

# Production of Paper vs Utilization of Cellulose, Lignin and Pentosan

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Earlier cotton was used as the main raw material for production of paper. Cotton is a pure cellulosic material which has got very little of other material. When cotton is used, it is simply to be beaten to separate cellulosic fibres which have thereafter to be felted to form paper. However, when the demand for paper increased, it was not physically possible to meet the increasing demand with available supply of cotton, cotton linters and rags and the cost of such material also would be such that it would not be possible for a paper mill to use it as a raw material. Therefore the use of cotton is confined now to only high quality rag paper. So new processes had to be developed to use cheaper and more abundant raw material for making paper. Therefore processes have been developed over the last century to use wood as the basic raw material for production of paper. Diverse type of wood is being used for production of paper.

However I would like to emphasise the point that when a paper mill buys a ton of wood, it will be able to use only a portion of this, say about 40%, being the cellulosic component, towards production of paper. The rest of the material (i.e., 60%) is not useful in the manufacture of paper although the mill has paid for it. The various components in wood are as follows :

Typical Composition of wood		
Cellulose	...	45%
Pentosans	...	25%
Lignin	...	20%
Others	...	10%

Basically the process of conversion of wood into paper involves reducing the cellulosic material in wood into fibres and separating the three basic components namely, cellulose, lignin and pentosans. In the process of conversion the mill uses not only mechanical and

chemical but other types of energy to separate these three basic components.

The large amount of coproducts created during this process have to be got rid of. Therefore an optimal system of production of paper could be, to find out, whether all the components in the wood, could be put to use such that whatever material has been bought, is fully used in generating revenue.

So far we have traditionally been interested in one component namely cellulosic material but the question we could legitimately ask is, whether it is feasible and desirable to use all the components found in the woody raw material. If instead of spending money for separation and then use more money to dispose of these components, will it not be better, if all the three components could be made to generate revenue?

Fortunately there have been very interesting developments during the last couple of years under which useful products could be generated from lignin and pentosans. Lignin could be a very versatile material as it is basically a complex polymer. If we look at the polymers market today, we find that various polymers fetch a price between Rs. 10 to Rs. 50 per kg. whereas the average price of paper may range from Rs. 8 to Rs. 15 per kg. So the question which one could well ask is, when the market value of the lignin and its derivatives could be higher than that of the paper, then how could the paper industry afford to ignore it and lose the possibility of generating additional revenue? Pentosans constitute the third component which could also be converted to some useful product

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## LIGNIN

Let's look at lignin and its properties. Some kind of wood are more resistant to decay than others. When the fast growing radiata pine was introduced into Australia, its wood was used by builders with disastrous consequences. Within a few years, most of it was rotting. At the other extreme is the Fallen Monarch, a dead sequoia tree, that has lain in the Sierra Nevada mountains in California for at least 400 years. Its wood is hard as a rock.

The difference is explained largely by the lignin content of the two trees. Lignin is a natural polymer that trees use for mechanical support, but it also provides resistance to decay, repels water etc. Some of lignin is burnt as fuel or converted to activated carbon etc. But a lot of it is thrown away.

Lignin is designed by nature to bind fibres together. Because all the molecular building blocks (Phenols) contained in a chunk of lignin are chemically bonded to each other, the structure resists heat and cannot be remoulded once set. Unfortunately, that is also its drawback. For lignin to be useful, its three-dimensional structure must be smashed open. White-rot fungus does this with an enzyme called lignase which biochemists are now trying to mass produce. The processes used in pulp-making get part of the way there. They produce lignin possessing enough active chemical groups to incorporate it directly into Bakelite resin by adding it to the ingredients of Bakelite-formaldehyde and phenol.

At the Virginia State University, Dr. Wolfgang Glasser and his associates are trying to modify lignin by making it react with propylene oxide. The resulting lignin derivative bristles with alcohol groups which can react with other chemical groups, notably isocyanates. The result is a "cross-linked" structure that is hard and fire resistant. Dr. Glasser plans next to develop lignin-based epoxy resins. It consists of elongated cells wrapped in helical bands of cellulose and encased in lignin sheaths. When it is stretched, the chemical bonds between successive turns of the cellulose break but the bands remain intact, so the cracks cannot spread.

There are various routes for obtaining lignin as a useful material. I will mention a couple of recent developments.

## ORGANIC SOLVENT AND CATALYST ROUTE

Kraft process, involves cooking chipped ligno-cellulosic materials in treatment liquor of sodium hydroxide and sodium sulfide. This is undesirable route in that pulping process inevitably degrades significant portion of desired cellulose component, substantially reducing pulp yield. The process that relies on sulfide components in treatment of liquors presents problems of disposal of sulfide pollutants. But a liquor made of alcohol, an amine, and water each present in amount of 1 to 12 part by volume, could be used in presence of a quinone and/or azine catalyst.

Aliphatic polyamines such as ethylenediamine in combination with aqueous alcohols such as ethanol in the presence of catalyst like anthraquinone provides an effective and efficient pulping agent for selective removal of lignin while protecting cellulosic materials from degradation.

