

UNITED STATES PATENT OFFICE

2,673,148

ALKALINE PULPING USING GASEOUS OXYGEN

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No Drawing. Application October 4, 1950,
Serial No. 188,487

6 Claims. (Cl. 92-9)

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This invention relates to a pulping process for cellulosic raw materials. More particularly, the invention is a pulping process wherein high yields of substantially pure holocellulose are obtained and wherein the ligneous and resinous materials present in the cellulosic raw material may be simultaneously recovered in a commercially valuable form.

Cellulose is found in nature associated with noncellulosic carbohydrate materials, lignin, resins, fatty acids, and various other impurities. The naturally occurring mixture of cellulose and carbohydrates, or hemicellulose, is called holocellulose. Many different pulping processes have been proposed and used in the removal of the lignin, resins, and other impurities from these naturally occurring cellulosic raw materials. Most of the methods known result in considerable attack on the cellulose itself and in the extraction of the carbohydrate materials normally associated with the cellulose. Some of the processes are reasonably effective in removing lignin, but are comparatively ineffective in removing the associated resinous materials. Consequently, the art has continually sought a pulping process which is more specific in its removal of lignin and resins and which solubilizes less of the hemicellulose during the digestion procedure.

An object of the present invention, therefore, is a process by which ligneous and resinous materials can be substantially completely removed from raw cellulosic materials.

A further object of the invention is a process for pulping raw cellulosic materials which gives a high yield of substantially pure holocellulose.

An additional object of the invention is a pulping process in which it is possible to obtain simultaneously high yields of substantially pure holocellulose and recover the ligneous and resinous materials in a commercially valuable form.

Generally described, the present invention is a process for simultaneously pulping cellulosic raw materials and removing the impurities therefrom which comprises digesting the cellulosic raw material in an aqueous medium maintained at a pH of from 7 to 9; said digestion being conducted at a temperature of from 125°-175° C. in an atmosphere of pressurized oxygen-carrying gas, said oxygen-carrying gas having, at reaction temperature, a partial oxygen pressure of at least 800 p. s. i. If pure oxygen is employed, the minimum pressure at reaction temperature is 800 p. s. i. If an oxygen-carrying gas such as air is employed, then a pressure must be em-

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ployed which will result in a partial oxygen pressure of at least 800 p. s. i. at reaction temperature. According to the preferred embodiment of the invention, the digestion is carried out at a pH of from 7 to 7.5, at a temperature of about 140° C., and in an atmosphere of pure oxygen at a pressure of 1000-1100 p. s. i. The preferred alkaline reagent is sodium bicarbonate.

No reagent penetration period is necessary to prevent degradation of the cellulose or hemicellulose in the process of the invention although minor improvements in yield may possibly result with a few raw materials. As will be seen, the unbleached pulp from the present process is comparable in strength to bleached sulfite pulps. The pulp obtained from the process of the invention may be bleached by conventional processes to produce a pulp of superior characteristics.

As will be seen from the subsequently presented examples, it has been found that several elements of the process in accordance with the invention are essential to operability. In the first place, substantially no pulping is obtained if, during the reaction, the pH of the medium is below 7; i. e., if the reaction medium is acid, unless very high temperatures are employed for long periods of time. However, the pulp thus obtained is too degraded to be of any value. Pulping is obtained at all pH's above 7 but the reaction becomes more drastic with higher pH's until at pH's of over 9, the oxygen used in the reaction attacks the cellulose and other carbohydrate materials as well as the lignin and resins. The result is that highly degraded celluloses are obtained in poor yields if the pH is over about 9. In fact, if the pH is raised substantially above 9, it is possible to solubilize wood and other cellulosic raw materials completely on treatment with oxygen under the conditions of pressure and temperature employed in the process of the invention. Furthermore, the pH must not only be within the range of 7 to 9 at the beginning of the operation, but must be maintained on the alkaline side substantially throughout the cook in spite of the formation of acidic materials by the oxidative degradation of the lignin. It will be appreciated that if the end pH of the reaction liquor is only very slightly on the acid side; e. g., in the order of 6.8 or 6.9, the reaction medium has been alkaline for substantially the entire cook in accordance with the invention. However, the reaction liquid must be substantially neutral at the end of the reaction so that the cook is not conducted under acid conditions for any substantial period. A buffering agent must,

