

Wood as resource for chemicals: Modern approach for optimum utilization without hampering its conventional use

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Abstract

Due to the dependence on petroleum to supply energy and chemical needs many countries have experienced problems because of declining reserves, increased demands, and political problems in oil exporting nations, which have also created problems for oil-importing countries. Demand on renewable resources to meet the needs for energy and carbon based chemicals in the wake of eventual depletion of fossil oil and natural gas reserves. Furfural, lignin, vanillin can be synthesized by extraction process from which vanillin and furfural are costlier products, which makes the process economically viable. Material balance was done to understand the material composition of wood. Comparison and costing of various processes are also evaluated which resulting into inexpensive than petroleum. A long-term solution would be to use renewable resources to produce many of the hydrocarbons. So, this work aims at finding feasible ways extracting the valuable chemicals such as furfural, lignin, vanillin, etc. from wood.

Keywords: Renewable resources; Chemicals; Wood; Extraction; Biomass; Lignin

1. Introduction

The rapidly increasing cost, dwindling resources and uncertain supply of oil have lent a sense of urgency to the need for developing new technologies for the use of alternative raw materials as petroleum substitutes. Plant biomass has become a likely choice, since unlike petroleum, it is renewable and enormous quantities are available on global scale. According to Glesinger, with proper management, the world's forests could produce up to 14 billion tons of wood per year perpetually: he has cited three unique attributes of wood, which make it a very attractive raw material:

- Wood has widespread availability.
- Forests cover nearly 25% of the earth's land area this is in contrast to the very limited area where coal, oil, iron ore, etc. are found.
- Wood is inexhaustible and replenishable.

Other attributes of wood are low ash and nitrogen contents and practically no Sulphur. The importance of wood as a raw material supplying fiber, energy, and chemicals is similar in magnitude to its use as a solid material. Lumber, plywood and reconstituted boards consume about one-half of the timber harvest; usage for fiber, chemicals and fuels accounts the remaining half. Although the relative value of wood as a source of energy and chemicals has varied considerably through the decade's wood continues to be an important source of specialty chemicals and renewable energy and may be even more important in the future. Wood is composed of 70 – 80% polymeric carbohydrates and 20

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– 30% lignin. The matrix can be degraded in various ways to produce practically all the industrially important organic chemicals produced by the chemical industry.

Also, lignin will have an important place in the chemical industry, when it starts shifting from a petrochemical base to coal and renewable materials. If such production of chemicals becomes feasible, India will benefit immensely, because vital feed stocks will remain available even as oil supply dwindles. In turn, oil will be used for the production of chemicals for which no petroleum substitutes exist.

