

Aug. 10, 1954

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2,686,120

ALKALINE PULPING OF LIGNOCELLULOSE IN THE PRESENCE
OF OXYGEN TO PRODUCE PULP, VANILLIN, AND OTHER
OXIDATION PRODUCTS OF LIGNIN SUBSTANCE

Filed Jan. 14, 1952

2 Sheets-Sheet 1

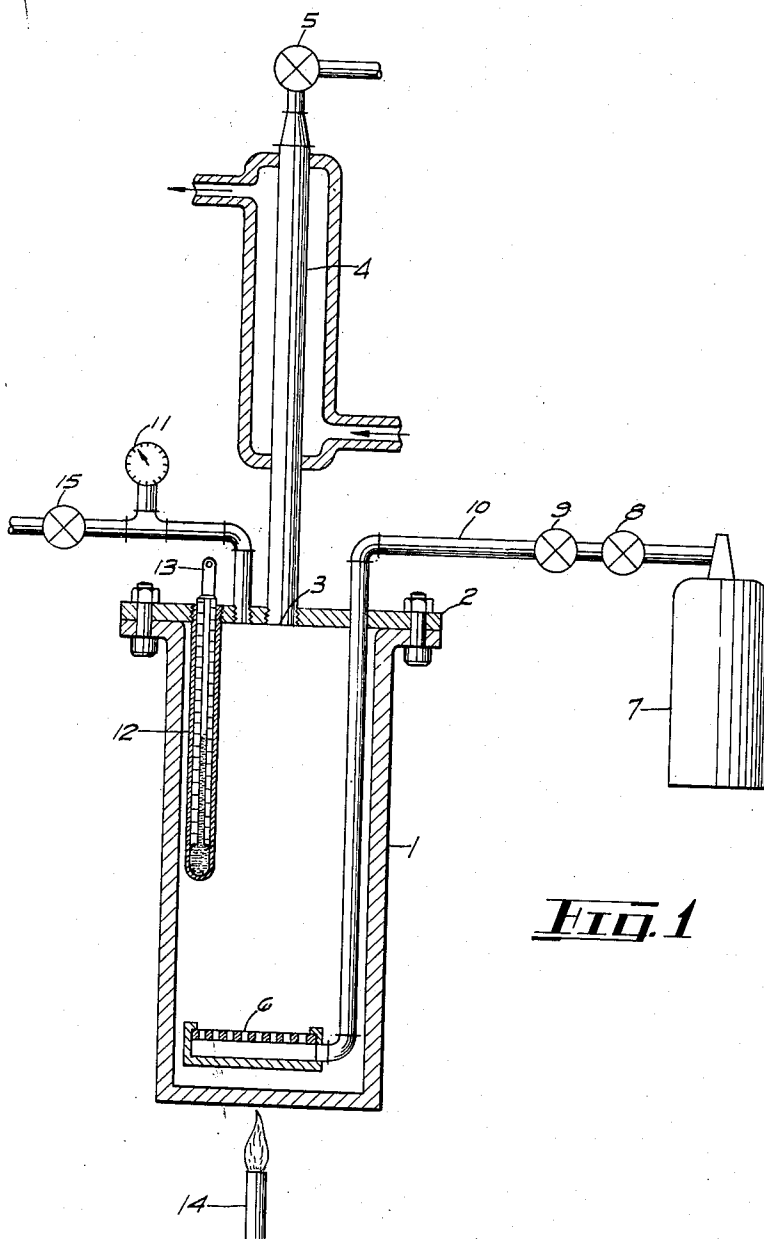


FIG. 1

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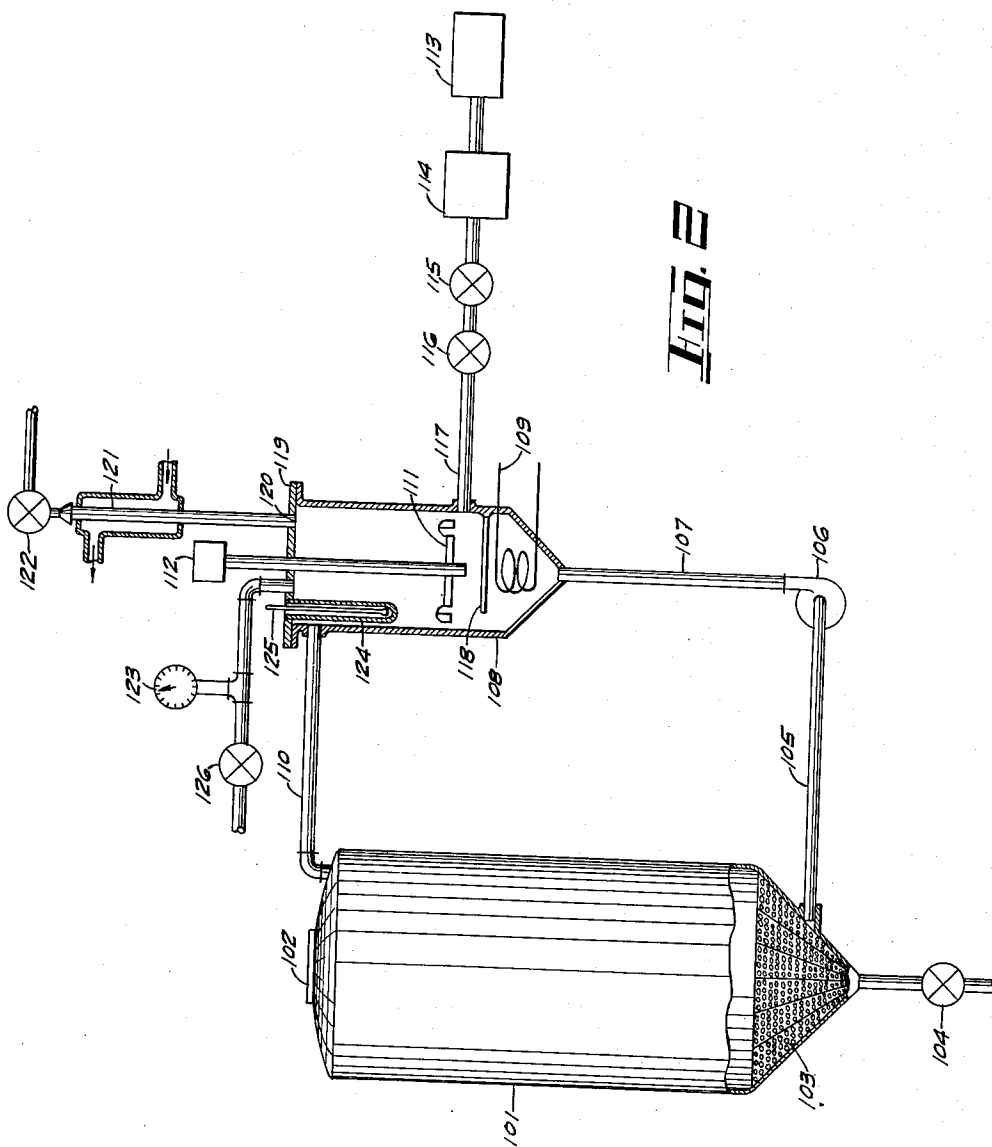
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4, 1952

2,686,120

Filed Jan. 14, 1952

2 Sheets-Sheet 2



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UNITED STATES PATENT OFFICE

2,686,120

ALKALINE PULPING OF LIGNOCELLULOSE
IN THE PRESENCE OF OXYGEN TO PRO-
DUCE PULP, VANILLIN, AND OTHER OXI-
DATION PRODUCTS OF LIGNIN SUB-
STANCE

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Application January 14, 1952, Serial No. 266,354

5 Claims. (Cl. 92—9)

1

2

This invention relates to the pulping of ligno-
cellulosic materials. It also relates to the pro-
duction of oxidation products, including vanillin,
from fibrous lignin-containing substances, in-
cluding wood, and the formation of the same, 5
during an alkaline pulping operation, and is a
continuation-in-part of application S. N. 700,018,
filed September 28, 1946, now abandoned, and
entitled "Method for Pulping Lignocellulose Ma-
terials and Simultaneously Producing Oxidation
Products Therefrom."

