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PROCESS FOR PULPING

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This application is made under the act of March 3, 1883, as amended by the act of April 30, 1928, and the invention herein described, if patented in any country, may be manufactured and used by or for the Government of the United States of America for governmental purposes throughout the world without the payment to us of any royalty thereon.

This invention relates to a novel process for manufacturing paper pulp from coarse fiber materials. It has among its objects the provision of a novel mechano-chemical pulping process which can be conducted at atmospheric pressures at reduced operating and equipment cost, at reduced pulping time and with improved quality and uniformity of product.

Coarse fiber material may be defined for the purpose of this invention as cellulosic material of a basic fibrous structure which occurs naturally or has been converted into material consisting substantially of fiber bundles or groups of fiber bundles which have a relatively thin cross section measured perpendicular to the axis of the fiber direction or "grain" of the material. In the case of woody materials the cross-sectional dimension should be less than or of the same order of magnitude as the individual fiber lengths. This limitation on the woody materials is necessary in view of the density or compactness of the woody structure, which in greater thicknesses would tend to restrict or resist the facile impregnation of liquids or liquid chemicals, when employing the process of this invention. Examples of coarse fiber material in accordance with this invention are such non-woody materials as straw, flax and hemp tow, cotton, sugar-cane bagasse, cornstalks, jute, reeds, manila and sisal fibers and the like. Included also are coarse fiber materials produced from wood, such as Asplund fiber, McMillan fiber, coarse groundwood fiber, chopped fine excelsior and the like.

Another object is the provision of a combined chemical digestion and mechanical defibering process which results in larger yields of pulp with higher hemicellulose content, requiring less power and equipment for beating and refining. Still another object is to provide a straw pulp substantially free from node or rachis material and seeds, and containing a minimum of fines.

Pulp from straw, flax and hemp tow, cotton, sugar-cane bagasse, cornstalks, jute, reeds, manila and sisal fibers or similar material is usually prepared by pressure pulping methods which involve heating for several hours in the chemical pulping liquor at temperatures substantially above 100° C. and at corresponding steam pressures. These methods are attended by the many hazards and other disadvantages which attend the heating of large volumes of material under considerable pressure for extended periods of time. Even though high quality paper pulp can be made by these methods, they are relatively tedious and costly due to the necessity for pressure equipment and the great amount of labor and time required.

Although it is known that agricultural residues such as straw can be pulped at atmospheric pressure, methods heretofore employed have required relatively large

amounts of chemicals and long cooking or digestion periods.

We have discovered that a large factor in the speed and proper conversion of raw stock to pulp is the rate of diffusion of the liquid containing the active chemical through the pieces of raw material to succeeding inner layers or surfaces. Thus the reaction between a pulping agent and the plant material to be delignified may be considered a topochemical reaction; that is, it takes place mainly at the contact surfaces or interfaces between the solid plant material and the liquid. When the reaction at this point is completed no further substantial action takes place until the reaction products have been removed, thus exposing new surfaces. During the early part of the conventional cooking, such removal may be accomplished by circulation of the liquor past the more or less stationary plant material in a stationary digester, or by the difference in motion of the liquor and plant material, relative to each other, in a tumbling or rotating digester. After the first action on the outside surfaces of the solid material, the reaction products from the reacting surfaces have to be removed, fresh chemical has to be brought to the reacting surfaces. These actions are normally brought about by diffusion, which is a relatively slow process. It is mainly for this reason that the rate of pulping by conventional methods decreases as the cooking progresses.

According to the instant invention a mechano-chemical process for producing pulp is provided. In this process, an undefibered non-woody fiber material, such as straw, bagasse, etc. is subjected to the action of a pulping liquor containing a chemical reagent in solution in a liquid medium, this reagent being capable of digesting the said non-woody fiber material by removing lignin and other encrustants therefrom. The process is carried out at a temperature ranging from about 90° to 100° C. and at atmospheric pressure and under these conditions the pulping liquor is essentially non-hydrolytic. Simultaneously with the foregoing chemical action, the individual pieces of the non-woody fiber material are subjected to vigorous non-cutting impact blows while submerged in the pulping liquor and while they are in a relatively free state, these non-cutting impact blows comprising mechanically-induced cycles of expression and absorption. Each cycle comprises compacting the pieces in an unconfined zone of impact to express liquid, immediately removing said pieces from the zone of impact to a zone of absorption of fresh liquid and returning said pieces containing absorbed liquid to another zone of impact. These blows are continued for from 30 to 60 minutes at which time a substantial proportion of liquor has been removed from the pieces and they have become broken up into individual fibers producing a pulp having a proportion of hemi-celluloses at least as great as that contained in the original non-woody fiber material. Where the non-woody starting material contains nodes, rachises, seeds, and similar materials, the pulp produced by the above-described process may be subjected to a riffling and screening operation to remove such nodes, rachises, etc., from the pulp.

