Aug. 7, 1956 R. K. ALLEN ET AL 2,758,017

APPARATUS FOR OXIDIZING RESIDUAL PULP LIQUOR

Filed July 30, 1949 2 Sheets-Sheet 1

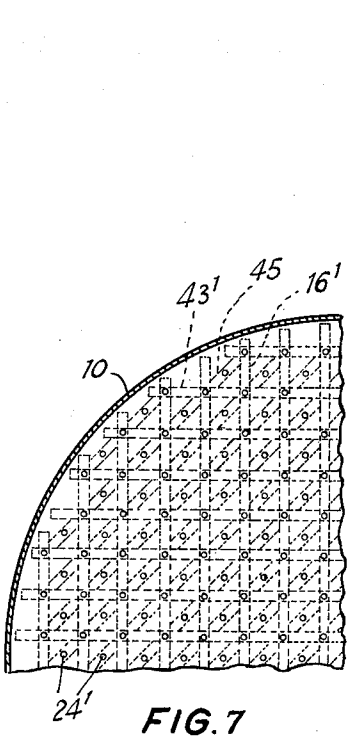


FIG. 7

FIG. 1

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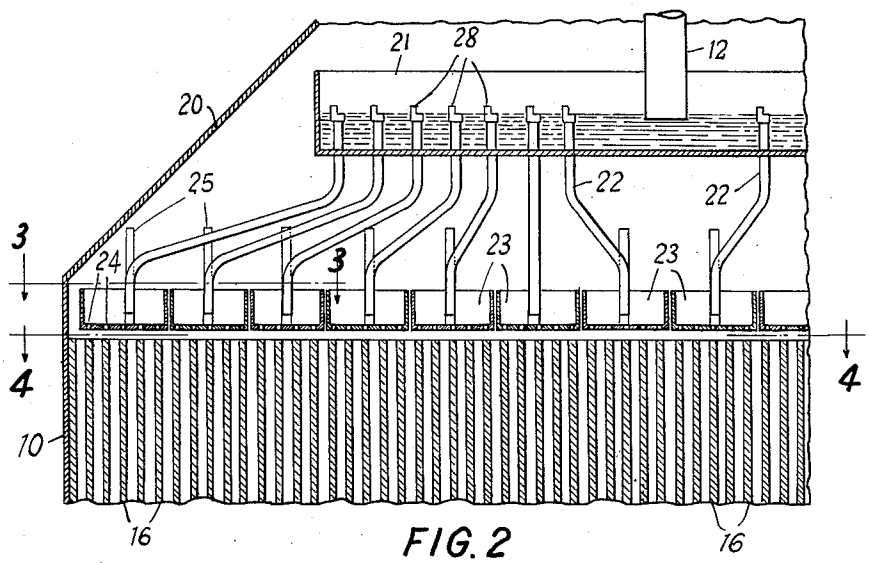


