Aug. 26, 1958 P. E. SHICK 2,849,292

PULP MANUFACTURE

Original Filed Nov. 16, 1953 3 Sheets-Sheet 1

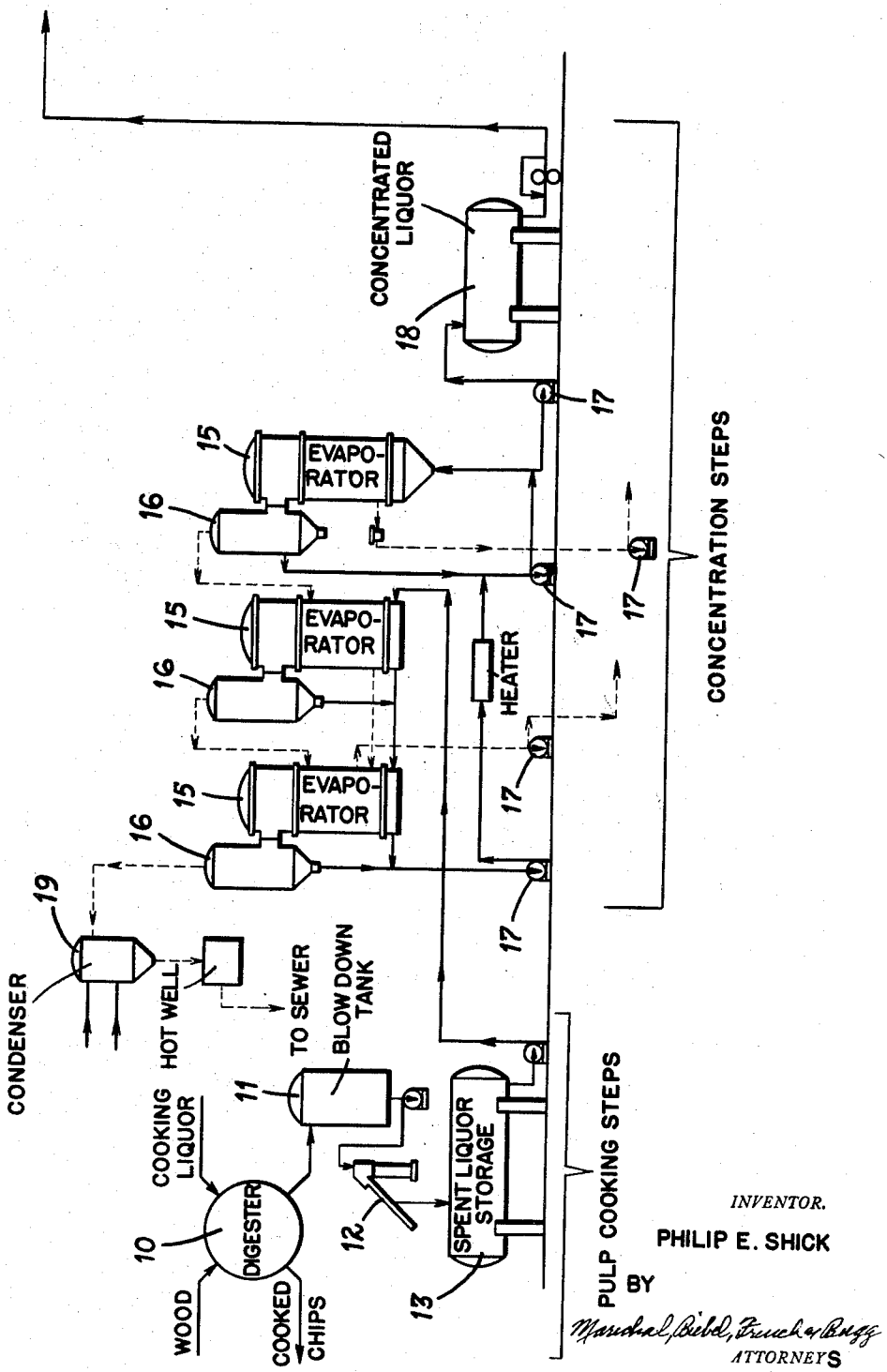


FIG-1

INVENTOR.

