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INTRODUCTION

The problem of pollution abatement is intimately associated with utilization of wastes. Raw materials in pulp and paper industry are ligno cellulosic materials such as wood, bamboo and agricultural residues; chemicals used for pulping, bleaching, stock preparation and water. While going through various operations and processes, waste is generated, which may be solid waste such as bamboo/wood dust generated in chipper house, wood/bark waste generated in wood yard, rejects of screening systems, sludges generated at water treatment plants, chemical recovery plants, effluent treatment plants or it may be in the form of spent pulping liquors, effluents from bleaching, stock preparation, recovery, machine section etc. Disposal of black liquor has always been the object of study in the pulp and paper industry. Direct disposal of spent liquors not only creates a grave problem of polluting ground water but also is wasteful.

Growing awareness about pollution free environment in public and Government makes it obligatory on the part of managements of pulp and paper industries to treat these wastes and recycle it as far as possible. Conventional treatment methods are capable of removing upto 90-95 per cent BOD. Other pollutants such as particulate matter, COD, sludges, acidity, alkalinity can also be removed by appropriate methods. The constraints in treatment of waste are more economical than technological, however. Paper mills having capacity upto 50 tons per day find it difficult economically to recover, renovate and reuse spent liquors using conventional recovery systems.

Utilization of spent sulphite liquor is well established in U.S. Canada, Norway and Sweden. In India almost all mills are using Kraft and Soda pulping and are using hard wood/bamboo/agricultural residues as raw material. These raw materials are not rich in resin acids and therefore Tall oil recovery is not practiced in India. Similarly because of complexity of hard wood lignins, commercial production of vanillin may not prove to be economical. Proper approach therefore appears to convert Ligno-cellulosic solid waste to useful organic chemicals; to separate organic chemical values in form of lignin prepolymers from spent liquors, recycle inorganic chemicals from spent liquors and then treat the effluents with available methods to reduce BOD, COD, colour, alkalinity, acidity etc.

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The use of lignocellulosic material as a base for production of chemicals although uneconomic, compared to petroleum as a base, is worth considering when it is viewed as a part of pollution abatement.

Following is a brief review of methods developed to get useful chemicals from pulp and paper industry waste.¹

CHEMICALS FROM WOOD/BARK WASTE

Activated carbon:

Lignocellulosic material such as saw dust, bamboo dust, broken chips partly pulverized bark is reported^{1a} to have been converted into activate carbon. The material was first treated with inorganic acid to remove sugars at low temperature range. Acid extracted material was then heated at 450°C for nine hours and for one hour at 800°C. While steam was being injected. The tar was removed as condensate in this high temperature range. About 22 % yield of activated carbon was reported.

Y. Shirai² and others have claimed continuous production of activated carbon by carbonization of cellulosic material impregnated with activating agent such as zinc chloride. The process involved continuous supply of activating agent-impregnated material into carbonizing zone containing previously carbonized cellulosic material at such constant flow rate as to allow the impregnated material to reside for fifteen minutes in the carbonizing zone. The impregnated material was carbonized with the carbonized cellulosic material heated to 350°C by counter currently supplied hot gases and which formed an agitated fluidized bed by being fluidized with hot gas stream and being stirred by a mechanical means. The total weight of the product was two third of the original weight of the wood material supplied.

Chemicals from Bark:

Bark along with other refuse creates a disposal problem for paper mills using hard wood as raw material. Utilization of bark can be developed on following lines.

- i) As a source of fuel for steam generation.
- ii) As a source of chemicals, particularly tannins and tannin like compounds, which would be recovered by water/acid/alkali extraction of bark prior to burning.

- iii) Marginal utilization as soil conditioner, extender for thermosetting resins³, oil well mud additive, reinforcing and stabilizing agent for polypropylene moulding compounds.⁴

Hydrolytic Degradation of Lignocellulosic waste to sugars:

Hard wood and agricultural residues are rich in pentosans which mainly contain xylan. Waste and refuse generated from hard woods/straw/bagasse while preparing these materials for pulping, could be degraded hydrolytically to D(t) Xylose and Xylitol, which are used in food stuff as sweeteners. H-Friese⁵ described a process in which hydrolysis was carried out in first stage with sodium hydroxide of 4 % concentration which removes acetic acid chemically bonded in the wood as sodium acetate. The liquid extract of this stage can be re-used after it has been brought to the alkali concentration to be used.

In the second stage of processing the residue from the first stage containing pentosan and cellolignin was further hydrolyzed with mineral acid e.g. sulfuric acid. When working without pressure, 1.5 to 6 % strength of H_2SO_4 , and a ratio of liquid to solid of 3 to 6 parts by volume was preferred. Temperature was preferably 50 to 125°C and time was 2-4 hours. After completion of the second stage, the batch was filtered, the filtrate could be worked to Xylose or directly to Xylitol.

The insoluble residue from the second stage could next be used to obtain organosolve lignin which was thermoplastic and very reactive; the material, this lignin preparation could be used as a base material for dyestuffs and pesticides. The residue remained after the removal of lignin, on treatment with sodium chlorite followed by sodium hydroxide could be converted to practically white cellulose which could be used for industrial applications. Thus all wood waste could be converted to useful chemicals.