FIG. 2

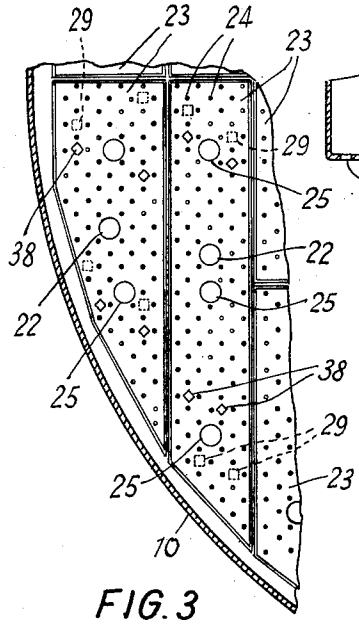


FIG. 3

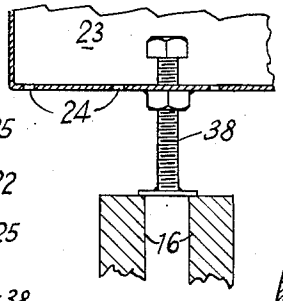


FIG. 5

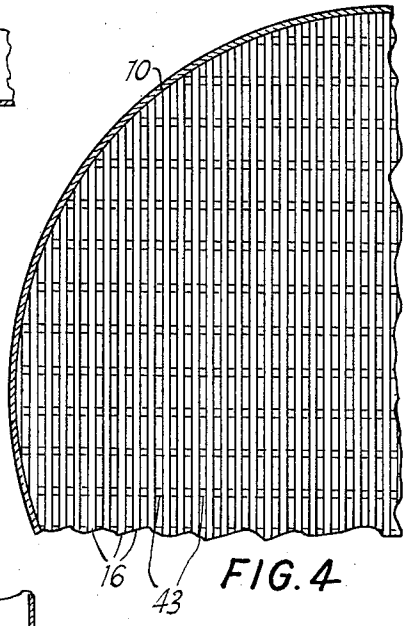


FIG. 4

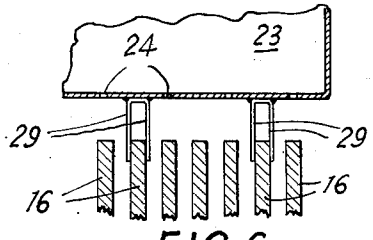


FIG. 6

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APPARATUS FOR OXIDIZING RESIDUAL PULP LIQUOR

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6 Claims. (Cl. 23—283)

The present invention relates to the recovery of chemicals in the residual liquor resulting from the chemical pulping of cellulosic fibrous materials. More particularly the invention relates to a method of and apparatus for the stabilization of sulphur compounds in sulphate residual liquors by the oxidation of the weak liquor at generally atmospheric temperatures.

The residual liquor resulting from the digestion of cellulosic materials in the sulphate process of paper pulp manufacturing contains sulphur compounds which are unstable when subjected to heat or heat in the presence of carbon dioxide gases. The principal unstable sulphur compound in the pulp residual liquor is sodium sulphide (Na_2S), although smaller amounts of other unstable compounds, such as mercaptans, are also present. These sulphur compounds evolve noxious gases, such as hydrogen sulphide, during concentration and incineration of the residual liquor. Such noxious gases not only are a nuisance, but upon their escape from the process also involve an appreciable economic loss of sulphur. However, it is known in the art that the unstable sulphur compounds can be stabilized by oxidation of the liquor in contact with an oxygen containing gas, such as air, at generally atmospheric temperatures and pressures. The oxidation of the liquor converts the sodium sulphide, for example, to a stable compound, sodium thiosulphate ($Na_2S_2O_3$).

In general, two methods of oxidation can be used to stabilize the sulphur compounds in a sulphate residual liquor. One method includes forcing air or other oxygen containing gases through a sheet or bath of the liquor. This results in an effective mechanical contact between the liquor and the gas, and a high degree of liquor oxidation. However, this method results in the formation of large quantities of foam, necessitating the use of a foam breaker or the provision of settling tanks for the foam. The second method of liquor oxidation seeks to avoid or minimize the formation of foam, so that the foam handling equipment will be but a minor portion of the apparatus required for the stabilization of the sulphur compounds in the residual liquor.

The present invention relates to a method of and apparatus for the oxidation of residual liquor under conditions of a minimum formation of foam. The liquor is passed through a tower in a plurality of films in countercurrent surface contact with the oxidizing gas, with the liquor films formed at the top of the tower in such a manner as to avoid the passage of oxidizing gases through any body of liquor. Any foam formed in the lower portion of that tower is removed, as formed, so as to avoid pluggage of the gas flow passages through the upper portion of the tower.

The various features of novelty which characterize this invention are pointed out with particularity in the claims annexed to and forming a part of this specification. For a better understanding of the invention, its operating advantages and specific objects attained by its use, reference should be had to the accompanying drawings and

descriptive matter in which the invention has been illustrated and described.

