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2,904,460

CONTINUOUS PULPING PROCESS

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This invention relates to the production of purified cellulosic pulp from wood chips and related ligno-cellulose materials for the manufacture of paper, synthetic fibers and the like.

It is a particular object of the invention to provide a method of producing wood pulp by a rapid continuous process.

A further object is the production of pulps from ligno-cellulose materials in high yield and in substantially short reaction times.

Another object of the invention is the production of cellulosic pulp having a high alpha cellulose content which is useful for the manufacture of rayon, cellophane and the like products.

A further object of the invention is the provision of such a process that is readily adaptable for the processing of various types of ligno-cellulose materials and wherein effective control is obtainable as to the yield and composition of the resultant pulp.

In the past it has been the common practice in the pulping industry to allow the reacting chemical agents to slowly penetrate into the wood chips for an hour or more at substantially low temperatures and concentrations in order to accomplish delignification without the destruction of a substantial portion of the cellulose materials. It has been customary to use a relatively low proportion of chemical to wood so that, by the time maximum reaction temperature has been reached, chemical concentration has been reduced sharply because of chemical consumed by the slow reaction during the warm-up period. Under these conditions, two to four hours of cooking time are required to delignify the chips sufficiently for paper making purposes.

When the warm-up period was eliminated, the reaction beginning at maximum cooking temperature, and sufficient chemical was used to insure sustained concentration, it was found that the speed of reaction was greatly increased but the outer portion of standard size chips were over-cooked while the chip centers were uncooked. The cellulose fibers in the outer portion of the chips were degraded from overexposure to the drastic cooking conditions while the fibers in the center of the chips were still encased in their protective lignin.

It has been found that the pulping reaction occurs substantially at the solid-liquid interface, and that the solid surface will vary from 100% wood at the beginning of the pulping reaction to a variable surface which is part wood and part cellulose fibers as the reaction progresses. As more wood surface per unit weight of wood is exposed to the initial action of the cooking chemical, more drastic cooking conditions can be employed because of decreased time of contact between cellulose and chemicals. The increased wood surface decreases the distance between the fibers at the outer portion of the wood particle and those at the center. Thus, the path which the reaction must follow is reduced and, consequently, the time during which the purified outer cellulose fibers can be degraded is shortened.

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However, there is a limit to which this surface expansion can be employed, if the initial physical strength of the cellulose fibers is to be retained for paper making purposes. If attempts are made to expand the wood surface to the point of complete fibrillation, as described in Asplund Patent No. 2,388,592, Offermanns Patent No. 2,164,040, Mason Patent No. 1,872,996, Walter Patent No. 2,454,532, Olsen Patent No. 1,979,341, and Australian Patent No. 12,149—Asplund, a high percentage of wood fibers are torn or broken, resulting in reduced strength of the purified cellulose. In addition, complete fibrillation requires the use of unnecessarily large amounts of power to effect the size reduction. I have found that fibrillation is not necessary in the use of high speed reaction under drastic pulping conditions, in fact such fibrillation should be avoided for efficient operation.

Sufficient increase in wood surface can be obtained by taking advantage of the mechanical weakness in the grain direction of ligno-cellulose materials. Mechanical forces can be applied so that the chips will split in the grain direction only. Cross-grain breakage is avoided by a presteaming operation which softens the chip to a leathery condition, resulting in bending rather than breaking when forces are applied. The presteaming operation leaves the chips in a leathery condition even when cold, permitting size reduction either at the presteaming temperature or at any temperature down to room temperature. It is quite important, in mechanical treatment, that the wood fragments remain, as far as possible, as long in the grain direction as the original chip. I have found that the optimum cross-section at right angles to the grain is between 2.3 and 4.7 mm. diameter, corresponding to the openings in 8 and 4 mesh standard screens. Material smaller in cross-section than that specified will, when converted to cellulose pulp, be low in physical strength because of fiber breakage during surface expansion. Woody material larger in cross-section than the specified range presents too great a length of travel for the reaction and results in degradation of cellulose.

Generally, the process of the invention for producing purified cellulosic material in substantially short reaction times comprises the following steps:

- (1) Softening the lignin in the material to be pulped;
- (2) Expanding the surface area of the softened material without appreciable breakage of the cellulose fibers;
- (3) Reacting the expanded ligno-cellulose material with cooking chemicals at substantially constant temperature and concentration throughout the cooking period.

