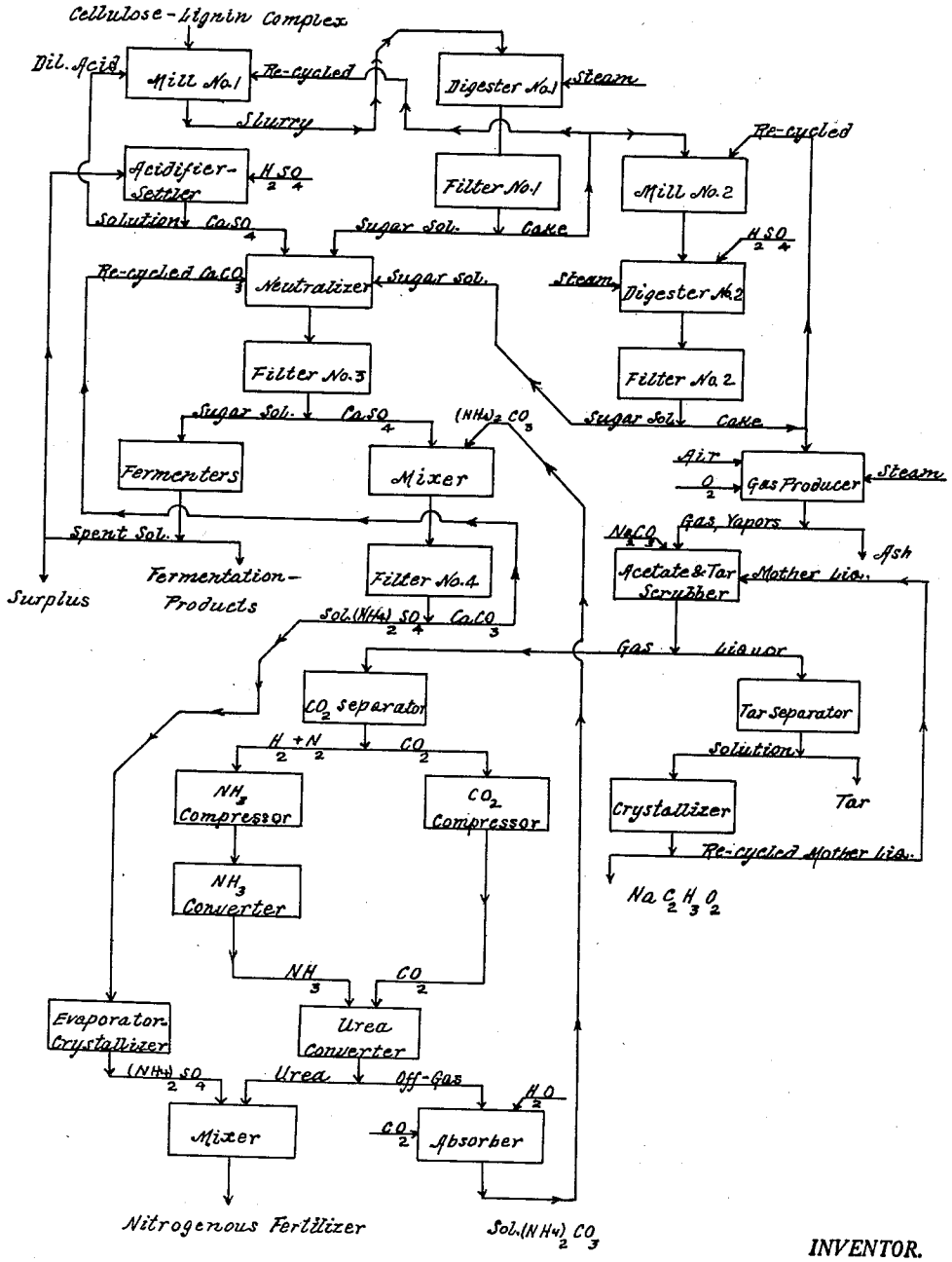
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METHOD OF PROCESSING A CELLULOSE-LIGNIN COMPLEX

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# METHOD OF PROCESSING A CELLULOSE-LIGNIN COMPLEX

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The term "cellulose-lignin complex" is used as a generic expression to describe what is probably the most abundant material present in the vegetable kingdom. Excluding fruits and seeds it embraces almost everything else as it has been nature's policy to produce the supporting structures of plants of lignified cellulose in the same manner as calcium phosphate serves in the animal kingdom. Obviously, wood and "woody" material is the principal form whether it be in the form of trees, brush, straw, or such "grasses" as bamboo and sugar cane. However, much of humanity's discards from the vegetable world also falls in this classification. Farm wastes and urban wastes alike fall into the same category when attention is called to the enormous amount of paper and paper products incinerated in most of our larger cities. In a generalized classification they all may be regarded as complexes of cellulose and lignin.