Of the drawings:

Fig. 1 is an elevation view of an oxidation tower constructed in accordance with the present invention;

Fig. 2 is an enlarged elevation view, in section, of a part of the upper portion of the apparatus shown in Fig. 1;

Figs. 3 and 4 are section views taken along the lines 3—3 and 4—4, respectively, of Fig. 2;

Figs. 5 and 6 are enlarged views of the support and guide elements, respectively, of the secondary distribution pans shown in Figs. 2 and 3; and

Fig. 7 is a plan view, in section, of a modified construction and arrangement of the tower walls shown in Fig. 1.

In general, as shown in the drawings, the liquor oxidizing apparatus of the present invention includes a vertically elongated cyclindrical shell 10 defining a liquor-gas surface contact tower. The tower is provided with a gas outlet 11 and liquor inlet pipes 12 and 13 in its upper end portion, and a gas inlet duct 15 intermediate the height of the tower connected with a source of supply such as a fan 18, and a liquor outlet pipe 14 in its lower end portion. Between the vertically spaced liquor inlet pipes and the gas inlet duct the tower is provided with a plurality of vertically extending horizontally spaced walls 16 arranged to present an extensive area of surface contact between the liquor and the oxidizing gas. Exteriorly of the tower shell 10, a liquor pump 17 is arranged to withdraw oxidized liquor through the pipe 14 and to discharge a selected portion of the liquor through the pipe 12 to recirculate through, and thereby to control the degree of liquor oxidation attained within the tower.

As shown in Figs. 1 and 2, the shell 10 of the tower is provided with a frusto-conical top 20 having a centrally positioned opening therein defining the gas outlet 11. The recirculated liquor supply pipe 12 and the make-up liquor supply pipe 13 project through the conical sides of the top 20 to discharge into a primary liquor distribution pan 21 of a generally circular plan section. From the pan 21 the liquor is discharged through connecting tubes 22 to a plurality of horizontally disposed secondary liquor distribution pans 23. Each of the pans 23 is provided with an individual tube 22 which is arranged with its lower end spaced above the bottom of the pan and generally centered with respect to the pan walls. The upper end of each tube 22 is fitted with a vertically adjustable notch or orifice, so that the intake height of each tube is equal to each of the other tubes, and each of the tubes 22 receives a substantially equal share of the liquor discharged to the pans 23. As shown in Fig. 2, the adjustable orifice on the upper end of each of the tubes 22 is formed from a pipe coupling 28 which is notched and threaded to the upper end of a tube.

The pans 23 are arranged in spaced horizontal relationship as shown in Figs. 2 and 3, and are each provided with a plurality of rows of spaced outlet ports 24 in the bottom thereof. The spacing between the rows of ports 24 corresponds with the spacing between the extended surface walls 16 of the tower, so that when the pans are properly positioned the ports are in vertical alignment with the walls with the discharging liquor forming a film on each of the vertical wall surfaces. The proper positioning of the pans is obtained and maintained by the use of guide clips 29 fastened to the under side of the pans, and each arranged to engage the upper end of one of the subjacent tower walls. For best results in the oxidizing tower, the liquor should be distributed to all of the subjacent wall surfaces so as to utilize the maximum available area of liquor film for gas contact

therewith. Best distribution of liquor is obtained by leveling each of the pans **23** with generally equal quantities of liquor passing through each of the ports **24**. Each pan is supported upon the subjacent walls **16** of the tower, with each of the pan supports formed by an adjustable screw jack **38**. The detailed arrangement of the guide clips **29** and the screw jacks **38** is shown in Figs. 6 and 5 respectively, while their assembled relationship to the pans **23** is shown in plan view in Fig. 3.

Each of the secondary distributing pans **23** is provided with two or more gas passage tubes **25** fastened to the bottom of the pan and arranged with their lower ends opening into the space between adjacent walls **16**. The tubes **25** extend upwardly above the surface of the liquor pool maintained in the pans **23**.

