

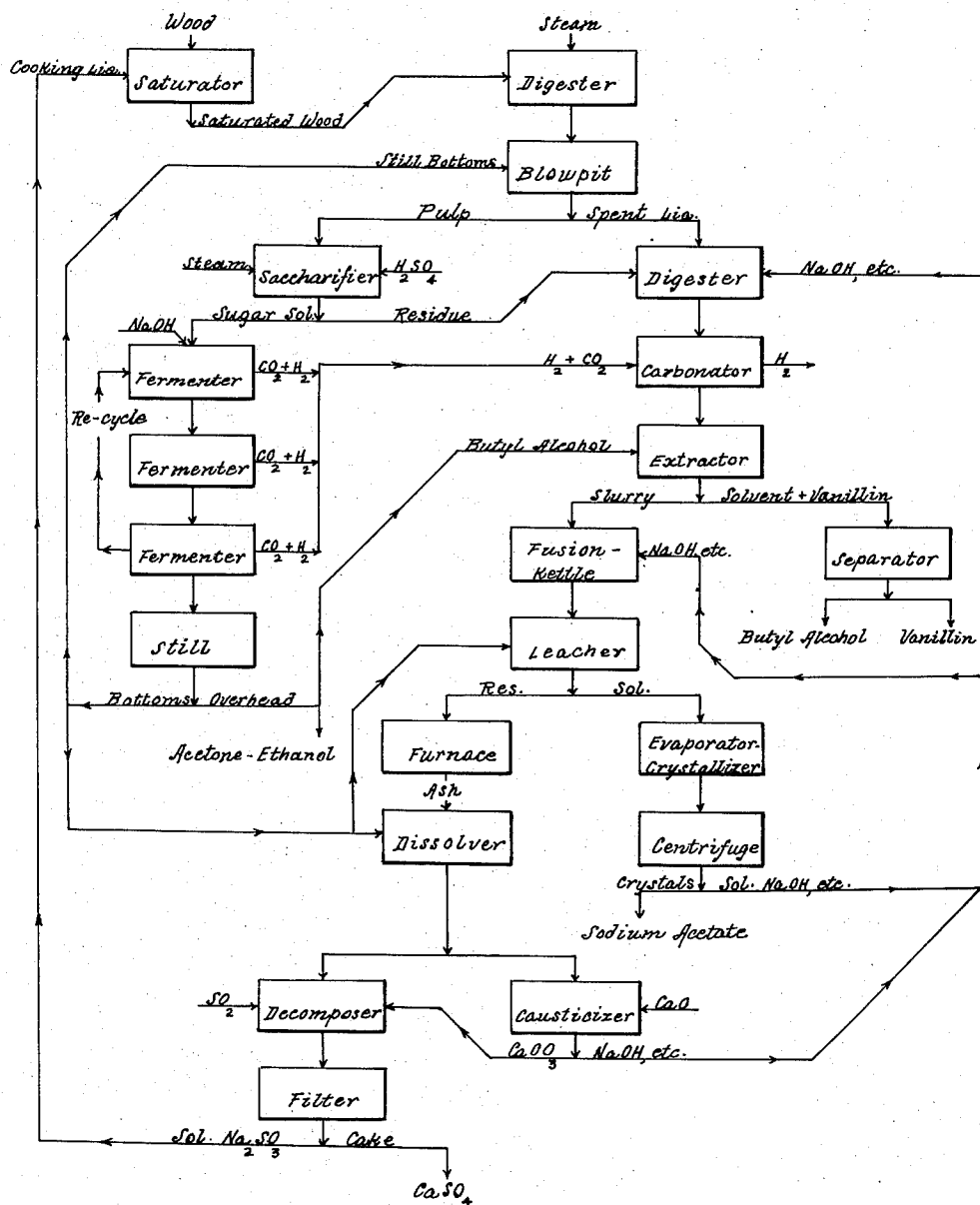
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METHOD OF PROCESSING LIGNIFIED CELLULOSE

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METHOD OF PROCESSING LIGNIFIED CELLULOSE

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The vegetable world furnishes us with substantially unlimited amounts of lignified cellulose. By this term I define the skeleton of most vegetable structures which serves as the support, in part, for softer tissues. While, obviously, it is best represented when used by itself as wood it has many other forms. It is the aim of my process to regard it as raw material for a chemical industry, not merely as structural material or as the source of paper pulp. In the instant case the cellulose will be converted into well known solvents, the methoxyl content of the lignin will appear as vanillin, the acetyl groups associated with both lignin and cellulose will become sodium acetate, and finally most of the chemicals used in effecting such transformations will be recovered for re-use in the process.