PHILIP E. SHICK

BY

Marshall, Bibb, Trucker & Boggs

ATTORNEYS

Aug. 26, 1958 P. E. SHICK 2,849,292

PULP MANUFACTURE

Original Filed Nov. 16, 1953 3 Sheets-Sheet 2

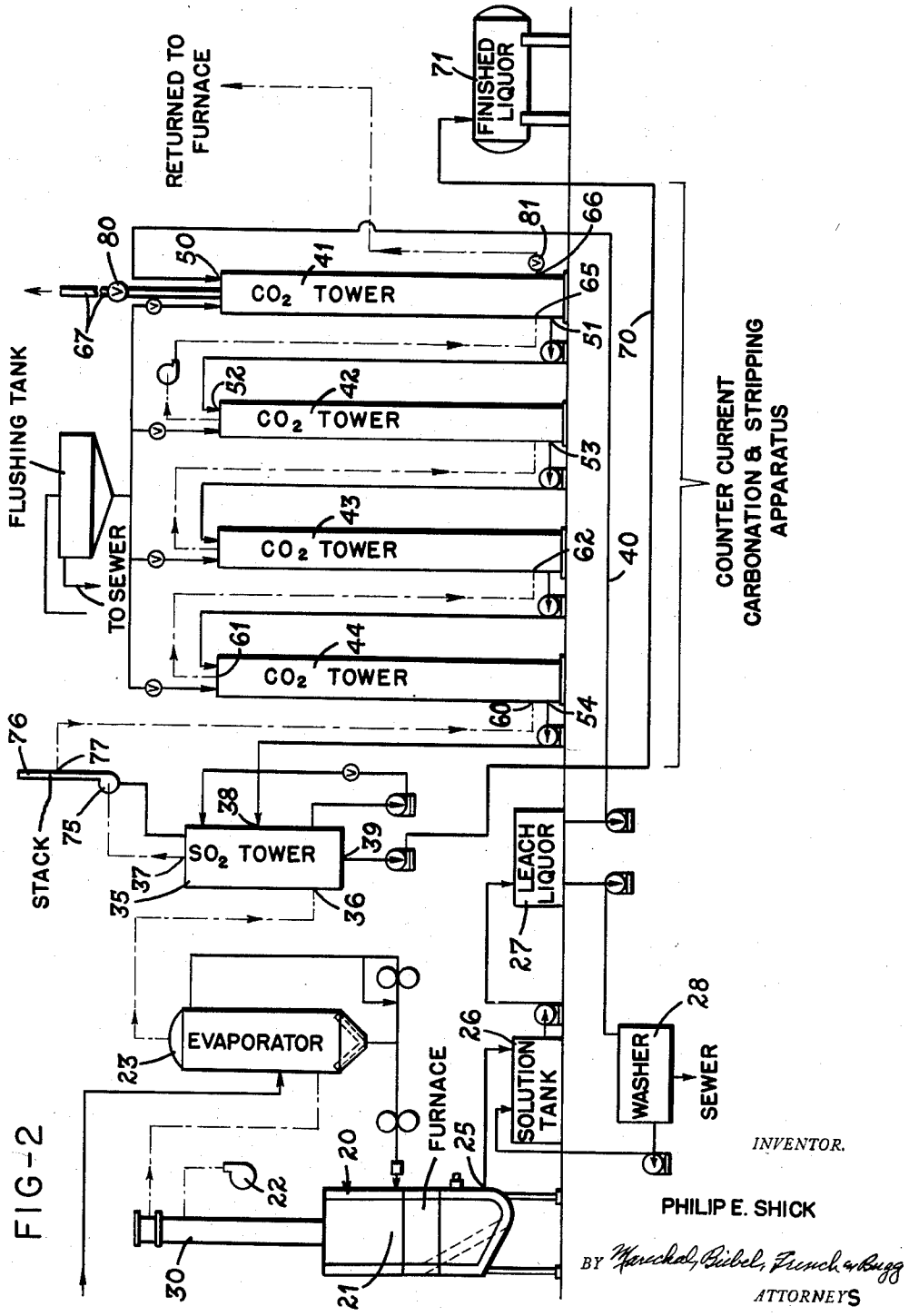


FIG-2

INVENTOR.