In general, processes that undergo less chemical reaction during pretreatment produce lignin that has larger molecular weight. This allows greater ease in separating lignin and produces a lignin closer to its native composition. These characteristics are important for some applications. Research workers classify existing and potential markets as polymers, modified polymers, prepolymers, low-molecular weight chemicals, and fuels. Polymers can be used as filters, extenders and encapsulants. When chemical groups are attached to lignin, modified polymers can be used in making surfactants, dispersants and coagulants. Prepolymers have low degrees of polymerization and are converted during processing to high-molecular-weight compounds. They can be used as adhesives and binders.

## BIO-TECH ROUTE TO SEPARATION OF LIGNIN.

Recently a solid sub-strate fungal culture reactor has been developed by Renewable Technologies, Inc., USA that could be used in lowcost production of lignin-degrading enzymes.

Reactor permits close control of all fungal culture parameters. Oxygen concentrations in culture air supply can be enriched and varied in response to culture performance. Oxygen appears to be the key to good ligninase production. In the past, biological delignification on a large scale has been hampered by white rot fungus' unusual oxygen requirements and slow

reaction rate of lignin-degrading enzymes. Also, chemical and mechanical means of separating lignin from cellulose tended to be energy intensive and/or ecologically undesirable. The new system that has been developed allows economical production and utilization of lignin-degrading enzymes. Economical lignin-degrading enzyme could be used in conjunction with cellulose degrading enzymes to get lignin and wood sugar.

#### ENZYME HELPS MAKE ADHESIVES AND RESINE.

Another route that is under development is by modifying lignin enzyme to work on industrially produced kraft lignin and other lignochemicals. The goal is to use modified products in adhesives and resins replacing petrochemical-based products in a variety of applications. It appears to be possible, for example, to use the modified kraft lignin resin adhesives in place of phenol-formaldehyde resin adhesives.

Detailed study has been done on enzyme from the basidiomycete *PHANFROCHAETE CHRYSOSPORIUM* (white-rot fungus). A genetic engineering company is producing an enzyme on a lab-scale volume. This enzyme can be produced four times faster by adding minerals such as manganese or copper, and veratryl alcohol. Researchers are trying to reach optimal adhesive/resin properties of low viscosity, high strength, and little colour. It is expected that enzymatic technology may be competitive with petroleum-based adhesives and that new adhesives will be used in applications that until now have been impossible. For example glues made from lignosulfonates have good adhesive qualities but are black and cannot be used eg. in book binding. New enzyme technology can produce a clear adhesive that could be used in binding.

#### BIOTECH SUGAR CONVERSION.

The Department of Energy (DOE) of the USA has been funding research into the biological conversion of sugar to alcohol, for various uses including eg. as fuel. The DOE has recently taken a patent in Britain. It is claimed to increase the bioconversion rate six fold, with an 80% reduction of chemical input. According to this patent, previous attempts at turning sugar into alcohol have been inefficient, because they relied on

dumping raw materials into a vat with micro-organisms and then adding extra nutrients to keep the organisms healthy. Most of the nutrients passed out of the vat unused and the micro-organisms became sluggish.

The way to do it, reports DOE, is to connect two separate containers, each of the form of a tall tube, by means of valves and pumps. In one container the flocculent strain of *Zymomonas mobilis* eats away at an aqueous solution of glucose, to produce ethanol and carbon dioxide.

The waste and ethanol are drawn off from the top and the tired micro-organisms are pumped to an adjacent "rejuvenating chamber" where they feast on a nutrient mix. The rejuvenated microbes are then fed back to the primary reactor to carry on with the job.

Tests have shown that without rest and recuperation the microbes start slowing down after 4 hours. But with 1.5 hours of recycling to the nutrient chamber, the bioconversion rate of glucose to ethanol increases again by more than 60%. Hence with such new processes which are more efficient, the pentosan component could be put to useful work and it could generate new revenue by sale of ethanol.

#### COMPOSITION OF SULPHITE LIQUOR.

Together with each ton of pulp, there is produced 8 to 10 tons of sulphite liquor, which contains from 10 to 12 percent of total solids. One analysis of sulphite liquor showed the presence of the following products for each 1,000 kg of cellulose obtained from Swedish spruce: lignin, 644 kg; carbohydrate, 311 kg; protein, 15kg; resin and fat, 73kg; sulphur dioxide combined with lignin, 235 kg; and calcium oxide combined with lignosulphonic acid, 102 kg.

The carbohydrates of 49.4 percent glucose, 15.6 percent mannose, 8.1 percent galactose, and 26.91 percent nonfermentable pentosans (arabinose).

Approximately 65 percent of the total reducing sugars are usually fermentable<sup>2</sup>.

Hence a thoroughly modified process technology may/should be adopted to produce simultaneously paper, lignin derived polymers and ethanol (or any

other fermentation derived products) from pentosans. The various components of new technology are available. It must be tried and it could make a world of difference in the revenue generated. At a time when paper industry is passing through a very critical period, it becomes all the more important that no opportunity is lost of generating higher revenue and turning the industry into a profitable one.

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