I commence with a pulping operation, i.e., I separate the cellulose as completely as possible from the non-cellulose portion and then treat each fraction separately. Of all conventional methods for doing this the best for my purpose is the so-called neutral sulphite cook as this has the least effect upon the cellulose portion. While soda is the base universally employed, potash could be substituted so in the claims, I use the term alkali or alkali metal as indicating either, or a mixture of both.

The best way to describe my process is to follow the drawing in which I have represented what I will call a preferred version of my process and then I will call attention to certain deviations therefrom. It will be obvious that certain parts of this composite operation could exist by itself, thus, if the object be to produce a good fiber, then the spent cooking liquor could be treated as I indicate in the drawing, thus constituting a "recovery system" for the neutral sulphite cook. Similarly, the solvents could be manufactured from any type of pulp. It is not essential that such deviations should be profitable, it would certainly be workable. Hence, I regard all such modifications as within the scope of my disclosure. Of course, as herein collectively represented, it forms what I regard as the best combination.

First, however, a word about the type of raw materials with which the process commences. On the drawing I have called it "wood" and that would be correct if wood waste were involved. At the last end of any process for the use of a tree there appears a "waste" which has no use save burning. In the pulp mill and the lumber mill this is a mixture of bark and sawdust, and at the end of the pulp mill it is the spent cooking liquor itself which is the "waste." Of course, it is always burnt in order to recover, for re-use, the resident soda salts and in such combustion there is some salvage of heat.

But apart from the tree there is an endless succession of "waste" vegetable products that could serve as raw material for my process, from sugar cane bagasse or the field waste from the pineapple plantation, to the "ferns" of the asparagus field. At best, any use made of such material is as fuel, but in many cases vegetable wastes are de-

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stroyed, at the place of origin, by fires, as the simplest solution.

In the drawing I show this wood as entering a "saturator" where it is thoroughly saturated with hot cooking liquor. It is then passed into the "digester" where it is further heated to a temperature corresponding to the gage pressure of about 175 lbs. This may be done on a batch basis but I prefer a continuous operation in which the cooked material, pulp suspended in spent cooking liquor, is continuously discharged through a nozzle so that the escaping steam may be utilized as "low-pressure steam" in some other location, such as an evaporator. The time of cooking is thus determined by the time of residence in the digester.

In the blowpit, where the nozzle discharge is collected, the resultant pulp is next thoroughly washed to free it from spent liquor, after which it is converted into sugar in the saccharifier. The process of saccharification consists of heating for a matter of minutes, only, until a partial conversion has taken place. Separation is then made between liquid and solids and the solids are recycled to the saccharification step until only a non-cellulose residue is left, the latter being sent to undergo the same treatment, described later on, to which the whole of the spent cooking liquor is ultimately subjected. I prefer to have said saccharifier operate as did the digester, continuously, so that the evolved steam may be similarly utilized.

The time in the saccharifier is governed by performance, i.e., the yield of sugar. The over-all effect should be one pound of sugar for each pound of cellulose, the increase in weight due to water of hydration balancing the inevitable loss due to decomposition. The actual saccharification is conventional, the acidity being equal to 1/2% of sulphuric acid and the temperature that corresponding to a gage pressure of 150 pounds. These conditions are but an approximation and may be varied at will by the operator in accordance with performance as previously explained under the factor of time.

The sugar solution thus produced is next treated in the conventional manner for the manufacture of that complex consisting of butyl alcohol, acetone, ethanol, carbon dioxide and hydrogen resulting from the life function of *Clostridium acetobutylicum*, or its equivalents of which several are well known. Obviously, it is first necessary to neutralize the acid sugar solution to the preferred pH and to add nutrients for the propagation of the added culture. I have shown the use of caustic soda but that is optional.

To the best of my belief all such operations are today conducted on a batch basis, each new batch starting from a pure culture. However, as I am utilizing a relatively pure medium which is absolutely sterile I can proceed in a continuous manner so I have shown the "broth" advanced from fermenter to fermenter until in the last the sugar is virtually exhausted. To equalize, therefore, I have also shown a continuous re-cycle of material from the last fermenter to the first, a step on which the continuity of the operation largely depends. If due care be taken that no foreign culture be permitted to enter, the organism will function smoothly and the violent evolution of gases so often encountered on a batch basis will be largely eliminated.

