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PROCESS OF MAKING VANILLIN FROM LIGNIN, LIGNIN DERIVATIVES OR OTHER MATERIALS CONTAINING LIGNIN

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This invention relates to a process of making vanillin from lignin, derivatives of lignin or other materials containing lignin.

The production of vanillin from materials containing lignin as used in practice can theoretically be explained from the formula for the constitution of lignin, as far as such formula is known. The commercial production of vanillin from lignin raw materials, however, had to be kept within narrow limits which in the first place is probably due to the fact that with all methods so far known for carrying out this process the attainable yields are relatively small and amount to only a very small fraction of the theoretical yield.

It is further known that vanillin may be produced from lignin sulpho-acids, the main constituents of sulphate cellulose waste-lye. In this case the process may for instance, be carried out in such a way that the sulphite waste lye which had been made strongly alkaline by ample addition of lime or caustic alkali is heated for some longer time to a temperature from 160 to 180° and that the vanillin formed is isolated by extraction with a suitable organic solvent (for instance benzol). However, the yield attained by means of this process is relatively very small and as a rule will only be 2 to 3 percent and in most favorable cases about 6 percent of the lignin used. (In accordance with this is also the statement "between 1 and 2.4 g per liter" which is found in Hägglund's book "Holzchemie", second edition, 1939, page 165, last line, the sulphite waste lye containing approximately 40 g of lignin per liter. See also the periodical "Holz als Roh- und Werkstoff" 1931, No. 1, page 20, right-hand column, stating that "there may be figured with a vanillin yield of about 5 to 6 percent of the weight of the lignin".) Other alledgedly much higher yields occasionally given in the older literature were later found to be based on grave errors mainly due to improper methods of determining the vanillin.

It is further remarkable that as lignin raw material for the production of vanillin hitherto solely sulphite cellulose waste-lye, that is lignin sulpho-acids, had been used and that it has not been possible to produce yields of vanillin or of vanillin derivatives sufficient for commercial purposes from other lignin substances (for instance from wood saccharification residues or from lignin isolated from wood by means of copper oxide ammonia or directly from wood or lignified vegetable matter or finally from derivatives of lignin.)

There has been no doubt that the process leading from lignin to vanillin is a process of oxidation. Accordingly it had been tried to expedite the process by introducing air or oxygen or by applying oxygen discharging or oxygen transmitting substances. However, no better yields could be obtained when carrying out the process in such a way. In the contrary, the cited book of Hägglund at the above cited place, for instance, states that "introduction of air had an unfavorable effect on the yield of vanillin."

The reason for these unsuccessful attempts, as careful tests have proven, was found to reside in the fact that the hitherto used processes of oxidation with the selected oxidizing agent or improper working conditions (temperature, and time of reaction) are either insufficient to attack the structure of the lignin or that too strong an action is exerted, with the result that the waste products first formed (phenols, oxy-acids, oxy-aldehydes etc.) are subject to further destruction. It has also been found that by carrying on the process under proper working conditions there may be attained considerably higher yields, eventually even a yield twice as large as hitherto obtainable, or also the same yields in a more convenient way and at smaller costs; furthermore, it has been found that like yields of vanillin may be produced, besides from cellulose waste lye, from the other above mentioned lignin raw materials.

The working conditions which are suitable for the present purpose from the basis of our new process. This process consists therein that the lignin raw material is heated in the presence of alkali (lime, caustic alkali) to a moderate temperature of 100 to 110°, in no case more then about 140°, under simultaneous action of finely distributed oxygen and/or oxygen discharging or oxygen transmitting compounds. Accordingly, air or a current of oxygen gas in fine distribution may be used at the stated temperatures either alone or in the presence of oxygen discharging or oxygen transmitting compounds. Such compounds may also be used alone (that is without introduction of air) in order to react onto the lignin raw material. In many cases the favorable action of the metal oxides may depend upon the surprising and hitherto unknown fact that several insoluble lignin raw materials readily enter into solution under the action of the metal oxides in the presence of alkali and thus are subject to a very uniform action of oxygen.

Heating of the reaction mass may be effected in accordance with prevailing conditions in an open container or under reflux or also in a closed container under pressure. Especially good results have been attained by addition of salts raising the boiling temperature. As may be seen from Example 7 and the subsequent Table, the yield will increase with increasing temperature. As oxygen discharging or oxygen transmitting substances, above all the several inorganic oxygen compounds or salts that are more or less known for such reactions have been found to be suitable for the present purpose, especially the compounds that may relatively easily be reduced in alkaline agents (for instance nickel oxide, cobalt oxide, cerium oxide, lead oxide, MnO_2, mangano-manganite, potassium ferri-cyanide etc.) Also gas-condensing adsorption substances, such as for instance active carbon, may well be used as oxygen transmitting substances (see Example 10).

