Dec. 1, 1931. G. A. RICHTER 1,833,975

CYCLIC PROCESS OF FIBER LIBERATION

Filed Sept. 6, 1923 5 Sheets-Sheet 1

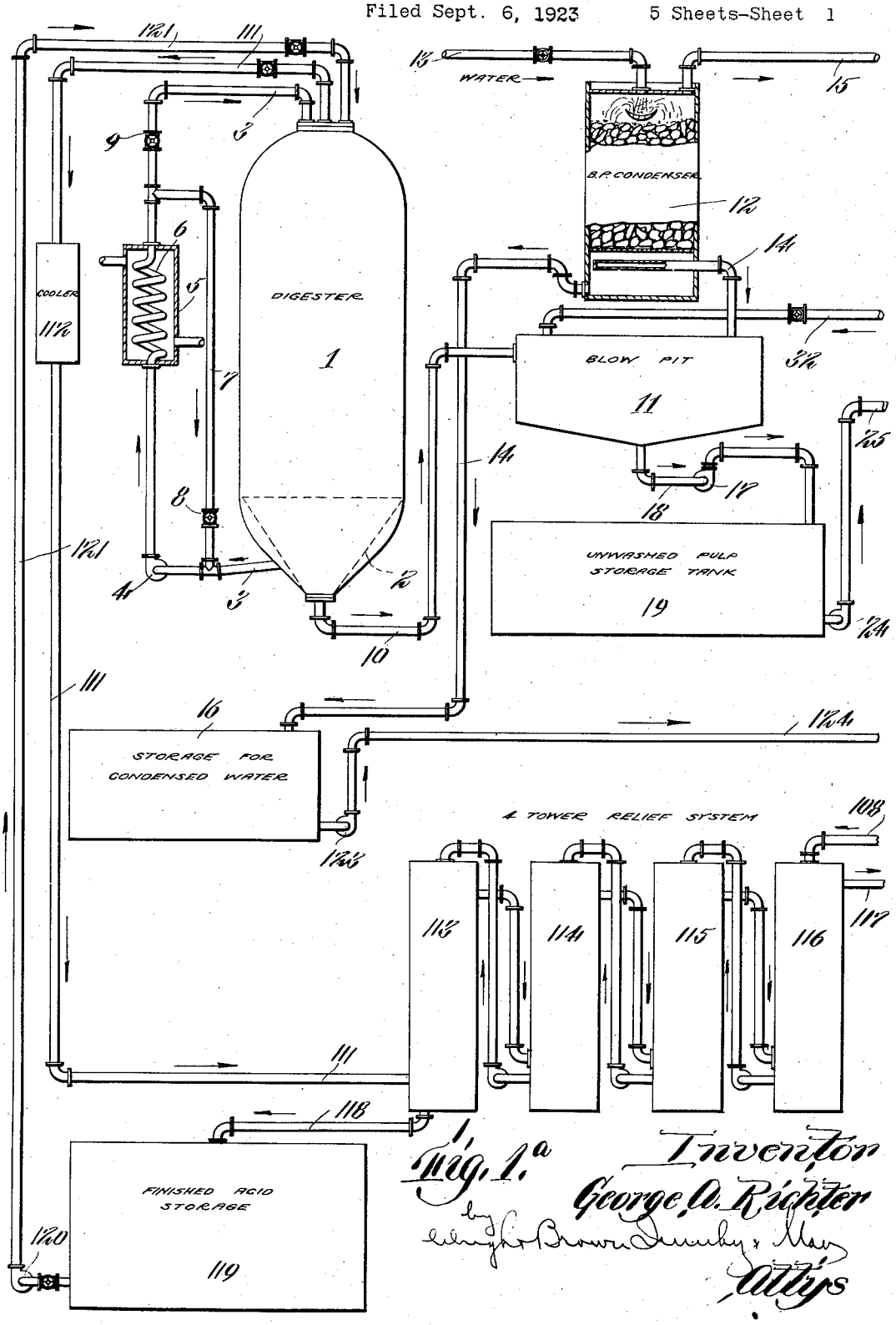


Fig. 1.

Fig. 1.a

Inventor
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CYCLIC PROCESS OF FIBER LIBERATION

Filed Sept. 6, 1923 5 Sheets-Sheet 2

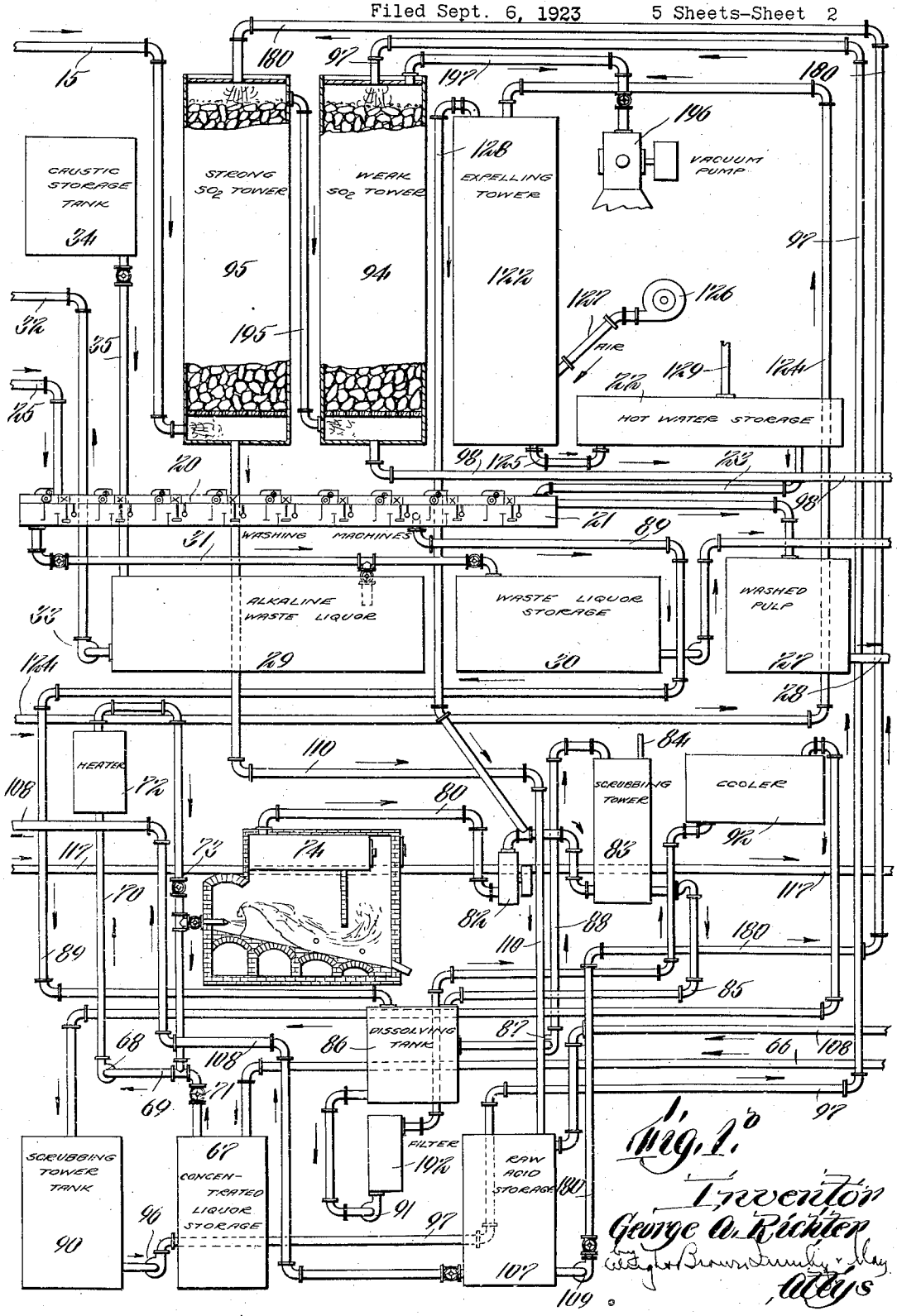


Fig. 1.