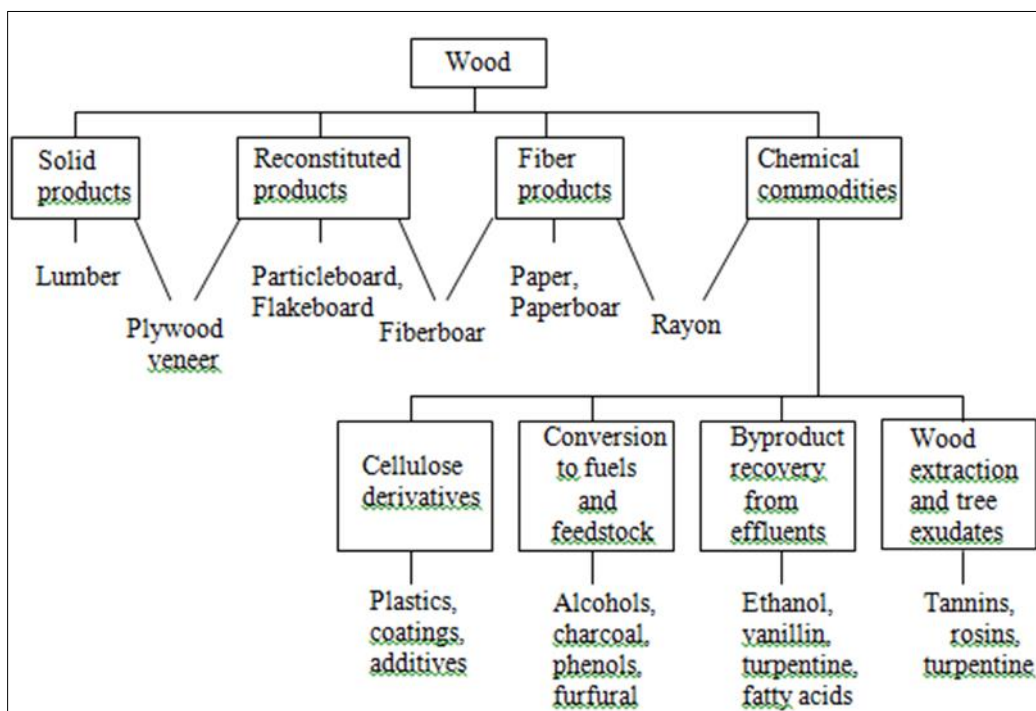


Figure 1 Summary of uses of Wood

2. The chemical composition of wood

The chemical composition of wood cannot be defined precisely for given tree species. Chemical composition of wood varies with tree part (stem, branch or root), type of wood, geographic location, climate and soil condition. Analytical data accumulated of many years of work and many different laboratories have helped to define average expected values for the chemical composition of wood. Wood is composed of three major polymeric materials are cellulose (40 – 50%) of the dry wood weight, Hemicelluloses (25 – 35%) and Lignin (15 – 35%). Elemental Composition are Carbon (50%), Hydrogen (6%) and Oxygen (44%) and trace amount of several metal ions. Wood is classified in two categories which is Hard woods and Soft wood. It is important to note that the terms “Hardwood “and “Softwood” have no direct relations to the hardness or softness of the wood.

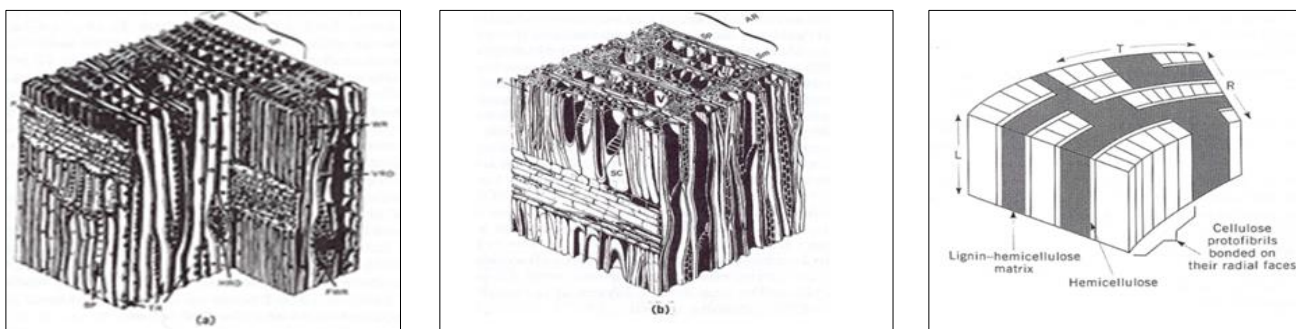


Figure 2 Cross section Of Softwood [1], Cross section Of Hardwood [1], Composition of Wood [5]

In fact, hardwood trees such as cotton wood, aspen, and balsa have softer wood than the western white pines and true firs, and certain softwoods such as long leaf pine and Douglas fir produced wood that is much harder than of basswood or yellow poplar. The term's hard wood and softwood have no direct application to hardness or softness of the wood of two classes.

