Dec. 21, 1954 C. C. HERITAGE ET AL 2,697,701

FRACTIONATION OF LIGNOCELLULOSE MATERIALS

Filed Feb. 9, 1951 3 Sheets-Sheet 1

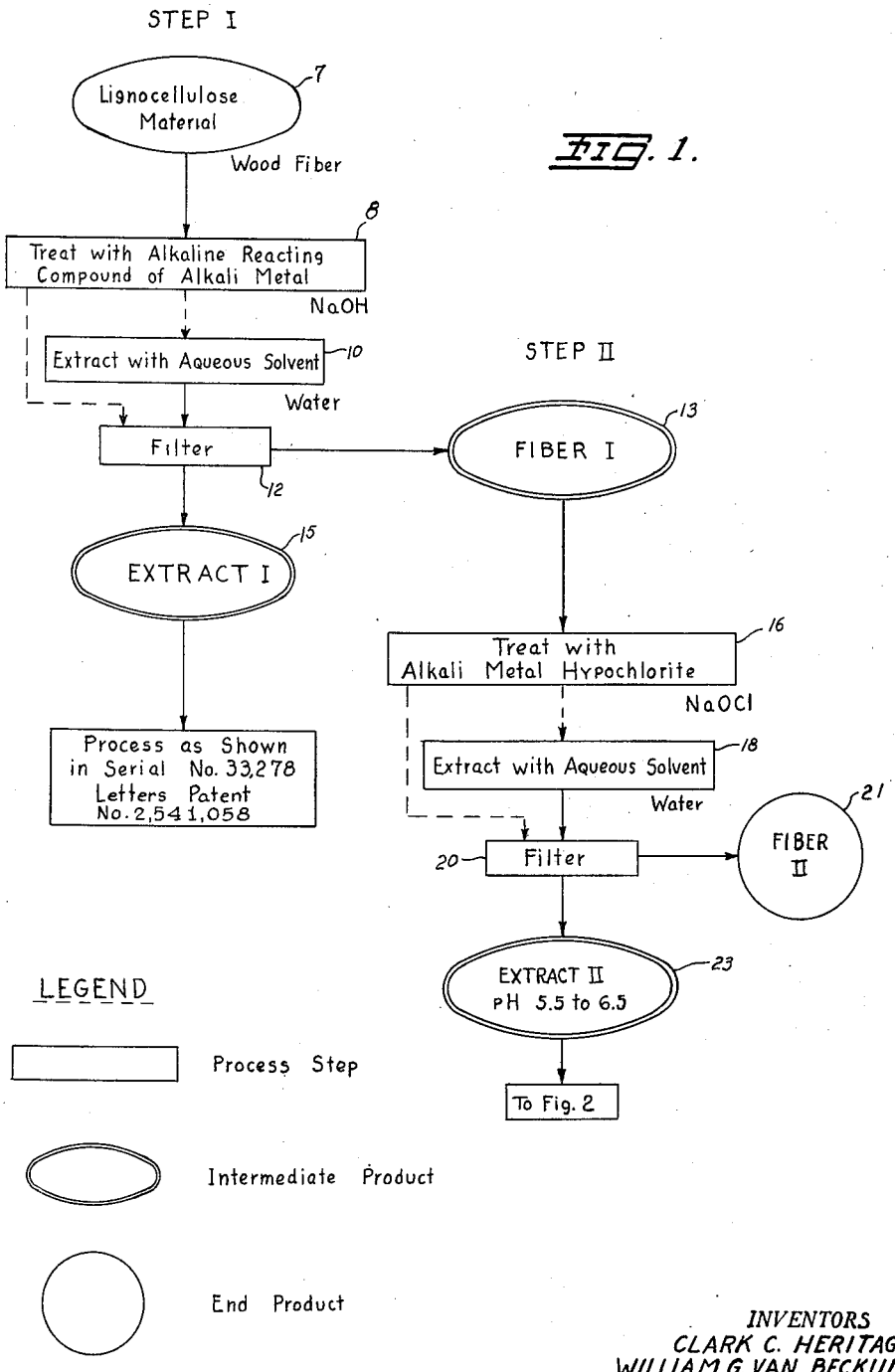


FIG. 1.

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FRACTIONATION OF LIGNOCELLULOSE MATERIALS

Filed Feb. 9, 1951 3 Sheets-Sheet 2

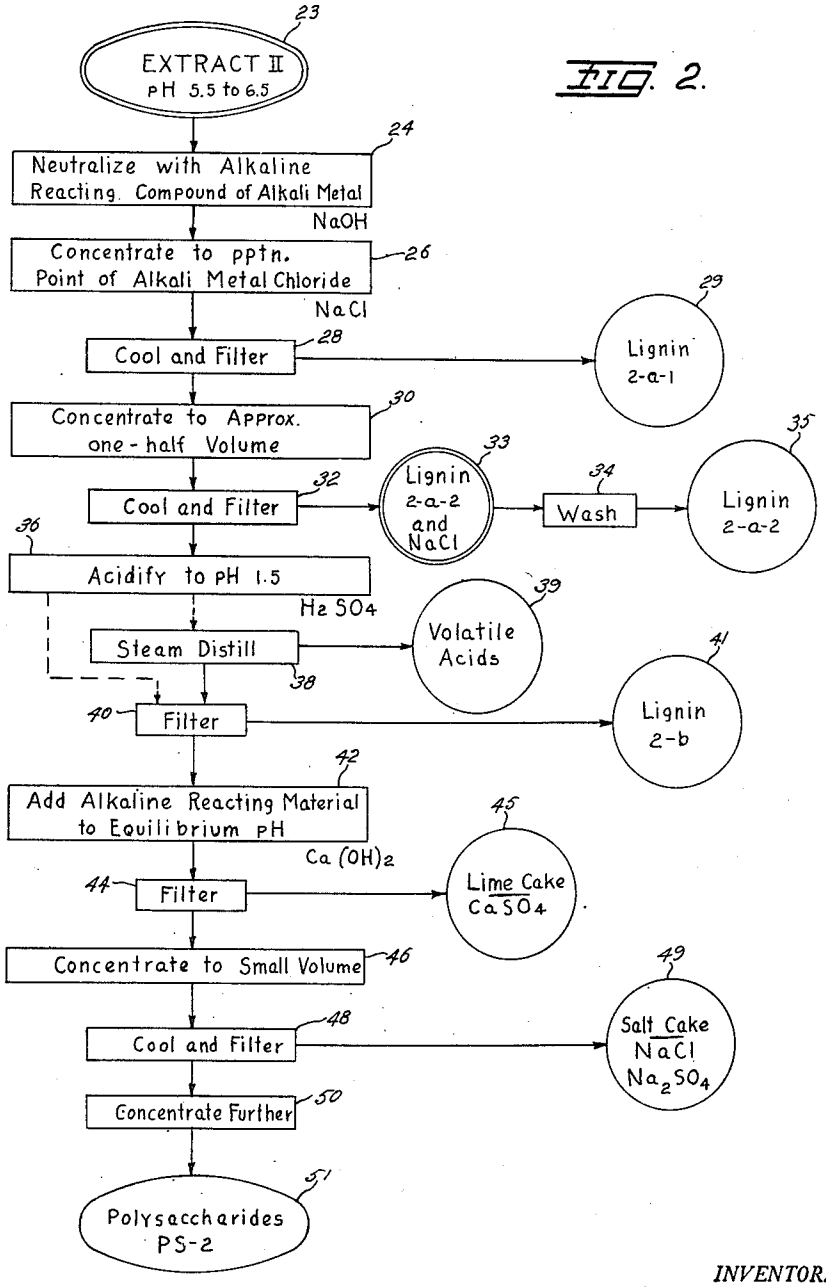


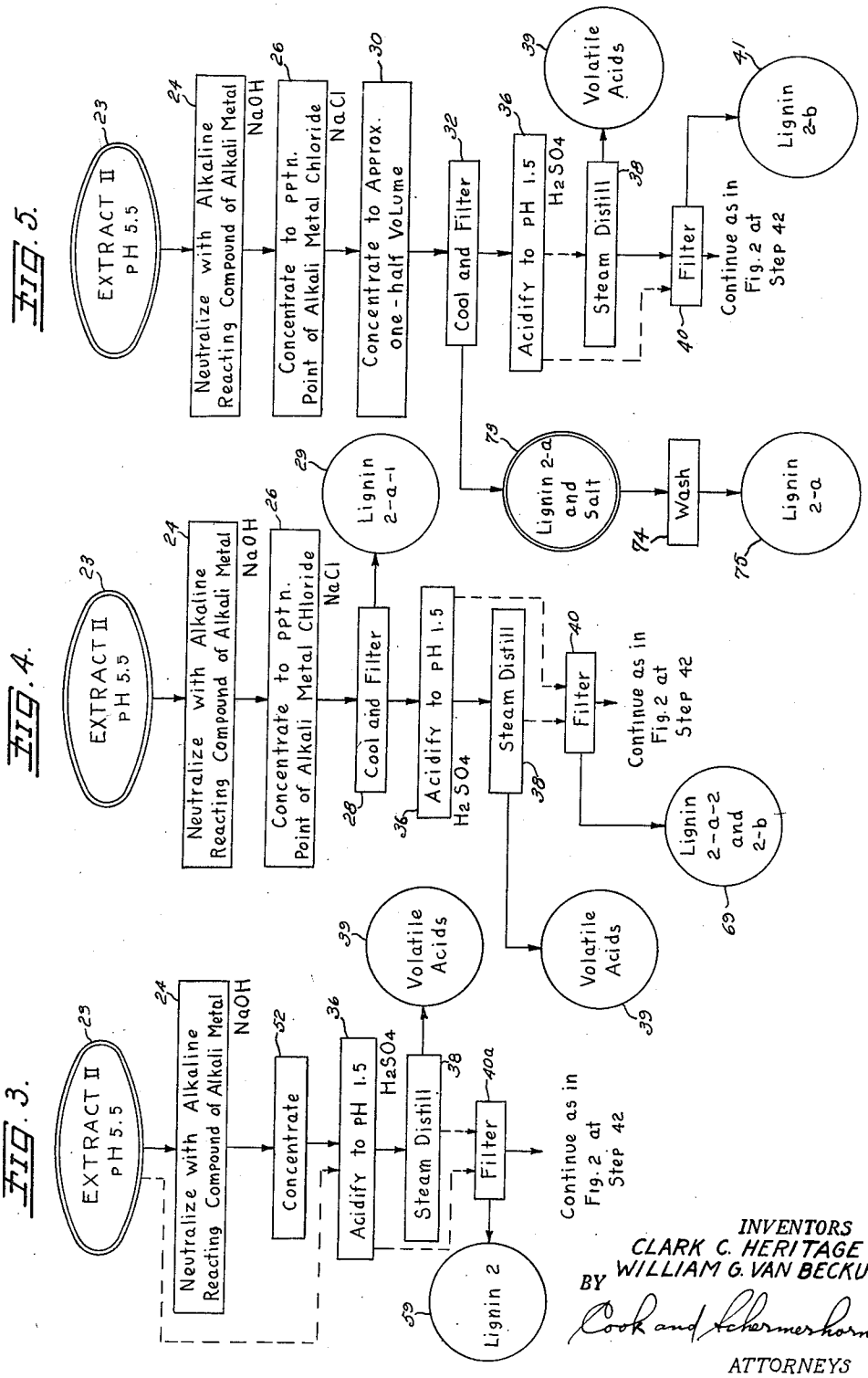
FIG. 2.