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CYCLIC PROCESS OF FIBER LIBERATION

Filed Sept. 6, 1923 5 Sheets-Sheet 3

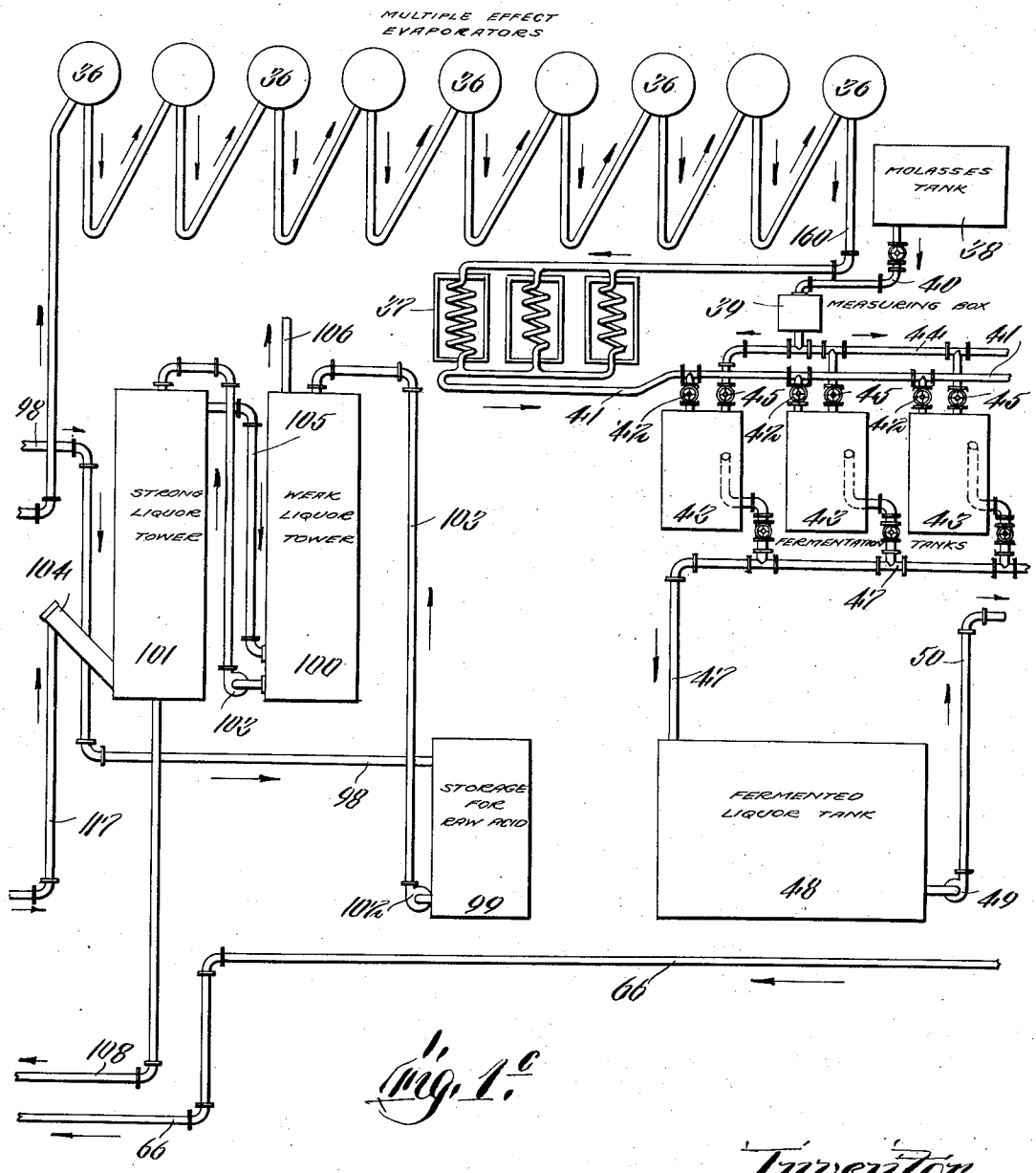


Fig. 1.c

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CYCLIC PROCESS OF FIBER LIBERATION