In our Patents Nos. 2,516,827, issued July 25,
1950 and No. 2,544,999, issued March 13, 1951,
there were disclosed methods whereby air or oxy-
gen could be employed to effect the production
of vanillin at highly satisfactory yields from 15
lignin-containing substances. The lignin-con-
taining substances referred to therein were char-
acterized in that the lignin content was avail-
able for oxidation either in solution (for example,
sulphite waste liquor) or in a substantially fine
state of subdivision (for example, wood meal). 20
The raw or starting material used in the above
mentioned patents did not, therefore, have the
full natural fibrous structure characteristic of an
original plant material but, on the contrary, the
lignin substance had been removed from such 25
original natural environment either in the form
of a soluble derivative (for example, in sulphite
waste liquor) or, in the alternative, made avail-
able for chemical action by cutting, abrading or
comminution to the extent that the original
fibrous structure of the plant material was sub-
stantially destroyed (for example, wood meal).

By "fibrous lignocellulosic material" we have
reference to and mean a lignocellulosic material,
the natural structure of which is of a fibrous
character and, furthermore, that such fibrous
character has not been substantially impaired by
abrading, comminution, other drastic cutting, or
process of maceration or the like prior to its
use as a raw or starting material for our pres-
ent invention. In particular we have reference
to the materials which are still of a lignocellu-
losic character as are discussed by G. S. Witham,
Sr., in "Modern Pulp and Paper Making," Rein-
hold Publishing Corp., New York, 1942, Chapter 2,
and by J. N. Stephenson (Editor in Chief) in
"Pulp and Paper Manufacture"; vol. 1, "Prep-
aration and Treatment of Wood Pulp," McGraw 50

Hill Book Co. Inc., New York, 1950, Chapter 1.
It will thus be understood that previously pulped
materials such as are described by Witham and
by Stephenson are no longer lignocellulosic in
character and do not fall within the definition
of the raw or starting material employed by us.
Our invention, therefore, relates to the class of
material here defined and when in the specifica-
tion and claims we make reference to "fibrous
lignocellulosic materials" we mean and have ref-
erence only to the class of materials above de-
fined.

The production of wood pulp by chemical pro-
cesses from fibrous lignocellulosic materials is
specifically directed toward the production of an
end product of fibrous character and having
such other qualities as are requisite for wood
pulp. For example, wood may be chipped into
units sufficiently small so that proper penetration
of chemicals into the unit chip can be obtained
under pulping conditions, but also sufficiently
large so that the fibrous structure of the wood
is not unduly damaged. During the pulping op-
eration, the lignin and other incrusting materials
of wood are subjected to the chemical action of
the pulping chemicals so that the fibrous units in
the wood become readily separable to form a 30
wood pulp. This balance in particle size of
fibrous lignocellulosic units, to permit adequate
chemical action for the production of a fibrous
end product, is the essence of the art of pulping
lignocellulosic materials.

We have now discovered that it is possible in
one single operation by the following process
which we have invented, to obtain from fibrous
lignocellulosic materials, both a fibrous pulp and
oxidation products of lignin, including vanillin.
Although vanillin is a principal oxidation prod-
uct from the ligneous content of the lignocellu-
losic materials employed by us when treated in
accordance with our present invention, other ox-
idation products are also formed. Among such
other products formed when soft woods are
treated in accordance with our invention, we have
identified acetovanillone, vanillic acid, and guaia-
col; when hard woods are employed, syringalde-
hyde and acetosyringone are formed in addition;
when certain fibrous annual crop materials such
as bagasse, wheat straw, flax straw, soya bean
stalks and oat hulls are employed, both vanillic

3
and syringic derivatives, as well as parahydroxy benzaldehyde have been identified in addition to vanillin.

In our Patent No. 2,516,827 referred to above, the effluent from alkaline chemical processes for producing wood pulp such as residual kraft liquor and residual soda liquor were cited as examples of lignin-containing substances to which the disclosures of that patent were applicable. The conditions for the production of vanillin according to the disclosures contained in the said patent were those of oxidation in an alkaline medium. The pulping process which we employ coincident to and simultaneously with the production of vanillin and other oxidation products from lignin substance is, therefore, an alkaline chemical process for producing wood pulp. We have also discovered that not only may simultaneous pulping action and alkaline oxidation of lignin to valuable end products be effected simultaneously, but also that by employing our present invention, the yields of vanillin are substantially increased over those which would be obtained were the pulping operation and the alkaline oxidation of lignin conducted as separate steps in series, i. e., in accordance with the known art of alkaline pulping, followed by the use of the invention disclosed in our Patent No. 2,516,827. Thus, in a process involving the use of wood chips, if a sample of such chips be divided into two portions, the first treated according to our present invention, and the second pulped by a known alkaline pulping process, for example, the soda process, and the residual liquor from the latter then subjected to oxidation in accordance with our previous invention as described in our Patent No. 2,516,827, there will result a substantially higher yield of vanillin by the former procedure.