The first step of the invention may be carried out by several different methods: the material may be subjected to the action of hot water at atmospheric pressure, the material may be steamed at high temperature for short periods of time, or a combination of high temperature steam and very dilute alkali may be used. It has been found that high temperature steaming will put the material in the best condition for obtaining optimum size reduction and the highest yields of correctly sized material. If the steaming treatment is carried out under slightly alkaline conditions acid hydrolysis of the ligno-cellulose material is prevented. The alkali is used primarily for the neutralization of woody acids released during steaming rather than for any pulping property of the alkali. The addition of small amounts of Na_2CO_3 to keep the pH of the treating fluid above 7.0 has been found to give very satisfactory results.

In the second step of the invention, that of surface expansion, mechanical disintegration such as hammer mills, attrition mills or crushing rolls may be used. If a hammer mill is used, the size of opening in the discharge screen is critical. Openings which are too small will result in excessive breakage across the grain while

openings which are too large will result in too much oversize material. The clearance between plates of an attrition mill is critical for the same reason. If crushing rolls are used, the pressure applied to the rolls and speed of the rolls should be adjusted so that excessive shear will not be induced, causing fiber breakage during size reduction. In the selection of a mechanical disintegrator care should be exercised to select a machine which will give the highest percentage of material in the optimum size range with a minimum of both oversize material and undersize particles which have suffered fiber damage.

Very satisfactory results have been obtained by passing steam-softened chips through a Sturtevant swing-hammer mill provided with a 1/2 in. expanded metal discharge screen through which the shredded chips must pass before leaving the hammer mill. The shredded material usually has a broomed-out appearance at the ends, which is an advantage because of increased wood surface. It is evident that other methods of mechanically shredding may be advantageously used in this step of the process as long as the surface area of the woody material is substantially increased without substantial reduction in the length of the cellulose fibers.

In the third step of the process of the invention, the softened and expanded ligno-cellulose material is rapidly purified at high and substantially constant temperatures, preferably in the range of about 300° to about 400° F., with alkaline cooking liquors, maintained at substantially constant concentration. These extremely rapid reaction rates are due to the facts that the expanded ligno-cellulose material is mixed with the chemical pulping solution at substantially the maximum desired temperature and that the concentration of chemicals in the pulping solution is maintained substantially constant, particularly during the first half of the cook. If standard size chips were subjected to this chemical process the resultant pulp would be extremely low in yield, high in screenings, and with a high degree of cellulose degradation.

I have found, in studying the effect of concentration of cooking liquor on the pulping reaction, that the numerical value of this concentration controls the quality of the resultant pulp. For example, when either NaOH or a mixture of NaOH and Na₂S is used as the active pulping chemical, a concentration of about 70 to about 100 gm. per liter (expressed as Na₂O) will result in a pulp of very low hemicellulose content. Such pulps are well suited for raw material for rayon, cellulose films, nitrocellulose etc. Heretofore, such a product has not been successfully produced by alkaline pulping without the aid of acid hydrolysis prior to the pulping reaction. If the concentration of the cooking liquor is held at a low level, about 20 to about 35 gm. per liter, the product will be high in hemicellulose and suitable for use in high strength papers. Any desired lignin content in the pulp may be obtained by adjustment of cooking temperature and time. Thus pulps of any desired combination of lignin, cellulose and hemicellulose content may be produced by this process.

The need for maintaining concentration of pulping chemical in the liquor is particularly important in the first half of the cook. In the latter stages of the process, concentration can be allowed to decrease in a controlled manner in order to increase yield of pulp.

When a mixture of Na₂SO₃ and Na₂CO₃ is substituted for either NaOH or NaOH and Na₂S, this effect of concentration is not nearly as important to the reaction. Here the cooking temperature and time are most important. Use of this chemical combination on expanded ligno-cellulose material with properly controlled temperature results in very high quality semi-chemical pulps of high yield in very short reaction time.

The following is a detailed description of a continuous pulping operation in accordance with the principles of

the invention as applied to turkey oak (*Quercus laevis*) chips.