As shown in Fig. 1, the walls **16** of the tower extend substantially vertically from an upper position, indicated at **42**, which is closely spaced below the distributing pan **23**, to a lower position intermediate the height of the oxidizing tower. The walls are supported at their lower ends by a support grid **44** attached to the shell **10**. As shown in Figs. 2 and 4, the walls **16** are constructed and arranged to extend transversely across the interior of the shell in closely spaced parallel relationship. The horizontal spacing between adjacent walls is maintained by a plurality of spacing strips **43** which are substantially uniform in cross-sectional dimensions and extend vertically for the full height of the walls **16**. Each surface of the walls is constructed to form a continuous, substantially planar surface throughout its vertical height, so that the liquor film flowing downwardly along the wall surface will be uninterrupted. In horizontal section, the walls are thus arranged to define a multitude of rectangular passageways for the upward flow of the oxidizing gas.

The walls **16** can be constructed of any suitable material that is substantially inert with respect to the liquor. Wood has been used successfully as a material, with the walls **16** fabricated from one inch lumber. When the tower is in use with new wood, the weak liquor will dissolve and remove the hemicellulose in the wood. This attack on the packing results in a loss of approximately **20** percent of the weight of the wood, without serious loss of structural strength, and is ended in the first hours of initial liquor and wood contact. After the removal of the hemicellulose the wood is substantially inert with respect to the liquor under the temperature and pressure conditions prevailing within the tower.

The spacing of the ports **24** in the bottom of the distributing pan **23** is selected to match the dimensions of the walls **16** and the spacing strips **43**, so that the liquor streams will impact the upper surfaces of the walls. The assembled relationship of the ports **24** with the upper ends of the walls **16** is shown particularly in Fig. 2. The spacing between the adjacent pans **23** and the gas passage tubes **25** will direct the oxidizing gas flow with a minimum interference in the formation of the liquor films on the walls **16**. This arrangement will tend to cause the liquor films on the wall surfaces to be formed with a minimum of liquor foaming, as may be created by a flow of gas through the liquor streams.

The lower portion of the tower is provided with vertically spaced inverted frusto-conical members **26** and **27** extending across the cross-sectional area of the shell **10**. The uppermost member **26** is spaced below the grid **44** and the gas inlet duct **15**, and is arranged to receive the oxidized liquor discharging from the lower ends of the walls **16**. The liquor collected in the member **26** passes through a centrally positioned outlet into a discharge pipe **30**. Since it is advantageous to avoid a free fall of liquor, so as to reduce foam formation, the pipe **30** is arranged to discharge liquor from the lower end thereof in a direction generally tangential to and adjacent the inner surface of the shell **10**. The lower member **27** is provided with a centrally located opening **31** which is connected with the pipe **14** by means of a vertically arranged stub pipe **32** and a connecting T fitting **33**. The fitting **33** is provided with a drain valve **34** so that the tower can be washed during periods of tower repair or cleaning.

The oxidized liquor flow rate through the pump **17** is regulated by the valves **35** and **36** in the pump inlet and discharge lines, respectively. The liquor leaving the pump is ordinarily divided into two streams, one stream passing through a valve **37** into the pipe **12** for recirculation through the oxidation tower, while the other stream passes through a valve **40** and a pipe **41**. The pipe **41** may be connected to an oxidized liquor storage tank, or directly connected with a liquor concentrating device, such as a multiple effect evaporator. The liquor flow through either of the pipes **12** and **41**, or through both in any selected proportion, can be easily regulated by adjustment of the valves **37** and **40**.

A pool of oxidized liquor is maintained within the bottom of the tower so as to provide a source of liquor, free of foam, for the pump **17** inlet. Any foam accumulated in the section of the tower defined between the members **26** and **27** will float on the top **47** of the liquor pool. When the height of the foam reaches the level of a foam discharge pipe **50**, the foam is removed by a foam pump **51** for delivery through a pipe **52** to a settling tank (not shown). While a source of foam-free liquor is desirable for the pump **17**, the level of the pool of liquor in the lower portion of the tower can also be used as a means for regulating the amount of unoxidized or make-up liquor supplied to the tower through the pipe **13**. With the operational adjustment of the amount of oxidized liquor recirculated through the pipe **12**, the actual amount of oxidized liquor removed from the system through the pipe **41** and thus the amount of make-up liquor required to maintain a generally uniform flow of liquor through the tower packing, may change. Any necessary changes in flow of liquor through the pipe **13** are readily accomplished by a float **53** operatively connected to a flow control valve **54** positioned in the pipe **13**, through a linkage **55**. The float **53** is selected with a weight and dimension sufficient to be effected only by the level **47** of the liquor pool, and not by any variation in the amount of foam present.