We have utilized our discoveries and have provided a pulping process which involves a simultaneous mechanical and chemical action on the stock during the pulping whereby the rate of diffusion is greatly increased. We accomplish the increase in diffusion rate by mechanical impact upon the liquid-swollen material in a relatively free state while submerged in the liquor. Upon a vigorous blow being struck while submerged in the cooking liquor, the turgid material is compacted, causing some of the liquid to be expressed, as liquid may be squeezed from a sponge, and immediately thrown from the zone of impact. After leaving the zone of impact, the mate-

rial tends to recover its original volume and absorb fresh liquid. Thus, by rapid mechanically induced cycles of expression and absorption, the diffusion of the chemical-containing liquid in and out of the material is speeded up greatly, resulting in astonishingly increased pulping rates, of the order of at least four times that of conventional pressure pulping.

This rapid increase in rate of diffusion can be accomplished by various mechanical means. A rapidly rotating plate fitted with non-cutting vanes submerged to the liquor, or a high-speed propeller stirrer produce satisfactory results. The impact action upon which our invention is based is not to be confused with the shearing or tearing action of the conventional pulp beater, jordan or other conventional refining engines. Moreover, prior methods for producing pulp employing a substantial degree of mechanical action have involved the use of beaters, mixers, paddle wheels, breaker beaters and the like.

In these prior processes, the pieces of material to be pulped are confined mechanically and cut or torn apart by the opposed action of relatively unyielding rubbing, grinding or cutting members or by the internal friction of a high consistency mass. Such action between two surfaces, squeezing and grinding the material, disintegrates the nodes and rachises and/or ruptures and cuts the fibers. In our process the particles are pulped and the cycles of diffusion are induced while in a free floating state in a medium of relatively low consistency, so that when the liquid is expressed from a particle, it immediately absorbs fresh liquid somewhat like the action of some conventional washing machines.

Our novel process is attended by numerous advantages, some of which have been previously mentioned. In addition, we have found that in the case of straw preliminary chopping and the like as a separate step prior to cooking may be eliminated, for whole straw may be fed into the hot liquor and transformed into pulp under our impact action almost as readily as pre-chopped straw. The straws are sufficiently tendered so that they are shredded easily by the action of the submerged impacting.

The nodes and rachises in straw have always been troublesome to the pulpmaker. They do not cook as readily as the culm or stem. The usual pulp beating or refining methods break down these relatively raw nodes and rachises to small particles which are not easily bleached and show up as specks in the final paper, and to the ultimate platelets and cells which slow down paper machine operation. In our process the nodes and rachises are swollen and softened, but not disintegrated, in contrast to results obtained with beaters or conventional refining engines. When our pulping operation is completed these nodes and rachises are substantially free of clinging fibers and can be removed by riffling and screening. Moreover, grain seeds which are normally digested and disintegrated by conventional pulping and refining methods are retained on the riffler and the screen, in a swollen and softened condition. The pulp from our process thus has a somewhat lower lignin content, better bleachability, and fewer specks than a similar pulp defibered in a beater or disc refiner before riffling and screening.

Our mechano-chemical pulping may be accomplished by means of a wide variety of mechanisms capable of producing impact upon the free submerged material pieces, i e., immediately free to move upon being struck a vigorous blow. For convenience, we employ mechanical devices designed for repulping paper, but our invention is not limited thereto.

One of the most important advantages of our process is our ability to produce a satisfactory pulp at atmospheric pressure. This increases the safety and reduces the cost of the process. It also increases the ease of control, since sampling can be done easily and rapidly and the necessary processing controls accomplished more efficiently. The lower temperatures result in a stronger pulp, since it is known that temperatures substantially above 100° C. tend to decrease the length of the cellulose molecular chains, resulting in shorter chains and lower strength. Probably also for the same reasons, higher yields of pulp are obtained by our process. Our pulp also contains a larger proportion of hemicelluloses, such as pentosans, than are present in the original straw. This is due to the mild essentially non-hydrolytic action of the cooking liquor at the lower temperatures. This process comes closer to the ideal pulping process, of removing the lignin with little or no attack on the carbohydrate portion of the straw or other fiber material, than any of the conventional pressure pulping methods.