Filed Sept. 6, 1923 5 Sheets-Sheet 4

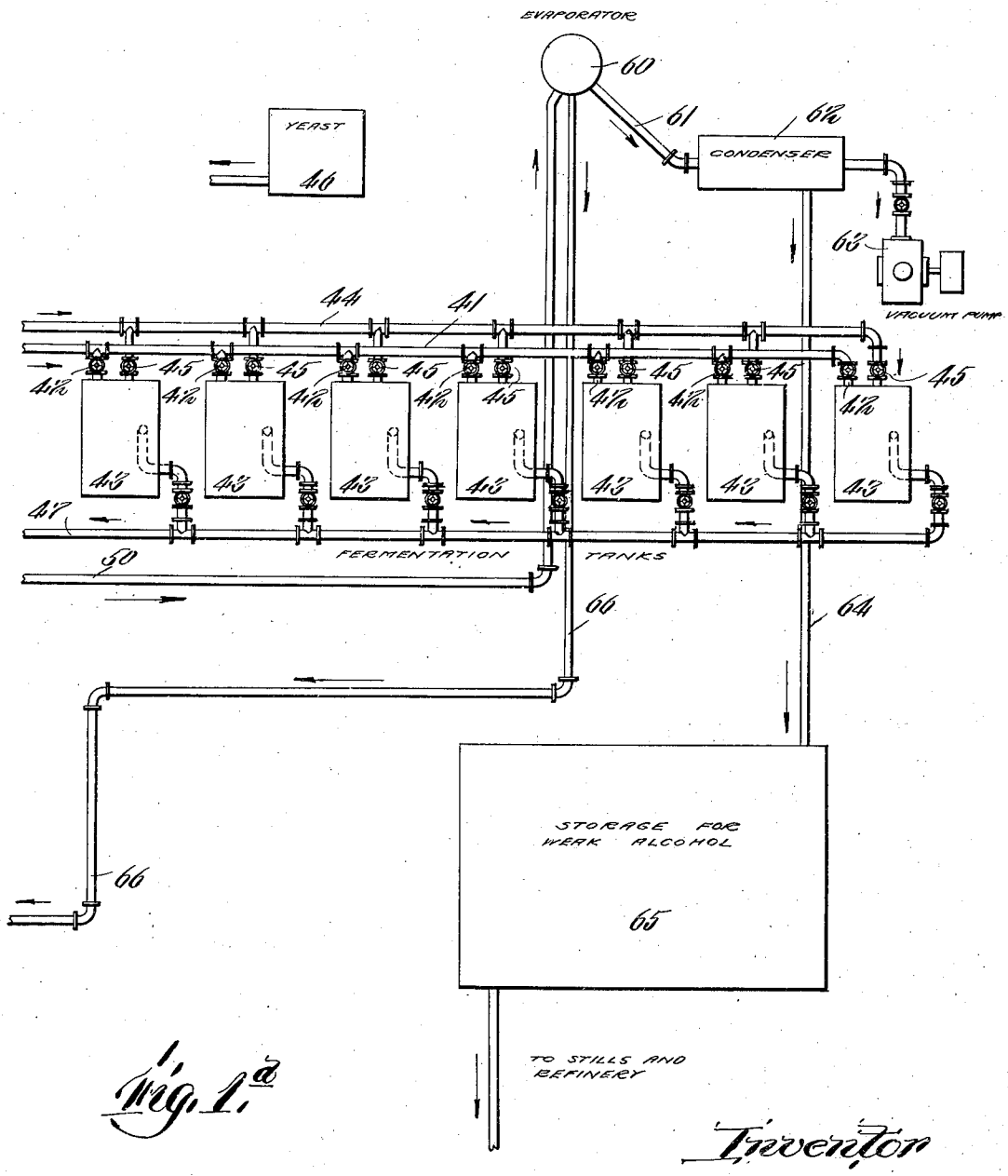


Fig. 1.

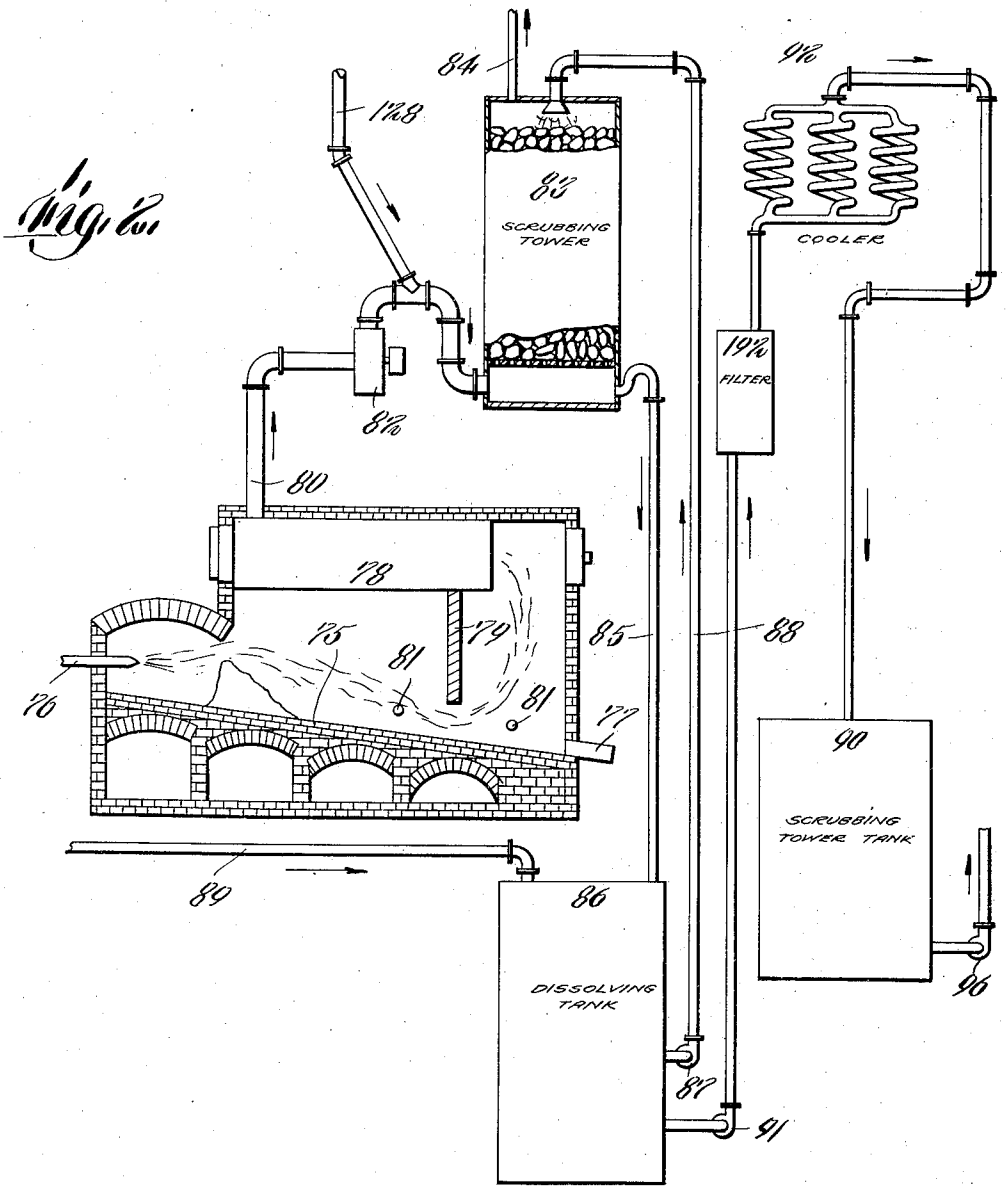
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CYCLIC PROCESS OF FIBER LIBERATION

Filed Sept. 6, 1923 5 Sheets-Sheet 5

Fig. 2.



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Patented Dec. 1, 1931 1,833,975

UNITED STATES PATENT OFFICE

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CYCLIC PROCESS OF FIBER LIBERATION

Application filed September 6, 1923. Serial No. 661,240.

This invention has among its objects to provide a process for the production of a high-grade cellulose pulp, the fibers of which are long and silky and capable of producing a strong paper when subjected to the usual processes of paper manufacture. The object of the invention further is to provide a process by which there is a greater yield of pulp with less loss through screenings than heretofore possible; to produce a pulp which is more easily bleached, so as to provide a final product of high color; and to accomplish the results by a quick cook in contradistinction to those processes in which the pulp is subjected to low temperature for a relatively long time.

Another object of the invention already stated is to utilize the combustible content of the waste liquor for the generation of steam and power, to recover the mineral or inorganic content of the waste liquor in the form of raw material which may be utilized in the formation of the cooking liquor, and to produce and recover alcohol from the waste liquor by the fermentation of the sugars therein contained resulting from the process of digestion.

A further object of the invention, broadly stated, is to reduce the cost of pulp production, to eliminate waste as far as possible, and reduce the cost of maintenance of the acid system. In accomplishing these results, it is possible to avoid the pollution of rivers and streams by the discharge of the waste liquor thereinto, such as is ordinarily practised in the manufacture of sulphite pulp so-called. Further objects of the invention are to provide certain improvements in the method of fiber liberation and in the various instrumentalities or combinations of instrumentalities which are employed in carrying out the process.