Said gases, consisting of hydrogen and carbon dioxide are shown as passing to the right hand side of the drawing where an advantageous use is found in the process itself, an advantage over conventional practice where the synthesis of methanol is introduced as a substitute. The fully fermented "broth" is then sent to a "still" where separation is made between the overhead products and the

"bottoms." The latter is divided into two parts, one of which is re-cycled in place of wash water to the blowpit so that any non-used ingredients may be utilized. It is obvious that the saccharifying liquor in which the pulp is suspended becomes, in this manner, the still bottoms previously described.

Probably the greatest advantage in this type of recycling is represented by the use thus made of the organisms abundantly represented, both living and dead. In the saccharification step there is thus not only the effect of the acid and temperature on the cellulose but also on the protoplasm of the bacteria. As a result, the corresponding amino acids of said protoplasm are set free as food for the organism in the fermentation step. This contributes amazingly to the speed at which propagation takes place as otherwise the organism would be compelled to manufacture its own. It thus influences as well the temperature it is desirable to maintain within the fermenters. While this, in general, is somewhere between 30° C. and 45° C. it will be varied by the operator according to the actual performance of the entire system.

Having thus described the various steps by which the fermentation and saccharification, per se, is much improved I will now show what happens to the spent liquor from the initial pulping step. In the digester, shown after the blowpit, an addition of caustic soda is made in such an amount that the total soda shall about equal the organics present. The charge is then held at a temperature corresponding to about 150 pounds gage pressure for about three hours and a large fraction of the methoxyl component of the lignin will have been converted into vanillin. To extract this compound and to use the carbon dioxide-hydrogen mixture as well, the digested material is cooled and then treated with this gaseous mixture in the device called a carbonator, which may be anything from a simple agitated tank to a bubble tower. Two purposes are thus served simultaneously. The caustic solution is neutralized, a necessary step to precede vanillin extraction, and simultaneously, the gaseous mixture loses much carbon dioxide and becomes correspondingly enriched in hydrogen, an equally necessary step in the further use of said hydrogen.

The carbonated material is next passed on to the extractor where it is thoroughly, progressively, extracted with the whole of the butyl alcohol fraction yielded by the still. Manifestly this is in an unrefined condition so two purposes are once more served. From the extractor the butyl alcohol plus the extracted vanillin passes to the separator, which is another still. Crude vanillin and the impurities of the butyl alcohol is thus obtained as one fraction, and refined butyl alcohol as another fraction.

The extracted material is next sent on to the "fusion-kettle," which is any agitated evaporative device. Here it is commingled with additional caustic soda until the ratio of organics to soda shall be approximately as 1 is to 3. Evaporation is continued until the temperature of the fused mass shall approximate 230° C. and it is then sent to the leacher. While not shown in the drawing it is obvious that any butyl alcohol left in the extracted material will have been volatilized by the rise in temperature and any methanol formed by the fusion step will likewise have been volatilized. Naturally, these vapors will be condensed and recovery of both methanol and butyl alcohol will be achieved.

In the leacher I have indicated the watery fluid in use as another portion of the "still bottoms" not used in the recycle step to the blowpit. Just enough will be used so as to remove the unused caustic and the sodium acetate formed during the fusion in the form of a solution. This solution is, in turn, sent to an evaporator-crystallizer for the crystallization of the sodium acetate, the mother liquor becoming a very strong solution of caustic soda, which is returned as a re-cycle material to the vanillin-digestion step and to the fusion step. This sodium acetate forms a very valuable by-product. I have shown its

separation from mother liquor by a centrifuge, which is optional.

From the leacher the residue is sent to a furnace which may be any type of a metallurgical roaster. In this device, carbon is burned off, organic salts of soda converted to carbonates and any accidentally formed sulphide is converted to sulphate. The ash leaving said furnace may, therefore, be considered as a mixture of sulphate and carbonate of soda. I have shown that as received in a dissolver, which is but another agitated tank. The liquid used to dissolve the ash is, once more, a part of the still bottoms, already used twice before. I will here explain why I elect to use this material in place of plain water. In view of the sulphuric acid added to the saccharification stage and the caustic soda used to neutralize said acid before fermentation, said still-bottoms must contain all such soda and acid previously added. This will be in the form of sodium sulphate and by my consistent policy of re-cycling this sodium sulphate will eventually become converted into the sulphite required for digestion, thus making up at least in part for any losses in the system. Obviously, it will be desirable to make the solution of ash as concentrated as possible but that is optional.