The temperature of our process may vary within the range of 90° C. to 100° C., preferably 96° C. to 98° C. Lower temperatures may be used, but the action is slower. Slightly higher temperatures can be effected, but are generally unnecessary and, unless measures are taken to confine the vapors, result in excessive steam consumption.

Practically complete defibering, i. e., the separation of the fibers from the nodes and rachises as well as the breaking up of the fiber bundles into the individual fibers is accomplished by our mechano-chemical process. We usually prefer to stop the process as soon as the straw is sufficiently pulped even though a small amount of fiber may still be attached to the nodes and rachises. This affords the advantage of a high-yield, high-quality pulp and avoids any effect of overcooking. If the material is not completely defibered within the pulping period, the final and complete defibering can be accomplished in the same vessel after removal of the pulping chemical, or in any of the well-known equipment used for defibering purposes.

In making fine pulps, equipment for this final defibering should be selected such that the nodes and rachises are not broken up in the defibering process. For example, a second treatment in the mechano-chemical vessel using water alone will accomplish this purpose, for the nodes and rachises will not be broken up or disintegrated, and it is easy to remove them from the pulp. Other defibering equipment which does not break up or cut the nodes and rachises may be used. In the production of coarser pulps, for example, in 9-point corrugating strawboard, where broken nodes and rachises are not necessarily disadvantageous, disc mills, beaters, jordan engines and the like may be used.

The invention is illustrated by the following experiments. In these experiments are described the preparation of strawboard pulp and fine pulp from wheat straw, but our invention is not limited thereto, since it is applicable to any non-woody material, such as straw, flax or hemp tow, cotton, sugar-cane bagassee, cornstalks, jute, reeds, manila and sisal fibers, and the like, and to coarse fiber material produced from wood, such as Asplund fiber, McMillan fiber, fiber produced from wood chips in a disc mill, coarse groundwood fiber, chopped fine excelsior and the like. Moreover, the invention is not to be understood as limited by the particular chemical cooking liquor employed, for our invention is based upon the mechanically induced diffusion of the chemical into and out of the material.

The pulping was carried out in a device consisting of a vessel fitted at the bottom with a rotating plate to which were affixed a plurality of blades so positioned that submerged particles of straw were given a vigorous blow as the plate rotated rapidly. Rotation was started after the addition of the pulping liquor and the straw was added as rapidly as possible. Direct steam was injected to maintain the temperature, and the period for combined digestion and defibering was measured from the time the last of the straw was added. Samples were removed frequently from the vessel during the period and examined visually for degree of pulping. At the end

of the cooking period the pulped straw was removed from the vessel and washed. The fine pulp suitable for bleached paper and board products was screened before it was tested for strength characteristics. Fine straw pulp and strawboard pulp were also prepared by conventional pressure pulping methods to serve as materials for comparative purposes. The tests reported herein were carried out in accordance with TAPPI standards.

In pulping straw for strawboard, the yields of washed pulp produced by our process, requiring one hour's pulping time at 90° to 98° C. were 78 to 79 percent, as compared with 75 to 78 percent for strawboard pulp produced by cooking for 5 hours at 140° C. (40 p. s. i.) using the same amounts of pulping chemical in both types of cooks (6 percent lime and 1.5 percent caustic soda, based on the dry straw). The pH of the black liquor from our process was 11.1 as compared with 8.8 for that of the black liquor from the pressure cook. This indicates less complete exhaustion of the active chemicals in our process.