Synthetic Fuel using Solar Furnace:

M.J. Antal⁶ described a process of producing gases such as CO_2 , CO , CH_4 and H_2 from pyrolysis and gasification of solid organic waste contained within a reactor. The process comprises solar heating of

working fluid (steam, CO_2 or a mixture of gases) to 600°C to 700°C by means of solar top furnace. The working fluid was contained in the lower section of the reactor situated at the focus of the solar top furnace. The heated working fluid was injected under pressure into porous reactant bed on which the catalyst (NaHCO_3)- mixed organic waste was situated. The catalyst-mixed organic waste was pyrolyzed causing the formation of CO_2 , CO , CH_4 and H_2 gases and char residue.

The hydrogen produced could be utilized to replace natural gas in a hydrogen economy, to make fertilizer or as a chemical feed stock. It is claimed that process did not require a source of pure oxygen, and provided an attractive method for using solar energy.

Basic Chemicals⁷:

Wood waste has a complex carbohydrate lignin structure requiring severe conditions to reduce it to such basic chemicals as Methanol, Ethanol, Furfural and Phenols. Chemical production costs are directly related to scale and complexity of operation. It is necessary to determine the quantum of the wood waste facility for the maximum size consistent with availability of raw material. A single product facility appears not to be competitive. In order to be economic utilization of the wood waste, multiple product facility is essential.

BY-PRODUCTS FROM SPENT PULPING LIQUORS

Pulp and Paper industry has a very huge lignin potential. According to rough estimate for every ton of bleached pulp produced, about 0.5 ton of lignin is either wasted to sewer or used as a low value fuel. If the means could be found to isolate it from spent pulping liquor and to convert it to usable chemicals, the financial returns might be sufficient to support separation and processing lignin preparations from spent liquor, thus helping abatement of stream pollution.

Lignin compounds from sulphate black liquor could be precipitated⁸ by bubbling CO_2 into it at about 60°C . The precipitated lignin was separated by filtration and purified by dissolving in dry hexane and reprecipitating in ether. Alkali lignin could be isolated from soda process black liquor by neutralizing it with CO_2 from stack gases to pH 8.3 to 8.5; about 40 % of the lignin was reported⁹ to have been

precipitated. The mix was heated to 85°C - 90°C to coagulate the lignin was filtered. Residual lignin could be further precipitated by addition of sulfuric/hydrochloric acid. Isolated lignin was washed first with cold water and then with dilute sulfuric acid and dried on double drum drier.

The slimy, gelatinous and hard to filter form of the precipitated lignin from black liquor could be changed to a crystalline, easily filterable and quick settling precipitate by mixing small amount of water-immiscible solvent such as chloroform, methylene bromide, 1-nitropropane or the like with lignin containing liquid such as kraft/soda black liquor. The chloroform or other agent, may then be recovered from the filtered liquid by vacuum or steam distillation.¹⁰

Lignin thus isolated could be converted to large surface area lignins¹¹ useful in drug formulations for adsorbing acids in the digestive system, due to their extremely high surface area and their acid-alkali resistance. Other suggested uses include carriers for adhesives, catalyst substrate, reinforcement for plastics and carriers for insecticides and herbicides.

A method to produce biodegradable uncoloured lignin solutions was described¹² wherein aqueous lignin solutions such as pulp mill effluent was treated with polyvalent metal cations. The amount of cation should be sufficient to react with lignins, and the aromatics to produce a water insoluble precipitate which was separated from remaining liquor. The precipitate was subsequently acidified with acid solution and was allowed to stand for sufficient time to permit digestion. The precipitate thus formed was separated by centrifugation; and was treated with alkali to produce aqueous basic solution. This solution was found to be effective in controlling scale formation in boiler water systems, when added to these systems in amount of 5-50 ppm. Thus method not only recovers valuable product from effluent but also reduces the amount of non-biodegradable and toxic materials prior to discharge. In addition colour of the final discharge is also reduced.

Sulpho methylated alkalilignins mixed with aqueous ferrous salt and dichromate and spray dried to a powdered product was reported¹³ to be useful as drilling mud thinner.

M.S.Dimitri¹⁴ described a method for forming lignin reinforced polymers by co-precipitating lignin/latex slurry and gas drying the slurry to leave a lignin reinforced polymer free of inorganic salts. In a process, alkali lignin was dissolved in ammonium hydroxides; and the ammonium lignate thus formed was then modified by adding hexamethylenetetramine to the lignate and heating to 90°-110°C for two hours. Thus treated lignin was mixed with latex to give emulsion, which was precipitated by CO₂. When the precipitate was dried at 300°F or below, inorganic salts formed in precipitation sublimed leaving lignin/latex polymer.

Lignin-polyisocyanate foam¹⁵: Polyethylene glycol solution of lignin when treated with toluene diisocyanate at 115°C afforded a foam having good compressive strength and 74 % recovery. Polyurethane type foam from lignin preparations and organic isocyanates are also reported by T.R.Santelli and R.T.Wallace¹⁶. These foams are useful as plastics and adhesives.