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therefore, be present or a similar buffering action must be obtained by the continuous addition of an alkaline agent to maintain the pH within the necessary range. In general, the salts of a strong base and a weak acid are preferred when used so that the reaction solution has a pH of between 7 and 9. Such substances include sodium bicarbonate, sodium tetraborate, sodium benzoate, sodium hydrosulfide, sodium phenolate, sodium acid tellurate, and sodium monohydrogen orthophosphate. Alkali metal salts of the weak acids are preferred. Pulping can be obtained when alkaline earth metal salts and higher valence metal salts are used, but because these metals form insoluble salts with constituents of the solubilized lignin and other noncellulosic materials and because these salts are difficult to remove from the resulting pulp, the use of such alkaline earth and other higher valence metals is undesirable except when certain special pulps are needed.

In order to obtain pulping, it is also essential that gaseous and dissolved oxygen be present. The oxygen may be in a pure state or in physical admixture with another gas as in the case of air. Substantially pure oxygen is preferred. The oxygen or oxygen-carrying gas should be introduced into the reaction vessel at a pressure which will result in a partial oxygen pressure of at least 800 p. s. i. at temperature. If the necessary pressure is not employed, the reaction rate is lowered to a point where the time necessary for pulping is undesirably increased. Under these conditions, the pulp is maintained at a high temperature for such an extended period that a degraded product is obtained. Consequently, if the pressurized oxygen or oxygen-carrying gas is admitted to the digester prior to raising the temperature, the gas should have a partial oxygen pressure of about 500 p. s. i.

The temperature of the reaction must be maintained between 125° C. and 175° C. Below 125° C., the reaction rate is too low and poor yields of degraded pulp are obtained. Above 170° C., a highly degraded pulp is obtained. The reaction time of the process of the invention is from about 2 to about 5 hours as compared with a minimum of about 8 hours for any known process resulting in acceptable yields of high-grade pulp.

The reaction rate is also affected by the degree of agitation employed. Faster reaction times are obtained with increases in agitation efficiency. Satisfactory agitation may be obtained by mechanical means or by liquor circulation.

The amount of water employed is not critical but is governed by practical considerations. Enough water must be employed, of course, to produce a workable slurry. The use of an excessive amount above this point necessitates the use of larger reaction vessels for a given charge and complicates the recovery of the reaction products and reagents. It is preferred, therefore, that water to raw cellulosic material ratios be kept between 6:1 and 20:1.

Having generally described the invention, the following examples are given for purposes of illustration.

EXAMPLE 1

Three hundred g. (dry weight) of solvent-extracted pine stump shreds, 150 g. of sodium bicarbonate, and 6 liters of water were placed in an autoclave and oxygen was introduced until a pressure of 750 lbs. was reached. The contents

of the autoclave were agitated and heated to a temperature of 140° C. over a period of one hour. The pressure within the autoclave at 140° C. was about 1000 p. s. i. At the end of 3 hours, during which time the contents of the autoclave were continuously agitated and maintained at 140° C., the contents of the autoclave were cooled to 70° C. The end pH of the reaction solution was 7.2. The resulting suspension was filtered. One hundred forty-eight g. (dry weight) of pulp was obtained for a yield of 49.5%. The pulp exhibited the following characteristics:

A. C. S. viscosity (5%)	-----sec----	693
α -Cellulose	-----percent----	82.4
Hemicellulose (soda soluble)	-----do-----	40.0
Pentosans	-----do-----	3.2
Lignin	-----do-----	1.3
Gums and resins (alcohol-benzene extraction)	-----percent----	0.14