The properties of any wood pulp are dependent on the pulping method employed and there are characteristic differences between wood pulps produced by different methods of pulping. In the case of any one pulping method, a wide range of pulp quality may also be obtained dependent upon the pulping conditions actually employed. The variation of such conditions in any given pulping process to produce a desired end result constitutes the basis of the art of chemical wood pulping.

The oxidizing conditions employed in our invention modify the pulping process from that which would obtain according to the well known alkaline pulping processes with the same pulping chemicals and the same temperature-pressure-time cycle. In general we have found that the rate and degree of pulping in accordance with our invention are less than when the oxidizing conditions, as herein described, are not employed. The yield of vanillin and of other oxidation products of lignin substance is also dependent on the reaction conditions. To assure both a satisfactory pulping action and a satisfactory yield of oxidation products, we recommend and prefer a digesting temperature in the range 150° C. to 200° C. The severity of oxidation of lignin substance is determined by temperature, partial oxygen pressure, time of reaction, and by the extent of circulation or mixing of the digester contents. For a satisfactory yield of oxidation products in the above temperature range, we recommend and prefer a reaction time of not more than four hours and conditions of digester pressure in the range 50 to 300 lbs. per square inch, the partial pressure of oxygen being that autogenically developed when using air as the source of oxygen

under the above conditions. The essential criteria of the reaction conditions of our invention are, however, first, that a fibrous wood pulp is produced and, second, that one or more of the oxidation products of lignin substance, as herein stated, are simultaneously produced. It will be obvious to anyone skilled in the wood pulping art that a wide variety of conditions may be employed from which a selection will be made with pulp quality and yield of oxidation products in mind. Examples of the application of our invention will be given which demonstrate that under certain conditions a wood pulp of useful quality may be obtained. Our invention is not limited to such conditions, however, but includes any conditions where oxidation of lignin to materials including vanillin and an alkaline chemical pulping process are combined in a single reaction.

Figure 1 shows in diagrammatic form an apparatus which we have used in some of our experiments and comprises a bomb 1, into which the reactants are introduced, a cover 2, containing an opening 3, leading to a condensing system 4, in which vapours from the bomb may be condensed and returned thereto by reflux through the opening 3, the condenser system terminating in the control relief valve 5, which limits the maximum pressure in the reaction system to a predetermined value. In the bottom of the bomb 1, is a porous plate 6, beneath which air or oxygen may be introduced and which serves as a gas diffusing means by which air or oxygen enters the reaction zone in a finely divided state. The air or oxygen is supplied from a pressure cylinder 7, through valves 8, 9, which control the pressure and rate of discharge from the cylinder into the gas diffusing means by tube 10.

The bomb is also equipped with a pressure gauge 11, and a thermometer well 12, containing a thermometer 13, by means of which the pressure and temperature of the reaction may be noted. The bomb 1, may be heated by any convenient means, for example, a gas flame 14. A relief valve 15, is provided for general pressure reduction.

Modifications of the equipment as described herein which will produce the combined action of pulping lignocellulosic materials and of the production of vanillin and other oxidation products therefrom will be apparent to those skilled in the art. For example, the pulping liquor may be circulated through the digester and subjected to the action of a gas containing oxygen, as described herein, in a vessel which comprises a portion of the circulation system external to the digester. Such modifications of the apparatus are to be considered as lying within the scope of our invention.

Apparatus for the practice of our invention utilizing a circulation system external to the digester and carried out during the pulping operation is illustrated in Figure 2. In this figure, the digester 101 may be of any design normally used for cooking by alkaline pulping processes. For example, as illustrated, it may have a removable top 102 for chip loading; a set of false bottom strainer plates 103 fastened to the digester wall and forming an annular space around the internal circumference of the bottom of the digester for liquor withdrawal; and a digester discharge valve 104. Any suitable heating system either direct or indirect may be employed. In Figure 2 an external indirect heating system is illustrated as an example and comprises the pipe 105, the liquor circulating pump 106, the