2.1. Cellulose

Cellulose is the main component of the wood cell wall, typically 40 – 50% by weight of the dry wood. Pure cellulose is a polymer of glucose residues joined by 1,4 beta glucosidic linkages. Cellulose is a glucan polymer consisting of linear chains of 1,4 beta bonded anhydro glucose units. The number of sugar units in one molecular chain is referred to as degree of polymerization (DP). Evidently, Cellulose is insoluble in most solvents including strong alkali. It is difficult to isolate from wood in pure form because it is intimately associated with lignin and hemicelluloses.

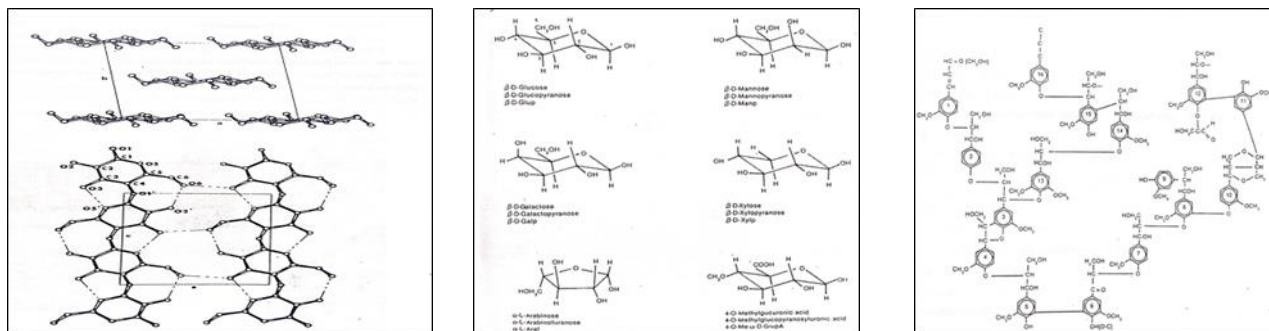


Figure 3 Structure of Cellulose, Hemicelluloses, Lignin [1]

2.2. Hemicelluloses

The hemicelluloses are lower molecular weight mixed – sugar polysaccharides. Hemicellulose is a mixture of amorphous branched chain polysaccharides consisting of a few hundred sugar residues. They are easily hydrolyzed to monomeric sugars and uronic and acetic acids (glucose, mannose, galactose, xylose, arabinose, 4 – O – methyl glucuronic acid and galacturonic acid residues). Hemicelluloses are largely responsible for hydration and development of bonding during heating. Pulp containing high percentages of hemicellulose are typically low in tear strength but develop high hydrogen bonding strength between fibrous elements. This leads to pulps having high internal bond strength.

2.3. Lignin

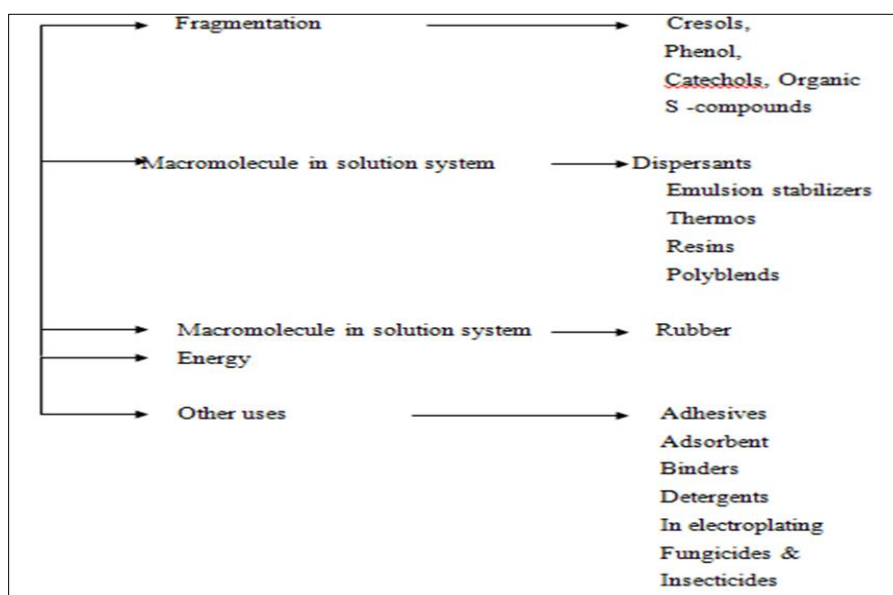


Figure 4 Uses of Lignin [4]