The selection of the working conditions to be used in individual cases as well as of the oxygen transmitting substance etc. depend in the first place upon the kind and exterior condition of the raw material. Accordingly, the proper working conditions and oxygen transmitting substances may easily be ascertained in every case by a few trials. Thus, for instance, it has been found as being of advantage in certain cases to subject the lignin raw material first to a preliminary boiling with alkali (lime, caustic potash or caustic soda) and thereupon to heating with oxygen metal oxides or the like in the presence of alkali (see Examples 8 and 9).

The working-up of the reaction mixture and the isolation of the vanillin is carried out in known manner, particularly as indicated in the examples given hereinafter.

A great advantage of our new process consists therein that the oxygen discharging or oxygen transmitting substances may easily be recovered and again be used with the materials to be subsequently treated.

As above stated, as oxygen transmitting substances there may also be used adsorption substances which owing to their large surfaces act condensing upon gases. As such "activators" there may be used, for instance, active carbon, platinum-sponge, finely distributed palladium and the like.

It has surprisingly been found that with a sufficiently fine distribution of the lignin material offering a greater surface of action to the oxygen high yields of vanillin may be attained under definite conditions also without addition of a special activator. For this purpose the lignin raw material is heated in a distribution as fine as possible, for instance in the form of finely powdered lignin or finely ground wood-flour in the presence of alkali under simultaneous action of oxygen (oxygen of the air) and under pressure to a moderately high temperature (not over 140°), while the isolation of the formed vanillin is preferably carried out in the above described manner.

It has furthermore been found that the yields may be essentially increased (for instance as far as to a double or quintuple value or more of the hitherto attainable yields), if the lignin raw material is heated under proper conditions in the presence of free alkali with aromatic nitro-compounds. The most suitable conditions (alkali concentration, temperature and time of heating, as well as the used quantity of the nitro-compound) depend mainly upon the kind of the lignin raw material and may easily be ascertained in every case by means of a few trials with the respective raw material.

Thus, for instance, for a definite raw material (cuproxamlignin) it has been found that the yield increases with the applied temperature and that upon surpassing a definite temperature (160°) the yield does not further increase or finally again decreases. A further comparative test has shown that with a boiling time of 72 hours (at 103°) more than the double yield was obtained, as compared with the yield obtained under otherwise like conditions with a boiling time of only 24 hours. Further information may be found in the examples given hereinafter.

Example 1

5 kg of lignin (consisting of finely comminuted pine-wood, isolated in known manner by means of highly concentrated muriatic acid or by treatment with copper oxide ammonia) were mixed with 50 liters of a 10% potash lye and cobalt hydroxide precipitated from 5 kg of cobalt sulphate in the presence of hydrogen peroxide with hot soda lye, heated under reflux and intensive agitation for 24 hours, and finely distributed oxygen passed through the mixture. Upon completion of the boiling the cobalt hydroxide is separated by a centrifuge, the substance still absorbed by the hydroxide removed by stirring several times with dilute lye, and carbonic acid introduced into the united liquids, until the caustic potash is converted into bicarbonate. The vanillin is thereupon withdrawn by extraction with ether, methylene chloride, benzol or the like and purified upon volatilization of the solvent, eventually by re-crystallisation. There are obtained 400 g of pure vanillin, that is 8 percent of the used lignin. From the bicarbonate-alkaline solution 100 g of vanillin acid, that is a yield of 2 percent may be obtained after acidulation and renewed extraction.

Example 2

5 kg of lignin (the same as in Example 1) are boiled with 50 liters of a 10% potash lye with addition of 10 kg of lead dioxide. The working-up is the same as stated in Example 1; the yield is likewise about the same as stated in this example.

Example 3

2 kg of de-resinized pine-wood flour (corresponding to about 500 g of lignin) are mixed with 20 liters of a 10% potash lye and cobalt hydroxide precipitated from 2 kg cobalt sulphate in the presence of hydrogen peroxide with hot soda lye and heated under reflux for 24 hours and agitation, at the same time passing oxygen therethrough. The reaction mixture is further treated the same as in Examples 1 and 2. This will furnish 45 g of vanillin, that is 9 percent with relation to the quantity of lignin contained in the used pine-wood. Besides, there may be obtained 10 g, that is 2 percent, of vanillin acid.