A modified arrangement of the tower packing is shown in Fig. 7. As in the arrangement of Figs. 2 and 4, all of the vertical surfaces of the packing are continuous and planar from top to bottom. In the arrangement of Fig. 7, the horizontal section of the spaces between the walls is triangular. The spacing between adjacent walls **16'** is substantially equal to the spacing between successive spacing strips **43'**, with the substantially square spaces therebetween divided by a diagonal member **45**. The ports **24'** through which the liquor is delivered to the top of the packing are spaced and arranged to discharge the liquor so as to form a downwardly moving film on each of the vertical surfaces of the packing.

The oxidizing function of the apparatus is initiated by starting the fan **18** to circulate the oxidizing gas through the packing of the tower. After a short period of gas flow, liquor is supplied to the top of the tower through the pipe **13**. The liquor pools maintained in the reservoir **21** and the distributing pan **23** are not subjected to a flow of gas therethrough, and thus any substantial foaming of the liquor is not encountered at these positions. Although the liquor ports **24** or **24'** are subjected to a slight gas pressure, such pressure is insufficient to overcome the head of liquor maintained in the pan **23**, so that gas flow upwardly through the liquor pool therein is avoided. The gas leaving the upper end of the walls of the packing will flow through the pipes **25**, between the spaced pans, and between the periphery of the pans and the interior of the shell **10**. While the streams of liquor discharging through the ports **24** fall through a short distance to the subjacent tops of the walls **16**, and in so falling are exposed to a limited cross flow of gas, the foam formed is slight and will

be washed downwardly through the tower by the liquor flow and will not interfere with either gas or liquor flow in the upper portion of the shell **10**.

The surface contact between the liquor films on the walls **16** or **16'** and the ascending gas effectively oxidizes the liquor to stabilize the unstabilized sulphur compounds therein, while minimizing foam formation. As the liquor falls through the gas inlet space between the support grid **44** and the member **26** foam is formed on contact with the latter. However, the foam will be washed down through the pipe **30** by the downflowing liquor and will not accumulate sufficiently to block or adversely restrict the gas flow passages between the walls of the tower packing.

As the liquor level **47** rises to the desired position, the inflow of make-up liquor is progressively reduced, as automatically regulated by the valve **54** and the float **53**. With a pool of liquor in the member **27** the pump **17** is started. During the initial operating period of the pump **17**, the oxidized liquor discharged therefrom is ordinarily recirculated to the reservoir **21** by adjustment of the valves **37** and **40**. As the desired degree of liquor oxidation is attained the valves **37** and **40** are readjusted to discharge oxidized liquor through the pipe **41**. When stabilized operating conditions have been established for the desired liquor oxidation, the apparatus will maintain such conditions automatically by reason of the make-up liquor flow control.

The amount of sodium sulphide contained in residual Kraft liquor will vary from plant to plant, depending upon the raw materials in use. However, for purposes of illustration a sodium sulphide content of approximately .006 pound per pound of liquor may be considered typical of the residual liquor obtained from the pulping of southern pine, for example. The height of the tower described, i. e. the vertical extent of the walls **16** required to oxidize sodium sulphide to sodium thiosulphate depends upon the sulphide content of the entering liquor and the degree of oxidation desired. For each .001 pound of the sulphide per pound of liquor supplied, the tower must be from approximately 6 to 13 feet high, where the smaller dimension represents the height necessary for the initial stage of oxidation and the larger dimension represents the height necessary to oxidize the last increment of the sulphide. Since the height of the tower is dependent upon the sulphide content of the entering liquor, it will be understood that the recirculation of oxidized liquor through the tower will reduce the average sulphide content thereof, and thus permit the use of a shorter tower to completely convert the sulphide to thiosulphate. However, recirculation increases the amount of liquor passing through the tower and necessitates larger areas of liquor-gas contact.