This solution of ash is next divided into two parts. One part is causticized in the conventional manner with lime giving a solution of caustic soda with inert sodium sulphate which is re-cycled wherever called for, and a residual sludge of calcium carbonate. This latter is commingled with the second part of the dissolved ash and with sulphur dioxide to form a solution of sodium sulphite and a precipitate of calcium sulphate. Separation is made between these substances, the calcium sulphate discarded, and the solution of sodium sulphite re-cycled to the saturation step with which my process was commenced. Here I will add another step not shown on the drawing. Any shortage of liquid at this point will be made up by re-cycling a portion of the spent cooking liquor, obtained from the blowpit, thus increasing the density of said spent liquor before and during all subsequent steps.

Another reason for my persistent "re-cycling" of dilute materials that normally go to waste but are recovered at no additional cost in my system will be found in the relatively small amounts of side-products produced along with the main items that I have already mentioned. Thus, from every one hundred grams of sugar consumed there is also produced about 5% of acetic acid and rather less than one-half as much butyric acid. Inasmuch as the "broth" rarely contains more than 3% of available products, all told, it is obvious that any plans of recovery would be absurd. However, let us trace these minute commodities through my process. In the still-bottoms sent to the blowpit these commodities are returned unchanged through the saccharification step. In neutralizing, they are converted to the corresponding soda salts and thus augment the percentage present in the "bottoms." Now when this enriched material is used in the leacher all such material ultimately comes out as crystallized sodium acetate and/or butyrate at the designated spot. Similarly, what is added to the dissolver is returned, in part, through the causticizing step to the same ultimate locus. It will also be simple to trace all the remainder through the decomposer, the saturator, the digester, the blowpit, until it finally has joined all the rest as a component of the spent liquor. When we consider that even the minute amounts herein considered will ultimately mount up to nearly a hundred pounds of crystallized salts per ton of "wood" employed it is obvious that it is not insignificant and that my process, in its entirety, is a method of processing lignified cellulose, not a mere mixture of unrelated factors. Similarly, the little ethanol represented on the drawing, could be passed through the quick vinegar process to form a dilute solution of acetic acid and then added to main, re-cycled flow, thus once more adding to the importance of the

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sodium acetate step as all such technique, incorporated in my process, would be inherently recoveries without additional cost.

Having thus proved that these diverse parts of my process do constitute a single, integrated process in order to obtain optimum results, and having fully described my process,

I claim:

1. The method of processing lignified cellulose which comprises; saturating said lignified cellulose with a cooking liquor consisting essentially of a solution of neutral alkali metal sulphite and digesting said mixture under conventional conditions as to sulphite concentration, time, and temperature until said resident cellulose shall have been substantially liberated from encrusting substances; separating the cellulose portion from the spent cooking liquor, reserving said liquor for future treatment; commingling the cellulose with a dilute acid medium containing approximately ½% of sulphuric acid and heating at approximately 150 pounds gage pressure to convert a portion of said cellulose into the corresponding sugar; separating the residual cellulose from the sugar solution and re-cycling same into the saccharification step until only a non-cellulose residue remains; neutralizing the resultant sugar solution and fermenting same with a culture suitable to the conversion of the sugar into volatile solvents represented principally by a mixture of butyl alcohol and acetone; distilling the fermented liquor to obtain volatile, overhead products and relatively non-volatile still-bottoms; separating the overhead into its constituent parts; re-cycling the still-bottoms, in part, as the liquid portion of cellulose mixture undergoing saccharification and, in part, as a dissolving medium in the further treatment of the reserved spent cooking liquor; commingling said spent liquor with sufficient caustic alkali until it shall approximately equal the total organic material present and with the non-cellulose residual from saccharification and heating at a temperature corresponding to a pressure of 150 lbs. gage until optimum conversion of the methoxyl content therein into vanillin shall have been effected; cooling and carbonating the resultant liquor using for said carbonation the mixture of carbon dioxide and hydrogen evolved during fermentation; extracting the carbonated mass with the butyl alcohol fraction obtained in the previous distillation step, and separating the solution of vanillin in butyl alcohol from the extracted residue; commingling said extracted residue with enough additional alkali metal hydroxide so that the additive alkali shall be approximately 3 times that of the organics present and fusing the mixture until a terminal temperature of approximately 230° C. shall be obtained; leaching the resultant mass with a part of the previously obtained still-bottoms until substantially all the unused alkali hydroxide and acetate, formed in the reaction, shall have passed into solution in the leaching liquor; removing the alkali acetate from the caustic liquor by crystallization and recycling the resultant mother liquor to the vanillin-digestion and fusion steps, respectively; roasting the residue from the leaching step to produce a mixture of sulphate and carbonate of the contained alkali metal as an ash; dissolving said ash in another portion of the still-bottoms previously produced and dividing the resultant solution into two parts; causticizing one part with lime in the conventional manner to obtain the caustic alkali required in the operations described and a calcium carbonate sludge; commingling the latter with the other portion of the solution of ash and with sulphur dioxide to produce calcium sulphate and alkali metal sulphite; separating the calcium sulphate and re-cycling the resultant solution of neutral alkali sulphite as the cooking liquor of the process.