PHILIP E. SHICK

BY Marshall, Bibel, French & Bugg

ATTORNEYS

FIG-3

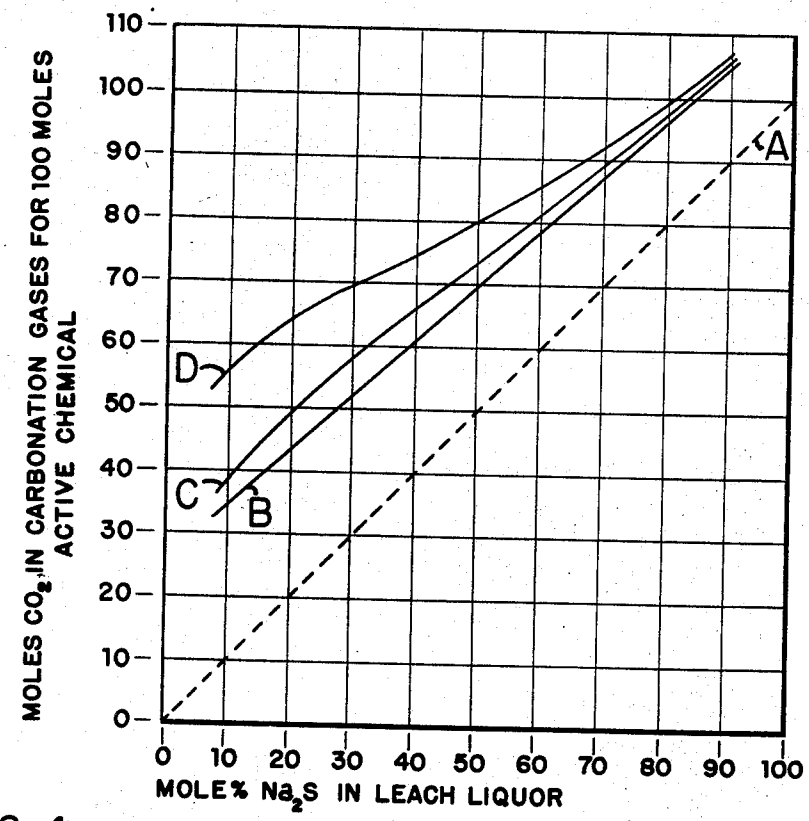
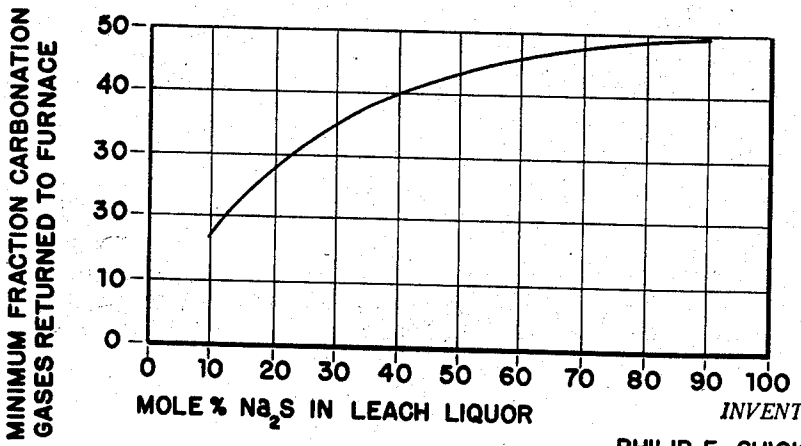


FIG-4



INVENTOR.
PHILIP E. SHICK
BY
Marshall, Bibel, French & Bugg
ATTORNEYS

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2,849,292

PULP MANUFACTURE

Philip E. Shick, Chillicothe, Ohio, assignor to The Mead Corporation, Dayton, Ohio, a corporation of Ohio

Original application November 16, 1953, Serial No. 392,182. Divided and this application April 9, 1956, Serial No. 582,312

8 Claims. (Cl. 23—262)

This invention relates to the manufacture of wood pulp and more particularly to a new and improved process for producing pulp by chemical action on wood or the like in such a way that the necessary chemical reagents may be substantially recovered for reuse.

This application is a division of my copending application Serial No. 392,182, filed November 16, 1953, now Patent No. 2,788,273, which is, in turn, a continuation-in-part of my copending application Serial No. 125,003, filed November 2, 1949, now abandoned.