pipe 107 leading to the bomb or heater-reactor 108 in which suitable means for heating are provided, for example, the steam coil 109. The liquor from the heater-reactor 108 is returned to the digester through the pipe 110. The treatment of the liquor with a finely dispersed gas containing free gaseous oxygen is accomplished in the heater-reactor 108 in which agitation is provided by the turbo-mixer 111 driven by the motor 112. Air is supplied from the compressor 113 through the tank 114 and after regulation as to pressure and rate of air flow by valves 115, 116 enters the heater-reactor 108 through the pipe 117 and is dispersed therein by the turbo-mixer 111 which is placed over the baffle 118, the latter serving to keep the air from the heating zone around the coil 109. It is understood, of course, that any suitable means of agitation may be employed. The bomb or heater-reactor 108 as in the case of the device, shown in Figure 1, is provided with a cover 119 provided with an opening 120, leading to a condensing system 121 terminating in the control relief valve 122. Pressure gauge 123, thermometer well 124 containing thermometer 125 and relief valve 126 are all provided as in the device shown in Figure 1 and for similar purposes.

By the practice of our present invention vanillin is present as an alkali salt in the liquor residual from the alkaline pulping operation and may be isolated therefrom and purified by known means. Other materials co-produced and capable of forming an alkali salt are similarly present in the liquor in the form of such alkali salt and known means may also be applied to their isolation and purification.

The following description of experiments which have been performed by us will serve to illustrate the application of our invention and it is to be understood that our invention is not limited to the materials and conditions described in these experiments which are to be considered as examples only. The apparatus in which the experiments were carried out was of small capacity and therefore required a higher ratio of liquor to lignocellulosic material and larger quantities of chemicals than would normally be necessary in commercial units. It is well known that this kind of relation exists between experimental cooking in small digesters and commercial operation in the known chemical processes for producing wood pulp. The experimental data are to be interpreted with this in mind.

The determination of lignin in the fibrous raw materials used for our process was in accordance with standard method T13m-43 of the Technical Association of the Pulp and Paper Industry (U. S.). All yields of materials when expressed on a lignin basis have reference to lignin as so determined.

In the evaluation of wood pulps the methods employed were the standard methods of the Technical Association of the Pulp and Paper Industry (U. S.) for example, method T222m-45 for lignin in wood pulps, T227m-43 for freeness (Canadian standard), T205m-42 for forming hand-sheets for physical tests of pulp, T220m-42 for physical testing of pulp handsheets, and so on.

In determining the presence and yield of vanillin and various co-products, the following techniques were employed. Where interference with syringyl derivatives did not apply, we used a gravimetric procedure involving the separation and estimation of vanillin in the form of its m-nitrobenzoyl hydrazone. This is described by Buckland, Tomlinson and Hibbert, Can. J. Re-

search 16B, 54 (1938), but employing ether as a solvent in place of trichlorethylene as described in the above reference. Alternatively, we used a spectrometric method of analysis according to the general method of Lemon, Ind. Eng. Chem., Anal. Ed., 19, 846 (1947). This is a rapid procedure which gives an overall measure of substances which are spectrometrically active at approximately 3500 Å., the vanillin being the principal substance present which is so active.

In the case of materials where syringyl derivatives were present, the above method of Lemon was also applied but here the result gives an overall indication of the total simple aromatic cleavage products of lignin as formed in the reaction. In the identification of specific compounds present among the cleavage products so formed, we have employed chromatographic methods as described by Stone and Blundell, Anal. Chem., 23, 771 (1951). Identification of vanillin, syringaldehyde, parahydroxy benzaldehyde, acetovanillone and acetosyringone were made by this technique.

Example 1

One hundred grams, wet weight, of spruce chips containing 41% moisture were heated with 60 grams sodium hydroxide dissolved in one litre of water in the previously described apparatus. Throughout the heating cycle a steady flow of compressed air was introduced through the diffuser, the valve 5 being adjusted to relieve gas at 110-115 lbs. per square inch pressure, the air flow as discharged being adjusted to 13.4 cu. ft. per hour. The apparatus reached a final observed temperature of 168-170° C. in approximately 25 minutes and was maintained thereat for 3 hours. No catalyst or special oxidizing agent such as copper sulphate was present. At the conclusion of this treatment the air flow was turned off, the system cooled to a lower temperature than its boiling point at atmospheric pressure and the pressure reduced to that of the atmosphere by the relief valve 15.