Example 4

2 kg of wood-flour are stirred-up in 20 liters of a 10% potash lye and mixed with freshly precipitated mangano-manganite obtained from the solution of 3 kg of $MnSO_4.7H_2O$ by precipitation with soda lye and subsequent oxidation with hydrogen peroxide or air or oxygen. The mixture is boiled for about 15 hours under reflux and agitation and at the same time air or oxygen is introduced in fine distribution. Thereupon separation from undissolved cellulose and the man-

gano-manganite is effected and the treatment continued with carbonic acid, until the caustic alkali is converted into bicarbonate, whereupon vanillin is withdrawn from the reaction mixture by extraction (with benzol or ether). This vanillin upon volatilization of the solvent will be obtained in beautiful crystalline form. The yield amounts to 40 g, that is 8 percent of the lignin contained in the wood material.

Example 5

1 kg of lignin bromide (obtained for instance in accordance with Ber. 1929, 62, page 1554) is stirred-up in 10 liters of a 10% potash lye and mixed with cobalt hydroxide obtained from 1 kg of $CoSO_4.7H_2O$ in the presence of hydrogen peroxide by precipitation with hot soda lye. The mixture is heated under reflux to boiling temperature for about 24 hours and oxygen simultaneously passed therethrough. The lignin bromide will be fully dissolved and converted into vanillin 6-bromide.

The reaction mixture is thereupon further treated as stated in Example 1. By extraction of the bicarbonate-alkaline solution with ether or benzol the vanillin bromide will be isolated and discharged upon volatilization of the solvent in the form of beautiful crystals. The yield is 70 g, that is 7 percent of the used lignin bromide.

Example 6

1 liter of commercial sulphite cellulose lye (corresponding to 40 g of lignin) is mixed with 300 g of caustic potash, the solution (boiling at 108° C) heated for 12 hours under reflux and at the same time oxygen passed therethrough. The reaction mixture is thereupon treated with carbonic acid and further worked-up as stated in Example 1. The yield amounts to 5 g of vanillin, that is 12.5 percent of the lignin contained in the waste-lye.

Example 7

1 liter of commercial sulphite cellulose waste-lye is brought to double alkalinity and mixed with common salt until saturation takes place. The solution having now its boiling point at 108° C is heated for 12 hours under reflux and at the same time oxygen is introduced in fine distribution; upon cooling this solution is further worked-up in the usual manner as stated in Example 1. The yield of vanillin is 4 to 5 g, that is 11 to 12 percent of the lignin contained in the sulphite cellulose lye.

The dependence of the yield from the action of the oxygen and from the boiling temperature is shown very instructively in the below Table giving the yields of vanillin for each liter of sulphite cellulose waste-lye obtained by treatment with and without oxygen as well as at several boiling temperatures (by adding different amounts of salt) but under otherwise exactly like conditions. These tests have been conducted without addition of an oxygen transmitting substance.

TABLE

Gas	Boiling temperature	Yield from 1 liter waste-lye	
		Vanillin	Lignin
	°C.	*Grams*	*Per cent*
Nitrogen	101	0.2	0.5
Oxygen	101	3	7.5
Do	104	3.6	9.0
Do	107–108	4.5	11.25

Example 8

A comparison of the processes hitherto in use (for instance according to U. S. Patent 2,069,185) with our new process (which is conducted in two steps, that is by preliminarily boiling with alkali) may be obtained in the following manner:

4 liters of sulphite cellulose waste-lye (which corresponds to 160 g of lignin) are mixed with 480 g NaOH and heated for two hours and one half to 160°. The solution is thereupon divided into two halves.

The one half corresponding to 2 liters of sulphite waste-lye, or 110 g of lignin, is worked-up in the usual manner which yields 4 g of pure vanillin, that is 4 percent of the lignin contained in the sulphite waste-lye.

The other half is boiled for 12 hours under agitation and with introduction of oxygen at the reflux cooler with the cobalt hydroxide freshly prepared from 300 g $CoSO_4.7H_2O$ by precipitation with NaOH and hydrogen peroxide. The working is carried out in the same manner as according to the above given Examples. There will be obtained from 8 to 9 g of pure vanillin which corresponds to a yield of 8 to 9 percent (figured with respect to the contents of lignin in the waste-lye). The yield obtained when working according to our invention, therefore, amounts to more than twice the yield obtainable with former processes.