W.I.Detroit¹⁷ reported the preparation of ozone treated lignin from kraft black liquor by treating lignin with oxygen containing 3 % ozone at 50°C for two hours; and spray drying the resulting solution. Oxidized lignin was found to be useful as dispersant for a variety of inorganic materials such as Clay, Cement, Calcium Carbonate, Titanium Dioxide.

Lignin adducts^{18,19} with 3-chloro-2-hydroxypropane-1-sulphonate, chloromethane sulphonate, acrolein and the like compounds are also reported to be useful as surfactants in dyestuff compositions.

An adhesive from Kraft or Soda black liquor was prepared²⁰ by reacting the black liquor (dry matter more than 25 %) with a formaldehyde and combining the product with separately prepared phenol-

formaldehyde adhesive.

Lignin preparations from pulping liquor chemically modified by reaction with compounds such as formaldehyde, triazines, alkylamines were found²¹ to be useful as coagulants in treatment of sewage and other wastes. Cationic water soluble lignin amines²² prepared by reacting Kraft/Soda lignins with the reaction product of epichlorohydrin and a tertiary amine were suitable for a variety of uses such as flocculating agents, coagulants, retention aids, dispersing agents, asphalt emulsifiers²³ and emulsion stabilizers.

Chlorobrominated lignins²⁴ were highly effective fire retarding agents. In one method, the inflammable material was coated or soaked with an aqueous slurry or alkaline solution of chlorobrominated lignin followed by drying. In addition chlorobrominated lignins could be combined with bonding compositions used for the production of bonded articles from particulate material, such as fibers, chips, granules, saw dust etc. eg. in the formation of chip board, particle board and the like. Chlorobromination was effected by adding chlorine and bromine concurrently or in two step operation. After completion of the reaction, the chlorobrominated lignin was filtered, washed and dried.

M.S.Dimitri and S.I.Falkehag²⁵ described composites of alkali lignin and biologically active agents such as fungicides, insecticides, nematocides, herbicides and the like which were useful as controlled release pesticides. These composites were prepared by intermixing ammonium salt of lignin with active agent under conditions of high shear mixing to form stable emulsion; acidifying the emulsion with mineral acid at pH 4-5 to precipitate the active agent/lignin emulsion with the active agent being physically absorbed within the lignin and drying the precipitate if desired.

Oxidation of Black Liquor:

Rapson and Reeve²⁶ developed a process in which kraft mill operation was integrated with a bleach plant to eliminate liquid effluents from bleach plant. In this process sodium sulphide-sodium chloride smelt was subjected to fractionation to obtain aqueous solution of sodium sulphide and to leave sodium chloride.

Oxidation of black liquor^{27,28} is one of the processes which not only reduces air pollution but also reduces sulfur losses from multiple effect evaporators, direct contact evaporators and recovery furnace.

G.G.Copeland²⁹ developed a process in which dried black liquor was burned in oxidation furnace to produce hot gases and molten smelt containing the inorganic constituents. Heat was recovered from the hot gases by heat exchangers, while the molten smelt was further regenerated by conventional means. The separation of steam generating heat recovery system from the oxidation furnace eliminates the possibility of accidental introduction of water into molten smelt in the furnace thus eliminating explosion hazard. The use of simple conventional waste heat boiler for steam generation in place of the complicated recovery furnace greatly reduces the cost of entire system.

Other Treatments of Black Liquor:

H.V.Hess and E.L.Cole³⁰ described the coking of black liquor. In a process black liquor was heated in absence of free oxygen to an elevated temperature (450°-625°F) and pressure to prevent vaporization of the water, for a period sufficient to produce granular coke. The coke was separated from the aqueous phase to yield an aqueous effluent of low COD. The coke produced might be burned to supply heat, or used as a soil conditioner or carbonized to produce high grade coke for metallurgical purposes or used to produce activated carbon.

Organic values of black liquor have been converted into heat energy and activated carbon by a method³¹ which eliminates the recovery boiler from pulping liquor regeneration systems. Black liquor containing 16 % solids or even lower or at any solids content upto 65 % was hydrolyzed under very high pressure at 550°-650°F. The organic matter separates as a water-insoluble precipitate along with inorganic constituents such as Na_2CO_3 , and minor amounts of Na_2SO_4 , Na_2S . The organic matter could be utilized to produce heat energy or activated carbon which itself could be used for purifying effluents from various section of paper mill.

Lime mud comprising calcium carbonate was found to be useful in removing colour from pulping liquid waste effluents. In a process³² effluents were treated with lime mud followed by clarification, separation of effluents from classifiers to remove colour bodies.

Utilization of spent liquor much depends on economic separation of its organic chemical values and inorganic chemical values from it. Modern techniques using Reverse Osmosis(RO), Ultrafiltration(UF), Electrodialysis (ED) have opened new horizons for treatment of spent pulping liquors particularly from small paper mills economically. Basu³³ and Co-workers have worked extensively on the applicability of these techniques and their results are encouraging.

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