The contents of the apparatus were emptied, the liquid portion separated by filtration, and the solid residue (soft chips and pulp) washed with several small portions of water which were added to the filtrate.

An aliquot portion of the filtrate was analyzed for vanillin and the amount so determined correlated with the lignin content of the original wood chips. On this basis a yield of 15% vanillin was obtained.

The soft chips and pulp as separated were subjected to a simple disintegration by stirring into a fibrous wood pulp. The lignin content of this pulp was 5%. The pulp was brownish in colour, had a freeness of 748 and handsheets prepared from it had a burst factor of 41.5 and tear factor of 158. These qualities indicate a usable pulp.

An additional sample of 100 g., wet weight, of the same spruce chips was heated in the apparatus with 60 grams sodium hydroxide dissolved in 1 litre of water and subjected to the same temperature-pressure-time cycle but without air flow. At the conclusion of the experiment the liquid portion was separated by filtration and the solid residue (soft chips and pulp) washed as before.

An aliquot portion of the filtrate when analyzed indicated a yield of 1% vanillin, based on the lignin content of the spruce chips.

The residue was easily disintegrated into a fibrous wood pulp which on analysis contained

4% lignin. The pulp was somewhat less brownish in colour than that previously described, had a freeness of 701 and handsheets prepared from it had a burst factor of 48.5 and a tear factor of 178.

It will be noted that in the last described above experiment the pulping conditions parallel those of the conventional soda pulping process except that the amount of alkali employed is substantially higher.

Example 2

Experiments similar to Example No. 1 were performed with the same spruce chips in which the alkali was 60 grams sodium hydroxide plus 30 grams sodium sulphide dissolved in 1 litre of water.

When subjected to air flow the vanillin content of the resultant liquor corresponded to a yield of 12.5%, based on the lignin content of the original wood chips. The corresponding pulp was of a brown colour, had a lignin content of 4%, and after disintegration a freeness of 704. Handsheets had a burst factor of 52.0 and a tear factor of 177.

In the experiment without air the residual liquor had a vanillin content corresponding to 2% of the original lignin content of the spruce chips and the resultant pulp a lignin content of 1.5%; freeness of 705; burst factor of 39.0 and a tear factor of 233.

It will be noted that in the last described above experiment the pulping conditions parallel those of the conventional kraft pulping process except that the amount of alkali is substantially higher.

Example 3

A sample of spruce chips was treated as in Example No. 1 except that the valve 5 was adjusted to relieve gas at 250 lbs. per square inch pressure. The air flow, as before, was adjusted to 13.4 cu. ft. per hour and the observed temperature was approximately 170° C.

In the residual liquor there were determined vanillin to the amount of 16.8% of the original lignin content of the chips and in addition acetovanillone to the amount of 10% of the lignin content of the original chips.

The pulp produced as before had a freeness of 701. Handsheets had a burst factor of 50.5 and a tear factor of 210.

It will be noted that the above example is under experimental conditions of higher pressure than in Example 1.

Our invention may also be applied to hardwoods. As is known, the ligneous content of hardwood is more complicated than that of soft woods and the oxidation products of hardwood lignin include compounds which are analogues of vanillin and its related compounds. The application of our invention to hardwoods produces therefore more complicated mixtures of oxidation products.

Example 4

A sample of poplar chips equivalent to 60 grams dry weight was subjected to a heating cycle as per Example 1. The valve 5 was set to relieve pressure at 110-115 lbs. per square inch. The observed temperature was approximately 171° C., the airflow 13.4 cu. ft. per hour.

The pulp produced had a freeness of 616. Handsheets prepared from it had a burst factor of 25.5 and a tear factor of 80.

In the residual liquor were identified vanillin, syringaldehyde, acetovanillone, and acetosyringone. Owing to the complicated character of the mixture, yields of each of the above were not determined. The combined amounts of vanillin and syringaldehyde were approximately 13.3% of the lignin in the poplar chips.

It will be noted that the above example illustrates the application of our invention to hardwoods.

