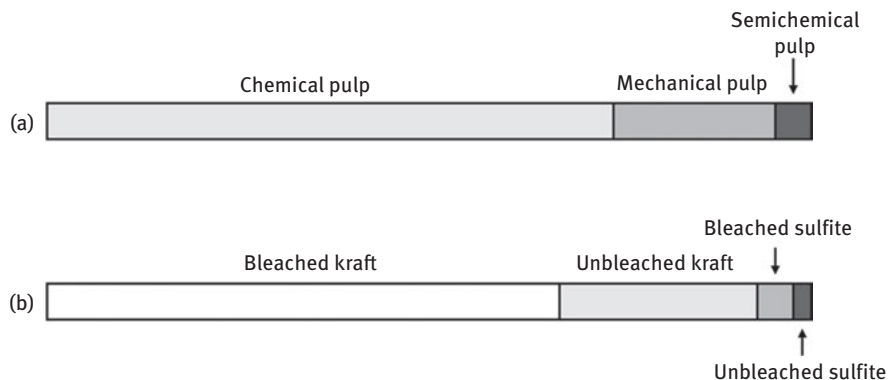
Zhao and Tran [32] studied the spent liquor of NSSC pulping (red liquor) and found that it contains lignosulfonates, hemicelluloses, organic acids, and ashes. The concentration of red liquor is quite low (5–8% dry matter) and for this reason its calorific value is small. The NSSC pulping plant is often integrated into a kraft pulp mill to facilitate chemical recovery by the so-called cross-recovery, where the red liquor is processed together with the kraft black liquor.

## 2.4 Chemical pulping

On a global scale, pulp is predominantly produced by chemical pulping processes, as shown in Fig. 2.5. Chemical pulp represents around two-thirds of total pulp production worldwide.

Figure 2.5 also shows that among chemical pulps, kraft pulp (bleached and unbleached) grades are the most produced if compared with sulfite pulp.

During the chemical pulping, reagents are used to split the macromolecule of lignin into fragments that are further dissolved in the cooking liquor. Fibers separation occurs when the lignin from the middle lamella is totally removed and, as a rule, no



**Fig. 2.5:** Sharing of chemical, semichemical, and mechanical pulps (a), and the distribution of chemical pulps (b).

mechanical action is necessary. Chemical pulping requires a large quantity of reagents and a high temperature and pressure. Besides lignin, polysaccharides are also chemically modified and dissolved, so that the pulp yield ranges between 45 and 60%. An important volume of spent liquor is generated.

There are two major grades of chemical pulp: papermaking pulp and dissolving pulp. Papermaking pulp includes unbleached pulp and bleached pulp and is characterized by yield, residual lignin content, brightness, and strength properties. Dissolving pulp differs substantially from papermaking pulp and it is characterized by high alpha-cellulose content, low noncellulosic carbohydrate content, defined cellulose molar mass and molar mass distribution, low extractives and low ash content, and high reactivity toward derivatising chemicals.

The main stages of a chemical pulping process are wood preparation, cooking, pulp washing and screening, pulp bleaching, and recovery of cooking chemicals.

## 2.5 Kraft pulping processes

### 2.5.1 General description

Kraft (or sulfate) pulping represents the main cooking process, accounting for nearly 90% of the global chemical pulp production as presented by Gavrilescu and Craciun [33]. The term *kraft* refers to the fact that kraft pulp exhibits good strength properties. The cooking liquor (usually called *white liquor*) contains sodium hydroxide and sodium sulfide as the active alkali, which reacts with lignin and promotes degradation of lignin polymer to fragments that dissolve in the cooking liquor.

Figure 2.6 shows the flowsheet of kraft pulping. Wood preparation includes logs debarking, logs chipping, and chips screening. Screened chips are temporary stored in piles and then transported into the digesters house.

