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Kurple

(54) **PULPING PROCESS WITHOUT A RECOVERY FURNACE**

(76) Inventor: **Kenneth R. Kurple**, Casco, MI (US)

Correspondence Address:
Kenneth L. Mitchell
Woodling, Krost & Rust
9213 Chillicothe Rd.
Kirtland, OH 44094 (US)

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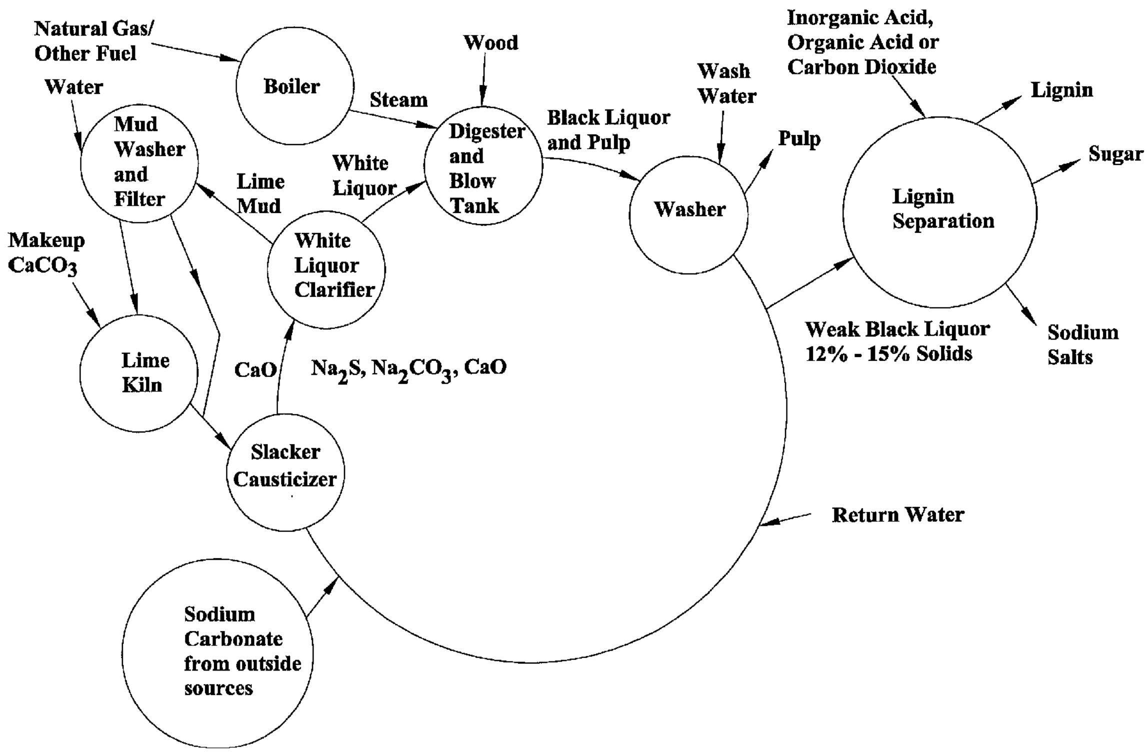
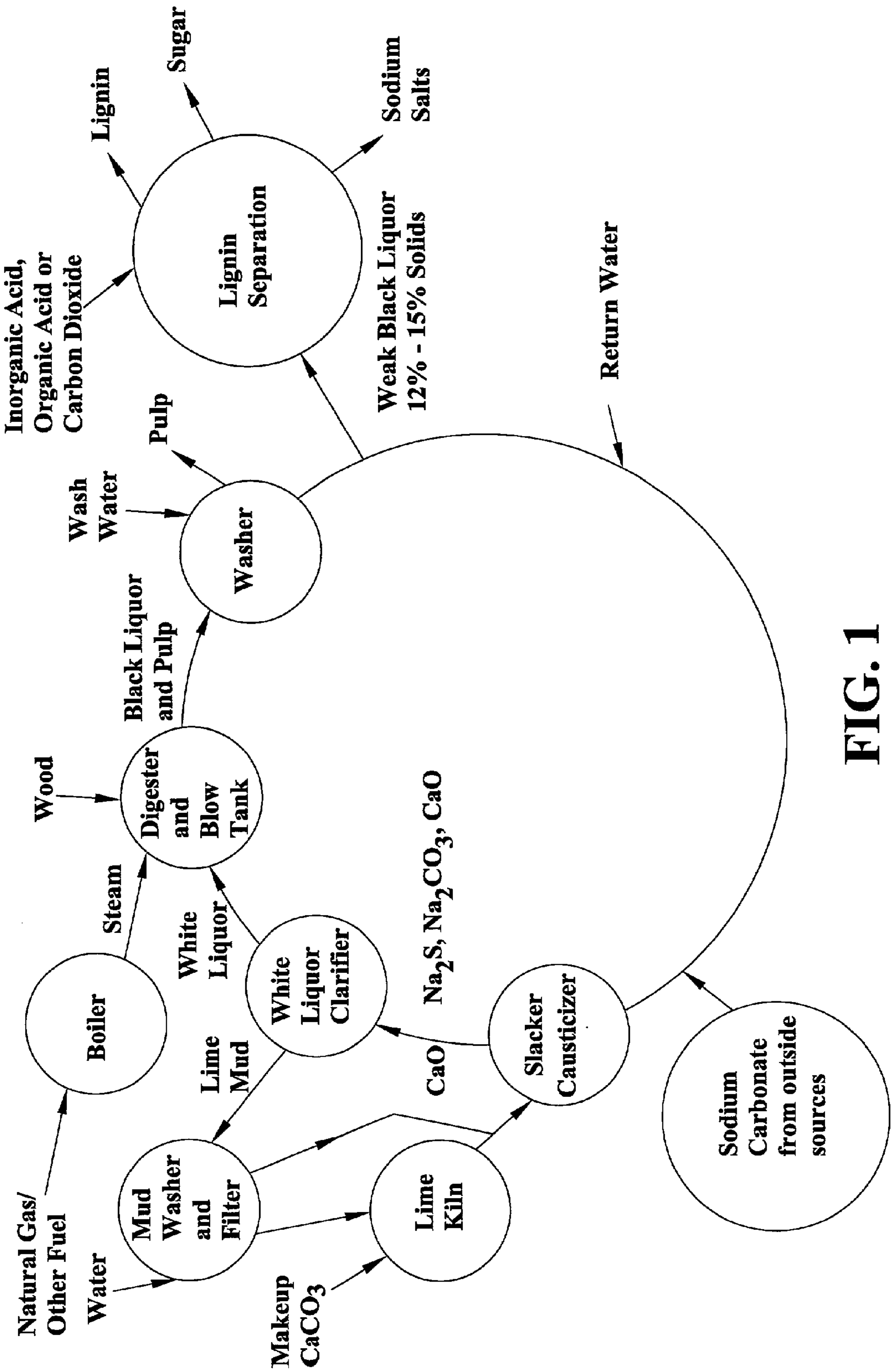
(57) **ABSTRACT**

