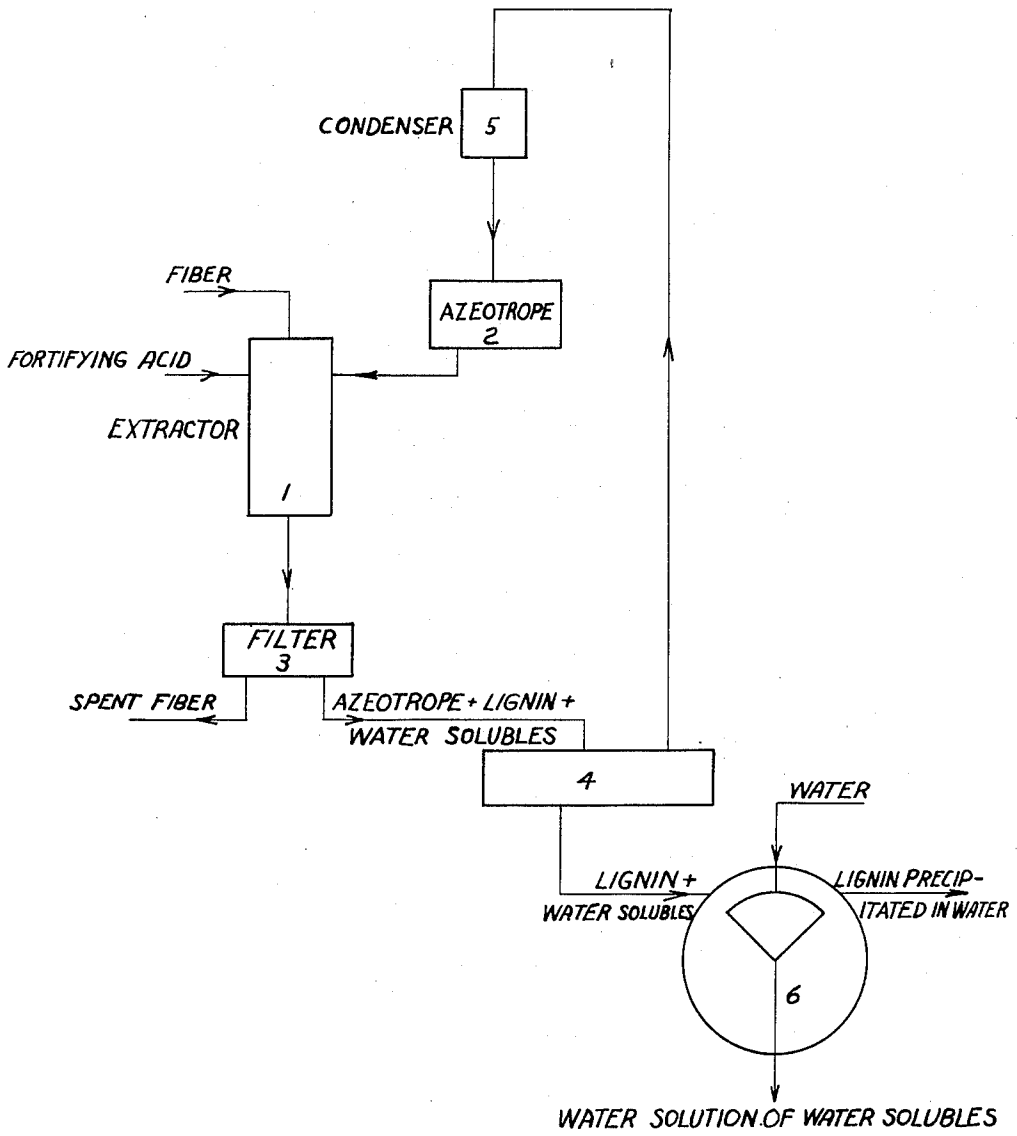
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PROCESS FOR EXTRACTION OF LIGNIN

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PROCESS FOR EXTRACTION OF LIGNIN

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This invention relates to a process of extracting lignin, and more particularly to the extraction of lignin from disintegrated lignocellulose materials by means of the azeotropic mixture of formic acid and water as the solvent.

It has been found according to the present invention in general that lignin can be extracted from disintegrated lignocellulose materials with the formic acid-water azeotrope, that the yield of lignin is greater than with non-azeotropic concentrations of formic acid, and that the azeotrope can be recovered and reused to extract lignin from additional lignocellulose materials.

Lignocellulose materials to which the invention is applicable comprise fibrous vegetable growths in general, such as the woody material of trees, bamboo, straw, cornstalks, grasses, sedges, and the like. The invention is applicable to extracting lignin from either raw or hydrolyzed material. The lignocellulose material can be either wet or dry.