The tower described has been successfully operated at liquor flow rates of from 50 to 400 pounds per hour of liquor per foot of wetted wall perimeter. Below the lower value the volume of liquor seems to be insufficient to cover the available surfaces of the walls **16** or **16'**. Above 400 pounds per hour the liquor film seems to become too thick for best contact with an oxidizing gas, such as air. In this range of liquor flow rates the oxidizing air, substantially at atmospheric temperature and pressure, is passed through the tower at a rate corresponding to from approximately .015 to .05 pound of air per pound of liquor. Apparently, the air flow velocity through the tower should be low, but velocity does not seem to be critical, as long as the velocity of the air flow does not interfere with the downwardly moving liquor films. The general proportions of the air flow passageways between the film supporting walls illustrated in the drawings, have proven satisfactory for this purpose.

It will be understood the tower of the present invention is constructed and arranged for the oxidation of unstabilized sodium compounds in a residual pulp liquor. For any particular tower, constructed according to the present invention, a reasonably consistent weight of sodium sulphide will be oxidized to sodium thiosulphate within the flow limits described for air and liquor. When the weight of sodium sulphide in the make-up or untreated liquor is sufficiently low, or when substantially complete oxidation is unnecessary, the tower can be operated without the recirculation of partially oxidized liquor. Several towers may also be connected for series flow of liquor, without recirculation, when a high weight ratio of sodium sulphide is present in the untreated residual liquor. Under desired operating conditions of partial liquor oxidation, the tower may be operated without the use of a fan, and with air flowing through the tower by reason of natural draft. Due to the very slight difference in entering air and liquor temperatures very little concentration of liquor occurs during its treatment in the oxidizing tower of the present invention. Ordinarily the contact between air and liquor will cause some evaporation of moisture from the liquor, but the amount is insignificant.

While in accordance with the provisions of the statutes we have illustrated and described herein the best form and mode of operation of the invention now known to us, those skilled in the art will understand that changes may be made in the form of the apparatus disclosed without departing from the spirit of the invention covered by the claims, and that certain features of the invention may sometimes be used to advantage without a corresponding use of other features.

We claim:

1. Apparatus for the oxidation of a pump residual liquor substantially without evaporation comprising a tower, a plurality of vertically extending continuous planar walls in the intermediate and upper portion on said tower, a liquor distributor having a perforate bottom positioned adjacent the upper end of said tower walls, said distributor arranged to maintain a pool of liquor therein and to deliver a plurality of streams of liquor to and in substantial vertical alignment with said walls, means for passing a flow of air between said walls in direct surface contact relationship with films of liquor thereon, and a plurality of air discharge pipes extending through said liquor distributor and the pool of liquor therein, whereby air leaves said tower without passing through said liquor pool.

2. Apparatus for the oxidation of a pulp residual liquor substantially without evaporation comprising a tower, wood walls within said tower arranged to form a plurality of vertically extending continuous planar surfaces arranged to form a plurality of gas flow passageways therebetween of substantially uniform horizontal configuration, a liquor distributor pan adjacent the upper end of said walls arranged to enclose a pool of liquor therein and having a plurality of perforations therein substantially in vertical alignment with the top of said walls to deliver streams of liquor to said walls, means for passing a flow of air through said passageways in direct contact surface relationship with the liquor on said walls, and a plurality of air discharge pipes extending through said liquor pan whereby air leaves said tower without passing through said liquor pool.