Pulp for the manufacture of paper and the like may be produced from wood by digesting or cooking the wood in the presence of suitable chemical reagents such as sodium sulphite or sodium acid sulphite which will act on or remove those organic constituents of natural woods which tend to bind the cellulose fibers together. If it is attempted to manufacture pulp in this way, the end products of such a cooking or digestion process include substances such as sodium compounds, sulphur compounds and organic substances. The dumping or discarding of such spent end products of the cooking or digestion operations not only is wasteful of the reagents and commercially expensive but also is extremely obnoxious to the area surrounding the mill in which such cooking and digesting processes are carried out.

In accordance with the present invention it has been discovered that pulp of satisfactory quality and characteristics for the manufacture of paper and the like may be produced from wood by the digestion or cooking thereof with sodium salts of sulphurous acid alone or in combination with other constituents such as carbonates or sulphur dioxide in such a way that the sodium and sulphurous components of the cooking or digestion reagents may be recovered for reuse in the cooking process, thereby eliminating wasteful use of chemicals and the production of obnoxious nuisance conditions in the vicinity of the mill utilizing the process of this invention. Such recovery of the cooking chemicals may be satisfactorily accomplished according to the present invention by utilizing in the operation of this invention controlled combustion, carbonation and sulphiting conditions to convert inorganic constituents of the spent end products of the cooking or digestion operation to suitable fresh cooking mixtures of sodium sulphite and sodium carbonate or bicarbonate or sodium acid sulphite and sulphur dioxide and to eliminate organic and undesirable inorganic substances in an inexpensive and unobnoxious manner.

Accordingly it is one object of this invention to produce pulp of satisfactory properties for the manufacture of paper or the like from cellulosic materials by the chemical digestion of such cellulosic materials to remove therefrom or to render ineffective as binders therein components of the cellulosic materials which tend to bind the cellulose fibers together, and to produce such pulp in the manner described so that the chemicals used in the cooking or digestion process may be economically recovered for reuse as cooking or digesting chemicals.

Another object of this invention is to provide a process and apparatus for the recovery of sodium and sulphur compounds from spent pulp cooking liquors of the character described.

Still another object of this invention is to produce pulp in the manner described so as to avoid wasteful and nuisance creating exhausting of expensive or obnoxious materials into the atmosphere or streams in the vicinity of the pulp mill.

A further object of this invention is the production of pulp in the manner described so that unwanted combustible by-products of the cooking or digestion process may be economically utilized for the production of heat, steam and power.

Still another object of this invention is the production of pulp in the manner described so that the pulp producing and reagent recovering process may be as nearly as practicable self-productive of the heat and other energy necessary for its use.

A still further object of this invention is to provide a cyclic process and apparatus therefor for continuous operation in conjunction with pulp manufacture of the character described to achieve substantially complete recovery therefrom of sodium and sulphur compounds for reuse as cooking chemicals.

Other objects and advantages of the invention will be clear from the following description, the accompanying drawing and the appended claims.

In the drawing—

Fig. 1 is a flow sheet or schematic representation of a portion of the various steps and stages of a process and a diagrammatic showing of apparatus embodying and for practicing this invention;

Fig. 2 is a continuation of the flow sheet or schematic representation of Fig. 1, and is shown as a separate figure merely because of the limitations of drawing size;

Fig. 3 is a chart of gas requirements and carbon dioxide distribution of a process embodying and for practicing this invention under typical operating conditions for a flue gas containing 16% carbon dioxide (on a dry basis) and an operating temperature of 160°–170° F.; and

Fig. 4 is a chart of minimum fraction of total carbonation gases to be returned to the furnace when operating a process embodying and for practicing this invention with a minimum total gas through-put.

In the preparation of cellulosic pulp from wood for the purpose of paper manufacture and the like, it is necessary to soften or remove from the wood or other cellulosic materials components thereof such as lignin and the like which tend to bind the cellulose fibers together. One satisfactory way of accomplishing this is by a chemical cooking or digestion process in which all or part of the binding material is removed or loosened or rendered ineffective as a binder by the action thereon under heat and pressure of sodium sulphite alone or of sodium sulphite in combination with suitable substances such as sodium bicarbonate. Whether sodium sulphite is used alone as the primary cooking or digesting chemical or whether it is used in combination with sodium bicarbonate is determined by the character of the cellulosic material to be digested as well as by the character of the pulp desired to be produced by the digestion operation.

The resultant products of such cooking or digesting process include, in addition to the freed or partially freed cellulosic fibers, fluids which may be referred to as "spent liquor" containing various inorganic sodium, sulphur, and carbon compounds in addition to organic residues of ligneous or cellulosic origin that have been removed from the wood during cooking. The exact composition of such "spent liquor" depends upon, among

other factors, the type of wood digested and the particular composition of cooking liquor employed.