EXAMPLE 2

Fifty g. (dry weight) of solvent-extracted pine stump shreds, 12.5 g. of sodium bicarbonate, and 1 liter of water were placed into an autoclave and sufficient oxygen was introduced to give a pressure of 1000 p. s. i. at a temperature of 175° C. The contents of the autoclave were maintained at 175° C. with agitation for a period of ½ hour. The end pH of the reaction solution was 4.8. When the resulting suspension was filtered, a 38% yield of very highly degraded pulp was obtained which had the following characteristics:

A. C. S. viscosity (5%)	-----sec----	2
α -Cellulose	-----percent----	53.5
Pentosans	-----do-----	6.2
Lignin	-----do-----	0.5

EXAMPLE 3

Three hundred g. (dry weight) of spruce chips, 150 g. of sodium bicarbonate, and 6 liters of water were introduced into an autoclave. The procedure of Example 1 was repeated except that the contents of the autoclave were maintained at 140° C. for 4 hours instead of 3 hours. The end pH of the reaction solution was 7.0. One hundred eighty-one g. (dry weight) of pulp was obtained for a yield of 60%. The pulp exhibited the following characteristics:

A. C. S. viscosity (5%)	-----sec----	977
α -Cellulose	-----percent----	81.4
Hemicellulose (soda soluble)	-----do-----	36.2
Pentosans	-----do-----	5.8
Lignin	-----do-----	1.5
Gums and resins (alcohol-benzene extraction)	-----percent----	0.07

EXAMPLE 4

Three hundred g. (dry weight) of spruce chips, 100 g. of sodium bicarbonate, and 6 liters of water were introduced into an autoclave. The procedure of Example 1 was repeated, the period of cooking at a temperature of 150° C. being 3 hours. The reaction solution at the end of the cook was substantially neutral, having an end pH of 6.8. A somewhat degraded pulp was obtained in 30% yield and had the following characteristics:

A. C. S. (viscosity (5%))	-----sec----	417
α -Cellulose	-----percent----	75
Hemicellulose (soda soluble)	-----do-----	35
Pentosans	-----do-----	4.8
Lignin	-----do-----	1.1
Gums and resins (alcohol-benzene extraction)	-----percent----	0.9

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Similar runs were then made using lower concentrations of sodium bicarbonate to give a pH on the acid side. In each case, unreacted wood was recovered showing incomplete reaction. As illustrated in Example 2, higher temperature cooks under acid conditions give almost completely degraded pulps.

EXAMPLE 5

Three hundred g. (dry weight) of aspen chips, 150 g. of sodium bicarbonate, and 6 liters of water were introduced into an autoclave. The procedure of Example 1 was repeated except that the reaction time at 140° C. was 4 hours. The end pH of the reaction solution was 7.1. One hundred seventy-eight g. (dry weight) of pulp was obtained for a yield of 59%. The pulp exhibited the following characteristics:

A. C. S. viscosity (5%)	-----sec	1833
α -Cellulose	-----per cent	79.7
Hemicellulose (soda soluble)	-----do	30.5
Pentosans	-----do	18.5
Lignin	-----do	0.9
Gums and resins (alcohol-benzene extraction)	-----per cent	0.17

EXAMPLE 6

Fifty g. (dry weight) of aspen chips, 25 g. of sodium bicarbonate, and 500 cc. of water were charged into an autoclave and cooked for 2 hours at a temperature of 150° C. and under an oxygen pressure of 800 p. s. i. The end pH of the reaction solution was 8.90. A partially degraded but acceptable pulp was obtained in 50% yield which had an A. C. S. viscosity (5%) of 212 seconds.

In a similar run with pine chips in which aqueous sodium hydroxide was employed to give a pH of 9.3, the charge was almost completely dissolved. Only an 18% yield of very highly degraded pulp was obtained.