The word lignin is derived from the Latin word lignum meaning wood. It is a natural polymer made up of phenylpropane units is a major component of vascular plants. After polysaccharides, lignin is the most abundant organic polymer in the plant world. In hard woods, the amount of lignin varies from 16 – 29% whereas in softwoods it ranges from 27 and 37%.

3. Material Used

Methylene dichloride (CH_2Cl_2), n-Butanol ($\text{C}_4\text{H}_9\text{OH}$), Methanol (CH_3OH), Sulfuric acid (H_2SO_4). Unscreened, mixed hardwood chips, not sorted by size, were taken. The length of the chips varied from 1 to 10 cm. The chips were oven dried to remove the unbound moisture contained in them.

4. Process Description and Material Balance

A variety of chemical and physical pretreatments have been developed for increasing the susceptibility of cellulose and lignocellulose materials toward acid and enzymatic hydrolysis. The ideal pretreatment should not only loosen the plant cell structure but also should use inexpensive chemicals and require simple equipment. In addition, the pretreatment should solubilize the lignin and hemicelluloses and decrease the crystallinity of the cellulose. Another important characteristic of a pretreatment but one which has been largely ignored is that the pretreatment needs to be effective with a wide range of biomass material. The commercial process involves first filling a vertical cylinder with wood chips. Once filled with chips, the cylinder is sealed and pressurized with saturated steam at pressures up to 17 to 20 kg/cm². The chips are permeated by saturated steam and develop high internal pressures. When the bottom of the cylinder is opened, the wood chips are defibrated by the sudden decompression. This steam explosion not only causes a physical change in the wood but also cause considerable chemical changes.

The following chemical changes occur in steam-exploded wood,

- The lignin is broken down into low-molecular weight products which retain the basic lignin structure and moderately reactive. Since the lignin has been extensively depolymerized by cleavage of the beta-aryl-ether bonds, it is soluble in alkaline solutions or certain organic solvents.
- The hemicelluloses are partially broken down and are predominantly soluble in water. In addition, some degradation products are formed which apparently condense with lignin, increasing the lignin content.
- The major effect of steam explosion is the large increase in the accessibility of the cellulose to enzymatic hydrolysis

4.1. Pressure vessel

The pressure vessel used was of approximately 1 ft³ mounted vertically and was fitted with pressure gauge for pressure measurement. The pressure of about 30 Kg/cm² could be reached in the pressure vessel. The feed was charged from the ball valve. The pressure vessel was heated from bottom with the gas cylinder. When it was desired to condense and recover all of the volatile material produced in the pressure vessel, including all if the steam a lid was attached to the pressure vessel. Various runs were made under different conditions. Four types of explosion experiments were carried out

- Explosion in open
- Explosion in closed
- Explosion in close and condensing the vapors
- Cooking of the pulp

4.2. Explosion in open

Hardwood chips 300 gm were taken and soaked with 100 gm of water containing 1.5% (or 5-6 gm.) H_2SO_4 . This was added to pressure vessel and about 800-900 gm. of water was added. The ball valve was closed and the pressure vessel was heated from bottom for about 1 hr. until the pressure was reached up to 18 Kg/cm². The pressure was maintained for about 15-20 min and the pressure vessel was inverted and the ball valve was suddenly opened. When the ball valve was opened, the charge of steam and lignocellulose material was violently discharged through the pressure vessel in the collector at the bottom. The pulp and aqueous solution was collected.