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FRACTIONATION OF LIGNOCELLULOSE MATERIALS

Filed Feb. 9, 1951 3 Sheets-Sheet 3



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United States Patent Office 2,697,701
Patented Dec. 21, 1954

2,697,701

FRACTIONATION OF LIGNOCELLULOSE MATERIALS

Clark C. Heritage, Tacoma, and William G. Van Beckum, Longview, Wash., assignors, by direct and mesne assignments, of one-half to Weyerhaeuser Timber Company, Tacoma, Wash., a corporation of Washington, and one-half to Wood Conversion Company, St. Paul, Minn., a corporation of Delaware

Application February 9, 1951, Serial No. 210,234

23 Claims. (Cl. 260—124)

This invention relates to a process for the isolation of non-cellulosic chemical products from lignocellulose materials with recovery of cellulosic fiber as an attendant product. More particularly the invention pertains to the separation of lignocellulose materials comprising cellulose, lignin, and polysaccharides-other-than-cellulose, into non-cellulosic substances, i. e., lignins, and other organics having a substantial content of polysaccharides-other-than-cellulose and a cellulosic fiber residue of variable but controllable composition.

The invention is a continuation-in-part of our copending application, Serial No. 33,278, filed June 16, 1948, for Processing of Lignocellulose Material, now Letters Patent No. 2,541,058, granted February 13, 1951.

The process of the invention is applicable to a diversity of lignocellulose materials, but is especially applicable to the fractionation of wood substance. Substantially all kinds of woods may be thus fractionated, representative and suitable woods being aspen, jack pine, western larch, Douglas fir, and many others. Substantially the same procedure and variations of it may be employed with all these varieties of woods, the results varying in degree.

In practicing the present invention, when wood is used as a source of lignocellulose materials, it is first reduced to finely divided or fibrous form by mechanical or other methods which do not subject the wood to the action of added chemicals other than water. Thus, wood fibers, sawdust, hogged fuel and similar forms of comminuted wood or lignocellulose materials are suitable raw materials for the practice of the invention. If the wood is fiberized, the fiberization is preferably carried to the point where it results in the conversion of the wood substance to fibers physically consisting substantially of ultimate fibers and opened-up bundles of ultimate fibers, hereinafter all referred to as fiber, and constitutionally consisting primarily of cellulose, lignin, and other organics including polysaccharides-other-than-cellulose, the latter being herein frequently referred to merely as "polysaccharides," these three constituents being present in mutual ratios in the range of compositions from those characterizing the raw wood from which the fiber is derived to those characterizing the water-insoluble content of the raw wood from which the fiber is derived. Fiber containing cellulose, lignin, and other organics including polysaccharides-other-than-cellulose in the ratios characterizing the water-insoluble content of the raw wood from which the fiber is derived, is exemplified by raw wood fiber which has been so treated with water as to extract the water-soluble constituents and leave as a fibrous residue the water-insoluble content of the raw wood. The production of such fiber from woods such as western larch, is of particular interest, since these woods contain high percentages of water extractable substances, e. g. about 23% in the case of western larch. It may therefore be commercially desirable in the case of these woods to extract them with water in order to isolate as commercial products the natural water-soluble fraction of the wood substance. A fiber form of the extracted wood may be employed to advantage as a rew material for the fractionation process of the instant invention.

The wood fibers to which the process of the invention may be satisfactorily applied may be produced, for example, by the method described in U. S. Patent No. 1,913,-607 to McMillan. This patent describes a mechanical defibering process entirely free from chemical action, which

comprises combing out fibers from wood by contacting logs of wood with high speed rotary radial elements, such as pointed pins projecting from an axle, like bristles. Fiber produced by this process is herein referred to as McMillan fiber, or pin fiber, and it is an excellent raw wood fiber for the present invention. Such pin fiber may be processed with or without an initial water extraction.

Wood fiber suitable for use in the process of the present invention may also be prepared by the method described in U. S. Patent No. 2,008,892 to Asplund. In this method wood substance is defibered by mechanically rolling and crushing the wood between relatively rotating opposing disks, while simultaneously applying steam under sufficient pressure markedly to soften the lignin in the middle lamella, thus permitting easy defibration of the softened wood. The fiber resulting from this practice, in efficient operation of the commercial Asplund machine, is termed herein "normal" Asplund fiber, or normal defibrator fiber. It is prepared, for example, by so defibrating the wood while exposing it for about one minute to high pressure steam at a temperature sufficient to effect the desired softening. The significance of the term "normal" is with reference to practical minimum operating time and temperature, as described, because increase of temperature or time has a chemical effect on the wood substance which may be measured in terms of water-soluble content formed by the action of the steam.

Any other process for reducing wood substance to said ultimate fiber or opened-up bundle form, may be employed. The wood substance may be affected by steam at any time or times before, during or after such defibration. Action by steam should be such as to avoid any substantial gasification of the wood substance which thus leads to loss or decomposition of wood substance, usually indicated by the formation of furfural, and evident in altered proportions of the three primary constituents, and by unduly altered forms of said constituents. Processes involving both defibering and steaming may be used. The fibers resulting from this process which includes those resulting from the Asplund process, differ from the raw wood in that their water-soluble content has been to a greater or less degree increased by treatment with the steam. In the case of normal Asplund aspen fibers made in about 1 minute at about 128 lbs. steam pressure, the increase in water-soluble content is about 4% to 5%, which is additive to a natural water-soluble content in raw aspen of about the same amount, variable, however, with the season of cutting and age of the tree. Thus, normal Asplund aspen fiber has about 8% to 10% of water solubles.

Other methods for producing fibers from wood substance may also be used, provided said methods do not subject the wood to the action of added chemical agents other than liquid water or steam, or substantially alter teh constituents in a manner other than those stated, excepting further, a treatment with an alkaline reacting compound of an alkali-metal for the described purposes of the present invention.

Heretofore, lignocellulose material has been converted to pulp suitable for use in the manufacture of paper, fiberboard, and other products, by various mechanical and chemical methods, or combinations of such methods. It is well-known, for example, to prepare paper-making pulp by treating raw wood with bisulfite salts, e. g. calcium bisulfite or magnesium bisulfite. It is also well known to subject raw wood to the action of numerous alkaline chemicals alone or in admixture, as in the well-known, soda, kraft or sulfate, and mono-sulfite processes. None of these methods, however, has effected the precise fractionation of wood substance by simple processes carried out under carefully controlled and standardized conditions at atmospheric pressures by a continuous process which facilitate the separation of useful lignin and polysaccharide products while at the same time producing a high yield of useful cellulosic fiber of reproducible properties.

By way of orientation, the present invention is part of a stepwise procedure devised for the carefully-controlled decomposition of lignocellulose material, particularly wood, into its various chemical constituents, including fiber or other lignocellulose residue. The total procedure

comprises, with variations, three basic steps, outlined as follows: treatment with sodium hydroxide (caustic), sodium hypochlorite, and sodium hydroxide (caustic). The total process is, therefore, generally referred to as the CHC process, with the letters "CHC" standing for caustic, hypochlorite and caustic, and the lignins produced by the process are referred to as CHC lignins, whether such lignins are produced by only one or all three of the basic steps. The three basic steps of the total process are also identified as Step I, Step II, and Step III, and the products of each step are designated by corresponding numerals, as for instance, Extract I, Fiber I and lignin 1 from Step I; Extract II, Fiber II, and lignin 2 from Step II; and similarly for Step III. Our copending application, Serial No. 33,278, of which this case is a continuation-in-part, which application matured as Letters Patent No. 2,541,058, granted February 13, 1951, dealt with the first of the three basic steps, i. e., the caustic or alkali treatment, identified as Step I and the corresponding chemical products. The present invention deals with the treatment through the first two basic steps, i. e., the caustic and hypochlorite treating steps, identified as Steps I and II, and also as the CH (caustic and hypochlorite) steps of the CHC process. The products of the present invention are those resulting from Step II, and are accordingly designated herein by either the Roman numeral II or the Arabic numeral 2, together with approximate sub-classification nomenclature. The further treatment of Step III of the full process is disclosed and described together with its products in our application Serial No. 210,235 filed February 9, 1951.

It is a general object of the present invention to treat lignocellulose materials of nature for isolating on the one hand mutually separable lignins and organics including polysaccharides-other-than-cellulose, and on the other hand a useful cellulosic product.

It is also an object of the present invention to separate lignocellulose materials into fractions together comprising isolated lignins, isolated organics including isolated polysaccharides-other-than-cellulose, and isolated cellulosic fiber of controllable quality.

In our copending application, Serial No. 33,278, Letters Patent No. 2,541,058, there is described and claimed a method of treating lignocellulose fiber of the types above referred to as the initial substance for treatment, by the action thereon of alkali metal hydroxide to provide a treated fiber identified as Fiber I, and a separable liquid, identified as Extract I, containing extractives derived from the initial fibers by the treatment. There are also described numerous process steps upon the separated liquid to win the said extractives. The fiber residue of the said treatment has utility as a special fiber, being composed of cellulose, lignin and organics, including polysaccharides-other-than-cellulose, but in new proportions as a result of removal of said extractives.

The present invention aims to use Fiber I as a raw material for a second processing to secure a Fiber II and an Extract II, and also to process Extract II for winning extractives therein derived from Fiber I, so that by this invention Fiber I is converted to one or more new lignin products, a concentrate of organics including polysaccharides-other-than-cellulose, and a new and useful fiber of increased cellulose content compared with Fiber I. Or, in another view, the present invention contemplates the provision of a two-step chemical treatment of lignocellulose material for the production therefrom of a cellulosic product and two different chemical extracts, followed by the processing of the second chemical extract to obtain different chemical products therefrom.

It is a particular object of the present invention to treat said Fiber I with aqueous alkali metal hypochlorite salt solution, as a solubilizing agent, which concurrently removes from the fiber a part of the lignin and other organics including polysaccharides-other-than-cellulose, and then to separate the resulting Extract II and the resulting Fiber II.

It is also an object of the present invention to process the resulting Extract II for separating one or more of the kinds of extractives contained therein.

It is also an object of the invention to process Fiber I to Fiber II which is richer in cellulose, and poorer in lignin and polysaccrarides - other - than - cellulose, than Fiber I.

It is also an object of the present invention to recover from Extract II one or more novel lignin products, and a concentrate of organics including polysaccharides-other-than-cellulose, which may be accumulated with like types of concentrates resulting from processing of Extract I, whereby the said accumulations and Fiber II of the present invention may represent substantially all of the original fiber employed to produce first Fiber I and then Fiber II.

Other objects and advantages of the invention will become apparent from the following description and explanation in connection with the appended drawings wherein process steps are shown in rectangular blocks, materials in process are shown in double-line curved enclosures, and end products are shown in single ring circles. Precipitates are shown in circles disposed laterally of the filter step by which they are separated and solutions resulting from filtration steps are shown in elliptical enclosures. Alternative sequences and steps are indicated by broken lines.

Preferred materials or reagents are shown at the lower left and right of the rings, blocks and enclosures that appear on the drawings.

Figure 1 is a flow chart diagrammatically representing the practice of the process for the production of Fiber I and an Extract I product, and the further treatment of Fiber I for the production of a Fiber II product and an Extract II product.

Figure 2 is a flow chart showing the processing of Extract II for the production of a number of products of the invention.

Figures 3, 4 and 5 are modifications of the process outlined in Figure 2 for obtaining particular combinations of the lignin products.

GENERAL DESCRIPTION

It has been found that the above and other objects of the invention may be accomplished by subjecting lignocellulose fiber, e. g. wood substance in fiber forms, to the action of a limited proportion of an alkaline reacting compound of an alkali metal in a strong or weak aqueous solution thereof, or in a solid form on moist fiber, separating a resulting solution from residual fiber using added water if necessary or desired, and treating the said residual fiber with an alkaline solution of a hypochlorite salt of an alkali metal, separating a second fibrous residue from the residual treating solution, and separating lignin and polysaccharides-other-than-cellulose from said residual solution.