EXAMPLE 7

Three hundred g. (dry weight) of spruce chips, 150 g. of sodium bicarbonate, and 3 liters of water were charged into an autoclave and cooked with agitation for 4 hours at 120° C. and under an oxygen pressure of 1000 p. s. i. The end pH of the reaction solution was 7.4. At the end of this time, only a small amount of pulp had been produced. Longer reaction time under these conditions resulted in greater yields but with undesirable degradation of the pulp. When the temperature was raised, increased yields of good quality pulp were obtained in normal reaction times.

EXAMPLE 8

Fifty g. (dry weight) of spruce chips, 25 g. of sodium bicarbonate, and 500 cc. of water were charged into an autoclave and cooked for 2 hours at a temperature of 175° C. under an oxygen pressure of 1000 p. s. i. The end pH of the reaction solution was 7.7. A 37% yield of partially degraded but acceptable pulp was obtained which had an A. C. S. viscosity (5%) of 70 seconds and an α -cellulose content of 59%. The use of a longer reaction time at 175° C. or the use of higher temperatures for the same period resulted in a highly degraded pulp.

EXAMPLE 9

Three hundred g. (dry weight) of solvent-extracted pine stump shreds, 150 g. of sodium bi-

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carbonate, and 3 liters of water were charged into an autoclave and cooked for 3 hours at a temperature of 140° C. and under an oxygen pressure of 800 p. s. i. A somewhat degraded but satisfactory pulp was obtained in 55% yield which had an A. C. S. viscosity (5%) of 385 seconds).

EXAMPLE 10

The run described in Example 9 was repeated under identical conditions except for employing an oxygen pressure at temperature of only 500 p. s. i. A 5% yield of partially degraded pulp was obtained which had an A. C. S. viscosity (5%) of 220 seconds. A much longer reaction time under these conditions increases the yield somewhat but results in a highly degraded pulp.

EXAMPLE 11

Three hundred g. (dry weight) of spruce chips, 300 g. of sodium tetraborate, and 3 liters of water were introduced into an autoclave. The procedure of Example 1 was repeated with the exception that the time of reaction at 140° C. was 4 hours. The end pH of the reaction solution was 7.2. One hundred seventy g. (dry weight) of pulp was obtained for a yield of 57%. The pulp exhibited the following characteristics:

A. C. S. viscosity (5%)	-----sec	461
α -Cellulose	-----per cent	72
Hemicellulose (soda soluble)	-----do	38
Pentosans	-----do	5.9
Lignin	-----do	2.0
Gums and resins (alcohol-benzene extraction)	-----per cent	0.14

EXAMPLE 12

Three hundred g. (dry weight) of spruce chips, 320 g. of sodium monohydrogen orthophosphate, and 3 liters of water were introduced into an autoclave. The procedure of Example 1 was repeated except that the reaction time at 140° C. was 4 hours. The end pH of the reaction solution was 6.8. One hundred seventy g. of pulp was obtained for a yield of 57%. The pulp exhibited the following characteristics:

A. C. S. viscosity (5%)	-----sec	570
α -Cellulose	-----per cent	72
Hemicellulose (soda soluble)	-----do	39.8
Pentosans	-----do	5.6
Lignin	-----do	1.4
Gums and resins (alcohol-benzene extraction)	-----per cent	0.08

EXAMPLE 13

Handsheets were prepared from unbleached pulps produced in accordance with the invention and compared with sheets prepared from Burgess bleached sulfite pulps produced from similar raw materials. The sheets compared were made from pulps beaten to a comparable freeness. The sheets made from the pulp produced according to the invention were found to possess superior dry burst and tensile strengths. Their dry tear strength was somewhat lower than the dry tear strength of the sheets prepared from the Burgess bleached sulfite pulp but was relatively high for a paper having such extremely high bursting and tensile strengths. The results of these tests are set forth in Table I. Basis weights were 40 lb.±1.0. All tests were conducted in accordance with TAPPI specifications.