A novel process has been discovered whereby acid is added to the lignocellulosic material (black liquor containing lignin). The acid renders the lignin insoluble thus enabling it to be separated from the lignocellulosic material. This allows the chemical value of various components to be reclaimed. This process enables important environmental and economic benefits to be achieved. The invention obviates the need for a recovery boiler which burns the sugars and the lignin. Additionally, sodium salts are precipitated out of the process. Sodium carbonate from outside sources is used in the novel process. The supply of energy to the separation process is from a source other than the recovery furnace.





Inorganic Acid, Organic Acid or Carbon Dioxide
Lignin
Sugar
Lignin Separation
Sodium Salts
Weak Black Liquor 12% - 15% Solids
Return Water
Wash Water
Pulp
Washer
Black Liquor and Pulp
Wood
Digester and Blow Tank
Steam
Boiler
White Liquor
White Liquor Clarifier
Na_2S, Na_2CO_3, CaO
Lime Mud
CaO
Slacker Causticizer
Natural Gas/ Other Fuel
Water
Mud Washer and Filter
Lime Kiln
Makeup $CaCO_3$
Sodium Carbonate from outside sources

FIG. 1

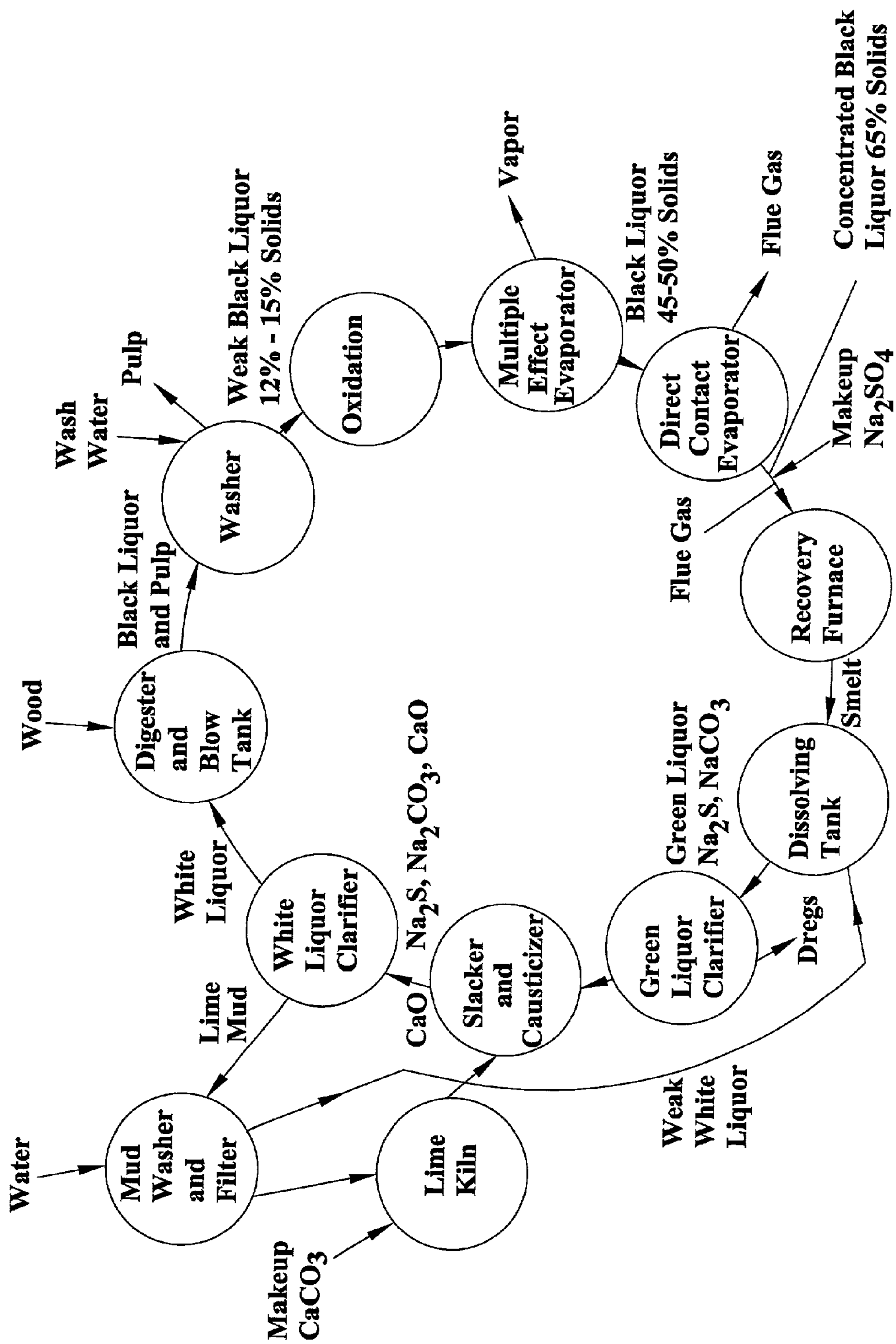


FIG. 2 (PRIOR ART)

PULPING PROCESS WITHOUT A RECOVERY FURNACE

[0001] This application claims the benefit of previously filed U.S. Provisional Patent Application No. 60/101583 filed Sep. 24, 1998. Further, this application claims the benefit of the filing date of Sep. 24, 1999 of copending application Ser. No. 09/405,207. This application is a continuation of Ser. No. 09/405,207.

[0002] After cellulose, lignin is the second most plentiful biopolymer on earth. Wood and other vascular plants are comprised of, by weight, approximately 25% lignin. As part of the processing in the pulp and paper industry to recover cellulose to make paper, lignin is treated as a by-product that is disposed of as part of the waste stream. Based on the amount of wood that is processed by a typical pulp mill, the removal of the lignin waste stream represents a significant disposal problem to the pulp and paper industry. The recovery furnace where the lignin is disposed of for fuel value is often a bottle-neck in the pulping process. Representing a tremendous capital investment to build, the recovery furnace is expensive to maintain as its emissions require additional machinery in order to reduce the environmental problem of air pollution release to the surrounding communities.