Desirably the lignocellulose material will be in a disintegrated state in order to render it more accessible to the extraction treatment. If it is desired to treat unhydrolyzed material, disintegration may be accomplished by grinding or by other mechanical means. If it is desired to treat hydrolyzed material, preferably the lignocellulose material will be disintegrated by a closed chamber (e. g. a gun such as that described in U. S. Patent 1,824,221 to Mason), although this may be done in other ways. This method comprises charging the gun with relatively small wood chips or other woody material, subjecting the chips to pressure of about 200–1200 pounds per square inch and a temperature of about 200°–300° C. for approximately 30 minutes to 5 seconds, respectively, in the presence of steam, and then discharging the woody material from the gun through a constricted discharge means therein, e. g. a valve, into a zone of lower pressure (preferably atmospheric pressure), thereby exploding the wood chips into comparatively finely divided elongated fibers and bundles of fibers, hereinafter called fiber. The gun conditions may be varied so as to be suited to changes in kind of wood, size of chips (desirably up to about one inch long), water content of the chips (preferably about 25%), extent of desired steam treatment, and the like.

Under this treatment the wood undergoes hydrolysis, and portions of the water-insoluble and readily-hydrolyzable constituents thereof are rendered soluble or dispersible or suspendible in water. The term "water soluble" is used to include dispersed and suspended material as well as dissolved material. The water solubles may be washed out of the disintegrated lignocellulose material before extracting the lignin or they may be extracted along with the lignin and separated

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therefrom with water. The invention will be described in most part with reference to extracting lignin from hydrolyzed lignocellulose fiber in which the water solubles are present.

The drawing is a diagrammatic representation of apparatus suitable for extracting lignin from unwashed fiber, i. e. fiber from which the water solubles have not been removed.

The following example illustrates a specific embodiment of this invention. Parts and percent are by weight unless otherwise indicated.

Example

Gum wood chips were fiberized in the gun mentioned herein under the following conditions: 30 seconds steam preheated to a pressure of 600 p. s. i., held 45 seconds at 600 p. s. i. and the charge shot from the gun. The fiber was air dried to a moisture content of about 5% and found to have a methoxyl of 6.3%. 100 parts of this fiber was slurried with hot (about 100° C.) formic acid of various concentrations, and the slurry filtered. The weight ratio of acid to fiber was approximately 20 to 1. The fiber was washed with fresh hot formic acid of substantially the same concentration as the initial acid, until the washings were substantially colorless, to remove occluded formic acid containing lignin. These washings were added to the filtrate. The formic acid was recovered by distilling from the filtrate. The residue (lignin and water solubles) from the distillation was dissolved in methyl cellosolve and the lignin precipitated therefrom into water. In experiments in which the azeotrope (77.5% formic acid—22.5% water mixture) was used, it was fortified with formic acid to compensate for water in the fiber. The azeotrope was reused to extract lignin from additional fiber. The concentrations of acid used and the yields of lignin obtained are tabulated below. The lignin had a methoxyl of about 17.5%.

Lignin Yield, Formic Acid Conc.	Formic Acid Concentration, percent by weight	Lignin Yield, percent by weight of air dried fiber
0.0	0.0	0.0
0.042	11.8	0.5
0.108	23.1	2.5
0.168	34.0	5.7
0.229	44.5	10.2
0.247	54.6	13.5
0.258	64.4	16.6
0.255	73.8	18.8
0.294	[1] 77.5	22.8
0.243	82.8	20.1
0.235	90.0	21.1

[1] Azeotrope.

Factors which affect the yield of lignin include the type of lignocellulose material used and the conditions under which it is disintegrated. Nevertheless, in any event, the yields are much high-

er than those obtained by extracting with conventional solvents.

In practicing this invention according to one embodiment thereof, hydrolyzed lignocellulose fiber, preferably gun fiber, is slurried with formic acid-water azeotrope and the slurry filtered. Some of the lignin-containing azeotrope is left behind with the fiber. To remove this the fiber is washed with fresh azeotrope until the washings are substantially colorless. These washings are added to the filtrate and the azeotrope distilled therefrom. Then the residue from the distillation is dissolved in a water-soluble organic solvent for lignin and the lignin precipitated into water from this solution. The distilled azeotrope is reused to extract lignin from additional lignocellulose material. While the azeotrope can be used at about room temperature, preferably the azeotrope will be used at an elevated temperature because the lignin yields are somewhat higher. Very good yields are obtained at a temperature of about the boiling point of the azeotrope. Water-soluble organic solvents for lignin which may be used include methyl cellosolve; dioxane; methyl, ethyl, propyl and tertiary butyl alcohols; and acetone.

Desirably this process will be varied somewhat depending on the condition of the lignocellulose material from which the lignin is to be extracted. These variations may best be brought out and the invention more clearly understood by describing the invention with reference to the drawing.