Pulp cooking steps

In practicing one embodiment of this invention for the manufacture of pulp for papermaking or the like, chips of various hard woods such as gum or poplar, or chestnut from which the tannin has been extracted, are charged or introduced into cooking or digestion apparatus well known in the pulp manufacture art such as a so-called rotary digester **10** commonly used in so-called "neutral sulphite semi-chemical cook" processes well known in the pulp making industry. These chips of wood may be steamed if desired in the digester. To the digester is then added a liquor which may be designated as "cooking liquor" in an amount approximately three and one-fourth times the dry weight of the chips in the digester. This cooking liquor contains sodium sulphite in an amount on a dry basis approximately 12% to 16% of the dry weight of the chips of wood and sufficient sodium bicarbonate to maintain a neutral pH in the digester at the end of the cooking operation, such an amount in this embodiment being approximately 4.8% to 6.4% of the dry weight of the chips. The sodium sulphite is of a concentration of approximately 40 to 50 grams per liter and the concentration of sodium bicarbonate may be approximately 15 to 20 grams per liter.

After the chips and cooking liquor have been introduced into the digester, it is closed as provided for in its well known construction and rotated while it is heated to approximately 100° C. at which time the rotation is stopped and the pressure which has accumulated within the closed digester due to the heating is relieved by releasing the gases to the atmosphere as provided by the well known construction of the rotary digester apparatus. Thereafter the digester is again closed and heated during the course of approximately two to three hours to a temperature of approximately 160° C. and is held at approximately this temperature for approximately three to four hours during which time a pressure of the order of from 75 to 100 pounds per square inch builds up in the closed digester. Thereafter the liquor is blown out of the digester into a suitable storage tank or "blow down tank" **11** by the action of the pressure which has accumulated in the closed digester and the cooked chips are dumped from the digester to be "defibered" and washed by common and well known procedures in the pulp making industry. The liquor blown from the digester, which, now that cooking is completed, may be designated as "spent liquor," contains approximately 40% to 50% of the original chemicals present in the cooking liquor originally introduced to the digester. Additional amounts of the original chemicals are added to this spent liquor by combining therewith the washings from the cooked chips from the digester. The above steps of the invention are indicated schematically on the drawing by the stage labeled "Pulp Cooking Steps."

Although this description of one preferred embodiment of this invention relates particularly to cooking or digesting steps of the character just described, the methods and processes of this invention are suitable for cooking or digestion operations which vary somewhat from that just described. For example, pulp may be produced in accordance with this invention as from a so-called "acid sulphite cook" in which the primary cooking chemicals are sodium acid sulphite and sulphur dioxide instead of the sodium sulphite and sodium bicarbonate mixture suggested above for a cooking or digesting process falling within the general class designated generally as a "neutral sulphite cook." Furthermore, pulp may be produced in accordance with this invention as from either a so-called "full chemical cook" or as from a "semi-chemical cook," the former designation indicating a digestion process in which substantially all of the material binding the cellulose fibers together will be removed or loosened or rendered ineffective as a binder by the cooking chemicals so that, upon completion of the cooking or digestion step, the cellulose fibers will be but loosely held together, and the latter designation indicating a cooking or digesting process wherein conditions are so controlled that only a portion of the binding material is effected during the cooking or digesting operation thus requiring further mechanical working or "defibering" to separate the cellulose fibers sufficiently for use in the manufacture of paper. The cooking or digesting operation above described, then, may be categorized as a so-called "neutral sulphite semi-chemical cook," such designation merely indicating to those skilled in the art that the cooking or digesting step of this embodiment is accomplished with sodium sulphite and is very generally of such a character that the pH at the completion of the cooking step will be substantially neutral and that the partially digested cellulosic material will require further mechanical defibering action to separate the cellulose fibers sufficiently.

Furthermore, in addition to the types of wood suggested in the particular description of one cooking or digestion operation above, sulphite cooking liquor prepared according to this invention may be used in the pulping of any of the ligno-cellulosic materials suitable for so-called sulphite pulp processes. These materials include not only hard woods such as aspen, poplar, oak and chestnut, but also soft woods such as pine, spruce and hemlock as well as various grasses and agricultural residues.