The pulp made in accordance with our invention had better beating and strength characteristics, particularly bursting strength and tear resistance, than the pressure-cooked pulps. The comparative values for the mechano-chemical and pressure-cooked pulps, respectively, were:

Table I

Type of Pulp	Beating time, min.	Freeness (Schopper-Riegler), ml.	Bursting strength, points/ream pound	Tensile strength, g./ream pound	Tear resistance, g./ream pound	Crush resistance (Riehle), pounds	Apparent density,
Mechano-chemical	45	340	66	131	58	46	0.76
Pressure-cooked	45	345	60	122	47	44	0.62

The somewhat higher apparent density of our pulps indicates better delignification, as compared with the pressure-cooked pulps, and consequently better hydrating and felting characteristics of the resulting fibers. This is corroborated by the chemical analysis of our pulps with 15.6 percent lignin and 30.4 percent pentosans as compared with 17.7 percent lignin and 25.5 percent pentosans for the pressure-cooked pulps. The color of the strawboard pulp was much lighter than that of the pressure-cooked pulp.

For producing fine pulp, runs were made in accordance with our process using as pulping reagents sodium sulfite and the usual kraft chemicals, sodium hydroxide plus sodium sulfide.

The results with strong pulping agents, such as the caustic soda and sodium sulfide of kraft liquor were better than those obtained with neutral sulfite. The neutral sulfite required a considerably longer time to produce pulp from straw. With 12 percent kraft chemicals, based on dry straw, the yield of screened pulp obtained by digesting straw for one-half hour at 98° C. in accordance with our invention was approximately 55 percent, about 8 percent greater than that obtained by cooking for two hours at 170° C. (100 p. s. i.) with the same amounts of chemicals. The beating and strength characteristics of the mechano-chemical and pressure-cooked unbleached kraft pulps, respectively, were very similar;

Table II

Type of Pulp	Beating time, min.	Freeness (Schopper-Riegler), ml.	Bursting strength, points/ream pound	Tensile strength, g./ream pound	Tear resistance, g./ream pound	Apparent density, g./ml.
Mechano-chemical	45	340	101	192	37	0.84
Pressure-cooked kraft (unbleached)	45	370	103	194	38	0.93

The kraft pulp produced according to our invention had a much lighter color than that of the usual pressure-cooked kraft straw pulp.

Decreasing the amount of kraft chemicals used for cooking resulted in increasing the time required to produce a pulp. The ash contents ranging from 1.9 to 3.7 percent with decreasing pulping chemical were lower than the ash of the pressure-cooked pulp (4.9 percent). The concentration of cooking chemical in our process had practically no effect on the pentosan content of the pulps, which were very high, ranging from 32.5 to 33.5 percent. This emphasizes the fact that our process approaches the ideal in pulping—delignification with relatively little action on the carbohydrate portion of the plant material.

Since the cooks of our process are carried out at lower consistencies than those used in pressure cooking, the concentration of organic materials in the black liquors is relatively low. A series of four cooks were made, using 10 percent kraft chemicals for the first cook. The drained liquor from the first cook was re-used in the second cook, more chemical being added to bring the total to 10 percent of the straw. This procedure was repeated twice more. The chemical characteristics of these pulps were quite similar except for the ash content which increased from 1.6 to 2.5 percent with repeated re-use of the waste liquor. Re-use of the black liquor had little or no effect on the yields or strength properties of the pulps.

We claim:

1. A mechano-chemical process for producing pulp comprising subjecting an undefibered non-woody fiber material to the action of a pulping liquor containing a chemical reagent in solution in a liquid medium, said reagent being capable of digesting said material by removing lignin and other encrustants therefrom, at a temperature of about from 90° to 100° C and at about atmospheric pressure, said pulping liquor being essentially non-hydrolytic under said conditions of temperature and pressure, while simultaneously subjecting the individual pieces of said material to vigorous non-cutting impact blows while submerged in the pulping liquor and while they are in a relatively free state, said non-cutting impact blows comprising mechanically-induced cycles of expression and absorption, each cycle comprising compacting the pieces in an unconfined zone of impact to express liquid, immediately removing said pieces from the zone of impact to a zone of absorption of fresh liquid and returning said pieces containing absorbed liquid into another zone of impact, and continuing the said blows for from 30 to 60 minutes at which time a substantial proportion of lignin has been removed from said pieces and they have become broken up into individual fibers producing a pulp wherein the proportion of hemicelluloses is at least as great as that contained in the original non-woody fiber material.

2. The method of claim 1 in which the undefibered non-woody material is straw.

3. The method of claim 1 in which the undefibered non-woody material is bagasse.

4. The method of claim 1 in which the undefibered non-woody material is straw, and wherein the straw pulp produced is subjected to a riffling and screening operation whereby nodes, rachises, seeds, and similar material are removed therefrom.

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