For the cooking of the wood and the liberation of the cellulose fiber, I employ an acid cooking liquor which comprises a soluble sulphate, a soluble sulphite and free SO_2 in the form of sulphurous acid. I have discovered that when a cooking liquor of this character is employed—namely, one having as its components a soluble sulphate (from 2% to 4%) and a definite fairly large proportion of combined SO_2 (from .2% to 2% which is considerably greater than that formed by metathesis of sodium sulphate in sulphurous acid solution), together with free SO_2 (4% to 7%)—that a pulp is produced, the fibers of which are relatively long and silky so that paper produced therefrom is comparable in strength with kraft paper. A solution such as referred to may be produced by using as the raw materials a soluble sulphate, oxalate or acetate or other sodium salt of a weak acid, and either a soluble sulphite, sodium carbonate or caustic soda, together with sulphur dioxide, which is bubbled through the aqueous solution to produce the cooking acid having the requisite percentage of free SO_2. As a sulphate I employ one having as its base only one of the alkali or alkali earth metals such, for example, as sodium, potassium, lithium, zinc, magnesium, but not calcium or any other base which produces an insoluble sulphate. The combined SO_2 is likewise in the form of a soluble sulphite, using for this purpose any one of the above-mentioned bases. The wood to be treated is placed in a digester of substantially the same character as that ordinarily employed in the manufacture of sulphite pulp so-called, but preferably the digester is heated by indirect heating instead of by the injection of steam, in order that the cooking liquor may not be diluted by the condensate of the steam. A quick cook is preferably effected, the temperature of the digester contents being raised to approximately from 275° to 300° F. and the cooking being continued for approximately nine to twelve hours. The liquor is circulated externally from the bottom of the digester to the top thereof and is passed through a heater wherein it is heated by steam coils or other suitable heating surface. After the cooking operation has been completed as ascertained by tests made in the usual way from time to time, the digester is blown into a blow-pit, and the vapors and gases arising therefrom are passed through a condenser wherein the steam is condensed by direct contact with water, and the chilled gases, comprising SO_2

passing from the condenser, are utilized in the acidification of cooking liquor.

The waste liquor which is separated from the pulp and which contains sodium sulphate, a certain percentage of sodium sulphite, a combustible organic content and various sugars, is now so treated as to effect the fermentation of the sugars and the recovery of alcohol, the combustion of the combustible content, and the recovery of the mineral content in the form of sodium sulphate and more or less sodium carbonate. In carrying out these several operations, I effect certain economies in operation by methods which will be explained in detail in this specification. The loss of sodium constituent in the cooking operation is made up by the addition, in the production of the fresh liquor, of the necessary sodium constituents, and the loss in SO_2 is made up by gases produced by the combustion of sulphur-bearing materials. In fact, after the process is in operation practically the only raw materials which are needed for making up losses are sulphur or sulphur-bearing material, and either sodium sulphate, sodium sulphite, sodium carbonate, caustic soda, or other soluble sodium salts of a weak acid, or a combination thereof.

Preferably, before the waste liquor is subjected to the recovery processes, its aqueous content is reduced by evaporation, which itself may take place in two steps. That is to say, the waste liquor may be evaporated to a certain degree of concentration prior to its being fermented, and the final step of evaporation may be accomplished after the fermentation and alcohol recovery, but prior to the delivery of the waste liquor to the retort in which the mineral content is recovered and the combustible content consumed. On the accompanying drawings,

Figures 1^a, 1^b, 1^c and 1^d on Sheets 1, 2, 3 and 4 illustrate diagrammatically and conventionally the various instrumentalities which may be utilized in carrying out my process, the said figures constituting an illustration of the entire system, when placed side by side in sequence.

Figure 2 represents a part of the system including the combined retort and boiler furnace, a scrubbing and recovery tower, a dissolving tank for receiving the effluent from the furnace, a scrubbing tower tank and a cooler.

The instrumentalities employed in the system are shown only conventionally and diagrammatically by the several figures of the drawings.

On the drawings 1 is a digester of the proper dimensions for carrying on the cooking operation. At the lower end of the digester I have indicated conventionally a screen 2 and a conduit 3 for the withdrawal of the screened cooking liquor, which is pumped by pump 4 through an indirect heater indicated conventionally at 5. From the upper end the conduit 3 leads back to the top of the digester. The heater 5 is illustrated conventionally as containing a coil 6 which constitutes the section of the circulating conduit 3. At 7 I have indicated a by-pass so that the liquor may be continuously circulated through the heater to maintain the efficiency thereof. The valves 8 and 9 may be used to regulate the passage of the liquor through the by-pass and into the digester so as to control the rate of flow of liquor in the digester and the temperature thereof. In this way it is possible to circulate the liquor rapidly through the heater, raising it to the desired temperature, and to draw off such liquor therefrom as may be needed in bringing the contents of the digester to and maintaining them at the desired cooking temperature and pressure. After the cooking operation is completed, the contents of the digester are blown through the blow pipe 10 to a blow-pit indicated at 11. The liberation of the digester contents in the blow-pits is accompanied by the formation of steam or vapor and the liberation of SO_2. The vapors and gases are conducted from the blow-pit into a direct condenser indicated as a whole at 12. This condenser may be substantially like that illustrated in my pending application Serial No. 405,915, filed on August 25, 1920, and it contains a mass of inert interstitial material such as spiral bricks, rocks, or the like, so that the vapors and gases are broken up into multitudinous small streams in passing upwardly through the interstitial material. Fresh cool water provided by pipe 13 is sprayed into the top of the condenser, and passing downwardly through the interstitial material therein, condenses the water vapor and cools the gases. Preferably the flow of water is so controlled that it leaves the condenser through pipe 13 at a temperature slightly less than the boiling point. The cooled gases containing from 30% to 60% SO_2 are conducted from the top of the condenser tower by pipe 15 and utilized in the formation of the cooking liquor, as will be explained. The heated cooling water delivered from the lower end of the condenser tower may be conducted by pipe 14 to a storage tank 16, from which it is drawn for purposes to be subsequently explained.

From the blow-pit the pulp and the waste liquor are forced by a pump 17 through a pipe 18 to what I may term for convenience an unwashed-pulp storage tank 19. It is now necessary to separate the pulp from the waste liquor and to wash the pulp so that it may be freed from the liquor and be in a condition to be sent to the usual screens which are employed for refining the pulp and removing the so-called screenings therefrom, which consist of knots, specks, particles of brick, cement, etc. At 20 and 21 I have