3. Apparatus for the oxidation of a pulp residual liquor comprising a closed tower having a top gas outlet and a bottom liquor outlet therein, a plurality of horizontally spaced substantally vertical walls extending from a position adjacent the top of said tower to a position spaced above the bottom of said tower, a liquor distributing pan positioned closely adjacent the upper end of said walls and having a plurality of perforations therein spaced to discharge streams of liquor to the top of each of said walls, means for maintaining a pool of liquor in said pan, a plurality of tubes extending upwardly through said pan with the lower ends thereof opening to the spaces between adjacent walls, a fan arranged to deliver oxidizing gas to said tower for upward flow between said walls and through said tubes to said gas outlet, an inverted frusto-conical liquor collecting member extending across

said tower at a position intermediate the lower end of said vertical walls and said tower bottom, a discharge tube connected with a centrally positioned opening in said member and extending to a lower position spaced above said tower bottom adapted to discharge liquor generally tangentially along the wall of said tower, and a pump arranged to withdraw liquor from the bottom of said tower.

4. Apparatus for the oxidation of a pulp residual liquor comprising a closed tower having a top gas outlet and a bottom liquor outlet therein, a plurality of horizontally spaced substantially vertical walls extending from a position adjacent the top of said tower to a position spaced above the bottom of said tower, a liquor distributing pan positioned closely adjacent the upper end of said walls and having a plurality of perforations therein spaced to discharge streams of liquor to the top of each of said walls, means for maintaining a pool of liquor in said pan, a plurality of tubes extending upwardly through said pan with the lower ends thereof opening to the spaces between adjacent walls, a fan arranged to deliver oxidizing gas to said tower for upward flow between said walls and through said tubes to said gas outlet, an inverted frusto-conical liquor collecting member extending across said tower at a position intermediate the lower end of said vertical walls and said tower bottom, a discharge tube connected with a centrally positioned opening in said member and extending to a lower position spaced above said tower bottom adapted to discharge liquor generally tangentially along the wall of said tower, a pump arranged to withdraw liquor from the bottom of said tower, and a float adapted to control the flow of liquor to said pan in response to the level of liquid in the bottom of said tower.

5. Apparatus for the oxidation of a pulp residual liquor comprising a closed tower having a top gas outlet and a bottom liquor outlet therein, a plurality of horizontally spaced substantially vertical walls extending from a position adjacent the top of said tower to a position spaced above the bottom of said tower, a liquor distributing pan positioned closely adjacent the upper end of said walls and having a plurality of perforations therein spaced to discharge streams of liquor to the top of each of said walls, means for maintaining a pool of liquor in said pan, a plurality of tubes extending upwardly through said pan with the lower ends thereof opening to the spaces between adjacent walls, a conduit opening into said tower at a position beneath the lower end of said vertical walls and arranged to deliver air to said tower for upward flow between said walls and through said tubes to said gas outlet, an inverted frusto-conical liquor collecting member extending across said tower at a position intermediate the lower end of said vertical walls and said tower bottom, a discharge tube connected with a centrally positioned opening in said member and extending to a lower position spaced above said tower bottom adapted to discharge liquor generally tangentially along the wall of said tower, a pump arranged to withdraw liquor from the bottom of said tower, and a float adapted to control the flow of liquor to said pan in response to the level of liquid in the bottom of said tower.

6. Apparatus for the oxidation of pulp residual liquor comprising a closed tower having a gas outlet in its top and a liquor outlet in its bottom, a plurality of horizontally spaced substantially vertical walls extending from a position adjacent the top of said tower to a position spaced above the bottom of said tower, a liquor distributing pan positioned closely adjacent the upper end of said walls and having a plurality of perforations therein spaced to discharge streams of liquor to the top of each of said walls, a plurality of gas flow tubes extending upwardly through said pan with the lower ends thereof opening into the spaces between adjacent walls, an inverted frusto-conical liquor collecting member extending across said tower at a position intermediate the lower end of said vertical walls and said tower bottom, a discharge tube connected with a centrally positioned opening in said member and extending to a lower position spaced above said tower bottom adapted to discharge liquor tangentially along the wall of said tower, a liquor pump arranged to withdraw liquor from the bottom of said tower and to discharge a selected portion of said liquor into said distributing pan, means for delivering make-up liquor to said pan, means for controlling the flow of make-up liquor in response to the level of liquor in the bottom of said tower, and a fan arranged to deliver an oxygen containing gas to said tower for upward flow between said walls.

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