Our invention may also be applied to annual crop lignin-containing material which is characterized in its natural state by a fibrous structure, for example, bagasse, wheat straw, flax straw, soya bean stalks, oat hulls and the like. The ligneous content of such materials differs from that of wood substance and the particular oxidation products which are formed depend both as to their nature and quantity on the fibrous raw material treated in accordance with our invention. It is a common characteristic of all such materials, however, that the oxidation products include vanillin. Other materials have been identified among the reaction products as noted in the following examples. Just as the quality of pulp obtainable from wood chips is dependent upon the wood species pulped, so is the quality of the pulp obtainable from annual crop fibres dependent upon the species of such annual crop material pulped. When such materials are used in accordance with our invention, we have found that the rate and degree of pulping are less than when the oxidizing conditions herein described are not employed. An analogous situation, however, maintains to that in the wood pulping art in that a skilled operator can readily make a selection from the wide variety of possible conditions to combine the objectives of satisfactory pulp quality and good yield of vanillin plus other oxidation products.

Example 5

A sample of wheat straw equivalent to 120 grams dry weight, containing 16.9% lignin and 7.6% moisture, was heated with 120 grams sodium hydroxide dissolved in 2 litres of water in an apparatus as previously described. The apparatus reached a final observed temperature of 170° C. in 12 minutes and was maintained thereat for 90 minutes. Throughout the reaction compressed air was introduced through the diffuser, valve 5 being adjusted to relieve gas at 135 lbs. per square inch, the air flow as discharged being adjusted to 13.4 cu. ft. per hour. No catalyst or special oxidizing agent such as copper sulphate was present.

As a result of the above treatment the residual liquor contained simple aromatic derivatives from lignin, spectrometrically determined, corresponding to 15.2% of the original lignin content of the wheat straw. Chromatographic analysis indicated a yield on a lignin basis of 5.3% vanillin, 6.2% syringaldehyde, and 0.9% parahydroxy benzaldehyde. Acetovanillone and acetosyringone were identified by chromatographic methods but were not quantitatively determined.

A straw pulp was removed from the reaction vessel in an amount corresponding to 34% yield on the original straw. This pulp had a freeness of 299, a burst factor of 31 and a tear factor of 82.

Example 6

We have also applied our invention to bagasse, flax straw, oat hulls, and soya bean stalks with

experimental conditions and yields as per table below:

160° C. in 11 minutes and was maintained thereat for 180 minutes. The pressure was maintained

	Whole Oat Hulls	Whole Flax- seed Straw	Soya Bean Stalks	Fresh-dried Sugar cane Bagasse
Raw Material:				
Moisture, Percent	7.9	7.6	9.5	6.4
Lignin, Percent	15.8	13.3	15.5	17.2
Reaction Conditions:				
Dry weight fibrous raw material, g.	120	120	120	120
Weight Alkali	120 g. NaOH	120 g. NaOH	120 g. NaOH	120 g. NaOH plus 60 g. Na ₂ S.
Final Temperature	170° C	150° C	200° C	170° C.
Time to Final Temperature, min	13	13	17	13
Time at Final Temperature, min	60	90	90	60
Gas Relief Pressure p. s. i. gauge	135	125	245	135
Rate of Gas relief cu. ft./hr.	13.4	13.4	13.4	13.4
Aromatic Reaction Products:				
3500's (see note x)	14.1%	12.8%	14.5%	14.5%
Chromatographic analyses—				
Vanillin	2.8%	5.1%	5.5%	1.7%
Syringaldehyde	3.7%	2.0%	2.9%	2.2%
Parahydroxybenzaldehyde	1.7%	1.4%	0.6%	0.9%
Pulp Properties:				
Yield, Percent	26	38	21	36
Freeness	382	(see note y)	215	437
Burst factor	7.8	do	7.4 (see note z)	26.4
Tear factor	36	do	36 (see note z)	86

Note x.—Determined spectrometrically as hereinbefore described.

Note y.—The pulp had the appearance of typical flax pulp characterized by great fibre length. Considerable refining was required, as with normal flax pulp, before it could be reduced to a condition where handsheets could be formed. Processing of our resultant pulp by methods known and employed in refining flax pulps results in the production of a pulp of useable characteristics of strength and drainage.

Note z.—The resultant soya bean pulp did not form satisfactory handsheets. The test data are for a mixture 25% soya bean pulp as produced, 75% groundwood pulp of freeness 100, burst factor 12, and tear factor 37. The soya bean pulp was over-cooked at the temperature employed in the experiment described.