indicated a series of pulp washers, arranged in two groups, one of which for convenience I may term the "strong liquor" washer and the other the "weak liquor" washer, the pulp passing continuously through both series of washers. These washing machines are preferably substantially like those illustrated and described in the patent of Brown, Martinson, Moore & Parker, No. 1,421,664, dated July 4, 1922, although if desired one may utilize the ordinary rotary vacuum type of washer. In the washers of the patent referred to, the pulp is carried continuously through agitator tanks in one direction, and the washing liquor is carried successively through such tanks in the opposite direction. For the purpose, the washing water is drawn from a hot water storage tank indicated at 22 and it passes through a pipe 23 to the pulp delivered at the end of the group of washers indicated at 21, the fresh water entering the last vat of the group 21 from which the pulp is delivered. The unwashed pulp and the waste liquor are forced by pump 24 from the tank 19 to a conduit 25 to the first of the group of washers indicated at 20, and the pulp which is delivered from said series passes to the second group of washers indicated at 21. The washed pulp delivered from the second group is delivered to a washed pulp tank 27, from which it may be drawn off and delivered to the usual screens (not shown) by a conduit 28. The purpose of subjecting the pulp to the operation of two groups of washing machines is so that I may employ the wash liquor which is relatively weak in inorganic chemicals from the group of washers 21 for one purpose and the strong wash liquor from the other group for another purpose which I will make clear, this making for a more efficient recovery of the valuable constituents of the waste liquor without entailing a corresponding dilution of the liquor which is subsequently evaporated. A certain amount of water from group 21 passes to group 20. The strong washing liquor delivered from the series of washers 20 is discharged into two tanks indicated at 29 and 30 by a conduit 31, having valved branches leading to the two tanks. The amount of liquor delivered to each tank is controlled as may be desired. A certain amount of the wash liquor which contains also the original waste blow-pit liquor is utilized for sluicing the blow-pit and removing any pulp which may remain therein after the blowing operation has been completed. For this purpose there is an outlet pipe 32 leading from the tank 29 and provided with a pump 33 by which the liquor may be delivered to the blow-pit for the sluicing operation and from which it passes back to the conduit 18 to the storage tank 19. As the waste liquor is acid, it is desirable to neutralize this acidity by an alkali, and for this purpose I preferably utilize a caustic soda solution which is contained in a caustic storage tank 34 and from which it is drawn as desired by an outlet pipe 35 leading to the tank 29. The proportionate amounts of the caustic delivered for admixture with the liquor from the first series of washers 20 are such as to make the liquor therein slightly alkaline and to compensate for losses in sodium sulphite occasioned in the cooking liquor during the process of digestion. The proportionate quantity of the liquor delivered from the series of washers 20 to the tank 29 is so regulated that a substantially constant amount of liquor is circulated from the tank back through the blow-pit, the unwashed pulp storage tank 19, to the washers 20 and thence to the tank 29, so that after the process is in operation the greater quantity of the liquor coming from the blow-pit and delivered to the washers 20 is passed to the waste liquor storage tank 30, from which it is drawn for evaporation and concentration. In effect, the tank 29 and the conduits last referred to comprise a by-pass between the washers 20 and the tank 30 so that waste blow-pit liquor may be circulated for the purpose of cleaning the blow-pit and supplying the necessary alkali for neutralizing the acidity of the waste liquor from the blow-pit. Of course, it will be understood that whereas I have shown but a single digester connected with the blow-pit, I may utilize a bank of digesters all discharging into the same blow-pit or a series of blow-pits all connected with the same tank 29 with proper valved connections for delivering the sluicing liquor to the several blow-pits if more than one be used.

The tank 30 contains substantially all of the waste liquor which was delivered from the blow-pit, together with a small amount of alkaline liquor delivered from the caustic storage tank 34, and this liquor is now treated for the production and recovery of alcohol, and thereafter for the recovery of its other valuable constituents. Prior to these operations, however, it is desirable that the liquor should be subjected to evaporation for the removal of a portion of the aqueous content. For this purpose I have illustrated conventionally at 36 a series of multiple effect evaporators, the details of construction of which it is unnecessary to describe. While I preferably employ multiple-effect evaporators, any other form of evaporator for removing a part of the aqueous content of the liquor may be utilized. From the last effect of the multiple-effect evaporators the liquor which has been concentrated to about 16° Bé., and which contains about 25% solids, is passed through a cooler indicated conventionally at 37, so that it is cooled to a temperature suitable for fermentation. The liquor which enters the evaporators is either slightly alka-

line or substantially neutral, and with the removal of the water becomes slightly acid due to the decomposition of certain organic constituents of the liquor, so that the liquor delivered from the cooler 37 is slightly acid. This liquor, while it contains sugars, is not per se suitable for the most efficient propagation and maintenance of yeast for the fermentation of the sugars, and it is therefore desirable to add to the liquor any suitable yeast nutrient. For this purpose I preferably employ molasses from sugar cane, such as ordinary black molasses, for which, on the drawings, there is indicated a tank at 38. From this tank the molasses may be drawn to a measuring box 39 by a valved pipe 40, so that a predetermined quantity of molasses may be measured out for admixture with a given quantity of the waste liquor. Inasmuch as the fermentation requires some hours, I provide a plurality of fermentation tanks which are preferably of relatively small size and arranged in groups. Thus they may be arranged in six groups of two, three groups of four, four groups of three, or the like, as most convenient. From the cooler 37 extends a pipe line 41 having valved branches 42 leading therefrom for delivery of the waste liquor to the various tanks indicated at 43. Similarly there is a pipe line 44 for the molasses and from it extend valved branches 45 to the several tanks 43. It has been determined that by the addition of, say, 3% to 4% by weight of molasses to a given quantity of waste liquor of say 16° Bé., it is possible by the addition of yeast taken from a yeast box 46, to cause the acclimation and propagation of yeast cells in the liquor for the fermentation of the sugars contained therein. In the present instance, the liquor is supplied from the cooler to the first group of three tanks at a temperature of approximately 80° to 90° F., and to the liquor in these tanks is added about 3% to 4% of molasses. A sufficient quantity of yeast is then added to each of these tanks and the liquor is permitted to remain therein until the yeast is propagated in sufficient quantity for the fermentation of the sugar. On certain occasions it may be desirable to add a small quantity of nitrogenous material such as ammonium phosphate or ammonium chloride. While the fermentation is going on in the first group of tanks, the waste liquor is next supplied to the second group of three tanks, to which molasses may be added, as is explained, together with yeast. There is a valved outlet from each of the fermentation tanks connected with a pipe line 47 by which the fermented liquor may be decanted to a tank therefor, indicated at 48. I do not herein claim specifically the process of adding a small predetermined quantity of a nutritive element, (together with yeast if required), to successive batches of the yeast liquor, as that process, per se, is not my sole invention. It is desirable now to remove the alcohol from the fermented liquor. This is accomplished by forcing the fermented liquor by a pump 49 through conduit 50 to an evaporator 60 in which the alcohol is evaporated, together with certain water content of the liquor, sufficiently to reduce it to that consistency at which it contains about 50% solids. The vapor containing the alcohol is conducted from the evaporator through a conduit 61 to a condenser 62, with which is connected a vacuum pump 63. The condensed water and alcohol are delivered by a conduit 64 to a storage tank 65. The aqueous alcoholic solution has approximately a 2%–3% content of alcohol, and by fractional distillation the alcohol is subsequently removed from the water and recovered, being subjected if desired to such refining processes as may be needed. The concentrated waste liquor delivered from the evaporator 60 is conducted by a pipe 66 to a storage tank 67, from which it is withdrawn for the combustion of the combustible content and the recovery of the basic inorganic chemicals, such as sodium sulphate and sodium carbonate. I do not herein claim specifically that process of treating fermented waste liquor which consists in subjecting it to evaporation for the concentration thereof and the simultaneous removal of alcohol and a part of its contained water, and the further separation and the qualitative evaporation of the water and alcohol by fractional distillation. The waste liquor which has been subjected to concentration and fermentation, and from which the fermentable sugar has been fermented and removed as alcohol, contains a large quantity of solid matter, comprising combustible sulphur organic substances, sodium sulphate and some sodium sulphite. In drawing the fermented liquor from the fermentation tanks, the yeast is permitted to settle in the bottom of the tanks and to remain therein. Consequently there remains in each tank sufficient yeast for the next batch of waste liquor, to which is added a given quantity of molasses,—together with fresh yeast if the latter is required.