[0003] The burden on the recovery furnace can be reduced by removing the lignin from the waste stream. Reducing the load on the recovery furnace allows the pulping process to operate more efficiently and more profitably. Furthermore, the removal of lignin from the recovery furnace will also greatly reduce the amount of material being burned which will result in significant emissions reduction of air pollutants and global warming gases such as carbon dioxide.

[0004] U.S. Pat. No. 5,635,024 to Shall does not disclose a pulping process which includes supplying energy to a digester for the generation of a lignin containing solution and pulp, with the energy being from a source other than a lignin-fired recovery furnace. Plus the main goal of Shall is to use defoamers and polymers to coagulate lignin while one of the objects of the present invention is to produce a polymer grade lignin from the pulping process instead of burning it as waste, while burning conventional fuels to supply energy to the pulping process, and while creating other valuable by products (salts) from the addition of acid to the lignin containing solution (black liquor).

[0005] Shall as stated above does not include supplying energy exclusively from a source other than a lignin fired recovery boiler. U.S. Pat. No. 5,820,830 to McIlroy et. al does disclose supplemental use of steam from a power boiler while using the remainder of the steam to make electricity with the amount of steam needed as a supplement to the pulp mill being a function of the efficiency of the process. Shall and McIlroy are really not amenable to combination because their respective teachings are divergent. Shall is teaching how to coagulate the lignin for burning and McIlroy is teaching make up power from conventional sources and those teachings are seemingly divergent as Shall is presumably trying to increase the efficiency of his process (lignin recovery) and McIlroy is admitting failure of the energy requirements of the lignin. Neither Shall nor U.S. Pat. No. 3,546,200 to Whalen et. al suggest a pulping process wherein the energy is totally supplied from a source other than a lignin-fired recovery furnace.

[0006] Lignin represents an abundant natural resource that, if utilized, can provide more efficient pulping processes and reduce environmental issues concerning its current method of disposal. Based on the natural abundance of lignin and the disposal problem it has historically posed for pulp mills, there are a number of environmental and economic incentives to this process.

[0007] U.S. Pat. No. 5,034,094 to Kurple discloses lessening the load on a recovery furnace used in a pulping process by recovering lignin from the process. This permits more efficient use of the plant and overall process efficiency while creating valuable byproducts. It does not, however, teach the elimination of the recovery furnace.

[0008] The present Kraft pulping system designed to maximize pulping efficiency is more than one hundred years old. When the Kraft pulping system was first put into use there was no polymer industry of any significance. As a result, the pulping process currently in use is based on the production of paper from the optimum recovery of cellulose from pulpable material like trees. However, today in the United States, over 70 billion pounds of various polymers are produced with the majority derived from a petrochemical feedstock. Worldwide production is over 270 billion pounds annually. Markets have been developed for a commercial grade of the lignin after the design of the pulping system. This demand for polymers creates a market for commercial grade polymers from lignin which is part of this process. In the current kraft pulping process the lignin is burned as a fuel and its only value is its BTU value. This is an inefficient use of the naturally occurring high molecular weight polymer (lignin) that is abundantly produced in trees. The process of this invention provides a way of obtaining both environmental and economic benefits from recovering this valuable material from the current inefficient processes for markets outside the pulp and paper industry.

[0009] Current technology has demonstrated that lignin can be used in the foundry industry, urethane foam industry and also the plastics industry. Lignin has more value when it is used in lignin based products in the polymer industry as compared to lignin used as a fuel. Once the lignin is removed from the black liquor it is possible to easily separate the sugars that are present and convert them into ethanol that can be added to gasoline. Obviously, the use of ethanol as a fuel supplement to gasoline was not popular or even known at the time of the Kraft pulping process.

[0010] Natural gas is readily available as a fuel and is environmentally clean. Natural gas boilers can provide the necessary steam requirements for a pulp mill at a fraction of the cost of a recovery boiler. Recovery boilers which burn lignin are difficult to control and maintain in compliance with environmental laws. Natural gas boilers are environmentally friendly and clean.