In brief, my process consists in converting the cellulose, or a part thereof, into some form of sugar by acid hydrolysis and separating said sugar in the form of solution from the residuum, the subsequent use of said sugar in industry being outside of the scope of this application. Said residuum is next processed so as to yield a mixture of gases suitable for the manfacture of ammonia and its derivatives, urea, and/or salts of ammonium. In these various steps a series of by-products is unavoidably produced and the recovery of such material has much influence on the economics of the process.

In so far as chemical reactions, per se, are concerned I have introduced nothing that is new. But in the way in which I have combined such material to form an economic structure I believe that I am entirely original. A complete description of my process, in its entirety, is best understood by following the various steps on the drawing which is attached hereto. This is my preferred illustration and I shall give time, temperatures, and concentrations as I go from step to step. It will thus be simple for the skilled operator to carry out these steps and to use the suggestions contained herein. However, I am assuming that said person is sufficiently familiar with the present state of the art that when I merely say "purely conventional" he will require no further guidance. Finally, as my process can exist without necessarily using all these steps I shall also call attention to sundry abbreviations that under certain conditions may be advantageous.

Commencing, therefore, at the upper left of the drawing I show such a complex, which for the purpose of the illustration we may call wood waste, or saw mill waste, entering mill No. 1, which can be a pebble mill, where it is ground to a slurry with dilute sulphuric acid. I have then shown this slurry advanced to digester No. 1, where it is heated by steam until only a relatively small part of the contained cellulose has been converted into sugar at which time it is discharged to filter No. 1. The acid concentration is optional. In industrial work in saccharification a ½% solution of acid is customary. At a later point this acid must be neutralized, generally with lime as CaO, so it is advantageous to make the acid as dilute as possible and substitute increased steam pressure. Obviously, the less time, and the less acid consumed per pound of sugar the cheaper the process. In my case, I ultimately recover said acid in the form of ammonium sulphate, and the lime is simultaneously re-cycled as precipitated calcium carbonate, hence I can afford to be liberal with acid use. In general I use from 1% to 3% of acid on the saccharifying liquid and, of course there is no consumption of lime. I can, therefore, much improve the saccharification step and decrease the optimum temperature, hence pressure, required.



Standard practice on pressure is around 150 p.s.i. or higher and the conventional approach is to fill a digester with sub-divided wood in a relatively dry state and then to permit the saccharifying liquor to pass through same at a definite rate, either continuously or in "surges" thus using a type of percolation technique and consuming many hours until virtually all the cellulose has been removed. Such technqiue involves much destruction of the sugar being formed and it leaves the digester partially filled with a solid compact mass of residuum. These difficulties, while combatted in Europe, have so far prevented the industry from obtaining a foothold in the United States. Apart from the difficulties of filling and emptying the digester there is the added fact that some eight hours is often required to service a single charge.

Contrariwise, I do not retain my charge in the digester more than an average of 15 minutes, both charging and discharging being, of course, continuous. With the higher acid concentration I can also keep my temperature down to a degree corresponding to a pressure of but little more than 100 p.s.i. Manifestly, with these guides actual performance will soon indicate at what point as to both acid and temperature the sugar yield becomes most advantageous.

Returning now to the operation of filter No. 1, I have shown this as yielding a sugar solution and a filter cake, the former going to the "neutralizer" and the latter divided into two portions. Part of said cake is directly re-cycled to mill No. 1, where the extracted "envelope" is removed from the central "core" by attrition, thus presenting fresh surfaces to the action of the acid on re-treatment. The remainder of said cake is then advanced to mill No. 2 where is is similarly treated without admixture with fresh charge as was the case with the portion sent to mill No. 1. After such grinding, the material is acidified once more and re-heated in digester No. 2, in the same manner as before described, and then discharged to filter No. 2. Time, temperature, etc., is assumed to be the same as in digester No. 1, but again, adjustment must be made according to actual results obtained in practice. Filter No. 2, is then shown as yielding another sugar solution, sent to the neutralizer, and a cake which is, in part re-cycled to mill No. 2, and in part diverted to the gas producer indicated immediately below.