The known art of alkaline pulping of fibrous lignocellulosic materials is normally based on the use of a caustic alkali, for example, with sodium hydroxide or sodium hydroxide plus sodium sulphide as the active alkaline pulping agent. Certain fibrous lignocellulosic materials can, however, according to the known art, be pulped under less severe conditions of alkalinity, for example, pulping of straw by lime as the active alkali is well known (see, e. g., G. S. Witham, Sr., "Modern Pulp and Paper Making," Reinhold Publishing Corp., New York, 1942, p. 41). In this case the pulp produced is a much more crude product than that which would be made from the same straw when a caustic alkali is employed and this is well known in the pulping art. Our invention can, however, be employed for alkaline pulping processes where less severe alkalinity than is typical of the use of caustic soda with or without the co-presence of sodium sulphide is employed. As already noted, according to the practice of our invention, the pulping action is less severe under a given condition of alkalinity than is normal for conditions where the oxidizing features of our invention are not employed. For this reason a usable pulp will not be produced in accordance with our invention if the conditions of alkalinity are insufficient to promote pulping according to the known art of alkaline pulping, for example, a cook of wood chips using lime only as the active alkali will result in failure to produce a usable pulp both under normal conditions of alkaline pulping and when our invention is employed under similar conditions. The application of our invention is therefore limited to conditions of alkalinity and the use of alkalis such that a pulping action is obtained according to the known art of alkaline pulping. The following example illustrates the application of lime base cooking to whole wheat straw.

Example 7

120 grams equivalent dry weight of the same wheat straw used in Example 5 was heated with 2 litres of water to which lime had been added equivalent to 84 grams calcium oxide. The apparatus reached a final observed temperature of

at 110 lb. per square inch, the airflow being adjusted to 13.4 cu. ft. per hour.

As a result of the above treatment a straw pulp was produced suitable for use in strawboard manufacture. The total simple aromatic derivatives from lignin, spectrometrically determined corresponded to 6.0% of the original lignin content of the wheat straw. By chromatographic analysis the following compounds were identified as being produced: vanillin, acetovanillone, syringaldehyde, acetosyringone, parahydroxy benzaldehyde.

When in the specification the word "pressure" is used, it is to be understood that we refer to gauge pressure and not absolute pressure.

We are aware that this invention may be embodied in other specific forms without departing from the substance thereof and it is, therefore, desired to comprehend within the invention such modifications as may be embraced within the claims and the scope of the invention.

What we claim as our invention is:

1. A process for simultaneously producing from wood chips a fibrous pulp and a vanillin product, which process consists essentially of digesting said wood chips in an alkaline pulping liquor at a temperature of 150° C. to 200° C. to produce a pulp, continuously passing into the digestion mixture during the pulping step, a finely dispersed gas containing free gaseous oxygen and recovering said vanillin product, said alkaline pulping liquor containing as the sole essential components, water and an alkaline pulping reagent selected from the group consisting of sodium hydroxide and a mixture of sodium hydroxide and sodium sulphide.

2. A process for simultaneously producing from fibrous lignocellulosic material a fibrous pulp and products of oxidation of lignin substance including at least one of the group of compounds consisting of vanillin, acetovanillone, syringaldehyde, acetosyringone, parahydroxy benzaldehyde, said lignin oxidation products being present in the form of their appropriate alkaline derivatives, which process consists essentially in digesting said material in an aqueous alkaline pulping

11

liquor at a temperature of 150° C. to 200° C. to produce a pulp, continuously withdrawing said liquor from the digester during the pulping step, continuously passing into said withdrawn liquor a finely dispersed gas containing free gaseous oxygen, continuously recirculating to the digester during the pulping step said liquor into which said gas has been passed and recovering from said liquor at least one of the said oxidation products of lignin substance.

3. The process of claim 2 in which the aqueous alkaline pulping liquor contains as its active pulping agent an alkali selected from the group consisting of sodium hydroxide and a mixture of sodium hydroxide and sodium sulphide.

4. A process for simultaneously producing from fibrous lignocellulosic material a fibrous pulp and a vanillin product which process consists essentially of digesting said material in an alkaline pulping liquor at a temperature of 150° C. to 200° C. to produce a pulp, continuously withdrawing said liquor from the pulping step, continuously passing into said withdrawn liquor a finely dispersed gas containing free gaseous oxygen, continuously recirculating, to the pulping step, said liquor into which said gas has been passed, and recovering a vanillin product.

5. The process of claim 3 in which the lignocellulosic material is wood chips.

12

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