More specifically stated, lignocellulose materials are fractionated in accordance with the present invention by treating such materials in comminuted form, either in dilute aqueous suspensions, or in moist condition of the lignocellulose particles with an alkaline reacting compound of an alkali metal, e. g., sodium hydroxide, at atmospheric pressure and at a temperature ranging from room temperature to an upper limit of atmospheric boiling point where aqueous suspensions are involved, or higher temperatures where superheated steam is used for the treatment of moist fibers, for a time sufficient substantially to complete to equilibrium the chemical reaction between the alkali and the wood substance, thereby converting substantially all that portion of lignin and organics including polysaccharides-other-than-cellulose which are so convertible under the conditions of the reaction, from a water insoluble state to a water soluble state with a substantial residue of lignocellulose remaining insoluble, separating the water soluble matter from the insoluble residue by washing with more water, if necessary, thereby obtaining an extract containing the lignin and said organics, and then subjecting to the action of an alkali metal hypochlorite salt the lignocellulose residue, either in an aqueous suspension, or, if in moist fiber condition, in the presence of sufficient water within the fiber to permit interaction with the alkali metal hypochlorite, thereby rendering soluble further quantities of lignin and polysaccharides-other-than-cellulose, separating the resulting lignocellulose residue from the resulting weakened or exhausted solution, and separating the lignin and polysaccharide contents from the residual solution.

The alkali is used in any amount, expressed in terms of caustic soda, upwardly from that which leaves an alkaline extract under the conditions employed, usually about 2.5 parts to 100 parts of oven dry fiber, to a large amount, for example an amount equal to the oven-dry weight of the fiber, i. e., 100 parts alkali to 100 parts fiber. The alkali may be used in dissolved form in suspensions of

the fiber in water, or may be applied as a solid to moist fiber without a suspending quantity of water. The ratio of fiber to a liquid mass containing it is expressed as "per cent consistency." A 4% consistency as a slurry may be used, or modified to a higher consistency, such as a 50% consistency, which is represented by a mass of suitably moist fibers. To minimize the effect of strong causticity on the fiber substance, low usage of water accompanies low usage of alkali-metal hydroxide, and high uses of each go together.

For example, a mass consisting by weight of 100 parts of dry fiber (oven-dry basis), 100 parts of water, and 8 parts of sodium hydroxide constitutes a moist mass. The reaction may be carried out over a range of temperature conditions. Usages of 5% and 9% at 50% consistency (100 parts dry fiber, 100 parts water and 5 or 9 parts sodium hydroxide) have been successfully employed in the Step I treatment, both at 140° C. and at room temperature. If desired, the caustic soda may be prepared in solution form before mixing with the fiber. When the treatment was conducted at room temperature, a caustic solution was prepared and sprayed on the fiber while mixing in a revolving agitator type mixer, such as a Hobart. The heat of reaction raises the temperature of the reacting mass up to possibly 60° or 70° C. and the reaction goes substantially to completion in 10 to 15 minutes. An advantage of this procedure is that by controlling the temperature of the caustic solution prior to addition to the fiber, so as to take into account the exothermic value of the reaction, the maximum reaction temperature of the treated mass is controlled. Superheated steam may be used to obtain treating temperatures as high as 140° C. while maintaining atmospheric pressures. In this case, the caustic soda, water and fiber are first thoroughly mixed together to form a moist mass and then transferred to a steam treating chamber where the mix is subjected to the superheated steam for from 40 to 60 minutes.

No disadvantage accrues with respect to yields or quality of fiber and chemical products from conducting the alkali treatment either in aqueous suspension or in a moist condition of the lignocellulose particles. The choice between the two types of treatment is largely dependent on available plant equipment engineering convenience, and economic considerations. Regardless of the various ways in which the treatment is conducted, the initial fibers or lignocellulose particles become acted upon by the alkali to produce a mixture of residual fibers and a spent liquor, both being the products of reaction and extraction between the lignocellulose, water and alkali material.

The objective of the caustic or alkali treatment, which is designated in the drawings and frequently referred to herein as Step I, is to provide a fibrous residue as Fiber I and a solution as Extract I. The fibrous residue, Fiber I, may be washed with water and is then subjected in a second step, designated Step II, to the action of an alkali metal hypochlorite salt in solution which has a pH of from slightly alkaline, say about 7.5, to about 10.5. A preferred pH range is from about 8.0 to about 8.3. During the treatment with the hypochlorite, the pH drops from the original values on the alkaline side to slightly acid in the range from about 5.5 to about 6.5. There is thus produced by the hypochlorite treatment, Step II, a lignocellulose residue designated herein as Fiber II and a mildly acid residual treating solution, designated herein as Extract II. The conditions for the practice of Step II will be described hereinafter in greater detail with reference to the drawing.

Description of Figure 1.—Step I

Referring to Figure 1 of the drawings, it will be seen that the process of the invention is practiced by treating lignocellulose material **7**, e. g., wood fiber, as the starting raw stock, with an alkaline reacting compound of an alkali metal as indicated at step **8**. The alkaline reagent employed is typically exemplified by sodium hydroxide. The treatment is conducted at atmospheric pressure and at a temperature in the range from room temperature to about 140° C. The time of treatment is variable, depending upon the type of wood being treated, but in general may be from 10 to 15 minutes up to about two hours, or such time as shows the interaction to be approaching completion. The reacted mass is extracted

at step **10** to separate the soluble matter from the thus treated fiber.

Step **8**, or steps **8** and **10**, herein referred to as the alkali treatment and sometimes herein referred to as Step I, extracts from the wood substance a substantial proportion of the content of lignin and of other organic materials such as polysaccharides-other-than-cellulose, and leaves a fibrous residue. Step **8** may be practiced by a batchwise procedure or by a counter-current or recycling procedure as hereinafter more fully discussed. Water is usually employed as the solvent in step **10**, but the water may also be admixed with minor amounts of other materials, e. g., water miscible organic solvents such as methanol, ethanol or acetone, in order to contribute specific properties to the solvent or for specific purposes. Water alone, or with such other materials admixed therein, is herein referred to as an aqueous solvent. Steps **8** and **10** may be efficiently combined when an aqueous solution of sodium hydroxide is used, but when moist fiber is treated with solid sodium hydroxide, or with solutions so concentrated as to amount to syrups, the separate aqueous extraction step **10** will be necessary. The extraction step as discussed and defined herein is deemed to include the extracting effect of the aqueous solution of sodium hydroxide without resort to a separate aqueous extraction where the solution of sodium hydroxide is sufficiently dilute to provide good extracting action. Variables of the alkali treatment, Step I, are discussed in detail hereinafter.

The mass or slurry, with the treated fiber in aqueous suspension is next filtered at step **12** or otherwise processed to separate Fiber I as product **13** from the soluble matter in the filtrate or solution **15** arbitrarily herein designated Extract I, which contains lignin and the organic materials including the polysaccharides-other-than-cellulose. Extract I may be processed for the recovery therefrom of the various lignin products and the polysaccharide stock solution, as disclosed and described in copending application, Serial No. 33,278, filed June 16, 1948, which matured as Letters Patent No. 2,541,058, granted February 13, 1951.

Description of Figure 1.—Step II

The fibrous residue **13** (Fiber I) resulting from the alkali treatment, Step I, is then subjected in step **16** to the action of an alkali metal hypochlorite solution. This comprises Step II. The treatment may be conducted on either moist fiber or with the fiber in aqueous suspension. Functionally, the hypochlorite is a fractionating agent for lignocellulose by partial solubilization, in a manner analogous to the alkali treatment of Step I. The prototype or prototypes of the lignin products and polysaccharides fractionated out by Step II are solubilized relative to aqueous media by the action of hypochlorite, whether the action be regarded as chlorination or an oxidation. The solubilization and fractionation effect of the hypochlorite applies as well to the saccharides as to the lignins. The reaction with the two classes of chemicals is concurrent. The alkali treatment of Step I renders soluble those organic materials which are most easily solubilized, but the Step I treatment reaches an asymptote beyond which further solubilization is negligible. The functional objective of the hypochlorite treatment of Step II is, therefore, to carry the solubilization of the wood substance further to remove a further quantity of lignin and saccharide products which were resistant to solubilization by the alkali treatment. Just as in the case of the Step I treatment, the Step II treatment reaches an asymptote and can go no further than a certain maximum removal. However, in the case of Step II, the hypochlorite changes the chemical nature of the lignocellulose residue which remains insoluble, both with respect to the hypochloriate treating solution itself and with respect to aqueous extraction, so that, although insoluble so far as Step II is concerned, a partial content of the lignocellulose residue is conditioned for solubilization by further chemical treatment in succeeding steps, such as with sodium hydroxide, as described in our application Serial No. 210,235, filed February 9, 1951. Although any of the alkali-metal hypochlorites may be used, sodium hypochlorite is a preferred member of the group because of its ready availability and its efficient action.

The hypochlorite salt may be a commercially available

product, or, if desired, it may be prepared immediately before use. Thus, a sodium hypochlorite solution of the desired concentration may be prepared by passing chlorine into a solution of sodium hydroxide having a pH of 11 to 12 until the precalculated quantity of chlorine for the quantity of NaOH used has been absorbed or until the pH of the alkali solution has been lowered to a value of about 8.0 to 8.3. The reaction ratio for the preferred pH, based on parts by weight, is about 100 parts of sodium hydroxide to 85 parts of chlorine. However, the pH of the hypochlorite solution may range from values slightly above 7.0 to about 10.5, in which case the ratio of NaOH to chlorine will vary accordingly. The solution is preferably kept cold during this process, as by mixing ice therewith.

The amount of hypochlorite salt used is variable depending upon the condition and species of wood being treated, low cellulose woods requiring a greater amount of hypochlorite salt than those of higher cellulose content. For substantially complete action by hypochlorite salt, the maximum amount will vary with the wood species and with the previous treatment. The usage of hypochlorite salt is herein expressed as the amount of sodium hydroxide equivalent of the hypochlorite salt actually used. Thus, an 80% usage signifies that for 100 parts by weight (dry basis) of fiber treated by hypochlorite salt, 80 parts of sodium hydroxide is treated, as at about 0° C., with chlorine to effect the desired pH, and the resulting solution is employed on the fiber. The hypochlorite treatment usually does not require higher than an 80% usage. Jack pine and other coniferous woods require about a 70% usage, while aspen requires about a 35% usage, for substantial completion of the step, where the original fiber is raw wood such as McMillan fiber.

The dilution of the hypochlorite salt solution and the consistency of the mass of fiber being treated to said solution are related by the above mentioned usage of hypochlorite salt. Thus, where the mass being treated is such that it may be stirred by an agitator in a containing vessel, a consistency of about 4% is a practical operating consistency, meaning, that about 4 parts by weight of fiber are present in 100 parts by weight of solution. Accordingly, an 80% usage of hypochlorite salt at 4% consistency designates that for every 100 parts by weight of fiber (dry basis) there are about 2500 parts of water, and that 80 parts of sodium hydroxide equivalent have been used. In terms of sodium hydroxide used to form hypochlorite salt, the solution is 3.1% in strength by weight.

Although it is possible in the first step of the invention, i. e., the step in which lignocellulose fibers are treated with dilute caustic alkali solution, to fortify and recycle the resulting extract into contact with fresh wood fiber, thereby building up the content of extractives by a substantial degree, it is usually not practical to replenish and recycle the aqueous alkaline hypochlorite solution employed in the second step to accomplish a similar result. This is in part because of the mineral content of the solution and also because a considerable amount of organic materials, which are present in the alkaline hypochlorite salt solution after it has been once used, react with and consume fresh hypochlorite salt which might be added thereto in order to build up the hypochlorite salt concentration to an effective degree. The operation is, therefore, preferably a single cycle operation.