[0011] At the present time in the kraft pulping process, the kraft soda pulping process and the semi-chemical pulping process it is necessary to have the black liquor concentrated and burned in a recovery furnace in order to have the sodium compounds converted into sodium carbonate. Then the sodium carbonate is reacted with calcium hydroxide to produce sodium hydroxide which is the desired pulping chemical. However the capital costs for such processing steps as oxidation of the black liquor, using a multiple effect evaporator and then further evaporation of the black liquor with a direct contact evaporator are very expensive. The most expensive piece of equipment is the recovery furnace and also the most dangerous to operate. Additionally, recovery furnaces fired by black liquor are not environmentally clean to operate. This novel process produces valuable byproducts from the black liquor and enables alternate, cheaper fuels such as natural gas, to be used in the process without a recovery boiler. Boilers fired by natural gas and other fuels are used in the process to produce the required steam. The recovery furnace greatly contributes to the cost of operating a pulp mill and can significantly limit the efficiency of the pulp mill based on excess accumulation of the waste stream. It is the major advantage of this present invention that allows all of this equipment to be eliminated from the pulp mill.

[0012] The economic impact of a more effective pulping process will be significant for a number of different aspects in the pulp and paper industry. In the pulp and paper industry which generates approximately 500 billion pounds of lignin containing waste annually, disposal costs are at a premium. Further, the control measures and maintenance costs involved in protecting the environment from the release of emissions from the burning of byproducts of the pulping process adds to the operating and maintenance cost of mill operations. Based on the fact the pulp and paper industry is the fourth largest industrial consumer of energy, improving the efficiency of the pulping process can also be a source of significant cost savings. The pulp and paper industry is coming under increasing pressure from the recent environmental regulations which cover the air and water discharges. Control technology to limit Volatile Organic Compounds and Hazardous Air Pollution (HAP) emission is an increasing cost to pulp mills.

[0013] Another major advantage of this invention is that by removing the lignin from the black liquor it now becomes possible and economical to produce a variety of other products such as sodium acetate, sodium sulfate, wood sugars, acetic acid, and lignin.

[0014] It is this equipment (recovery furnace) that contributes to the high cost of operating a pulping mill and significantly affects the profitability of a pulp mill. It is the major advantage of this present invention that allows all of this equipment to be eliminated from a pulp mill.

[0015] By acidifying the black liquor with an acid, it is possible to precipitate the lignin and produce a sodium salt which has a commercial value in the marketplace. Organic acids and inorganic acids may be used. As an example one such acid is acetic acid whereby sodium acetate is produced or phosphoric acid may be used which produces a sodium phosphate salt. These salts, sodium acetate and sodium phosphate, are considerably more valuable as compared to sodium carbonate which is much cheaper than the salts produced. By producing sodium salts which are more valuable than sodium carbonate, it is more economical and more profitable than using the present recovery furnace to produce sodium carbonate by using the present recovery furnace and its auxiliary equipment. Also, sodium salts do not have to be more valuable than sodium carbonates to make this process economical. The reasons include the equipment cost savings by not having a recovery furnace, the value of the recovered lignin which can be further processed into polymer grade lignin (i.e., low sodium lignin), and recovery of sugars.

[0016] In the prior art process, the smelt from the recovery furnace includes the sodium ion which is later used to form sodium hydroxide for use in the digester and blow tank. Smelt is generated by burning the lignin which contains the sodium ion. The carbon in the lignin is burned in the recovery furnace leaving the sodium ion behind in the salt. In the present invention, sodium carbonate which is inexpensive is added to the return water. The sodium ion from the sodium carbonate is used to form sodium hydroxide which is used in the digester and blow tank.

[0017] In the digester and blow tank, lignin is separated from a lignocellulosic material, for example from trees, as black liquor. The black liquor and pulp are then washed in a washer and pulp is extracted therefrom for the processing of paper and other well known products. Lignin, sugars and sodium salts are then separated out of said black liquor as is disclosed herein.

[0018] **FIG. 1** is a schematic representation of a pulping process without a recovery furnace.

[0019] **FIG. 2** is a schematic of a known pulping process with a recovery furnace.

[0020] As an example, addition of acetic acid to the black liquor until the lignin is insoluble, will render the lignin insoluble and will be filtered from the liquor by various means. A filter press, vacuum filter belt or ordinary filters are some of those means.