The concentrated liquor in tank 67 after the removal of the alcohol is now subjected both to heat and pressure to generate an explosive force therein, substantially as described in Patent No. 1,326,414 to Moore & Quinn, dated December 30, 1919. To this end the concentrated liquor is drawn from the tank 67 by a pump 68 through a pipe 69, and it is circulated through a circulating system comprising the pipe 70 which is connected to the pipe 69, the latter being provided with a check valve indicated at 71. The liquor in passing under pressure through the circulating system is heated to a temperature above the boiling point by a heater 72 and is delivered from the circulating system by a pipe

or series of pipes 73, terminating in nozzles extending into a combined boiler furnace and retort indicated as a whole at 74. In the present instance it is desired that the sodium compounds recovered from the furnace should contain sodium sulphate and sodium carbonate. If this recovery takes place in an oxidizing atmosphere, there is no difficulty in recovering the desired salts. One may, however, operate the furnace as most convenient, taking precautions to eliminate the presence of sodium sulphide prior to the point in the system where the alkaline liquors come in contact with the strong sulphur dioxide gases of the acid system. One may employ a furnace as shown in Fig. 2. In this case what may be termed the combustion chamber of the furnace is provided with a floor 75 which preferably extends rearwardly and downwardly from the front of the furnace into which project the nozzles 76 for the emission of the waste liquor. The floor at the rear wall of the furnace is provided with spouts 77 from which the molten effluent escapes from the furnace. Opposite the nozzles and projecting downwardly from the flues 78, there is a bridge wall 79 which terminates a short distance above the floor 75 so that the gaseous products of combustion will pass downwardly thereunder before passing through the flues and upwardly through the stack 80. Notwithstanding that an explosive force is generated in the waste liquor and the waste liquor is disrupted, leaving the nozzles so that it is more or less consumed in transit before reaching the floor of the furnace, yet there are drops of the waste liquor which form on the nozzle and fall to the floor of the furnace. By inclining the floor rearwardly, such waste liquor as is dropped upon the floor must flow downwardly through the hottest part of the combustion chamber and be subjected to an oxidizing atmosphere, as in the present instance. To supply an oxidizing atmosphere the sides of the furnace at suitable points may be provided with air inlets indicated at 81, certain of these inlets being located in the rear and others in front of the bridge wall 79. By provision of the bridge wall, the gaseous products of combustion including CO_2 are brought into contact with the smelt to insure the conversion to carbonate and sulphate of any sodium sulphide that may be formed in the portion of the furnace where there is, because of the nature of things, a reducing atmosphere. A fan 82 connected with the stack assists in maintaining a reduced pressure in the stack and back through the furnace and also delivers the escaping products of combustion under pressure to a scrubbing tower 83. This scrubbing tower consists of an elongated vertical shell of wood or other suitable material containing a mass of spiral brick or other inert interstitial material supported by a perforated diaphragm spaced from the bottom of the tower. The stack is connected with the lower end of the tower so that the gaseous products of combustion, together with sublimed salts, and such SO_2 as may be formed in the furnace, are caused to pass upwardly through the tortuous passageways afforded by the interstitial material and meet the downflowing stream of the liquor (derived from a source to be explained) which is supplied to the top of the tower, as a result of which I am able to recover many valuable constituents which otherwise would be wasted in the atmosphere, and all without the use of an electrical precipitator or other expensive recovery apparatus. In fact, by the provision of the scrubbing tower constructed as described, I am able to recover sulphur in the form of SO_2 which is not recoverable by the employment of a Cottrell or other electric precipitator. The waste gases, (consisting substantially of nitrogen and carbon dioxide), emerging from the top of the tower are delivered to the atmosphere through a vent 84. The liquor which emerges from the bottom of the tower is conducted by a conduit 85 to what I have termed a dissolving tank 86 for the purpose to be explained. The molten effluent from the furnace consisting of a soluble sulphate and a soluble carbonate are delivered from the spouts 77 to the dissolving tank 86 and are dissolved in the liquor supplied to that tank from the scrubbing tower. A part of this liquor is circulated back to the scrubbing tower by a pump 87 and pipe 88, so that it will be seen that there is substantially continuous circulation of liquor from the dissolving tank to the scrubbing tower and back again. The fresh liquor which is supplied to the dissolving tank is drawn from the series of weak liquor washers indicated at 21 and is conducted therefrom to the dissolving tank by a pipe 89. Inasmuch as a part of the liquor from the dissolving tank 86 is circulated through the scrubbing tower and as there is a constant fresh accretion of liquor from the washing machine 21, it is desirable to provide a storage tank for the surplus prior to its subsequent use, and for this purpose I employ a storage tank 90, to which liquor is pumped from the dissolving tank 86 by a pump 91 through a cooler 92 and a filter 192. By passing this liquor through the filter, I am able to remove any adventitious solid matter that may be contained in the liquor.

As thus far explained, it is quite clear that the only fresh water which has been added to the system is that which was supplied for the direct condensation of the moisture and the cooling of the gases in the condenser tower connected with the blow-pit, and that which was added in forming the caustic solution introduced into the tank 29 prior to the first washing of the pulp, all of the liquor which is utilized for scrubbing, for the forming of

the fresh solution, and the like, being provided by the wash liquor and the added water previously referred to, but an additional supply of hot water may be provided by pipe 129 to the hot water storage tank 22. The effluent from the furnace, when dissolved in the wash liquor in the dissolving tank, to which the weak liquor from the second series of washing machines was delivered after being filtered and delivered to the storage tank 90, is in condition to be acidified by SO_2. This may be accomplished in any suitable way, by bubbling SO_2 gas through the liquor or causing such liquor and the SO_2 to pass in countercurrent flow through a suitable tower or series of towers containing inert interstitial material. Preferably, however, it is desirable for increasing the strength of the liquor in SO_2 so as to provide cooking liquor having a relatively high free SO_2 content, to effect the acidification of the liquor by a series of steps which may be carried on continuously. It will be understood, however, that in describing the preferred process for acidifying the liquor the present invention is not limited to the employment thereof, as any suitable method of acidifying the liquor to produce one having a predetermined percentage of combined SO_2 and a predetermined percentage of free SO_2 may be utilized. The liquor containing the dissolved effluent from the combined boiler furnace and retort comprises, as has already been stated, a soluble sulphate,—e. g., sodium sulphate—and sodium carbonate. The sodium carbonate by reaction with SO_2 is formed into sodium sulphite, sufficient caustic soda having been supplied to the original waste liquor to provide for a sufficient proportion of the carbonate to be formed into sulphite as may be desired. In the case as previously stated, I produce a liquor having from 0.2% to 2% combined SO_2 as sodium sulphite, approximately 2% to 4% sodium sulphate, and from 4% to 7% free SO_2. The acid system so-called by which the liquor is acidified may comprise the following instrumentalities: Towers indicated at 94, 95 are provided with inert interstitial material, and the liquor from the tank 90 is forced by a pump 96 through pipe 97 to the top of the tower 94. The liquor from the lower end of the tower is conducted by a pipe 98 to a storage tank 99. The liquor which leaves the tower 94, in order to distinguish it, may be termed weak acid liquor, since in leaving the tower it contains only from 0.2% to 0.4% free SO_2, from 0.2% to 2% combined SO_2, and from 2% to 4% Na_2SO_4. This liquor is now ready to be delivered to what may be termed the raw acid liquor system which comprises towers indicated at 100 and 101, and consequently is pumped by pump 102 through pipe 103 to the top of the tower 100. These towers, like those at 94 and 95, are provided with a mass of inert interstitial material such as spiral brick, rock and the like, and after the liquor is passed downwardly through the tower 100, it is forced by pump 103 to the top of the adjacent tower 101. In passing downwardly therethrough, it comes in contact with burner gas which is delivered to the bottom of tower 101 by a conduit 104 leading from a sulphur burner. The sulphur burner gas passing upwardly through the tower 101 is conducted therefrom through pipe 105 to the bottom of tower 100, and after passing upwardly therethrough, it may be vented to the atmosphere through an outlet or vent pipe 106. The weak acid liquor, after being passed in series through the two towers 100 and 101, emerges from the latter as what may be termed for convenience a raw acid liquor, and is conducted from the tower 101 to a storage tank 107 through the pipe 108. This liquor as it reaches the storage tank 107 contains from 2% to 2.5% free SO_2 in addition to the combined SO_2 and the sodium sulphate originally in the weak liquor. From this last-mentioned storage tank 107 the liquor may be drawn for further strengthening by the addition of sulphurous acid.