As the reaction of the hypochlorite with the lignocellulose Fiber I proceeds, the hypochlorite is consumed, and the pH of the reaction mass is lowered until at the conclusion of the reaction, the reaction solution, Extract II has a pH on the acid side, usually in a range from 5.5 to 6.5.

The consistency of the mixture of hypochlorite and fiber may vary throughout a wide range. Consistencies of from 4% to 25%, i. e., 4 parts by weight of fiber per 100 parts of solution to 25 parts by weight fiber per 100 parts solution, have been satisfactorily used. Consistencies in aqueous suspension up to 15% may be satisfactorily employed for the hypochlorite treatment, but the use of consistencies above 15% with aqueous suspensions results in the production of a non-uniform Fiber II product, which means, of course, that the chemical content of the wood is not being uniformly extracted, and that the yield and identity of the chemical products obtained from the solution will vary in a greater degree.

Treatment with consistencies above 15% should be effected by spraying the hypochlorite solution in a strong jet onto a moist or dry fiber while vigorously mixing the same in order to insure uniformity of treatment. Under such conditions a usage of 35% sodium hypochlorite solution has been used with a consistency of 25% to produce a high quality Fiber II. A typical, preferred treatment is that of spraying a hypochlorite solution on moist fiber so as to provide a 20% consistency and a 20% usage of hypochlorite salt. The reaction is continued for from 15 to 30 minutes. The advantages of the more dilute versus the more concentrated consistencies are substantially similar to the advantages discussed herein in connection with the variables of the alkali treating Step I.

Treating times for Step II of from 15 to 20 minutes up to about one hour usually effect substantially complete removal of the wood content susceptible to removal by the hypochlorite solution, with but little further action being observed during more protracted treatments. The proper time within the range mentioned depends on various factors, but principally on the consistency and usage employed, which in turn determines the temperature of the reaction.

The temperature of the hypochlorite treatment may vary over a wide range, for example, from below normal room temperature up to at least 75° C. Higher temperatures up to the boiling point of the hypochlorite solution may be used under some conditions. Superatmospheric pressures, and the temperatures which accompany such pressures are avoided at all times, as such pressures and temperatures would cause excessive degradation of the fiber residues and the chemical products of decomposition. In other words, it is essential to the carefully controlled decomposition of the lignocellulose in accordance with the principles of the present invention that each treating step be conducted at atmospheric pressure.

The exothermic heat of reaction is sufficient to raise the temperature from room temperature to 60° to 70° C., and the mixing is continued until the mass cools to a temperature of approximately 25° C. which is usually from about 30 minutes to 1 hour in the case of treatment in aqueous suspension. Where the spraying technique is used, the reaction is substantially complete in 15 to 20 minutes.

Temperature variously affects the treatment as to extracted content and as to the properties of the residual fibers. The higher the temperature the more polysaccharides-other-than-cellulose are removed from the fiber. Where the residual fiber is to be used in making fiber board or paper, it is preferred to operate at a temperature below 40° C. Temperatures lower than 25° C. have been used satisfactorily, and chilling to below room temperature has been practiced. When it is desired to limit the rise in temperature, the treatment may be conducted in the presence of ice or in refrigerated apparatus. As pointed out hereinbefore, the sodium hypochlorite solution is preferably kept cold during its formation by chilling with ice. It is therefore convenient to use this solution in its chilled condition, directly as formed. Where Fiber II is to be extracted subsequently by a dilute sodium hydroxide treatment, as described in Serial No. 210,235 filed February 9, 1951, the over-all extraction by the hypochlorite salt and then by the alkali metal hydroxide, is substantially the same regardless of the amount extracted by the hypochlorite. Hence, where such a subsequent extraction is practiced, the actual temperature for the hypochlorite treatment is relatively immaterial when the production of high quality fiber is not an objective. However, little advantage is gained by operating at higher temperatures and in fact so doing may result in removal or undesirable degradation of the polysaccharide content of the fiber.

After the hypochlorite treatment of Step II the fibrous residue may be separated from the spent hypochlorite solution. Ordinarily the consistency of the mass during the hypochlorite treatment will be sufficiently low that the water of solution accomplishes the extraction of the chemicals rendered soluble by the hypochlorite simultaneously with the treatment. This step is separately indicated at **18**, however, to portray the function. On the other hand, when the consistency of the hypochlorite

treating solution is quite high, a separate aqueous extraction step 18 is necessary as illustrated. Separation of the fibrous residue 21 (Filter II) is most practically done by filtering, as shown at step 20, but other methods of separation may be employed. The extraction step as discussed and defined herein is deemed to include the extracting effect of the aqueous solution of hypochlorite salt without resort to a separate aqueous extraction where the hypochlorite solution is sufficiently dilute to provide good extracting action. The fiber residue 21 may then be washed and further treated or used without further treatment for a variety of uses, as is further described hereinbelow.

Description of Figure 2

The hypochlorite treatment solution 23 (Extract II) may be processed for the separation of valuable lignin and polysaccharide products therefrom. This procedure is represented in Figure 2. It provides for the separation of the lignin content of the extract into products herein arbitrarily designated as lignins 2–*a*–1, 2–*a*–2, and 2–*b* and a product consisting of other organics including polysaccharides-other-than-cellulose herein arbitrarily designated as product PS–2. In accordance with this procedure, extract 23 is first neutralized to approximately pH7 at 24, and then concentrated (dewatered) by evaporation at step 26. Since the said extract 23 is acid in reaction, having a pH of about 5.5 to 6.5, the neutralization is effected by the addition of a suitable alkaline reacting compound of an alkali metal, preferred reagents being sodium hydroxide or carbonate. It will also be understood that ammonium hydroxide may be used, as it is an equivalent of sodium hydroxide for this purpose.

The concentration of the neutralized solution is carried on approximately until reaching the point of incipient crystallization of the sodium chloride content of the extract. In a typical case this requires evaporation of the solution down to about 12% of its original volume. The concentration at which the saturation point of the alkali metal chloride content of the solution is achieved can be calculated in advance from the quantity of reagents used. In order to avoid contamination of the lignin product, which is concurrently being precipitated with the reduction in volume of the solution, the concentration should be stopped before the volume has been reduced in quantity to the point at which crystallization of the alkali metal chloride will occur. The neutralized, concentrated solution is then cooled and filtered in step 28. This results in the separation of lignin 2–*a*–1 in the solid state as product 29. This product will be relatively free from contamination by the alkali metal chloride salt, if the foregoing instructions of reducing the volume to an amount just above the saturation point of the salt are observed. In the event that any salt is obtained with the lignin 2–*a*–1, it may be removed by washing with an aqueous wash, preferably slightly acidified. The filtrate remaining after the separation of the solid lignin 2–*a*–1, product 29, is then further concentrated, as to about half its volume at step 30, this degree of concentration being necessary since the hypochlorite extract (Extract II) is not a recycled extract as was the case with Extract I, and the dissolved organic content is correspondingly low. The concentrated solution is then cooled and filtered at step 32 to separate a further insoluble lignin product 33, designated as lignin 2–*a*–2. This product will necessarily be contaminated with a considerable quantity of crystallized inorganic salt. (NaCl when sodium hydroxide or other sodium compound was used as the neutralizing agent in step 24.) The salt is removed by an aqueous wash indicated at step 34, the wash water being preferably slightly acid, resulting in the production of a purified lignin 2–*a*–2, product 35.

The filtrate from step 32 is next acidified to a pH of 1.5 at step 36 and if desired, it may be steam distilled at step 38 to separate the volatile acids 39 from the acidified solution. Any acid, or acidic agent, having an ionization potential sufficient to lower the pH to 1.5, may be employed, but preferred acidic materials are sulfuric acid or sodium acid sulfate, inasmuch as the sulfate radical lends itself to easy removal during subsequent steps. The solution from which the volatile acids may or may not have been removed is then filtered at step 40 in order to separate a further lignin product 41, i. e., solid lignin 2–*b*.

After removal of lignins 2–*a*–1, 2–*a*–2, and 2–*b* as described above, there is added at step 42, to the filtrate obtained from step 40, an alkaline reacting material, preferably of the group consisting of hydroxides, oxides or carbonates of an alkaline-earth metal, in an amount sufficient to bring the pH to equilibrium in order to neutralize the acidity of the solution and thus facilitate its further processing, storage and handling. Neutral or slightly alkaline solutions present much less processing difficulties than acidic solutions, and also avoid corrosion of metal containers to a much greater extent. Hydrated calcium hydroxide is the preferred reagent. Assuming that sulfuric acid or sodium acid sulfates have been used as the acidifying reagent in step 36, and that calcium hydroxide or carbonate are used as the neutralizing agent at step 42, an amount of calcium sulfate is precipitated equivalent to the amount of sulfate ion due to free sulfuric acid, which is then removed by filtration at step 44 as lime cake 45. The filtrate from step 44 now includes in addition to its polysaccharide and other organic content a substantial quantity of sodium or other alkali salts.

If desired, calcium carbonate or any other alkaline material may be used as the neutralizing agent in step 42. If calcium carbonate is employed, the treated solution must be heated in order to drive off the dissolved carbon dioxide. While, ordinarily, the neutralization pH is 7.0, it will be found that an equilibrium pH ranging from 7.0 to about 8.5 may be obtained at this step, due to the presence of salts of weak acids. When the salts of the alkaline materials employed in step 42 are soluble, as, for example, when sodium hydroxide is used, the inorganic salt content of the final solution is increased.

A further amount of the inorganic content of the filtrate from step 44 is removed by concentrating the solution at step 46 thereby effecting the precipitation of sodium chloride and sodium sulfate, as the salts obtained when sulfuric acid is used as the acidifying agent at step 36, which are then removed as salt cake 49 by filtration at step 48. Separation of the sodium sulfate as a solid is facilitated by the technique known as "freezing out" in which the solution is cooled prior to filtering to lower the solubility product value of the sodium sulfate. Further concentration of the solution at step 50 results in the production of a solution of organics including polysaccharides, product 51, designated as PS–2, which may be used without further treatment as a source of polysaccharides or which may be processed further to separate solid polysaccharides therefrom.

Modifications.—Figures 3, 4 and 5

It is apparent that the foregoing scheme for the processing of the hypochlorite extract (Extract II) may be modified as desirable or necessary to suit extracts of varying characters derived from various types of woods. Or, again, the process may be modified when it is desired to obtain certain specified combinations of lignin products, in which event, it would be needlessly expensive and time consuming to practice all the steps outlined in Figure 2. For instance, it may be desired to obtain all the lignin from Exarct II as one product, lignin 2. A suitable modification of the process to accomplish this purpose is illustrated in the flow chart of Figure 3. In this modification, Extract II, which already has a pH of about 5.5, may be further acidified directly to pH 1.5 (step 36) which will cause all the lignin to precipitate and it may be obtained as a composite lignin product 59 by filtration (step 40*a*). The filtrate from step 40*a* may be further processed as shown and described in connection with Figure 2, beginning with step 42.

Precipitation of the lignin is more complete and is more readily accomplished when the solution is more concentrated than it occurs as obtained in Extract II. It is, therefore, preferred, for processing advantages, still to conduct the first treating step 24 of adding an alkaline reacting material and then concentrating the solution at 52 to the extent desired before acidifying. Neutralization of Extract II is preferred before concentrating because the neutralized or slightly alkaline solution is easier to process and less corrosive of the equipment than would be the acidic solution. Introduction of corroded material from the equipment as a contaminant is also avoided in this way.