[0021] As an additional example, 10% solution of sulfuric acid may be added to the black liquor until the lignin is insoluble enabling the lignin to be filtered from the liquor by various means. Most of the lignin is insoluble at pH of approximately 2-3. After the lignin is removed, the solution is concentrated by evaporation or other means forming crystals of sodium sulfate. Then the sodium sulfate crystals are filtered from the solution thereby producing a sugar solution which can be used to produce alcohols or other products. A filter press, vacuum filter belt or ordinary filter may be used to filter the sodium sulfate crystals.

[0022] Optionally, carbon dioxide and sulphur dioxide may be added to the black liquor. These gases become acids when added to the black liquor as they react with water.

[0023] A separation process whereby lignin is separated from a lignin containing material is disclosed and claimed. The lignin is precipitated from the lignin containing material by the addition of an acid such as sulfuric acid, acetic acid, or phosphoric acid. A simplified chemical equation is, for example:

$$C_6H_{12}O_6+2Na\text{-}L+H_2SO_4\longleftrightarrow 2H\text{-}L+2Na+SO_4+C_6H_{12}O_6$$

[0024] Where L represents lignin, Na represents the sodium ion, SO4 represents the sulfate ion, and C6 H12O6 represents the sugar.

[0025] The lignin can them be removed by various filtration means such as filter press, vacuum filter belt or various other filtering or extraction methods. The extraction of the lignin from the solution leaves behind a solution containing inorganic ions (such as sodium Na) initially present in the lignin containing material, the anion from the acid (such as the sulfate ion SO4), as well as the sugars initially present in the lignin containing material.

[0026] Once the lignin is removed the difficulty in separating and extracting the remaining salts and sugars is greatly reduced. The salt is formed from the cation, sodium, already present in the lignin containing material with the anion from the acid that is added initially to the beginning solution. In this case, sodium from the lignin containing material and the anion from the acid, sulfate, combine to form sodium sulfate.

[**0027**] The remaining salt, sodium sulfate, an inorganic material, can be removed by filtering the salt crystal from the remaining solution which will contain primarily sugars (organic material).

[**0028**] Those skilled in the art will recognize that many changes may be made to the invention heretofore described without departing from the spirit and the scope of the appended claims. Commercially valuable sodium salts are also produced by the addition of the acid to the black liquor. This process enables the pulping process to occur without a recovery furnace.

I claim:

1. A pulping process without a lignin-fired recovery furnace, said process includes recovering lignin and sugars from a lignin containing solution, comprising the steps of:

supplying energy to a digester and blow tank for the generation of a lignin containing solution and pulp, said energy being totally supplied from a source other than a lignin-fired recovery furnace;

separating said lignin containing solution and said pulp;

precipitating polymer-grade lignin from the lignin containing solution by adding an acid selected from the group consisting of sulfuric acid, acetic acid and phosphoric acid or by adding a gas selected from the group consisting of carbon dioxide and sulphur dioxide;

removing said precipitated lignin from said lignin containing solution leaving inorganic ions to react with said selected acid forming inorganic salts and leaving organic sugars in solution; and,

separating said inorganic salts and said organic sugars from said solution.

2. A process as claimed in claim 1 wherein said acid is acetic acid which produces sodium acetate.

3. A process as claimed in claim 1 wherein said acid is phosphoric acid which produces a sodium phosphate.

4. A separation process for separating lignin from a lignocellulosic material without using lignin as a fuel, comprising the steps of:

supplying energy to said separation process, said energy being totally supplied from a source other than said lignin:

separating lignin from said lignocellulosic material creating a lignin containing solution;

precipitating lignin from said lignin containing solution by adding an acid selected from the group consisting of sulfuric acid, acetic acid, and phosphoric acid or by adding a gas selected from the group consisting of carbon dioxide and sulfur dioxide; and,

removing said precipitated lignin from said lignin containing material leaving inorganic salts and leaving organic sugars from said solution.

5. A separation process for separating lignin from a lignocellulosic material without using lignin as a fuel, comprising the steps of:

supplying energy to the separation process, said energy being totally supplied from a source other than said lignin:

separating lignin from said lignocellulosic material creating a lignin containing solution;

precipitating lignin from said lignin containing solution by adding an acid selected from the group consisting of sulfuric acid, acetic acid, and phosphoric acid or by adding a gas selected from the group consisting of carbon dioxide and sulfur dioxide; and,

adding a compound having a sodium ion as part thereof.

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