It will be recalled that during each blow of digester contents there emerges from the blow-pit condenser 12 a large quantity or volume of cooled gases containing approximately 50%–60% SO_2. Consequently for the recovery of these gases it is desirable to use a portion of the liquor which is undergoing acidification. The cooled gases are delivered from the blow-pit condenser at intervals or intermittently so that when this is occurring it is necessary to supply for the time being a quantity of liquor for the recovery of the SO_2. This is accomplished by drawing the raw acid liquor contained in the storage tank 107. Hence, leading from the last-mentioned tank there is a valved conduit 180 including a pump 109, for delivering the raw acid liquor to the top of the tower 95; and the conduit 15 for the gases from the condenser 12 is connected to the lower end of the last-mentioned tower so that when the liquor passes downwardly through the tower it meets a strong acid gas by which its free SO_2 content is materially increased to a point where it contains from say 2.7% to 3% free SO_2. From the lower end of this tower the fortified liquor is conducted by pipe 110 back to the storage tank 107. Thus the pipe 180, the tower 95 and pipe 110 afford a circulating system for circulating the raw acid liquor through the tower 95 for the absorption and recovery of SO_2 delivered from the condenser during a blow of the digester. It may be noted that the gas, after passing through tower 95, is conducted by pipe 195 to the lower end of tower 94. A vacuum pump 196 is connected to the vent pipe 197 from tower 94. Even with the addition of free SO_2 to

the liquor in storage tank 107, it is desirable ordinarily to increase its strength in sulphurous acid, and for this purpose I preferably employ the relief gas discharged from the digester during the cooking operation. The relief gas pipe 111 leading from the top of the digester conducts the gas through a cooler 112 and thence to the first of a series of towers indicated at 113, 114, 115 and 116. These towers may be substantially as illustrated and described in my application Serial No. 503,846, filed September 28, 1921, and I do not herein specifically make claim thereto. It is sufficient to say that for the present purposes each of these towers contains inert interstitial material through which gas and the liquor may pass in series and in countercurrent flow. Thus the gas conduit 111 conducts relief gas to the lower end of tower 113 whence it passes in series through towers 114, 115 and 116, and the tail gas which contains about 16% SO_2 is conducted by a pipe 117 from tower 116 to the burner gas conduit 104, so that it may be passed with the burner gases through the series of towers 101 and 100. The raw acid liquor is drawn from the storage tank 107 and delivered first to the top of tower 116, and passing in series through the towers, in countercurrent flow to the gas, is finally delivered to a conduit 118 to a large "finished acid" storage tank 119, whence it is drawn by pump 120 and valved pipe 121 as may be desired for the cooking of chips in the digester 1. The finished acid liquor as delivered to the final storage tank 119 now contains the desired proportion of (say, 4% to 7%) free SO_2, combined SO_2 (say, 0.2% to 2%) in the form of sodium sulphite, and (say, 2% to 4%) sodium sulphate, for it will be recalled that the sodium carbonate delivered as a part of the effluent from the furnaces has been acted upon by SO_2 with the consequent formation of sodium sulphite.

The water which is employed for cooling the gases and condensing the vapors, in the blow-pit condenser, notwithstanding that it is delivered at a relatively high temperature from the condenser, contains a certain amount of SO_2 which may be recovered. This I accomplish by passing such water, while heated, through an expelling tower 122, to which it is passed by pump 123 through pipe 124, and from which it passes through pipe 125 to the hot water storage tank 22 hereinbefore referred to. The tower 122 contains a mass of inert interstitial material, e. g., spiral brick. Air is blown by a fan or pump 126 through an inlet pipe 127 to the lower end of the tower, and in passing upwardly in contact with the trickling streams of water sweeps and removes therefrom substantially all of its contained SO_2 and delivers the same through a conduit 128 to the stack 80 of the boiler furnace for recovery in the scrubbing tower 83.

It will be understood by those skilled in the art that whereas I have described certain preferred arrangements and combinations of the various instrumentalities, nevertheless many changes may be made thereof without departing from the spirit and scope of the invention as set forth in the claims. Because of the nature and small size of the drawings it is impossible to illustrate the various instrumentalities in their exact relationship or at their different levels or in their relative proportions. Moreover, various by-passes, fittings and valves which are used in the actual construction of the entire system are omitted from the drawings in the interests of clarity. In Letters Patent No. 1,427,125, granted on the 29th of August, 1922, I have described a process of fiber liberation in which the cooking liquor comprises essentially an acid solution of a soluble sulphate, and I have pointed out that there were, at times, small adventitious quantities of soluble sulphite accidentally produced in the recovery of the sulphate from the waste liquor. I have since discovered, however, that by providing a material and appreciable definite quantity of soluble sulphite in the cooking liquor, I am able to produce a pulp of higher grade than it is possible to produce when the cooking liquor contains only a soluble sulphate or a soluble sulphate with a negligible portion of sodium sulphite. Consequently in accordance with the present invention I add to the liquor to be used in cooking a definite quantity of either a soluble sulphite or a salt which in the process of recovery and acidification by reaction produces a soluble sulphite in sufficient predetermined quantities. In describing the apparatus which is illustrated upon the drawings, I have called attention to the employment of a caustic soda storage tank 34 from which caustic soda is added to the waste liquor, to the end that in the oxidation furnace the caustic soda may be recovered as sodium carbonate and later converted to sodium sulphite by reaction with SO_2, but it is quite evident that instead of adding caustic soda at the point indicated, sodium carbonate might be added to the contents of the dissolving tank 86 for admixture with the solution produced by the addition of the molten effluent of the liquor, or I may add to the finished acid liquor a certain definite proportion of previously formed sodium sulphite. These all produce equivalent results, and I should not regard the adoption in lieu of the others as a departure from the spirit and scope of the present invention.