In Figure 4 there is illustrated a modification of the process in which Extract II is treated to provide as one product lignin 2–*a*–1 and all the remaining lignin as a

second product. This process is identical to Figure 2 through the production of lignin 2–*a*–1 at step **28**. The process differs from Figure 2 at this point by next directly acidifying to pH of 1.5 without further concentration, thereby omitting step **30** of concentrating to one-half the volume. Both the lignin 2–*a*–2 and lignin 2–*b* are then precipitated and obtained by filtration as one product **69**. This modification of the process is particularly advantageous where the main interest is in obtaining product lignin 2–*a*–1, or where there is no objection to combining lignin 2–*a*–2 and 2–*b*, because it avoids the tedious and difficult step of concentrating to one-half the volume, and also avoids contamination, with inorganic salts, of the lignin product **69** precipitated thereby.

Still a third modification of the process is shown in Figure 5 wherein Extract II is processed to provide the lignin in two products, lignins 2–*a* and 2–*b*. It will be appreciated that lignin 2*a* is a combined product consisting of lignins 2–*a*–1 and 2–*a*–2. The first product **73**, lignin 2–*a*, is obtained in the same manner as shown in Figure 2 for the production of lignin 2–*a*–2, except that the cooling and filtering step **28**, at which point lignin 2–*a*–1 is precipitated, is omitted. Lignin 2–*a*–1 is, therefore, carried along and obtained in combination with lignin 2–*a*–2 and the inorganic chloride salt which crystallizes at that stage of the process. The salt in product **73** may be removed by washing at step **74** to provide lignin 2–*a* as a purified product **75**. The remainder of the process from step **36** on, illustrated in Figure 5, is the same as the corresponding part of the process illustrated in Figure 2. This process has the obvious advantage of providing a minimum procedure for obtaining lignin 2–*b*, product **41**, in purified form where that product is particularly desired, and where there is no particular interest in obtaining fractionation of lignin 2–*a* into its two component lignin products, 2–*a*–1 and 2–*a*–2.

Other variations in the process will occur to those skilled in the art. There is illustrated in all the figures from Figures 2 to 5 the optional variation of the steam distilling step **38** prior to the production of the last lignin product in order to obtain volatile organic acids, if desired.

It will also be understood that the processes described in connection with Figures 2, 3, 4, and 5 are not limited to the specific manipulative procedures described. For instance, decanting or centrifuging procedures may be used in lieu of filtration and are to be regarded as equivalent manipulations as is well known in the art.

VARIABLES.—THE ALKALI TREATMENT.—STEP I

The operating conditions of the alkali treatment step 8 or the extraction step 10 may be varied within limits as desirable or necessary to suit the particular lignocellulose material being treated, or to adapt the process to the plant equipment in which it is to be practiced, or to provide particular end products, or end products of particular yield, quality or properties. It is the teaching of the invention, however, and critical to its success and practical operation, to use and maintain operating conditions and reagents of strong enough character to effect the cleavage of the lignin polysaccharide complexes existing in the lignocellulose materials, and the separation of lignin, and at the same time the character of such operating conditions and reagents should be sufficiently mild not to cause substantial or drastic changes in constitutional composition of the constituents, thereby preserving the lignin products of this invention, and particularly those obtained from Extract I, the relatively greater inherent reactivity of naturally occurring lignin.

While the preferred alkali treating agent for step 8 is sodium hydroxide, various alkaline materials may be employed. Suitable alkaline materials include in general the hydroxides of the alkali metals as well as those alkali metal compounds which, being salts of strong bases and weak acids, undergo hydrolysis in aqueous medium to form the alkali metal hydroxides, or their equivalent in alkali-metal ions and hydroxyl ions. Such compounds are, therefore, the basic-acting compounds of the alkali metals, i. e., of lithium, sodium, potassium, rubidium and cesium. Basic acting compounds of ammonium may also be used. The hypothetical metal represented by the ammonium radical NH_4^+ is to be regarded as an equivalent of an alkali metal for the purpose of this invention. The hydroxides are generally preferred to other types of compounds, but the carbonates, especially sodium carbonate, may be used to good advantage.

Since the alkali treatment step 8 and the extraction step 10 may be, and frequently are, combined in the ordinary practice of the invention, the considerations affecting these treatments will be hereinafter discussed together except as specifically pointed out when the steps are separated. Three factors are involved relating to the amount of alkali treating agent employed, to-wit: usage, strength and consistency. "Usage," as the term is used herein, is defined as the quantity by weight of alkaline reacting compound, calculated in terms of caustic soda, used per 100 parts of fiber on an oven dry basis. For example, a mass consisting by weight of 100 parts dry fiber and 100 parts sodium hydroxide, regardless of the actual water content of the fiber, and reegardless of the amount of water of solution of the sodium hydroxide, has a usage of 100%. "Strength," as used herein, has its normal meaning when speaking of chemical solutions, and defines the percentage composition of the alkaline compound, calculated as sodium hydroxide, in the aqueous solution employed. "Consistency," as the term is used herein, defines the ratio of oven dry fiber to a liquid mass containing it and is expressed as the percentage of fiber in the mass. It will be seen that the factor of consistency is a resultant factor determined by the usage and strength.

It has been found that the alkaline reagent may be used in a wide range of strength, provided conditions of usage and consistency are correlated thereto. It has likewise been found that the usage may vary over a wide range provided that the strength and consistency are correlated thereto. Similarly, the consistency may vary over a wide range provided the strength and usage is correlated in a predetermined manner. The usage will usually range from about 2.5 to 100 parts for each 100 parts of oven dry fiber. Strengths of solution are practical in a range varying from .05% up to the use of solid caustic material on moist fiber.

As hereinbefore stated, the invention is ordinarily practiced by the use of the alkali material in aqueous solution, but the alkali may be applied as a solid to moist fiber without the presence of free water. Fiber ordinarily contains absorbed moisture in amounts ranging from 50% to 200% on an oven dry basis. A 100% moisture content, oven dry basis, means 100 parts by weight of oven dry fiber and 100 parts by weight of water. This is a 50% moisture content on a total basis. By way of example, treatment of fiber in a moist mass has been conducted with a mixture of 100 parts of fiber (oven dry basis), 100 parts of water (derived from the moist wood), and 8 parts of sodium hydroxide. When solid caustic is used with moist fiber, containing, say 100% moisture, the usage of caustic is preferably limited to about 10 parts per 100 parts of fiber (oven dry basis), which fixes, in effect, an upper limit of about 10% for the strength of the caustic solution.

Consistencies have been used ranging from as low as 2% up to about 50%. In a typical embodiment of the invention, a .6% strength and a usage of 15% were used which resulted in a consistency of 4%. Such a consistency provides a slurry, whereas the treatment of moist fibers with solid sodium hydroxide as in the preceding example resulted in approximately a 50% consistency represented by a moist mass. Consistency is of fundamental importance as a measure of the relationship between usage and strength and is valuable as a control for determining the extent of solubilization to be effected.

The alkali agent may be used in any amount from that which leaves an alkaline extract under the conditions employed upwards to larger amounts which may be desired to effect a greater degree of solubilization of the lignocellulose material for certain desired end purposes of the process, or to facilitate economy of operation of the process. The stronger the solution, the greater its solubilizing power within limits, the relationship being asymptotic, and the more severe its side effects upon the insoluble fibrous residue. However, strength of solution alone is not of independent significance, because it is related to the relative proportions of the alkaline compound, water and fiber employed, and to the reactivity of the fiber. Experience

has shown that an increase in strength accompanied by a constant or increased usage, or an increase in usage accompanied by a constant or increased strength, will result in greater solubilizing action. On the other hand, the extent of the solubilizing action decreases as dilution with water increases, or stated otherwise, as the strength of solution, or the consistency, decreases. To minimize the effect of strong causticity on the fiber substance, low usage of water accompanies low usage of alkali and high uses of each go together.

Of still further consideration is the fact that wood fiber has a natural pH of about 4, and exhibits a neutralizing or consuming power for the alkali. The fibers are characterized by content readily rendered soluble in dilute alkali solution, and other content readily rendered soluble only in much stronger alkali solution, as well as content of intermediate responsiveness. It, therefore, appears that as the natural composition of the wood or fiber is solubilized by the action of alkali, the resultant products exhibit a neutralizing capacity beyond that of the original fiber composition. Thus, when alkali at a given initial strength is supplied to the fiber, the alkali content is depleted and the solution becomes weaker. Hence, the usage of alkali, and consistency of the mass wherein the chemical action takes place, are advantageously employed as control means to regulate the degree of solubilizing of the fiber. The alkali is therefore preferably used in an amount and in a concentration such that the reaction comes to an equilibrium with the residual fiber, and presents a mildly alkaline solution as it reaches or approaches that equilibrium.

Differences in the amount of soluble components formed and obtained by increasing the usage and concentration while maintaining consistency constant at 4% are shown from the yields obtained from three samples of Western red cedar which were extracted with caustic soda at boiling temperature for one hour. These tests show that as the caustic usage was increased from about 5% to 15% to 25%, with a corresponding increase in the concentration, the yield of solubles increased from about 17% to 22% to 24%, thereby showing a direct relationship but of constantly diminishing ratio. The results are summarized in Table I below:

Table I

Usage	Percent Concentration of Alkali Solution	Percent Solubles based on Original Fiber Weight
5.4	0.2	17.3
15.2	0.6	22.6
25.0	1.0	23.9

Results of the same effect were obtained from another series of experiments conducted on normal Asplund aspen fiber with the consistency kept constant at 2% and the usages of caustic soda varied as shown in Table II below. The treatment was continued for two hours at boiling temperature.

Table II

EFFECT OF VARYING USAGES ON EXTRACTION OF SOLUBLE MATTER

Usage	Percent Concentration Alkali Solution	Percent Solubles based on Original Fiber Weight	Percent Composition of Extract	
			Lignin	Polysaccharides
2.5	.05	11.5	34.0	66.0
5.0	.10	14.8	32.4	67.6
15	.30	23.7	30.8	69.2
25	.50	26.6		
50	1.00	29.0	27.6	72.4
100	2.00	29.7	27.6	72.4

In another case water extracted raw aspen wood fiber was boiled for one hour with a 5.5% solution of caustic soda at 10.4% consistency, corresponding to a usage of 55% (composition—9 parts fiber; 86 water; 5 NaOH). A soluble yield of 33% was obtained. Thus, it can be seen that a wide range of "solubles" can be extracted by the exercise of the controls as described.

Other factors or variable conditions of treatment in step 8 are the matters of temperature, pressure and time of treatment. These factors are closely related and interdependent, and, therefore, will be discussed together. The alkali extraction with a bulk of liquid is desirably carried out at an elevated temperature, preferably a temperature which is about the boiling temperature of the mixture and at atmospheric pressure. For porous masses of high consistency the temperature may be higher, using superheated steam. In ordinary operation, where the process is carried out at normal atmospheric pressure in open vessels at relatively low consistencies and low concentrations, the temperature of operation will be in the range from 80° to about 100° C., for at or near the boiling point as provided by applied heat or steam injection. This temperature is chosen for ease of control and for simplicity in standardizing the process for reproducible results. When a moist or porous mass of fibers at high consistency is to be treated, it is easier and preferable to apply the heat by subjecting such mass to the action of superheated steam, but still at atmospheric pressure. Reaction temperatures somewhat above the normal boiling point of water are obtained by the use of superheated steam. For instance, temperatures as high as 140° C. have been obtained. The reaction, in the case of the use of moist fiber and solid caustic soda, may also be conducted at room temperature. The reaction being exothermic, the temperature of the reacting mass rises to possibly 60 to 70° C. Treatment with caustic soda solution at high consistencies may also be conducted at room temperature, provided the caustic solution is preheated to 70° C. or above.

The time or treatment is variable, depending upon the type of lignocellulose or species of wood being treated and other conditions of treatment, but, in general, may be up to about 1 to 2 hours, or such time as shows the extraction to be advancing only slowly or to be substantially complete. The reaction has often been found to be essentially complete in 10 to 15 minutes. Continuation of the extracting conditions beyond substantial completion of the reaction has no harmful results. When superheated steam is employed, the treatment is continued for one hour. In the case of aspen, jack pine, and similar wood, maximum treating times of the order of one hour are used, relatively little advantage being obtained from longer treating durations. The attainment of substantial equilibrium is an indication of maximum time.