Table I

Designation	Freeness cc. S.-R.	Burst (lb./ sq. in.)	Dry Tear (g./sheet)	Dry Tensile (lb./in.)	Air Re- sistance (sec./100 cc./sq. in.)
Burgess bleached sulfite...	840	14.9	78.6	13.8	4
Alkaline oxidation pulp...	840	28.1	51.4	21.8	4
Burgess bleached sulfite...	400	23.0	40.1	26.8	700
Alkaline oxidation pulp...	350	37.5	41.5	32.7	930
Burgess bleached sulfite...	300	22.0	---	26.0	1,492
Do.	160	---	27.4	25.5	---
Alkaline oxidation pulp...	160	31.8	23.9	30.1	16 hrs. +

¹ Contained 3% K gum size (sodium salt of K gum resin).

EXAMPLE 14

Aspen pulp prepared by the process of this invention was bleached in a three-stage process consisting of the following steps: (a) chlorination with 2.3% chlorine based on pulp weight at pH 2.0 and a consistency of 3.0% for 0.5 hour at 24° C., (b) extraction with 0.25% sodium hydroxide at a consistency of 10% for one hour at 96° C., (c) alkaline bleach with 1.0% chlorine (hypochlorite at pH 9.8) in 10% consistency for one hour at 55° C. The bleached pulp was a bright white and was characterized by an Excitation Purity of 3.3% and a dominant wave length of 576.5 millimicrons with respect to Illuminant C.

The bleached pulp was refined as follows: It was treated with 11.1% sodium hydroxide at a consistency of 10% for 2 hours at 0° C. The product had an α -cellulose content of 92.8%. The yield of this product is 29% on the aspen chips, 52% on the unbleached pulp, and 54% on the bleached pulp.

EXAMPLE 15

Samples were taken from the reaction liquors obtained in the pulping of softwoods and hardwoods by the alkaline oxidation process of the invention. The individual samples were partially evaporated and then acidified to precipitate the ligneous and resinous compounds solubilized in the particular process. These materials were analyzed with the following results:

Table II

	Alkaline Oxidation		Sulfate, Softwood
	Softwood	Hardwood	
Acid No.	444.0	111.0	90.0
Methoxyl, percent	1.8	13.5	13.1
Hydroxyl, percent	19.0	16.0	3.2
Hydroxyl corrected for acid number	6.0	12.0	0.5
Molecular wt.	190.0	500.0	840.0+
Solubilities in:			
Acetone	Soluble	Soluble	Insoluble.
Methanol	Partially soluble	Partially soluble	Do.
Chlorinated hydrocarbons (CH ₂ Cl ₂), (CHCl ₃), (CCl ₄)	Soluble	Soluble	Do.
Dilute alkali	do	do	Soluble.
Hydrocarbons (aliphatic and aromatic)	Insoluble	Insoluble	Insoluble.

¹ Although it is accepted that the insolubility of the ligneous compounds which are by-products of the various pulping processes is due to their high molecular weights, there are no definite molecular weight values available. It is widely believed, however, the molecular weight of the basic lignin building unit is about 840.

From the foregoing examples, it is seen that high yields of substantially lignin-free holocellulose may be obtained by treating cellulosic raw materials in accordance with the invention. Furthermore, it is apparent from the data in Table II that the lignin and resins recovered from the liquors of the process of the invention are in a form quite different from that recovered from the liquors of prior processes such as the sulfate process. The acidity of the materials recovered from the alkaline oxidation liquor is due

to the carboxylic acid groups produced on oxidative degradation of the lignin molecule. The acidity of the ligneous substances recovered from sulfite liquors is due to some phenolic acidity and the sulfo groups introduced into the large, undegraded lignin molecule. The acidity of the ligneous material in the sulfate liquor is entirely due to phenolic acidity. In all cases, the alkaline oxidation process of the invention produces more highly acidic and more highly hydroxylic solubilized noncellulosic material of greatly decreased molecular weight. As illustrated, this decreased molecular weight results in solubility characteristics which give the materials commercial value.