Although I have previously adverted to the fact, nevertheless I desire once more to call attention thereto, that in the recovery and utilization of the waste liquor, which includes the evaporation of the aqueous content, the formation and recovery of alcohol,

and the recovery of the inorganic content, only such water as is employed in making the fresh liquor by addition of the recovered soda thereto is that which is used in condensing and cooling the gases and vapors from the blow-pit, omitting from condensation the water which is used in forming the caustic soda solution contained in the tank 34, and consequently the whole process is highly economical, although additional water may be drawn from a suitable source if desired. The acid-making system is easily and cheaply maintained, as there are no insoluble sulphates or other waste products formed which require removal from time to time. The only waste resulting from the entire system comprises those waste or tail gases from the combined boiler furnace and retort and from the tower 100, which are indeed negligible, since these gases comprise substantially only nitrogen and CO_2. The combustion of the combustible content of the waste liquor furnishes heat and power for operating the various pumps and a sufficient excess of steam or power is provided for heating the digester contents and in utilization in other parts of the plant. As a result of the invention as herein set forth, I not only produce a fine, high-grade pulp which is easily bleached and which consists of long and silky fibers, but I also effect marked economies in the operation of the entire apparatus, in addition to saving and recovering valuable products which would otherwise be wasted.

I have herein described the smelting and boiler furnace as provided with an oxidizing atmosphere for the recovery of soda in the form of sodium carbonate and sodium sulphate, but it should be understood that since the furnace-operating conditions bear a direct relationship upon the final ratio of combined SO_2 and sodium sulphate in the cooking liquor, these conditions may be changed according to any given circumstances. As hereinbefore described, the conditions are preferably such as to avoid the formation of sodium sulphide, but under conditions in which the sulphide could without trouble be converted to carbonate, the atmospheric conditions in the retort could be changed. The process as herein outlined provides for a practicable recovery of chemicals, and a cyclic operation, in addition to the production of pulp of the character hereinbefore described. This follows from the use of both soluble sulphate and soluble sulphite in the cooking liquor.

What I claim is:—

1. A process of fiber liberation, which comprises digesting cellulosic material in a sulphurous acid solution comprising 0.2% to 2% combined SO_2 as a soluble sulphite and 2% to 4% of a soluble sulphate.

2. A process of fiber liberation, which comprises digesting cellulosic material in a sulphurous acid solution comprising 0.2% to 2% combined SO_2 as a soluble sulphite and 2% to 4% of a soluble sulphate, together with 4% to 7% free sulphur dioxide as sulphurous acid.

3. A process such as herein described, which comprises cooking in a digester raw cellulosic material in a sulphurous acid solution of a sodium salt, condensing the vapors from the hot waste liquor resulting from such digestion by direct contact with water, smelting and recovering in such water sodium salts of such waste liquor, and acidifying the resulting solution for use in digesting fresh raw material.

4. A process such as herein described, which comprises cooking in a digester raw cellulosic material in a sulphurous acid solution of a sodium salt, condensing the vapors from the hot waste liquor resulting from such digestion by direct contact with water, washing the pulp with the resulting hot water, smelting and recovering in the water from such washing sodium salts from said waste liquor, and acidulating said water containing said salts for digesting raw cellulosic material.

5. A process such as herein described, which comprises cooking in a digester raw cellulosic material in a sulphurous acid solution of a sodium salt, condensing the vapors from the hot waste liquor resulting from such digestion by direct contact with water, washing the pulp with the resulting hot water, smelting and recovering in the water from such washing sodium salts from said waste liquor, recovering in said water soluble salts from the products of combustion in said smelting operation, and acidulating such water for use in digesting raw cellulosic material.

6. A process such as herein described, which comprises cooking in a digester raw cellulosic material in a sulphurous acid solution of a sodium salt, condensing the vapors from the hot waste liquor resulting from such digestion by direct contact with water, washing the pulp with said water, smelting and recovering in the water from such washing sodium salts from said waste liquor, recovering in said water soluble salts from the products of combustion in said smelting operation, recovering free SO_2 from the waste cooking liquor, and acidulating said water-sodium-salt solution with said recovered SO_2 for use in digesting raw cellulosic material.

7. A process such as herein described, which comprises cooking in a digester raw cellulosic material in a sulphurous acid solution of a sodium salt, condensing the vapors from the hot waste liquor resulting from such digestion by direct contact with water, removing free SO_2 from such water, washing the pulp with such water, recovering free SO_2 from the waste cooking liquor, concentrating

and burning the combustible content of the waste cooking liquor and smelting and recovering the contained sodium salts in said water, and acidulating the resulting solution with said recovered SO_2 for use as cooking liquor.

8. A process such as herein described, which comprises cooking in a digester raw cellulosic material in a sulphurous acid solution of a sodium salt, condensing the vapors from the hot waste liquor resulting from such digestion by direct contact with water, smelting and recovering in such water sodium salts of such waste liquor, acidifying the resulting solution for use in digesting fresh raw material, and supplying to said solution such sodium compounds and sulphurous acid as required to bring the same to proper strength as acid cooking liquor.

9. A process as herein described, comprising cooking raw cellulosic material in a sulphurous acid solution of a soluble sulphur compound of the alkali or alkali earth groups, during which the cooking liquor is heated by heating surfaces and not by direct steam, condensing the vapors from the resulting waste cooking liquor by direct contact with water, recovering SO_2 from said waste cooking liquor, washing the pulp in said condensing water, smelting and recovering in said water the inorganic content of said cooking liquor, and acidulating such water with said recovered SO_2.

10. A process as herein described, comprising cooking raw cellulosic material in a solution of a soluble sulphur compound of the alkali or alkali earth groups, during which the cooking liquor is heated by heating surfaces and not by direct steam, evaporating and concentrating the waste cooking liquor, subjecting such concentrated liquor to fermentation for the formation and recovery of alcohol, burning the combustible content, and smelting and recovering the inorganic content of the remaining waste liquor.

11. A process as herein described, comprising burning the combustible content and smelting the inorganic content of a waste cooking liquor resulting from the digestion of raw cellulosic material containing compounds of the alkali or alkali earth groups, recovering said smelted inorganic compounds in an aqueous solution, conducting the products of combustion through a confined mass of inert interstitial material, and circulating said solution through said inert material in contact with said products of combustion for the absorption and recovery of the soluble products thereof.

12. A process of fiber liberation, which comprises digesting cellulosic material in an acid solution containing substantial amounts of both a sulphate and a sulphite of a metal of the alkali-metal group, the amount of said sulphite being considerably more than that formed by metathesis of the sulphate in sulphurous acid solution.

13. A process of fiber liberation, which comprises digesting cellulosic material in a sulphurous acid solution containing substantial amounts of both sodium sulphate and sodium sulphite, the amount of said sulphite being considerably more than that formed by metathesis of the sulphate in sulphurous acid solution.

14. A process of fiber liberation, which comprises digesting cellulosic material in a sulphurous acid solution containing a substantial amount of a soluble sulphate and at least 0.2% of a soluble sulphite.

15. A process of fiber liberation, which comprises digesting cellulosic material in a sulphurous acid solution containing a substantial amount of sodium sulphate and at least 0.2% of sodium sulphite.

16. A process of fiber liberation, which comprises digesting cellulosic material in a sulphurous acid solution containing at least 2% of a soluble sulphate and at least 0.2% of a soluble sulphite.

17. A process of fiber liberation, which comprises digesting cellulosic material in a sulphurous acid solution containing at least 2% of sodium sulphate and at least 0.2% of sodium sulphite.

In testimony whereof I have affixed my signature.

GEORGE A. RICHTER.