The mechanics of the combined alkali treatment and liquid extraction may vary in well known ways. Both batch and continuous operations variously involving the principle of counter-current contact may be employed. Such continuous type operations are recycling, wherein the alkali solution is used repeatedly on new batches of fiber until the alkali solution becomes so saturated with solubles that a condition of equilibrium with the fiber is approached. Another counter-current process is that in which the alkali solution is used repeatedly and the fiber is subjected to successive or repeated treatments with successive batches of alkali solution in inverse relation to the freshness of the solution; i. e., the first treatment of the fiber is made with the oldest or last use of the solution and the last treatment of the fiber is conducted with the first use or newest solution. This practice is based on the principle that the first soluble content is most easily extracted and the last soluble content is most difficultly extracted, and that, therefore, the strongest and freshest solution should be used on the last step treatment of fiber.

The type of mechanical treatment employed to a large extent determines the proper or optimum consistency at which the treatment should be conducted. The optimum consistency is obviously dependent upon many factors, but principally upon the method of handling the fiber mixture. Thus, varying consistencies may be used depending upon whether the fiber is treated batchwise, or continuously, as in counter-current operation. Where a batch mixing procedure is employed, using fiber and a solution of alkali, the consistency of the reaction mixture is maintained at a level such as to afford ease of manipulation and thoroughness of treatment. When carrying out the extracting treatment in a batch mixer equipped with a mechanically operated agitator resulting in a tumbling

action, it has been found possible to provide a consistency of up to about 50%, but 10% is preferred as a control objective, and consistencies at 4% have been extensively used. The slurry of 4% consistency has the advantage that it is readily stirrable by simple mechanical means for laboratory or pilot plant operations. In general, disadvantages of the use of higher consistencies are that they result in harsher chemical treatment of the lignocellulose constituents, increase the cost of chemicals used and make for more difficult aqueous extraction of the solubilized components. The use of higher consistencies is advantageous in that they tend to increase the yield of solubles, provide greater concentration of solids in the extract and ordinarily necessitate less evaporation in the subsequent treatment of the extract.

Largely for reason of economy and efficient operation, it is usually preferred to recycle the caustic extract solution. In this manner the caustic soluble content of the wood substance is built up in alkaline solution to a point where the said solution becomes a more valuable source of extracted materials. Since some of the alkali is consumed by reaction with the wood substance during the extraction process, it is a practice in recycling to add a further quantity of alkali before each treatment of fresh fiber. In the case of woods, such as aspen and jack pine, when extracted at 4% consistency with a .6% solution of caustic soda (a 15% usage), about 60% replacement of the original alkali usage after each extraction is sufficient to fortify the solution to the desired degree, e. g., to a concentration of about 0.6% in the case of caustic soda. This replacement represents consumption in extraction and also mechanical losses. Although the number of times that a caustic alkali solution which has been thus fortified may be used for the extraction of the specified fibers of wood substance is variable, depending largely upon the nature and treatment of the wood, it has been observed that extracting 8 times in the manner stated above, results in the production of an alkaline extract rich in lignins and organic materials including polysaccharides-other-than-cellulose and at the same time leaves a fiber residue of satisfactory composition and properties. The extent to which recycling, or its equivalent operation, may no longer be profitably practiced is determined by the point where the contribution in extract equals the amount of extracted material retained by the fibers upon separating the fibers and the extract.

A preferred process of the invention is illustrated in the following examples, as applied to different species of wood. The yields and composition of the products obtained are summarized in tables following the examples.

EXAMPLE 1

McMillan aspen fiber, i. e., fiber prepared from aspen wood by means of a McMillan defibrator, was treated with a 0.6% aqueous solution of sodium hydroxide. A sufficient amount of this solution was used to provide a total sodium hydroxide usage equivalent to 15% based on the dry weight of the raw wood fiber. This resulted in a reaction mixture having a consistency of about 4%, i. e., a mixture containing about 4 parts by weight of fiber per 100 parts of solution. The treatment was effected at the boiling temperature of the solution at atmospheric pressure for a duration of one hour. The fiber was then separated from the sodium hydroxide solution and washed with water for subsequent uses. The alkaline extract was fortified by the addition of caustic soda in an amount sufficient to build up the sodium hydroxide concentration to a level substantially that of the original solution. This required replacement of about 60% of the original sodium hydroxide. The fortified solution was then employed in the treatment of a further quantity of raw wood fiber. A total of 8 treatments of raw wood fiber was carried out in this manner, replenishing the concentration of sodium hydroxide in the treating solution between each treatment. This resulted in the production of an alkaline extract rich in materials removed from the wood substance, i. e., rich in lignins and in polysaccharides-other-than-cellulose.

This alkaline extract was processed for the recovery of its lignin and polysaccharides-other-than-cellulose content substantially in accordance with the process in copending application Serial No. 33,278 now Letters Patent No. 2,541,058, granted February 13, 1951. The separation of these substances from the solution and from each other was accomplished by neutralizing with sulfuric acid the alkaline extract, which had a pH of about 10 to a pH of about 7, and concentrating the neutralized extract by evaporation while adding further sulfuric acid as necessary to maintain the solution neutral. The solution was thus concentrated to about 12% of its original volume. It was then cooled and filtered. This resulted in the separation of a lignin fraction designated herein as lignin 1–*a*.

The neutral solution remaining after the separation of lignin 1–*a* was then acidified with sulfuric acid to a pH of about 1.5, sufficient sodium sulfate being added to satisfactorily coagulate the lignin forming a solution saturated or partially saturated with respect to this compound. The acidified coagulate was then steam distilled to separate volatile organic acids, after which it was filtered in order to separate lignin 1–*b*.

Sufficient lime was added to the liquid remaining from the separation of lignin 1–*b* again to bring the pH of the solution to a value of 7.0, thereby neutralizing the excess free mineral acid and at the same time forming a precipitate of calcium sulfate (lime cake), corresponding in amount to an equivalent weight of the neutralized sulfuric acid. After removal of the calcium sulfate by filtration the liquid was concentrated to a small volume, cooled and filtered to remove in the form of a crystallized salt cake the remainder of the sulfate radical which was present in the form of molecular sodium sulfate. This left a syrup containing organic bodies including polysaccharides-other-than-cellulose.

The fiber I residue remaining after the alkaline extract, carried out as described above, was next treated with a solution of sodium hypochlorite. The sodium hypochlorite solution employed in this treatment was prepared by passing chlorine gas into a solution of sodium hydroxide which contained a sufficient amount of sodium hydroxide to be equivalent to 35% by weight of the fiber residue to be treated. Chlorine gas was passed into this solution until the pH of the solution was decreased from about 11 to 12 to about 8.0 to 8.3. This required the reaction of the sodium hydroxide with approximately an equal weight of chlorine. The reaction mixture was cooled with ice during this addition. A sufficient amount of this solution was used in the treatment of the fiber to form a mixture having a consistency of about 4%, i. e., one containing about 4 parts of fiber per 100 parts of solution.

The fiber was treated with this solution for about one hour at a temperature of about 25° C. At the end of this time the mixture had become acid, the final pH being about 5.5 to 6.0. The spent solution was separated from the fiber, the fiber being washed with water and as fiber II applied without further processing to a diversity of uses, or if desired used as a starting material for further refining steps.

The acid hypochlorite extract (Extract II) obtained from this extraction was neutralized with sodium hydroxide and concentrated to about 12% of its original volume. It was then cooled and filtered to separate lignin 2–*a*–1.

The filtrate was concentrated further to about 6% of its original volume. It was then cooled and filtered to separate lignin 2–*a*–2. The filtrate remaining after removal of lignin 2–*a*–2 was acidified with sulfuric acid to a pH of about 1.5 and steam distilled to separate volatile acids, after which it was filtered to remove lignin 2–*b*.

After removal of lignin 2–*b*, the solution was brought to a pH of 7 by the addition of lime, and filtered to remove the precipitated calcium sulfate. Thereafter it was concentrated to a sufficiently small volume to effect the precipitation of a substantial proportion of its sodium chloride content. This was removed by filtration, and the solution further concentrated to yield a syrup rich in organics including polysaccharides-other-than-cellulose.

EXAMPLE 2

Fiber prepared from aspen wod by means of the Asplund defibrator wherein the wood is subjected during defibration to the action of steam at about 128 to 135 pounds pressure per square inch gauge for about 1 minute was also treated successively with dilute sodium hydroxide solution and sodium hypochlorite solution and the extracts processed substantially as described in Example 1.

EXAMPLE 3

McMillan jack pine fiber was also treated with dilute sodium hydroxide solution and then with sodium hypochlorite solution and the extracts separated into lignin and organic fractions as described in Example 1. In this case, however, because of the low cellulose content of the fiber employed it was necessary in Step II to use an amount of sodium hydroxide for the hypochlorite formation equivalent to about 70% by weight of the fiber used rather than about 35% as was the case in Example 1.

EXAMPLE 4

Fiber was prepared from jack pine by means of the Asplund defibrator wherein the wood was subjected during defibration to the action of steam at about 150 pounds per square inch gauge pressure (365° F.) for about 1 minute and was then treated successively with dilute sodium hydroxide solution and sodium hypochlorite solution, and both extracts processed as described in Example 1. In this case, as in Example 3, a usage of about 70% of sodium hydroxide based on the weight of fiber treated was employed for the hpyochlorite reagent of Step II.

The yields of the various products obtained by the application of the alkali treatment, Step I, of the process of the invention to the various types of wood fibers, as described in the foregoing examples, may be summarized as follows:

Table III

YIELDS OF PRODUCTS FROM STEP I

[In percent by weight of original fiber.]

	McMillan Aspen (Example 1)	Asplund Aspen (Example 2)	McMillan Jack pine (Example 3)	Asplund Jack pine (Example 4)
Product:				
Fiber I	81.3	79.6	84.1	78.9
Extract I	18.7	20.4	15.9	21.1
COMPOSITION OF EXTRACT I				
Lignins:				
1-*a*	4.3	2.0	2.2	5.0
1-*b*	1.2	4.1	1.3	1.5
Total Lignins	5.5	6.1	3.5	6.5
Total Polysaccharides	5.1	6.8	6.7	7.1
Volatile Acids	5.8	5.9	2.9	4.4
Total Organics Recovered	16.4	18.8	13.1	18.0
Remainder Unaccounted For	2.3	1.6	2.8	3.1

The yields of the various products obtained by the operation of the hypochlorite treatment, Step II, on Fiber I, i. e., the fiber residue remaining after extraction of wood fiber with dilute sodium hydroxide solution, are summarized in Table IV.

Table IV

YIELDS OF PRODUCTS FROM STEP II

[In percent by weight of Fiber I.]

	McMillan Aspen (Example 1)	Asplund Aspen (Example 2)	McMillan Jack pine (Example 3)	Asplund Jack pine (Example 4)
Product:				
Fiber II	78.3	75.5	73.6	68.0
Extract II [1]	21.7	24.5	26.4	32.0
COMPOSITION OF EXTRACT II				
Lignins:				
2-*a*-1	3.8	5.2	4.4	16.7
2-*a*-2	3.0	2.1	9.0	13.7
2-*b*	3.4	3.7	3.7	7.9
Total Lignins	10.2	11.0	17.1	38.3
Total Polysaccharides	7.0	11.8	8.5	14.2
Volatile Acids	0.9	0.9	1.4	2.0
Total Organics Recovered	18.1	23.7	27.0	54.5
Gain or Loss	3.6 (Loss)	.8 (Loss)	.6 [2] (Gain)	22.5 [2] (Gain)

[1] The initial total organics content of Extract II is determined by difference.