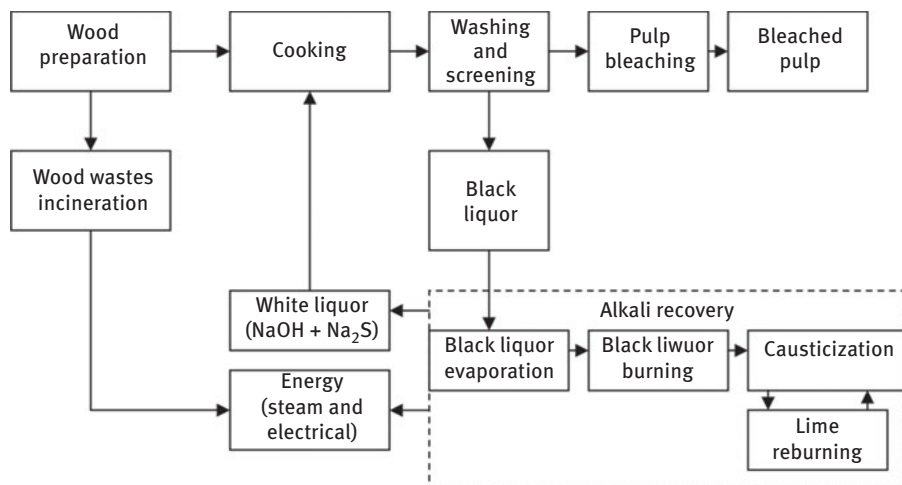


Fig. 2.6: Flowsheet of kraft pulping.

Cooking is performed in discontinuous or continuous digesters at a high temperature and pressure. After cooking, pulp is washed and screened and is finally bleached to obtain the bleached pulp, which is used for printable paper grades, while unbleached pulp is used for the production of packaging paper grades. Kraft pulping generates spent liquor (denoted as black liquor) that contains the organic compounds removed from wood and the inorganic chemicals originating from white liquor. The black liquor must be processed to recover the cooking reagents and to valorize the heat of the organic matter; the alkali recovery process includes black liquor evaporation and burning, causticizing of green liquor, and lime reburning.

White liquor is characterized by the quantitative and qualitative parameters presented in Tab. 2.2. The most important are the concentration of active alkali (AA) and sulfidity (S).

Detailed studies were made regarding the composition of kraft cooking liquor. Gierer [34] found that in the white liquor, the main ionic species are  $\text{Na}^+$ ,  $\text{HO}^-$ ,  $\text{HS}^-$ , and  $\text{CO}_3^{2-}$ . Other ionic species ( $\text{S}^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ) are of negligible importance in the electrolyte equilibria of the cooking liquor. Gierer also stated that hydroxide ions ( $\text{HO}^-$ ) and hydrogen sulfide ions ( $\text{HS}^-$ ) are the only species that react with lignin during kraft pulping.

The typical composition of white liquor is listed in Tab. 2.3. The major components are sodium hydroxide and sodium sulfide and the minor components are

**Tab. 2.2:** Parameters of white liquor.

White liquor parameter	Formula
<b>Quantitative parameters</b>	
Active alkali (AA)	$\text{NaOH} + \text{Na}_2\text{S}$
Effective alkali (EA)	$\text{NaOH} + 0.5\text{Na}_2\text{S}$
Total alkali (TA)	$\text{NaOH} + \text{Na}_2\text{S} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4$
<b>Qualitative parameters</b>	
Sulfidity (S)	$S = \text{Na}_2\text{S} / (\text{NaOH} + \text{Na}_2\text{S})$
Causticity (C)	$C = \text{NaOH} / (\text{NaOH} + \text{Na}_2\text{CO}_3)$
Degree of reduction of sodium sulfate (DR)	$\text{DR} = \text{Na}_2\text{S} / (\text{Na}_2\text{S} + \text{Na}_2\text{SO}_4)$

**Tab. 2.3:** Typical composition of white liquor (expressed as  $\text{Na}_2\text{O}$  and  $\text{NaOH}$ ).

Component	Concentration (g/L)	Concentration ( $\text{Na}_2\text{O}$ ; g/L)	Concentration ( $\text{NaOH}$ ; g/L)
NaOH	100	$100 (31/40) = 77.5$	100
$\text{Na}_2\text{S}$	35	$35 (31/39) = 27.8$	$35 (40/39) = 35.9$
$\text{Na}_2\text{CO}_3$	20	$20 (31/53) = 11.7$	$20 (40/53) = 15.1$
$\text{Na}_2\text{SO}_4$	6	$6 (31/71) = 2.6$	$6 (40/71) = 3.4$
Active alkali concentration	–	105.3	135.9
Total alkali concentration	–	119.6	154.4

sodium carbonate and sodium sulfate. Under kraft pulping condition, sodium carbonate and sodium sulfate are not able to react with lignin.