2. The method of processing lignified cellulose which comprises; saturating said lignified cellulose with a cooking liquor consisting essentially of a solution of neutral alkali metal sulphite and digesting said mixture under

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conventional conditions as to time, temperature, and sulphite concentration until said resident cellulose shall have been substantially liberated from encrusting substances; separating the cellulose portion from the spent cooking liquor; commingling the said cellulose with an acid liquor containing approximately ½% of sulphuric acid, made by acidifying still-bottoms obtained in a later step, and digesting for a partial saccharification only at a temperature corresponding to 150 lbs. gage; separating the sugar solution formed from un-reacted cellulose and recycling said cellulose to the saccharification step until only a non-cellulose residual shall remain; performing the saccharification in a continuous manner so that the sugar solution, mixed with unreacted cellulose and residuum shall emerge continuously as a jet from the saccharifying vessel; neutralizing the resultant sugar solution and fermenting it with a culture suited to the conversion of sugar, essentially, into butyl alcohol and acetone; performing said fermentation in a series of closed vessels to collect the carbon dioxide and hydrogen formed during fermentation; passing the fermenting broth successively from vessel to vessel until in the last vessel the sugar shall have been essentially converted, meanwhile re-cycling a portion of said fermenting material, continuously, from the last vessel to the first vessel in the series; distilling the resultant liquor to obtain still-bottoms for re-cycling as herein prescribed, and an overhead product consisting essentially of butyl alcohol, acetone, and ethanol for subsequent separation and refining.

3. The method of processing lignified cellulose which comprises; saturating the lignified cellulose with a cooking liquor consisting essentially of a solution of neutral alkali metal sulphite and digesting said mixture under conventional conditions as to sulphite concentration, time, and temperature until the resident cellulose shall have been substantially liberated from the encrusting substances; performing said digestion in a continuous manner so that the mixture of liberated cellulose and spent cooking liquor shall issue, continuously, in the form of a jet emerging from the digesting vessel; separating the liberated cellulose from the spent cooking liquor; commingling said spent liquor with sufficient alkali metal hydroxide that there shall be present approximately as much such hydroxide as there is organic material; heating said mixture to a temperature corresponding to a pressure of about 150 pounds, gage, until optimum conversion of the resident methoxyl into vanillin shall have been obtained; carbonating the resultant material to liberate the vanillin thus produced; extracting the resultant material with butyl alcohol and separating the solution of vanillin in butyl alcohol from the extracted residue; commingling said residue with sufficient additive alkali until said alkali shall be equal to approximately three times the amount of organics present and fusing the mixture until a final temperature of 230° C., approximately, shall have been obtained; condensing the vapors evolved in such fusion to recover butyl alcohol and methanol, the latter formed during said fusion; leaching the resultant mass with an aqueous liquid in sufficient amount to extract substantially all of the un-used caustic and of the alkali metal acetate, formed during fusion; evaporating the solution, crystallizing the resident acetate and separating it from the mother liquor, consisting essentially of caustic alkali, and re-cycling it to the vanillin-digestion and fusion steps, respectively; roasting the residue from the leaching step to produce as an ash a mixture of sulphate and carbonate of the contained alkali metal; dissolving said ash in a watery liquid and dividing into two parts; causticizing one part with lime in the conventional manner to produce the caustic alkali required in the process, and a calcium carbonate sludge; commingling said sludge with the remainder of the solution of ash and with sulphur dioxide to produce a solution of alkali metal sulphite and a precipitate of

calcium sulphate; separating said calcium sulphate and re-cycling the solution of alkali metal sulphite as the cooking liquor of the process.

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