[2] The increase in the total organics recovered is probably due to combined chlorine.

The yields of Fiber II, Extract I and Extract II, and of the composition of Extract II, based on per cent by weight of the original fiber, which enables comparison with Table III, are shown in Table V below:

Table V

YIELDS OF PRODUCTS FROM STEPS I AND II

[In percent by weight of original fiber.]

	McMillan Aspen (Example 1)	Asplund Aspen (Example 2)	McMillan Jack pine (Example 3)	Asplund Jack pine (Example 4)
Product:				
Extract I	18.7	20.4	15.9	21.1
Fiber II	63.7	60.1	61.9	53.7
Total Organics Extracted From Fiber I (Extract II) [1]	17.6	19.5	22.2	25.2
COMPOSITION OF EXTRACT II				
Lignins:				
2-*a*-1	3.1	4.1	3.7	13.0
2-*a*-2	2.4	1.7	7.6	10.8
2-*b*	2.8	3.0	3.1	6.2
Total Lignins	8.3	8.8	14.4	30.0
Total Polysaccharides	5.7	9.4	7.2	11.2
Volatile Acids	0.7	0.7	1.1	1.5
Total Organics Recovered	14.7	18.9	22.7	42.7
Gain or Loss	2.9 (Loss)	0.6 (Loss)	0.5 [2] (Gain)	17.5 [2] (Gain)

[1] The initial total organics content of Extract II is determined by difference.

[2] The gain in the total organics recovered is probably due to combined chlorine.

Table VI

FIBER COMPOSITIONS BY WEIGHT

	Original Fiber		Fiber I		Fiber II	
	Percent Lignin	Percent Other Organics Not Cellulose	Percent Lignin	Percent Other Organics Not Cellulose	Percent Lignin	Percent Other Organics Not Cellulose
McMillan Aspen (Example 1)	20.1	21.6	20.0	22.4	1.8	23.8
Asplund Aspen (Example 2)	20.8	21.8	18.5	20.0	1.1	21.7
McMillan Jack Pine (Example 3)	29.6	15.1	29.6	14.0	6.2	9.0
Asplund Jack Pine (Example 4)	29.6	13.6	30.4	9.0	2.8	7.4

Components of the original fiber, of Fiber I, which has been treated with sodium hydroxide solution; and of Fiber II which has been treated with sodium hypochlorite solution, are shown in Table VI.

SUMMARY

Each of the products obtained by this invention has many developed and potential industrial uses. The cellulosic fiber residue, Fiber II, may be used as is, or may be used as a raw material to be processed further for the production of technical cellulose, and also for the production of chemical cellulose, or alpha cellulose. When the raw lignocellulose material is sawdust, hogged fuel, or similar comminuted material, the cellulosic product corresponding to Fiber II is useful where a non-felting cellulosic fibrous product is desired.

The extracted substances likewise have important uses. The lignins, for example, may be used in the manufacture of plastic clad plywood, impregnated papers, the tanning of leather, and as reagents for the recovery of metals from dilute solutions of metal salts. The polysaccharides obtainable by the process of the invention may be used, for example, as humectants and crystallization controllers, and may be fermented or otherwise treated to form other valuable products. Both the lignin and the polysaccharide extracts may be utilized as raw materials for the preparation of valuable organic compounds, as by controlled oxidation processes.

The present invention permits on a commercial economic scale the separation of lignins and polysaccharides from the same solution. The process also results in the production of a cellulose residue without loss of the valuable lignin and polysaccharides-other-than-cellulose products, since, as has been described herein, the procedure is such as to recover substantially all of the original lignocellulose substances. Since the operating conditions and the concentration of the reagent used are relatively mild, the procedure does not drastically change the chemical constitution of the wood substance beyond the changes desired for permitting the separations. On the other hand, the extracted substances are obtained in forms approaching, if not almost identical with, the forms in which they are found in the wood itself. The chemical reactivity and therefore the usefulness of the extracted substances is far greater than the reactivity of corresponding substances obtained from liquors from conventional pulping processes that employ drastic cooking conditions. By using different woods and slightly varying the operating procedures, it is possible to produce a variety of products having a substantial range in properties so as to be useful for a diversity of purposes. These manifold advantages are achieved, furthermore, by a process which makes use of relatively inexpensive reagents and apparatus and does not require the use of pressure vessels and protracted cooking operations.

It is also apparent from a consideration of the flow plan that the process of the invention for the separation of the constituents of the hypochlorite extract is flexible and may be varied as desirable or necessary when processing different materials, especially different species of woods, over a wide range of operating conditions and with different reagent concentrations. Thus, although it is usually desirable to separate the total lignin content into specific component lignins, because of the differences in properties of these lignins, and also because of the simplicity of operation obtainable when the total lignin content is isolated stepwise, it may be desirable in the case of certain hypochlorite extracts to effect the total precipitation of the lignins of Extract II in a single step, as by acidifying the extract to a pH of 1.5 and effecting the necessary concentration. It is also possible to recombine the lignins resulting from stepwise isolation in order to form a lignin product containing substantially all of the lignin content of the extract.

All the various modifications that may be practiced within the spirit of the disclosure herein and the novel products which may be obtained from the practice of the invention are deemed included in the invention.

What is claimed is:

1. The process of treating comminuted lignocellulose raw material to produce a fibrous product and chemical products therefrom, which comprises the steps of reacting the lignocellulose material with an alkaline reacting compound of an alkali metal in the presence of water at atmospheric pressure and at a temperature in the range from room temperature to about 140° C., extracting with an aqueous solvent the soluble products of reaction of said lignocellulose material with said alkaline reacting compound of an alkali metal, separating the extractives from said lignocellulose material to obtain the same as a first product and a fibrous residue, treating the fibrous residue of said lignocellulose material with an alkali metal hypochlorite reagent having an equivalency of from 35 parts to 80 parts sodium hydroxide for each 100 parts by weight dry fiber, extracting with an aqueous solvent the soluble products of reaction of said fibrous residue with said alkali metal hypochlorite reagent, separating a second fibrous residue from the solution embodying said last named aqueous solvent to obtain the same as a second product, adjusting the pH of the last named solution after separation of said second fibrous product to a pH value of about 7, increasing the salt concentration of said aqueous solution to a value approaching saturation, adding acid to said solution to precipitate its lignin content, separating therefrom the precipitated lignin as an intermediate product or products, and leaving as a last product a resulting solution containing other organics including polysaccharides.

2. The process of treating comminuted lignocellulose raw material to produce a fibrous product and chemical products therefrom, which comprises the steps of reacting the lignocellulose material with an alkaline reacting compound of an alkali metal in the presence of water at atmospheric pressure and at a temperature in the range from room temperature to about 140° C., extracting with an aqueous solvent the soluble products of reaction of said lignocellulose material with said alkaline reacting compound of an alkali metal, separating the extractives from said lignocellulose material to obtain the same as a first product and a fibrous residue, subjecting said caustic extracted fibrous residue to the action of a dilute alkali metal hypochlorite solution in quantity of from about 35 parts to about 80 parts of sodium hydroxide equivalent of the hypochlorite salt for 100 parts by weight of said fibrous residue, the reaction with the hypochlorite being conducted for about one hour and at a temperature below the boiling point of the solution, separating the resulting fiber from the hypochlorite solution to obtain the fiber as a second product, acidifying said hypochlorite solution after removal of the fiber as a second product to a pH of about 1.5 to effect precipitation of substantially all of its lignin content, and separating as a third product a solid form of lignin from the said hypochlorite solution.

3. The process of treating comminuted lignocellulose raw material to produce a fibrous product and chemical products therefrom, which comprises the steps of reacting the lignocellulose material with an alkaline reacting compound of an alkali metal in the presence of water at atmospheric pressure and at a temperature in the range from room temperature to about 140° C., extracting with an aqueous solvent the soluble products of reaction of said lignocellulose material with said alkaline reaction compound of an alkali metal, separating the extractives from said lignocellulose material to obtain the same as a first product and a fibrous residue, reacting the fibrous residue of said lignocellulose with an alkali metal hypochlorite reagent having an equivalency of from 35 parts to 80 parts sodium hydroxide for each 100 parts by weight dry fiber, extracting with an aqueous solvent the soluble products of reaction of said fibrous residue with said alkali metal hypochlorite reagent, separating said fibrous product from the hypochlorite solution as a second product, adding an alkaline reacting compound of an alkali metal to neutralize to a pH value of about 7 the solution obtained after separating the said second fibrous product, concentrating said last named solution to a value approximating the saturation point of the inorganic chloride salt content, and filtering to remove precipitated lignin as a third product.

4. The invention as defined in claim 3 together with the further steps of concentrating the solution remaining after separation of the precipitated lignin to about one-half its volume, and filtering the same to remove further precipitated lignin as a fourth product.

5. The invention as defined in claim 3 together with the further steps of acidifying the solution remaining after separation of the precipitated lignin to a pH of about 1.5 to effect precipitation of substantially all of the re-

maining lignin content thereof, and separating said last mentioned lignin from the residual solution.

6. The process of treating comminuted lignocellulose raw material to produce a fibrous product and chemical products therefrom, which comprises the steps of reacting the lignocellulose material with an alkaline reacting compound of an alkali metal in the presence of water at atmospheric pressure and at a temperature in the range from room temperature to about 140° C., extracting with an aqueous solvent the soluble products of reaction of said lignocellulose material with said alkaline reacting compound of an alkali metal, separating the extractives from said lignocellulose material to obtain the same as a first product and a fibrous residue, treating the fibrous residue of said lignocellulose material with an alkali metal hypochlorite reagent having an equivalency of from 35 parts to 80 parts sodium hydroxide for each 100 parts by weight dry fiber, extracting with an aqueous solvent the soluble products of reaction of said fibrous residue with said alkali metal hypochlorite reagent, separating said fibrous product from said hypochlorite solution to obtain a second fibrous product, adding an alkaline reacting compound of an alkali metal to the solution obtained after separation of said second product to neutralize said solution to a pH value of about 7, removing water of solution to about the point of incipient crystallization of the inorganic chloride salt content thereof and then further concentrating the solution to about one-half its volume to precipitate a composite lignin product and the inorganic chloride salt content, and filtering the same to remove the precipitated lignin product and inorganic chloride salt.

7. The invention as defined in claim 6 together with the further steps of adding to the solution obtained after separating said precipitated first lignin product an inorganic acid of sufficient ionization potential to bring the pH to about 1.5, and filtering the solution to obtain substantially all of the remaining lignin content thereof as a second lignin product.

8. The process of treating comminuted lignocellulose raw material to produce a fibrous product and chemical products therefrom, which comprises the steps of reacting the lignocellulose material with an alkaline reacting compound of an alkali metal in the presence of water at atmospheric pressure and at a temperature in the range from room temperature to about 140° C., extracting with an aqueous solvent the soluble products of reaction of said lignocellulose material with said alkali reacting compound of an alkali metal, separating the extractives from said lignocellulose material to obtain the same as a first product and a fibrous residue, treating the fibrous residue of said lignocellulose material with an alkali metal hypochlorite reagent having an equivalency of from 35 parts to 80 parts sodium hydroxide for each 100 parts by weight dry fiber, extracting with an aqueous solvent the soluble products of reaction of said fibrous residue with said alkali metal hypochlorite reagent, separating said fibrous product as a second product, adding to the solution obtained from the separation of said second fibrous product an inorganic acid having an ionization potential sufficient to bring the pH to about 1.5, and filtering the solution to obtain the lignin content thereof as a third product.

9. The invention as defined in claim 8 in which there is further included the steps, before adding the inorganic acid as specified in claim 8, of neutralizing with an alkaline reacting compound of an alkali metal to a pH value of about 7 the solution obtained from the separation of said second fibrous product and concentrating the same to a reduced volume.