I. Softening operation

2000 grams of oak chips of standard pulping size are mixed with 4 liters of a water solution of Na₂CO₃, containing 9 grams of Na₂CO₃ per liter, at a temperature of 365° F. and steam pressure of 148 pounds per square inch. The mixture is maintained at this pressure for 10 minutes. The pH of the solution immediately before releasing the pressure is about 8.5.

It has been found that under these conditions about 94 percent of the oak chips are recovered as softened material readily adapted to surface expansion by splitting along the grain. Substantially the same high yields may be obtained by using higher pressures and a correspondingly shorter reaction time or lower pressures and longer reaction times.

II. Mechanical expansion of the softened chips

The softened oak from step I are passed once through a mechanical swing-hammer mill provided with a 1/2 inch expanded metal discharge screen. A satisfactory screen analysis of the product from the hammer mill is as follows:

Screen size	+2 mesh	-2+4 mesh	-4+10 mesh	-10 mesh
Percent of product	19	39	30	12

Any adjustment of milling conditions which will reduce the percent of the product held on 2 mesh or passing through 10 mesh will increase the efficiency of the overall process.

III. Chemical pulping

The expanded chips are treated for 15 minutes at 347° F. with a cooking liquor comprising NaOH and Na₂S in water. The concentration of the solution is 80 grams per liter of solution, expressed as Na₂O, having a sulphidity of 25 percent. Throughout the cooking period heat and concentrated pulping liquor are added to the reactor to maintain the temperature and concentration of the mixture substantially constant. At the end of 15 minutes the pressure on the cook is immediately reduced to atmospheric.

It has been found that under these conditions the resulting cellulosic material consists of about 42 percent of the original oak chips and contains about 93.5 percent alpha cellulose, 3.5 percent lignin and 2.9 percent hemicellulose. This pulp is well suited for dissolving purposes.

When pine is substituted for oak and cooking conditions are 20 grams per liter concentration, 75° F. temperature and about 20 minutes cooking time, yield of pulp is about 51 percent of the original chips and the pulp contains about 9 percent lignin, 8 percent hemicellulose and 83 percent alpha cellulose. This pulp has very good strength characteristics and is particularly suited for wrapping papers of very high tearing strength.

From the foregoing description it will be evident that many variations in the process of the invention are possible, only a limited number of which have been shown by way of example. It will be evident to those skilled in the art that variations in temperature time and concentration of chemical may be used to effect changes in purity and yield of cellulosic material and grade of pulp. For example, the mixture of NaOH and Na₂S in the chemical solution may be varied from 100 percent NaOH to as high as 50 percent Na₂S, and other alkaline compositions such as mixtures of Na₂SO₃ and Na₂CO₃ may be used to produce pulps with varying characteristics with very satisfactory results in the process of the invention. In brief, very many cooking liquors of an alkaline nature may be formulated which will accomplish the purposes indicated.

This application is a continuation-in-part of my applica-

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tion Serial No. 236,453, filed July 12, 1951, now abandoned.

I claim:

1. A process for pulping wood chips comprising sub-
jecting the wood chips to be pulped to an alkaline solu-
tion having a pH of about 8 at an elevated temper-
ature and pressure for relatively short periods of time
to soften the lignin of the wood to permit subdivision
thereof in the fiber direction, subjecting the softened wood
to a mechanical shredding action to expand the surface
area of the wood normal to the fiber direction into chip-
length splinters having a cross-sectional dimension of
from about 2.3 to about 4.7 mm., and then subjecting the
splinters to a delignification treatment of the cellulosic
material by the action of a solution of sodium hydroxide
and sodium sulfide at substantially constant concentration
at a temperature of from about 300° to about 400° F.

2. The invention defined in claim 1 wherein the con-
centration of the alkaline solution is maintained substan-
tially at about 70 to about 100 grams per liter expressed
as Na₂O to provide a substantially lignin free pulp having
a low hemi-cellulose content.

3. The invention defined in claim 1 wherein the con-
centration of the alkaline solution is maintained from

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about 20 to about 35 grams per liter expressed as Na₂O
to provide a substantially lignin free pulp high in hemi-
cellulose content.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,904,460

September 15, 1959

William J. Nolan

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, lines 52 and 53, for "75° F. temperature" read -- 375° F. temperature --.

Signed and sealed this 22nd day of March 1960.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

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