Example 9

1 kg of lignin (produced from wood-flour in known manner by means of copper oxide ammonia (cuproxam) or muriatic acid is heated with 20 liters of 2n-alkaline lye for one hour in a closed container to 165°. Upon cooling the solution is mixed with 3 kg of potassium ferri-cyanide and the mixture heated 3 hours to 110°. Working-up the reaction product in the above indicated manner yields 50 g of vanillin, that is 5 percent of the original material.

Example 10

2 kg of wood-flour are stirred-up in an autoclave with agitator in 20 liters of a 10% potash lye and thoroughly mixed with 100 g of active carbon (Merck). Thereupon oxygen is pressed-in and the mixture is heated for about two hours under agitation to 120°. Upon cooling the solution is separated from undissolved matter and the vanillin isolated therefrom by extraction subsequent to treatment with mineral acid or carbonic acid according to the above given statements (see for instance Example 4). There are obtained 50 g of pure vanillin, that is a yield of 10 percent of the weight of the wood.

Example 11

1 kg of finely ground wood-flour is thoroughly mixed with 10 liters of alkaline lye of double normal value in an autoclave with agitator, thereupon oxygen is pressed in (at about 10 atmospheres over-pressure) and the mixture heated for two hours under thorough agitation to 120°. Now separation from the undissolved residue is effected and carbonic acid introduced into the solution until the whole of the caustic potash is converted into bicarbonate, whereupon the vanillin is withdrawn from the reaction mixture by extraction (with benzol or ether). Upon evaporation of the solvent there will be obtained 28.5 g of raw vanillin containing approximately 85 percent of pure vanillin yielding by re-crystallisation 24 g of pure vanillin, that is 9.6 percent figured with respect to the amount of lignin (250 g) present in the original wood-flour.

Example 12

50 g of "cuproxam lignin" produced from wood-flour or the like by extraction and treatment with copper oxide and ammonia are stirred-up in 2 liters of 2n-lye, mixed with 100 ccm nitro-benzol and boiled under entensive agitation and reflux for 72 hours. Upon removal of the nitro-benzol and its reduction products (at last with ether) the alkaline solution is acidulated, neutralized with bicarbonate and de-etherized. Upon evaporation of the ether there remains a yield of 6.25 g of a 90% raw vanillin corresponding to 12.5 percent of the used lignin. The degree of purity may suitably be ascertained with m-nitrobenz-hydracide. From the acidulated bicarbonate solution further oxidation products, such as vanillin acid, may be produced in small quantities.

Example 13

The same mixture of lignin, lye and nitrobenzol as given in Example 1 is heated in an autoclave with agitator. The working-up of the materials is likewise the same as according to Example 1. After heating for twenty hours to 160° the yield of raw vanillin amounted to 22 percent of the original material. Raising the temperature to 180° does not result in an increased yield. However, if heating is carried on to only 140° (same time) the yield will be smaller (18 percent).

Example 14

The same mixture of lignin and alkali as given in Examples 1 and 2 is heated with 100 ccm of nitrotuluol for 10 hours to 160° in an autoclave with agitator and further treated in the manner above stated. The yield was 12 percent raw vanillin.

Example 15

40 g of dry pine-wood flour (corresponding approximately to 12 g of lignin) are treated for 20 hours in an autoclave with agitator with 400 ccm of 2n-lye and 50 ccm nitrobenzol at 160° which yields 1.5 g of raw vanillin corresponding to 12.5 percent of the used lignin.

Example 16

400 ccm of commercial sulphite cellulose waste-lye corresponding to 22 g of lignin are brought to alkalinity of double normal value by addition of solid alkali, thereupon mixed with 50 ccm of nitro-benzol and treated in an autoclave with agitator for 6 hours at 150°. Upon working-up in the above indicated manner there will be obtained approximately 4 g of raw vanillin corresponding to 18 percent of the used lignin.

Example 17

100 g of lignin residues (11 percent methoxyl content) originating from a wood saccharification process are treated as above indicated in an autoclave with agitator for 3 hours together with alkali and nitro-benzol at 160° and worked-up as above stated. There are obtained 8 to 9 g of raw vanillin corresponding to about 12 percent of the lignin contained in the raw material.

The amount of the used aromatic nitro-compound may be considerably reduced especially in case of greater treated quantities.

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