10. The invention as defined in claim 1 in which the processing of the solution obtained by said last mentioned aqueous solvent comprises acidifying said solution with sulfuric acid to a pH of 1.5 to separate therefrom substantially all of the remaining lignin content, and then the further steps after separating the lignin content of adding to the residual solution containing other organics including polysaccharides an alkaline earth metal compound of the group consisting of hydroxides, carbonates and oxides, to raise the pH thereof to an equilibrium value thereby precipitating alkaline-earth metal sulfate, and separating the resulting alkaline-earth metal sulfate from the solution to provide as a last product a solution containing other organics including polysaccharides.

11. The method which comprises reacting at atmospheric pressure the system: wood in defibered form, water and alkali metal hydroxide all as a liquid suspension; said wood containing substantially all of the substance of the water-insoluble content of the natural wood of its origin, and constitutionally consisting primarily of cellulose, lignin and other organics, said three constituents being present in mutual ratios in the range of contents from those characterizing the said wood in natural form to those characterizing the said water-insoluble content of said wood in natural form; in which system the alkali metal hydroxide is present in amount by weight in the range from 2.5 to 100 parts calculated as NaOH per 100 parts of oven dry wood, and the reaction is substantially completed to an equilibrium condition between the spent liquid and the fiber-form residue of the system at a reaction temperature in the range from about 80° C. to about 100° C.; separating the fibrous residue of the wood from the water-soluble products of reaction of said wood with said aqueous solution of alkali metal hydroxide, subjecting the said fibrous residue to the action of an aqueous solution of an alkali metal hypochlorite reagent having an equivalency of from 35 parts to 80 parts sodium hydroxide for each 100 parts by weight dry fiber, separating the fiber product from the water-soluble products of reaction of said fibrous residue of wood with said alkali metal hypochlorite reagent, adding acid in successive increments to the hypochlorite solution remaining after separation of said fiber product, and removing the lignin product precipitated by the addition of each increment of acid, thereby providing a residual solution containing dissolved organics including polysaccharides.

12. The method which comprises reacting at atmospheric pressure the system: wood in defibered form, water and alkali metal hydroxide all as a liquid suspension; said wood containing substantially all of the substance of the water-insoluble content of the natural wood of its origin, and constitutionally consisting primarily of cellulose, lignin and other organics, said three constituents being present in mutual ratios in the range of contents from those characterizing the said wood in natural form to those characterizing the said water-insoluble content of said wood in natural form; in which system the alkali metal hydroxide is present in amount by weight in the range from 2.5 to 100 parts calculated as NaOH per 100 parts of oven dry wood, and the reaction is substantially completed to an equilibrium condition between the spent liquid and the fiber-form residue of the system at a reaction temperature in the range from about 80° C. to about 100° C.; separating the fibrous residue of wood from the dissolved water-soluble products of reaction of said wood with said aqueous solution of alkali metal hydroxide, subjecting the said fibrous residue to the action of a dilute alkali metal hypochlorite solution in quantity from about 35 parts to about 80 parts of sodium hydroxide equivalent of the hypochlorite salt for 100 parts by weight of said fibrous residue, separating the fiber product from the solution of water soluble products of the reaction of said fibrous residue with said alkali metal hypochlorite reagent, adding acid to the hypochlorite solution remaining after separation of said fiber product, and removing from said solution the lignin product precipitated by the addition of said acid.

13. The method which comprises reacting at atmospheric pressure the system: wood in defibered form, water and alkali metal hydroxide all as a liquid suspension; said wood containing substantially all of the substance of the water-insoluble content of the natural wood of its origin, and constitutionally consisting primarily of cellulose, lignin and other organics, said three constituents being present in mutual ratios in the range of contents from those characterizing the said wood in natural form to those characterizing the said water-insoluble content of said wood in natural form; in which system the alkali metal hydroxide is present in amount by weight in the range from 2.5 to 100 parts calculated as NaOH per 100 parts of oven dry wood, and the reaction is substantially completed to an equilibrium condition between the spent liquid and the fiber-form residue of the system at a reaction temperature in the range from about 80° C. to about 100° C.; separating the fibrous residue of the wood from the water-soluble products of reaction of said wood with said aqueous solution of alkali metal hydroxide, subjecting the said fibrous residue to the action of a dilute alkali metal hypochlorite solution in quantity from about 35 parts to about 80 parts sodium hydroxide equivalent

of the hypochlorite salt for 100 parts by weight of said fibrous residue, separating the fiber product from the solution of water soluble products of the reaction of said fibrous residue with said alkali metal hypochlorite reagent, adding to the solution remaining after said last mentioned separation an alkaline reacting compound of an alkali metal to obtain a pH of about 7, dewatering the neutralized solution until a solids concentration is attained in which undissolved lignin is present at about 20° C. to about 25° C., and separating the solid form of lignin from the residual liquid.

14. The invention as defined in claim 13 together with the further steps of acidifying the residual liquid by adding an acid to lower the pH below 7 in at least one stage and thereby effecting precipitation of at least one lignin fraction, and separating precipitated lignin from the acid solution.

15. The invention as defined in claim 13 together with the additional steps of acidifying the residual liquid by adding an acid to lower the pH to about 1.5, said acidification being effected in at least one stage and thereby effecting the precipitation of at least one lignin product, and separating from the acid solution any precipitated lignin material.

16. The invention as defined in claim 13 together with the further steps of acidifying the residual liquid with sulfuric acid to a pH of about 1.5, thereby precipitating lignin therefrom, adding alkaline-earth metal hydroxide to the said liquid to attain an equilibrium pH thereby precipitating alkaline-earth metal sulfate, and separating the resulting alkaline-earth metal sulfate from the acid solution to provide said solution rich in dissolved organic bodies including polysaccharides.

17. The method which comprises reacting at atmospheric pressure the system: lignocellulose in defibered form, water and alkali metal hydroxide; said lignocellulose containing substantially all of the substance of the water-insoluble content of the natural lignocellulose of its origin, and constitutionally consisting primarily of cellulose, lignin and other organics, said three constituents being present in mutual ratios in the range of contents from those characterizing the said lignocellulose in natural form to those characterizing the said water-insoluble content of said lignocellulose in natural form; in which system the alkali metal hydroxide is present in amount by weight in the range from 2.5 to 100 parts calculated as NaOH per 100 parts of oven dry lignocellulose, and the reaction is substantially completed to an equilibrium condition between the spent liquid and the fiber-form residue of the system at a reaction temperature in the range from room temperature to about 140° C.; separating the resulting fibrous residue of the lignocellulose from the dissolved water-soluble products of reaction of said wood with said aqueous solution of alkali metal hydroxide, subjecting the said fibrous residue to the action of a dilute alkali metal hypochlorite solution having an equivalency of from 35 parts to 80 parts sodium hydroxide for each 100 parts by weight dry fiber at a temperature of not over about 75° C. for a time period of up to about one hour, and separating the fiber product from the solution of water soluble products of the reaction of said fibrous residue of lignocellulose with said alkali metal hypochlorite reagent.

18. The method which comprises reacting at atmospheric pressure the system: wood in defibered form, water and alkali metal hydroxide all as a liquid suspension; said wood containing substantially all of the substance of the water-insoluble content of the natural wood of its origin, and constitutionally consisting primarily of cellulose, lignin and other organics, said three constituents being present in mutual ratios in the range of contents from those characterizing the said wood in natural form to those characterizing the said water-insoluble content of said wood in natural form; in which system the alkali metal hydroxide is present in amount by weight in the range from 2.5 to 100 parts calculated as NaOH per 100 parts of oven dry wood, and the reaction is substantially completed to an equilibrium condition between the spent liquid and the fiber-form residue of the system at a reaction temperature in the range from about 80° C. to about 100° C.; separating the fibrous residue of the wood from the dissolved water-soluble products of reaction of said wood with said liquid suspension of alkali metal hydroxide, subjecting the said fibrous residue to the action of a dilute alkali metal hypochlorite solution having an equivalency of from 35 parts to 80 parts sodium hydroxide for each 100 parts by weight dry fiber at a temperature of not over about 75° C. for a time period of up to about one hour, and separating the fiber product from the solution of water soluble products of the reaction of said fibrous residue of wood with said alkali metal hypochlorite reagent.

19. The process of treating comminuted lignocellulose raw material to form fibrous and chemical products therefrom, which comprises the steps of reacting at atmospheric pressure and at a temperature in the range of from room temperature to about 140° C. the lignocellulose material with an alkaline reacting compound of an alkali metal in the presence of water, extracting with an essentially aqueous solvent the reaction products soluble therein, separating the solution thus obtained to leave as one product the extracted fibrous residue, and subjecting the said fibrous residue to the action of a dilute alkali metal hypochlorite solution in quantity from about 35 parts to about 80 parts sodium hydroxide equivalent of the hypochlorite salt for 100 parts by weight of said fibrous residue.

20. The invention as defined in claim 19 together with the further steps of separating the solution thus obtained to leave as one product the extracted fibrous residue, and thereafter precipitating from the aqueous hypochlorite solution a plurality of separate, distinct lignin products by reducing the pH value of the solution in successive stages and removing the lignin product which forms at each stage.

21. The process of increasing the extractable solubles from a given amount of lignocellulose material which consists in the sequence of treating comminuted lignocellulose raw material at atmospheric pressure and at a temperature in the range of from room temperature to about 140° C. with an alkaline reacting compound of an alkali metal in the presence of water, separating the lignocellulose residue remaining after said treatment, and thereafter treating said lignocellulose residue with an alkaline solution of an alkali metal hypochlorite in quantity from about 35 parts to about 80 parts sodium hydroxide equivalent of the hypochlorite salt for 100 parts by weight of said lignocellulose residue.

22. The process of producing a plurality of separate, distinct lignin products from an alkaline solution of lignin, which consists in the sequence of treating comminuted lignocellulose raw material at atmospheric pressure and at a temperature in the range of from room temperature to about 140° C. with an alkaline reacting compound of an alkali metal in the presence of water, separating the lignocellulose residue remaining after said treatment, thereafter treating said lignocellulose residue with an alkaline solution of alkali metal hypochlorite in quantity from about 35 parts to about 80 parts sodium hydroxide equivalent of the hypochlorite salt for 100 parts by weight of said lignocellulose residue, separating the solution thus obtained to leave as one product the extracted fibrous residue, and thereafter adding acid to the last named solution to reduce the pH value of the solution in successive stages, thereby precipitating from said solution a plurality of separate, distinct lignin products, and removing the lignin product which forms at each stage.

23. The process of producing a plurality of separate, distinct lignin products from an alkaline solution of lignin, which consists in the sequence of treating comminuted lignocellulose raw material at atmospheric pressure and at a temperature in the range of from room temperature to about 140° C. with an alkaline reacting compound of an alkali metal in the presence of water, separating the lignocellulose residue remaining after said treatment, thereafter treating said lignocellulose residue with an alkaline solution of alkali metal hypochlorite in quantity from about 35 parts to about 80 parts sodium hydroxide equivalent of the hypochlorite salt for 100 parts by weight of said lignocellulose residue, separating the solution thus obtained to leave as one product the extracted fibrous residue, and thereafter adding acid to the last named solution in successive increments, and removing the lignin product formed upon the addition of each increment of acid.

(References on following page)

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,541,058	Heritage et al.	Feb. 13, 1951
2,541,059	Heritage et al.	Feb. 13, 1951
2,541,127	Van Beckum	Feb. 13, 1951

OTHER REFERENCES

"Wood Chemistry" (Wise), published by Reinhold Publ. Corp., New York city, 1946.

"Chemistry of Lignin" (Brauns), published by Academic Press Inc., New York city, 1952.