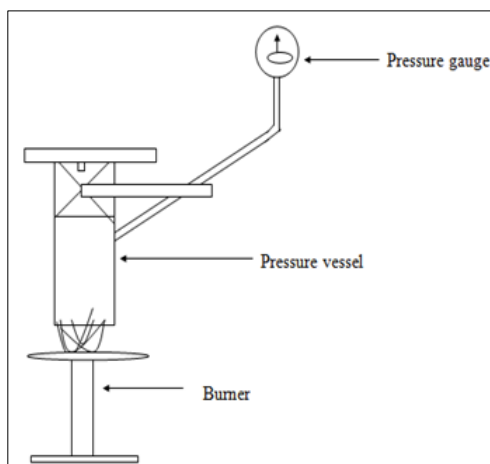


Figure 5 Experimental set up for Explosion in open [5]

4.3. Furfural Extraction

The liquid collected after explosion contains furfural. The pulp and the liquid collected are boiled for about 2 hr. to dissolve all the hemicellulose in the hot water and the mixture is then filtered. As the furfural is steam volatile. The filtrate obtained is steam distilled and the condensed steam is collected. Common salt NaCl is added to the distillate to reduce the solubility of furfural. Methylene Dichloride (MDC) is added, two layers are formed one is of MDC containing furfural and aqueous layer. The bottom layer of MDC is then decanted and aqueous layer is wasted. The MDC extract is the simple distilled and distillate obtained is pure MDC, which is recycled for extraction, and residue is furfural.

4.4. Explosion in closed

In the second run closed pipe attached with the ball valve was mounted on the top of the autoclave. Wood chips soaked with water and sulfuric acid as catalyst is charged in the autoclave and the pipe was mounted on the top and both the ball valves were closed. The autoclave is heated with the burner for about 1 hr. after reaching the pressure up to 18 kg/cm² it was maintained for 15 min. The ball valve attached to the autoclave was opened and the pressure was suddenly reduced to 3 kg/cm², the pipe was allowed to cool to condense the vapors formed. The ball valve of the pipe was opened and the pulp and condensed vapors were collected.

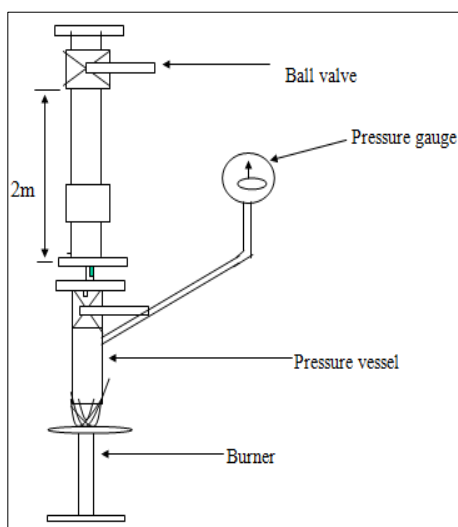


Figure 6 Experimental Set up For Explosion in closed [5]

4.5. Cooking of Pulp

In the fourth run the cooking of the pulp was carried out. The same feed was charged as in the other runs. After reaching the pressure in the autoclave and maintaining for 15 mins the vapors formed were taken out from the lid attached to

the autoclave. The condenser was attached to the lid. The vapors taken out from the autoclave were condensed and collected in the round bottom flask. The autoclave was allowed to cool and the pulp was collected.