Passing now to the neutralizer, I have shown the sugar solution from both filter No. 1 and filter No. 2, commingling with a re-cycled $CaCO_3$ obtained in subsequent steps, manifestly, in sufficient amount to neutralize the sulphuric acid contained therein with attendant production of calcium sulphate. After neutralization, the magma is passed to filter No. 3, where separation is made between the neutral sugar solution and the precipitated calcium sulphate. The sugar solution is shown as going to "fermenters" but its subsequent use, as previously stated, is no part of this disclosure. The future use of the calcium sulphate I shall reserve to a later time. However, if fermentation be the next step then the spent solution from said fermentation can advantageously be used in place of water in saccharification, hence I have shown it, in part, re-cycled to an "acidifier-settler" where acidification with sulphuric acid takes place with attendant formation of some additional calcium sulphate, due to the reaction between added acid and organic lime salts present in the sugar solution after neutralization with calcium carbonate. The calcium sulphate produced in

the acidifier-settler is passed unchanged through the neutralizer and finally is obtained as a part of the calcium sulphate separated on filter No. 3. The spent liquor from fermentation not thus re-cycled is on the drawing designated as "surplus," it being obvious that some discard must take place. However, the organic acids unavoidably produced in the saccharification will consistently increase in amount and, hence, may be recovered by purely conventional means from said "surplus" before the remainder is discarded.

Attention is now once more directed to the gas producer where the narrative was interrupted in order that the path of the sugar solution might be followed. Said producer, which may advantageously be in the form of a multiple hearth roaster, is well known in chemical technique. As said cake is passed downward in said producer against a current of hot gas it becomes first carbonized and said carbon is then completely decomposed by means of the steam, oxygen, and air admitted in controlled amount. It is the object of this invention to obtain from said producer a mixture of hydrogen and nitrogen in the conventional ammonia ratio of 3:1. The ratio is easily maintained by adding just enough nitrogen to serve this purpose and to supply the rest of the needed energy by the use of oxygen, the nitrogen being supplied in the form of air.

Two well known reactions between carbon and water, at elevated temperatures, may be represented by the following equations: $C+H_2O=CO+H_2$, and

$$C+2H_2O=CO_2+2H_2$$

Both are, of course, endothermic; but the heat requirement of the latter is less than that of the former though the yield in terms of $H_2$ is twice as great. In practice, the former equation is almost universally used, so it is supplemented by an exo-thermic reaction between water and carbon monoxide in the presence of a catalyst as follows: $CO+H_2O=CO_2+H_2$. Preference is given to this double reaction because, with fossil fuels, the direct reaction to $CO_2$ is extremely slow and incomplete. In the case of a carbon, derived from a vegetable source, the reverse is true. At a temperature of 1100° F., very little CO is produced so the one step reaction is suitable. I avail myself of this peculiarity of my raw material. I have, therefore, indicated the gas from the producer, consisting of a mixture of hydrogen, nitrogen, and carbon dioxide, with impurities in the form of tars and organic acids, going through a scrubber wherein the tar and acetic acid is removed by washing with a solution of $Na_2CO_3$. The scrubber liquor passes through a tar separator, entirely conventional, and then through an equally conventional crystallizer where separation is made between sodium acetate and a mother liquor, the latter being re-cycled to the tar scrubber. Parenthetically, at 1600° F., carbon will be present only as CO.

The gas, thus purified, is then sent to a $CO_2$ separator, also conventional, both in design and in fluid used. Ethanolamine is much used but I prefer the older technique of a strong solution in water of potassium carbonate. That is optional. Said separator yields two products, the ammonia synthesis gas before referred to, and carbon dioxide. Both of these are subsequently used. The former is converted to ammonia in conventional manner, the latter simply compressed to the relatively low demands of the urea synthesis. The urea converter, shown in the next to the last line on the drawing, is serviced by the ammonia from one source, and carbon dioxide from the other source. This is entirely conventional so no description is needed. I have shown said urea converter delivering urea and off-gas, the mixture of carbon dioxide and ammonia not converted to urea. Instead of re-cycling this undesired product, in some manner, back to the urea converter which is standard practice, I use it at a place in my process where it is needed.

I have shown this "off-gas" entering an absorber, which is only any type of a packed column, where it is converted into a solution of ammonium carbonate with a little extra $CO_2$ introduced as it is advantageous to have a little bicarbonate present. This solution is then sent back to a "mixer," placed just above filter No. 4, where it meets the calcium sulphate before described. The result is, of course, a water solution of ammonium sulphate with a suspension of calcium carbonate. These items are separated from one another on filter No. 4, the calcium carbonate being re-cycled to the neutralizer, and the solution of ammonium sulphate to the "evaporator-crystallizer" at the lower, left hand, corner of the drawing. I have then finally shown the mixing of this compound with the urea before described to make an "all-purpose" nitrogenous fertilizer, but such a final step is, of course, optional.