Concentration steps

The spent liquor, after removal from the digester **10** as above, may conveniently be filtered as at **12** to insure freedom from fibers or chips or other undesirable foreign matter, and collected in a storage tank **13**. The spent liquor is preferably concentrated before introduction into the next step of the process. Although any suitable means may be employed for concentrating the spent liquor and apparatus for effecting such concentration may be of well known form, a well known steam operated triple effect evaporator system is shown for purposes of illustration as having produced satisfactory results in a process embodying and for practicing this invention. This apparatus comprises evaporators **15**, separators **16**, pumps **17**, condensor **19** and the appropriate conduits and pipe lines as well understood in the art. In this connection it should be noted that, throughout Figs. 1 and 2, conduits and/or pipe lines carrying liquid material are indicated in solid lines with direction of flow indicated by arrows, whereas conduits and/or ducts or pipes carrying gaseous or vaporous material are indicated by dotted lines, also with arrows indicating the direction of flow. Small amounts of sodium carbonate may be added to the spent liquor immediately prior to the concentration step (e. g., in the storage tank **13**) for the purpose of inhibiting precipitation of solid matter from the spent liquor or "scaling" of the evaporator surfaces.

Spent liquors produced according to the above have been successfully treated at concentrations above 50% to 65% total solids. For maximum utilization of the heat of combustion in the next step of this process, however, it is desirable to concentrate the spent liquor as far as practical while avoiding precipitation therefrom. The solids content of spent liquor consists of approximately 40% inorganic constituents and approximately 60% organic constituents. Because of the relatively high ash content that combustion of such spent liquors produces, it has been found that spent liquor may not support its own combustion at concentrations lower than approximately 40% to 50% total solids. Although more dilute spent liquor may satisfactorily be treated in the next step of this process with heat from oil or coal burning furnaces as is common in so-called "rotary furnace" operation, it is economically desirable and pre-

ferred in the practicing of this invention that the spent liquors be concentrated in the evaporators to a degree which will admit of the evaporated liquid supporting its own combustion in the next step of this process. As one example, satisfactory results have been obtained according to this invention with a concentrated spent liquor having 62.5% total solids, a specific gravity of 1.370 at 149° F., and a sulphated ash content of 46.2% of the total solids.

Combustion steps

After adequate concentration, the concentrated spent liquor is introduced into suitable combustion apparatus **20**, wherein the spent liquor is treated under controlled combustion conditions to eliminate organic constituents by oxidation to gaseous carbon compounds and water and to convert sodium and sulphur compounds present into recoverable sodium sulphide, sodium carbonate, and sulphur dioxide.

One form of apparatus for satisfactorily accomplishing such controlled combustion step of concentrated spent liquor according to this invention is the well known Wagner spray-type recovery furnace or modifications thereof such as the well known Tomlinson recovery furnace. Such apparatus has means at various points and levels in the sides of the combustion chamber for the controlled introduction of air through controllable air ports, the individual adjustment of which enables the atmosphere within the combustion chamber to be controlled so that reducing or oxidizing conditions are obtained at various levels within the combustion chamber. In practicing this invention such air admitting ports near the bottom of the furnace are controlled so that only limited quantities of air are admitted thereby causing the atmosphere at the bottom of the furnace to be of a substantially reducing nature. The air admitting ports at higher levels in the walls of the combustion chamber are controlled so that some excess of air is admitted to maintain an oxidizing atmosphere in the upper portion of the combustion chamber.

The concentrated spent liquor from the storage tank **18** is further concentrated and/or heated by passing through an evaporator **23** in heat exchange relation with hot flue gases from the furnace combustion chamber, and then into the furnace **20** where the liquor is sprayed into the combustion chamber **21** to be first dried and charred and then reduced as it falls to the bottom of the furnace with the gaseous products being oxidized in the upper portion of the furnace.