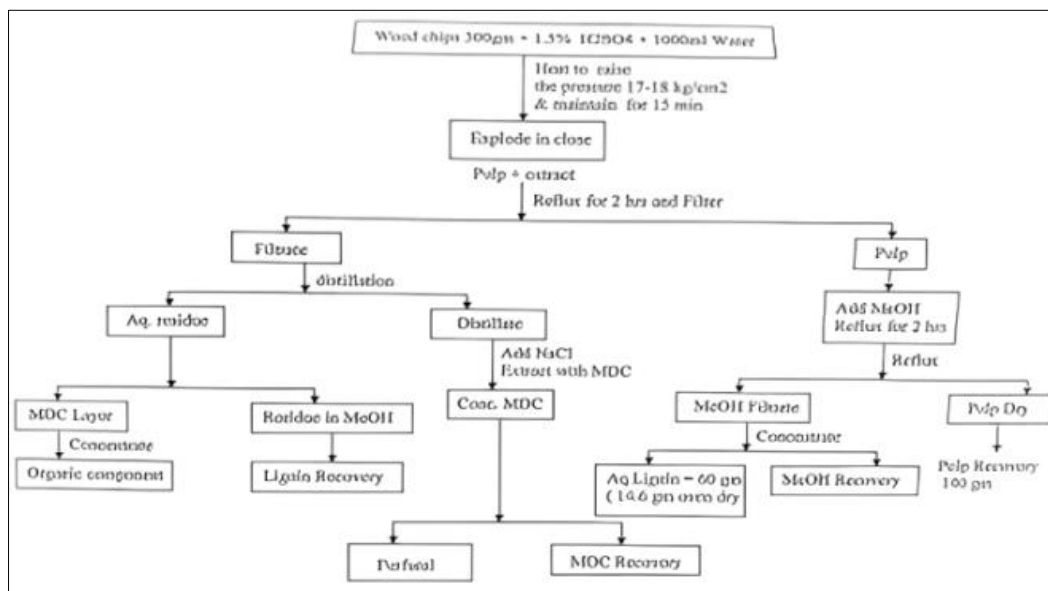


Figure 7 Flow sheet of Cooking of Pulp [5]

4.6. Vanillin preparation

The aqueous lignin was taken and about 100 ml of water was added along with NaOH flakes. This alkaline liquor was refluxed for 20 hr. and oxygen was passed continuously to the reactor. The mixture from the reactor was then extracted with n-Butanol and filtered and the filtrate further extracted with 15% sodium bisulfite solution. The sodium bisulfite addition compound was decomposed by acidifying with H_2SO_4 . The SO_2 formed was blown away with nitrogen. The solution was then extracted with MDC and then MDC was evaporated to give vanillin crystals.

Analysis of vanillin was also with a solution of Ferric Chloride is added to cold saturated vanillin solution a blue color appears. It changes its color to brown upon heating to 20 °C for few minutes. On cooling white pearly gray precipitate of silky needles forms.

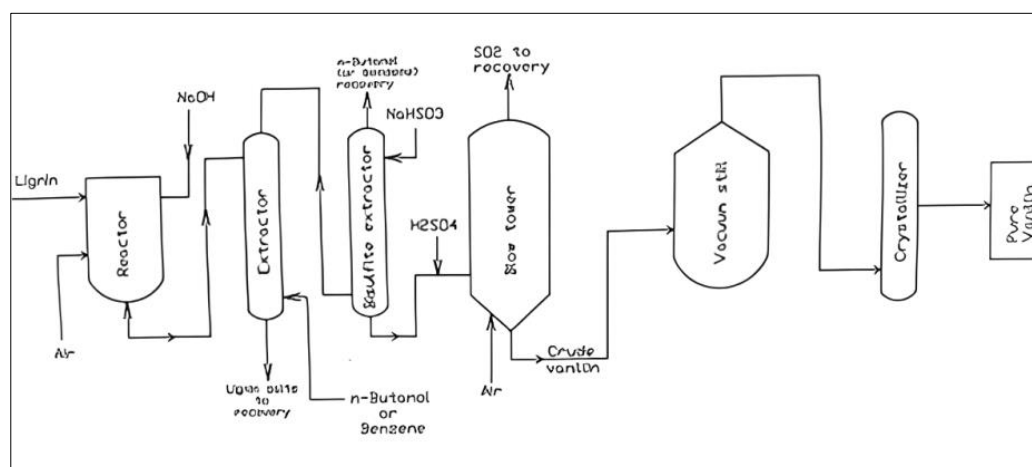


Figure 8 Flow sheet of Cooking of Pulp [5]