Describing the invention with reference to the drawing, gun fiber is charged into the extractor 1 and the azeotrope is passed into the extractor from tank 2. The fiber and azeotrope are slurried while heating the azeotrope at a temperature of about 100° C. Application of heat is discontinued and the charge discharged into a filtering means 3, such as a filter press, and filtered, whereby the lignin-water-soluble-azeotropic solution is separated from the spent fiber and passed into tank 4. The spent fiber contains occluded azeotrope with dissolved lignin and water solubles. If desired, this can be recovered by washing with fresh azeotrope and adding the washings to the first filtrate in tank 4. The azeotrope is distilled from tank 4 through condenser 5, and the azeotropic distillate passes into tank 2 from which it is reused to extract lignin from additional fiber. Additional azeotrope may be added at this point as make-up for process losses. The lignin-water soluble mixture is discharged from tank 4 onto a countercurrent washer 6. Countercurrent washing of this mixture separates the lignin and water solubles as shown. This same apparatus minus the countercurrent washer 6 is suitable for extracting lignin from washed fiber (i. e. fiber from which the water solubles have been previously removed as by washing with water).

The residue (lignin or lignin and water solubles) obtained in tank 4 after evaporation of the azeotrope, may be dissolved in a water soluble organic solvent for lignin and the lignin precipitated therefrom into water. Extraction can be carried out at the reflux temperature of the azeotrope. In this event, a reflux condenser (not shown) is attached to the extractor. Alternatively the filter 3 can be eliminated. Instead of filtering, the major portion of the azeotrope is decanted from the fiber and passed into tank 4. Then the fiber is washed with fresh azeotrope and decanted into tank 4. The last

traces of the azeotrope in the fiber are recovered by distilling from the extractor into tank 2. These last traces of azeotrope can be removed from the fiber by washing with water, preferably by means of a countercurrent washer (not shown); however, this method is less desirable. It complicates the recovery of the azeotrope in that means, such as a fractionating column, would be required to remove excess water from the acid to increase the concentration to that of the azeotrope. Moreover, there is a tendency for the lignin to precipitate prematurely since it is for the most part insoluble in water.

If the fiber to be extracted is not substantially bone dry, the formic acid-water azeotrope is fortified with formic acid prior to use in order to offset dilution of the azeotrope by the water in the fiber.

An outstanding advantage of this invention resides in the finding that the azeotropic concentration (77.5% formic acid, 22.5% water) of formic acid is a better solvent for lignin than other concentrations of formic acid (even 90% formic acid), and that the azeotrope can be reused to extract lignin from additional lignocellulose materials. The relative ease of recovering the azeotrope increases the significance of these advantages.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments thereof except as defined in the appended claims.

We claim:

1. Process of extracting lignin from hydrolyzed lignocellulose material which comprises slurrying said material with a formic acid-water azeotrope at a temperature of about the boiling point of the azeotrope, distilling the azeotrope from said material, recovering the lignin from the azeotrope, and reusing the azeotrope to extract lignin from additional lignocellulose material.

2. Process of extracting lignin from hydrolyzed lignocellulose material which comprises slurrying said material with a formic acid-water azeotrope at a temperature of about the boiling point of the azeotrope, filtering the slurry, washing the resulting lignocellulose material with additional hot azeotrope until the washings are substantially colorless to remove occluded azeotrope containing lignin, adding these washings to the filtrate, distilling the azeotrope from the resulting filtrate, washing the residue with water to remove water solubles therefrom, and reusing the distilled azeotrope to extract lignin from additional lignocellulose material.

3. Process of extracting lignin from hydrolyzed lignocellulose materials which comprises slurrying said material with a formic acid-water azeotrope at a temperature of about the boiling point of the azeotrope, filtering the slurry, washing the resulting lignocellulose material with additional hot azeotrope until the washings are substantially colorless to remove occluded azeotrope containing lignin, adding these washings to the filtrate, distilling the azeotrope from the resulting filtrate, dissolving the residue in a water-soluble organic solvent for lignin, precipitating the lignin from said solution by adding water thereto, and reusing the distilled azeotrope to extract lignin from additional lignocellulose material.

4. Process of extracting lignin from hydrolyzed lignocellulose fiber which comprises slurrying the

fiber with a formic acid-water azeotrope at a temperature of about the boiling point of the azeotrope, filtering the slurry, distilling the azeotrope from the filtrate, washing the residue with water, and reusing the distilled azeotrope to extract lignin from additional lignocellulose material.

5. Process of extracting lignin from hydrolyzed lignocellulose fiber which comprises removing the water solubles from said fiber, slurrying the resulting fiber with a formic acid-water azeotrope at a temperature of about the boiling

point of the azeotrope, filtering the slurry, distilling the azeotrope from the filtrate, washing the residue with water, and reusing the distilled azeotrope to extract lignin from additional lignocellulose material.

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