Having thus described the preferred version of the drawing in such a complete manner that the technically proficient operator will have no trouble in making my process workable, I will next describe sundry modifications. These are all abbreviations of the central theme. Thus, saccharification could be used in a single step, with lower sugar yield and more residuum of unused cellulose. Inasmuch as I have much use for this residuum such an abbreviation might even be preferred. Wood itself, could be sent to the gas producer, gasified, purified, and converted to urea and off-gas, the latter being converted to a concentrated solution of ammonium carbonate. A solution of urea, to saturation, in said ammonium carbonate solution would constitute an exceedingly satisfactory type of a nitrogenous fertilizer in this day and age when a liquid is much cheaper handled than anything in a bag though the unit of nitrogen may be a little less. With sodium acetate, and phenolic oils and pitch, derived from the tar, and a far cheaper method of making the ammonia synthesis gas than standard practice of today there would be no actual need of the removal of the cellulose if all other matters were suitable. Urea can, of course, be marketed by itself and so can ammonium sulphate. Doubtless, the method set forth on the drawing has a great advantage over all such abbreviations, but the suggestions made herein are equally workable, and will in the main be found quite profitable. I, therefore, consider them as within the scope of my disclosure.

Having thus fully described my process and given sundry modifications thereof, I claim:

1. The method of processing a cellulose-lignin complex which comprises; milling said complex with a dilute form of sulphuric acid to form a slurry; heating said slurry in continuous flow to a temperature corresponding to a gage pressure of between 100 and 150 p.s.i. for an approximate 15 minutes; separating the sugar solution thus formed from the solid residue; re-cycling a portion of said solid residue to the milling step to undergo once more the milling and heating operation; converting the remainder of said residue into a mixture of nitrogen, carbon dioxide, hydrogen, acetic acid vapor and tarry impurities, by the controlled addition to the gasifying solids of steam, air and oxygen, the addition of air and oxygen, relative to ane another, being such that the gas shall have three times as much hydrogen as nitrogen, by volume, the temperature during gasification being maintained at approximately 1100° F.; purifying the gas thus formed from acetic acid and tarry impurities by washing with a water solution of sodium carbonate; further purifying said gas by the removal of the resident carbon dioxide, and reserving said separated carbon dioxide for later use; the residual gas now being a suitable gas for ammonia synthesis with a hydrogen: nitrogen ratio of 3:1; converting said synthesis gas into ammonia; commingling said ammonia with the reserved carbon dioxide in conventional urea practice to produce urea and an offi-gas consisting of a mixture of ammonia and carbon dioxide.

2. The method of processing a cellulose-lignin complex set forth in claim 1, with the added step that the sugar solution produced therein be neutralized by commingling

with a re-cycled calcium carbonate with the simultaneous production of calcium sulphate and a solution of sugar; separating the calcium sulphate and commingling it with the solution of ammonium carbonate produced by dissolving the off-gas in water; separating the resultant solution of ammonium sulphate from the calcium carbonate formed in the reaction and re-cycling the calcium carbonate thus produced to the neutralization step above specified.

3. The method of processing a cellulose-lignin complex which comprises; converting said complex into a mixture of nitrogen, carbon dioxide, hydrogen, acetic acid vapor, and tarry impurities by the controlled addition of steam, air and oxygen at temperatures approximating to 1100° F. the proportion of air to oxygen being so regulated that there shall be present in the gas three times as much hydrogen as nitrogen, by volume; purifying the gas thus formed from acetic acid and tarry impurities by washing with a water solution of sodium carbonate; further purifying said gas by the removal of the resident carbon dioxide, and reserving said carbon dioxide for future use, the residual gas now being suitable for ammonia synthesis with a hydrogen to nitrogen ratio of 3:1; converting said synthesis gas into ammonia; commingling said ammonia with the reserved carbon dioxide in conventional urea practice



to produce a solution of urea and an off-gas consisting of a mixture of ammonia and carbon dioxide.

4. The method of processing a cellulose-lignin complex set forth in claim 1, with the added step that milling and saccharification be accomplished in two successive operations in each of which a residue is re-cycled in part to the originating step and in part to the next successive step, two sugar solutions being produced with a single residue advanced to the gasification step.

5. The method of processing a cellulose-lignin complex set forth in claim 1, with the added step that the sugar solution obtained therein be fermented, the fermentation products removed, and the resulting spent liquor recycled, after acidification, as the saccharifying liquor therein specified.


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