The uses to which the solubilized materials recovered from the alkaline oxidation liquor can be put are mainly due to the greatly enhanced solubility, high acidity, and high alcoholic hydroxyl content. Complete esterification with low molecular weight acids and alcohols produces low melting substances usable as plasticizers. Inter-molecular condensation with polyhydroxy and polycarboxylic materials results in high melting resins usable in protective coating finishes of all sorts where color is not a factor.

The solubilized materials in the alkaline oxidation reaction liquor may be recovered in a number of ways. The resins and lignin are present in the liquor as soluble salts and are most easily recovered by partial evaporation and acidification as illustrated in Example 15. It is also possible

to pass the liquor through ion-exchange resins to remove the cation, then concentrate the liquor and acidify to precipitate. In this way, both the lignin-resin mixture and the cation can be recovered.

It is a particular feature of the invention that any cellulose-containing material may be treated regardless of the lignin or resin content. Such materials include softwoods, semihardwoods, hardwoods, bamboo, straw, hemp, jute, and flax seed.

Since modifications within the scope of the present invention will become apparent to those skilled in the art, it is intended that the invention be limited only by the scope of the appended claims.

What I claim and desire to protect by Letters Patent is:

1. In the process for the production of substantially lignin-free holocellulose from cellulosic raw material by pulping the material, under pressure, with alkaline solution and in the presence of an oxidizing material at elevated temperature, the improvement comprising pulping the said material with an alkaline solution of at least one material of the group consisting of sodium bicarbonate, sodium tetraborate, sodium benzoate, sodium hydrosulfide, sodium phenolate, sodium acid tellurate, and sodium monohydrogen orthophosphate at a temperature between 125° and 175° C. for a period from about 2 to about 5 hours in the presence of at least one oxidizing material of the group consisting of substantially pure oxygen and air having a partial oxygen pressure of at least 800 pounds per square inch while maintaining the alkaline solution at a pH of between 7 and 9 throughout said pulping, whereby a high yield of the substantially lignin-free holocellulose is obtained and the lignin and resins recovered from said solution have low molecular weight and good solubility characteristics.

2. The process in accordance with claim 1 in which the oxidizing material essentially consists of substantially pure oxygen.

3. The process in accordance with claim 1 in which the oxidizing material essentially consists of air.

4. The process in accordance with claim 1 in

which the alkaline solution essentially consists of sodium bicarbonate.

5. The process in accordance with claim 1 in which the alkaline solution essentially consists of sodium tetraborate.

6. The process in accordance with claim 1 in which the alkaline solution essentially consists of sodium monohydrogen orthophosphate.

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References Cited in the file of this patent UNITED STATES PATENTS

Number	Name	Date
21,077	Lyman	Aug. 3, 1858
1,831,032	Richter	Nov. 10, 1931
1,902,916	Strecker	Mar. 28, 1933
1,996,797	Dreyfus	Apr. 9, 1935
2,022,654	Dreyfus	Dec. 3, 1935
2,234,188	Morgan	Mar. 11, 1941
2,243,050	Plant	May 20, 1941
2,516,827	Marshall et al.	July 25, 1950
2,538,742	Willey	Jan. 16, 1951

FOREIGN PATENTS

Number	Country	Date
312,618	Germany	May 31, 1919
185,421	Great Britain	1924
238,305	Great Britain	Aug. 17, 1925
284,846	Great Britain	Feb. 9, 1928
271,524	Great Britain	Mar. 29, 1928
559,405	Germany	Sept. 20, 1932
815,651	France	July 20, 1937

OTHER REFERENCES

Ser. No. 318,386, Freudenberg et al. (A. P. C.), published April 20, 1943.