5. Material Balance

The first step is to look at the three basic categories: materials in, materials out and materials stored. Then the materials in each category have to be considered whether they are to be treated as a whole, a gross mass balance, or whether various constituents should be treated separately and if so what constituents. To take a simple example, it might be to take dry solids as opposed to total material; this really means separating the two groups of constituents, non-water and water. More complete dissection can separate out chemical types such as minerals, or chemical elements such as carbon. The choice and the detail depend on the reasons for making the balance and on the information that is required. A major factor in industry is, of course, the value of the materials and so expensive raw materials are more likely to be considered than cheaper ones, and products than waste materials.

5.1. Material Balance for Explosion in closed

5.1.1. Input

- Wood = 300 gm
- Water = 1000 gm
- H₂SO₄ = 1.5% (4.5 gm)

Pulp + Extract refluxed for two hours, to dissolve all hemicellulose in hot water and then filtered

5.1.2. Output

- Wet pulp = 460 gm.
- Brownish black color
- Aqueous solution = 1000 gm.

Furfural extraction

5.1.3. Input

- Extract = 1000 ml
- MDC = 500 ml
- NaCl = 80 gm.

5.1.4. Output

- Recovered MDC = 486 ml
- Furfural = 6.43 gm.
- Aqueous = 995 gm. to waste

Pulp mixed with Methanol + 1% conc. and refluxed for 2 hours to dissolve maximum lignin in Methanol and filtered. Filtered methanol concentrated, residue heated up to 80 °C under vacuum to remove max. Methanol, Residue was up to 60 gm (Lignin) and the Pulp is then oven dried, brown in color = 140 gm.

5.2. Explosion in close and condensing the vapors

5.2.1. Input for explosion

- Wood - 300 gm
- Water - 1000 gm
- H₂SO₄ - 1.5% (4.5gm)

5.2.2. Output

- Condensate collected = 550 ml
- Wet Pulp = 370 gm.

Furfural extraction is then done on the condensate collected

5.2.3. Input

- Condensate = 550 ml
- MDC = 500 ml

- NaCl = 40 gm.

5.2.4. Output

- Recovered MDC = 490 ml
- Furfural = 7.93 gm.
- Aqueous = 580 gm. to waste

Pulp mixed with Methanol + 1% conc. HCl and refluxed for 2 hours to dissolve maximum lignin in Methanol and filtered. Filtered methanol concentrated, residue heated up to 80 °C under vacuum to remove max. Methanol, Residue was 65 gm. (Lignin). Pulp is then oven dried, brown in color = 143 gm.

5.3. Cooking of Pulp

5.3.1. Input for explosion

- Wood - 300 gm
- Water = 1000 gm
- H₂SO₄ = 1.5% (4.5 gm)

5.3.2. Output

- Condensate collected = 650 gm.
- Wet pulp = 357 gm.

Furfural extraction is then done on the condensate collected

5.3.3. Input

- Condensate = 650 ml
- MDC = 500 ml
- NaCl = 40 gm.

5.3.4. Output

- Recovered MDC = 485 ml
- Furfural = 6.3 gm.
- Aqueous = 690 gm. to waste

Pulp mixed with Methanol + 1% conc. HCl and refluxed for 2 hours to dissolve maximum lignin in Methanol and filtered. Filtered methanol concentrated was 59 gm. (Lignin). Further concentrated to give 16.86 gm. Pulp was 180 gm. (not oven dried) and if pulp not formed properly, the wood chips were softened.

5.4. Vanillin preparation

5.4.1. Input

- 15 m of lignin
- 50 gm. NaOH flakes
- 100 ml water
- 500 ml n-butanol
- 15 % NaHSO₃ solution 750 ml
- H₂SO₄ twice as mole % of NaHSO₃ solution
- MDC 100 ml

5.4.2. Output

Output of the solution was 2 gm. of vanillin

6. Comparison of alternatives used

The pressure vessel used was of approximately 1 ft³ mounted vertically and was fitted with pressure gauge for pressure measurement. The pressure of about 30 Kg/cm² could be reached in the pressure vessel. The feed was charged from

the ball valve. The pressure vessel was heated from bottom with the gas cylinder. When it was desired to condense and recover all of the volatile material produced in the pressure vessel, including all if the steam a lid was attached to the pressure vessel.