Extensive researches have been carried out to elucidate the chemistry of kraft cooking. Potthast [35] and Sakakibara and Sano [36] showed that the reactions of lignin during kraft pulping can be divided into two main categories, degradation reactions, and condensation reactions, respectively.

Degradation reactions split the lignin macromolecule into fragments that are able to dissolve in the cooking liquor. According to Gellerstedt [37] and Gierer [38], the common degradation reactions occurring during kraft pulping include the cleavage of  $\alpha$ -aryl ether and  $\beta$ -aryl ether bonds of lignin.

Condensation reactions are not desirable as they lead to the formation of alkali-stable linkages, thereby increasing the molecular size of lignin fragments, as was found by Gellerstedt and Lindfors [39]. These reactions occur if wood impregnation with white liquor is not finished and/or cooking temperature is raised too fast. According to the same authors, during a normal kraft cook, no extensive condensation involving the aromatic rings of the lignin takes place [40].

It is known that kraft spent liquor is black in color and kraft pulp is darker in comparison with pulp obtained by other pulping procedures. Robert and coworkers [41] showed that the reason for this behavior is the formation of lignin chromophores like quinonoide structures and stilbenes.

A particular reaction that occurs in kraft pulping studied by Gierer [42] involves the cleavage of methyl aryl ether bonds and generation of mercaptans represented by methylmercaptan, dimethylsulfide, and dimethyldisulfide. Mercaptans are responsible for the specific smell of the kraft pulp mill.

Sixta [43] studied the evolution of pulp yield and pulp delignification degree, and found that lignin is eliminated on a large scale during kraft pulping. Besides lignin, nonlignin components, mainly carbohydrates, are removed in some extent and, as a result, pulp yield decreases.

The reactivity of carbohydrates in kraft pulping depends on their structural features such as morphology, crystallinity, and degree of polymerization. Gentile and coworkers [44] found that hemicelluloses are degraded more than cellulose in alkaline media at high temperature.

Sjöström [45] reviewed the alkaline degradation of carbohydrates during kraft cooking and concluded that there are two basic degradation reactions: peeling and alkaline hydrolysis. In the peeling reaction, a step-by-step depolymerization occurs at the reducing end sites of the carbohydrates. The reaction generates a monosaccharide that finally transforms it into an isosaccharinic acid. During the reaction a new reducing end on the remainder carbohydrate is also formed, which can undergo further peeling reactions. The same authors also showed that the carbohydrate material lost in the peeling reaction is converted into various hydroxy acids, which consume active alkali and consequently reduce its concentration in the pulping liquor. Hemicelluloses (glucomannans and xylans) are more engaged in peeling reactions compared with cellulose. About 50–60 monomer units are peeled off from the carbohydrate macromolecule and, after that, a stopping reaction occurs.

Gustavsson and Al-Dajani [46] showed that alkaline hydrolysis of cellulose takes place at the end of the cook and determines the reduction of polymerization degree of cellulose. Due to the high temperature and strong alkaline medium, a random cleavage of cellulose macromolecule occurs. The resulting fragments may dissolve in the cooking liquor or participate in the peeling reactions. Alkaline hydrolysis of cellulose explains the severe loss of pulp yield in the final part of the kraft cook.

An important reaction of the carbohydrates in alkaline pulping is the formation of hexenuronic acids, which are formed by the alkaline degradation of 4-O-methyl-D-glucuroxylans. It was established that the presence of hexenuronic acids in the kraft pulp influences the reagents consumption during pulp bleaching and stability of pulp brightness [47].

Olm and Tistad [48] studied the kinetics of kraft pulping and showed that the dissolution of lignin and carbohydrates proceeds in three phases denoted as initial, bulk, and final delignification. Table 2.4 lists the characteristics of kraft pulping phases.



**Tab. 2.4:** Phases of delignification during kraft pulping.

Phases of delignification	Features
Initial	Slow delignification; lignin content is reduced by 15–25% of the initial amount, as compared to about 40% of the hemicelluloses (cooking selectivity is low)
Bulk	High delignification rate; about 70% of the lignin is dissolved as compared to 5–7% of carbohydrates (high selectivity)
Final (residual)	Slow delignification; intensive degradation of carbohydrates. Low selectivity

Initial delignification is a slow phase and only 15–25% of initial lignin is dissolved. In this stage, around 40% of hemicelluloses are dissolved so that the cooking selectivity is low. Bulk delignification is the main stage of cooking, with around 70% of the lignin being dissolved. The delignification rate is high as is the process selectivity. Final delignification begins at a delignification rate of about 90%. To avoid excessive pulp yield loss, kraft cook is often stopped before the final delignification [49].

Besides the major chemical constituents (cellulose, lignin, and hemicelluloses), wood contains a large number of low molecular organic compounds, denoted as extractives. The extractives can be separated from wood with hot water or organic solvents. Umezawa [50] found that the extractives are complex mixtures of fats, fatty acids, fatty alcohols, phenols, terpenes, steroids, resin acids, rosin, waxes, and other minor organic compounds.

During kraft pulping, extractives show a complex behavior. Some of them are volatile and accumulate in the gaseous phase of the digester; this fraction is recovered from the digester relief condensate and is called *sulfat turpentine*. Most of extractives are soluble in cooking liquor and may react with alkali. Fatty acids and resin acid esters are neutralized and recovered as tall oil soap. Lindström and coworkers [51] found that crude tall oil from pine contains 40–60% resin acids, 40–55% fatty acids, and 5–10% neutral constituents. Abietic and dehydroabietic acids cover over 60% of the resin acids, while oleic and linoleic acids predominate in the fatty acid fraction.

### 2.5.2 Kraft pulping parameters

Kraft pulping parameters include those factors influencing delignification rate, pulping selectivity, pulp properties, and specific consumption of raw materials and energy. MacLeod [52] showed that kraft pulping variables can be divided into key factors and minor factors. The key factors exert a significant influence on pulping results and they

are active alkali charge, white liquor sulfidity, cooking temperature and cooking time, wood specie, and chip quality. The minor factors are liquor-to-wood ratio, black liquor addition, and the presence of sodium carbonate in the white liquor.

The active alkali charge represents the ratio between active alkali quantity (expressed as NaOH or Na<sub>2</sub>O) and wood mass. Casey [53] established that the theoretical consumption of active alkali in kraft pulping is 15% NaOH on wood. In order to enhance the delignification rate, the practical active alkali charge is 50–60% higher, so that the cook is performed with an excess of active alkali. At the end of the cook, the concentration of active alkali must be 5–10 g/L NaOH to avoid the reprecipitation of dissolved lignin on fibers.

As the active alkali charge is higher, more lignin dissolves from the wood, so that this parameter determines the degree of pulp delignification. The active alkali charge ranges between 17 and 19% NaOH for obtaining hard kraft pulps and 20 and 25% NaOH for bleachable pulp grades. Softwoods require 10–12% more active alkali compared with hardwoods.

Casey [53] also showed that the active alkali concentration depends on active alkali charge and on liquor-to-wood ratio. The kraft cooking requires at least 25 g/L NaOH active alkali for fibers separation. At higher values, the delignification rate increases at the given temperature. Practically, kraft cooking requires an initial active alkali concentration of 40–60 g/L NaOH.

The sulfidity of white liquor is expressed as the percent ratio between sodium sulfide and active alkali. According to Kleppe [54], the sulfidity strongly influences the cooking rate and process selectivity. The pulping rate significantly increases if sulfidity rises up to 16%. The delignification rate continues to increase up to 35–40% sulfidity at a constant active alkali charge. As the sulfidity increases, the cooking selectivity enhances, which means that the pulp yield increases at the same pulp lignin content. A high sulfidity is advantageous for other many reasons: reduces the lime consumption for green liquor causticization and decreases fuel consumption of lime kiln, enhances the sedimentation velocity of lime particles during white liquor clarification, and raises the fluidity of the black liquor. The sulfidity ranges between 25 and 35% for cooking of hardwoods and 35 and 40% for softwoods.

Cooking temperature is the main factor influencing the delignification rate with the rate approximately doubling for an increase in cooking temperature of 8 °C. Temperature negatively influences process selectivity; in other words, at the same lignin content, increasing the temperature will decrease the pulp yield. The cooking temperature depends on the wood species, pulp grade, and cooking plant (discontinuous or continuous). Cooking of softwoods uses temperature of 170–175 °C, while cooking of hardwoods is performed at 165–170 °C.

The pulping time must be correlated with the cooking temperature in order to obtain pulp with the same properties. The *H*-factor is a kinetics model that combines cooking temperature and time into a unique parameter that measures the degree of