Various runs were made under different conditions. Four types of explosion experiments were carried out

- Explosion in open
- Explosion in closed
- Explosion in close and condensing the vapors
- Cooking of the pulp

Table 1 Comparison of alternatives used

Sr.No	Process Type	Input	Output	
			Furfural (gm.)	Lignin(gm.)
1	Explosion in open	Wood: - 300 gm	5.6	72
2	Explosion in close	Water: -1000 gm	6.43	60
3	Explosion in close & condensing vapors	H2SO4 :- 1.5%	7.93	65
4	Cooking of pulp	Total- 4.5 gm.	6.3	59

7. Cost estimation

Cost Estimation is a statement that gives the value of the cost incurred in the manufacturing of finished goods. It helps in fixing the selling price of the final product after charging appropriate overheads and allowing a certain margin for profits. It also helps in Inventory Reports drawing conclusions regarding the cost of production and in determining the necessity to introduce cost reduction techniques in order to improve the manufacturing process. Total product costs can be determined by adding together the total direct materials and labor costs as well as the total manufacturing overhead costs. To determine the product cost per unit of product, divide this sum by the number of units manufactured in the period covered by those costs. Cost estimation takes into consideration all expenditure involved in the design and manufacturing along with all related service facilities such as machines setting; tool making as well as a portion of sales marketing and administrative expenses or what we call overhead costs. **Basis:** Two batches/day (50 kg of wood chips /Batch)

Table 2 Raw Material Cost

Item	Rate	Requirement per year	Cost (Rs. /year)
Wood	7 Rs. /kg	1,46,000 kg	1022000
H2SO4	15 Rs. /kg	2190 kg	32850
NaCl	2 Rs. /kg	38933 kg	77866
Steam	900 Rs. /ton	438000 kg	394200
M.D.C.	33 Rs. /lit	2468.08 lit	81447
Methanol	38 Rs./lit	9810 lit	372780
		Total Material Cost	1981143

Total Raw Material Cost = Rs. 1981143= Rs 20 lacs

Total Operating Cost = 1 x Total Raw Material Cost (Assumed) = Rs 20 lacs

Total Production Cost = Rs 40 lacs

Table 3 Product Sales

Product	Rate	Production/year	Sales (Rs)
Furfural	210 Rs. /kg	4866.67 kg	1022000
Lignin	55 Rs. /kg	9733kg	535315
Pulp	62 Rs. /kg	68133 kg	42242646
		Total	5781562

$$\text{Profit/Year} = \text{Sales} - \text{TPC} = 5781562 - 4000000 = 17.81562 \text{ lacs}$$

8. Conclusion

Today the choice of feedstock for chemical production depends upon complex technical, economic, environmental and political factors. Most of the basic chemicals currently produced from synthetic chemical resources can also be produced from wood using demonstrated technology. It is the best solution for reducing the use of petroleum and its derivatives, which are limited. Furfural, lignin, vanillin can be synthesized from which vanillin and furfural are costlier products, which makes the process economically viable. The output of the lignin was greater than the furfural. The maximum result for furfural was obtained from explosion in close & condensing vapors and the maximum result for lignin was obtained from explosion in open. Total sales per year profit were much higher than then the operating cost and the total expenses. The pulp remaining can be further used for producing conventional products particleboard, paper, and enzymatic treatment for production of alcohol or as a fuel. Thus, all the fractions from wood are used up resulting into "Optimum Utilization without Hampering Its Conventional Use."

Compliance with ethical standards

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Disclosure of conflict of interest

The authors have no conflicts of interest to declare.

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