It has been found advantageous in practicing this invention to limit the excess of combustion air introduced into the furnace in order to limit the volume of flue gases produced by the furnace while still obtaining the complete chemical conversion desired. For example, too little excess air produces incomplete combustion of the organic constituents, whereas too great an excess may produce substantial quantities of sulphur trioxide (instead of sulphur dioxide) or sodium sulphate (instead of sodium sulphide) not desired for the subsequent steps of this process. Also too great an excess dilutes the carbon dioxide in the furnace flue gases disadvantageously in terms of the carbonation step to be described below. It has been found that 5 to 10% excess of air over the stoichiometric amount is necessary for complete combustion, although up to 25% of excess air is preferred. It has been found that the combustion air admitted to the furnace should be controlled so as to provide substantially complete reduction of sodium sulphur compounds to the sulphide at the bottom of the furnace while maintaining a carbon dioxide concentration in the effluent flue gases of approximately 12% to 18%, although 14% to 18% is preferred. Satisfactory results have been obtained according to this invention with furnace operating temperatures within the range of 800° C. to 1100° C., although temperatures approximately 950° C. are preferred.

A further influence on furnace operation is exercised by the recycled gases containing hydrogen sulphide returned to the furnace for combustion therein as described below. For example, satisfactory results have been obtained by controlling furnace operation with the concentrated spent liquor described above so that the furnace flue gases contain, on a dry basis, approximately 15% to 18% carbon dioxide, 0.5% to 1.5% sulphur dioxide, 2% to 4.5% oxygen, and 79% to 81% nitrogen, with approximately an additional 40% of the gases being made up of water vapor.

Molten inorganic compounds may be continuously drawn off from the bottom portion of the furnace, as at **25**, in the form of a molten furnace product and are dissolved or leached in water in a solution tank **26** to produce a leach liquor which is pumped to a clarifying or settling tank **27** the dregs of which are returned to a dregs washer **28** and, after washing, to the sewer, with the washings being admixed in the solution tank **26** with leach liquor. This leach liquor or water solution of soluble incombustible products from the furnace is then ready for passage through the counter-current carbonation and stripping apparatus as indicated in Fig. 2.

Furnace products in which the active components are present in widely varying proportions may be utilized in subsequent steps of a process embodying this invention. For purposes of illustration, however, satisfactory results have been obtained with the above example producing a clarified leach liquor having a specific gravity of 1.230 at 106° F. and the following chemical composition in terms of equivalents of sodium per liter:

Na_2CO_3	3.05
Na_2S	2.05
NaHS	0.07
$Na_2S_2O_3$	0.10
Na_2SO_3	0.02
Na_2SO_4	0.42
Total	5.71

Thus, satisfactory results have been achieved according to this invention utilizing a concentrated spent liquor in which the active inorganic constituents are present in such molar proportions as approximately 12 moles of sodium sulphite to 4 moles of sodium carbonate. After treatment as described in the controlled combustion step under oxidizing and reducing conditions, such spent liquor yields a molten furnace product having molar proportions of approximately 12 moles of sodium carbonate, 7 moles of sodium sulphide, to 1 mole of sodium sulphate. Substantially the remainder of the combined sulphur introduced into the furnace with the concentrated spend liquor is oxidized in the furnace to gaseous sulphur dioxide and becomes a part of the furnace flue gases as noted above.

Sulphur dioxide absorption

Such gaseous furnace products leaving the furnace combustion chamber as flue gases at **30**, as optionally aided by forced draft fan **22** and after having preferably although optionally been passed through the heat exchange tubes of a boiler or evaporator **23** conventionally associated with a furnace for the purposes of utilizing the excess heat contained in these gases to further concentrate and/or preheat incoming spent liquor, are conducted to the sulphur dioxide absorption apparatus. This apparatus may be any suitable well known equipment for scrubbing, absorbing, or otherwise removing sulphur dioxide from a gaseous mixture by absorption thereof in a liquid.

Satisfactory results have been obtained by introducing the flue gases at **36** to the bottom of a conventional gas absorption tower **35** packed with wood or ceramic grids. The gases are passed upwardly through the tower to emerge at **37** while a carbonated solution from the carbonation steps described below is introduced into upper

portion of the tower at **38** and passes downwardly in countercurrent contact with the gases to emerge at **39**. According to this invention, the solution admitted to the SO_2 tower **35** at **38** is alkaline and substantially free of sulphur compounds, being primarily composed of sodium carbonate and sodium bicarbonate. Thus sulphur dioxide in the furnace flue gases is readily absorbed by the carbonate solution to produce a sodium sulphite solution appropriate for reuse as a cooking liquor in the digestion step of the process. Also, the effluent gases leaving the SO_2 tower at **37** are substantially free of sulphur compounds, being primarily composed of carbon dioxide, which is utilized in the carbonation steps described below.

Using the above example as illustrative, satisfactory results have been obtained with gases leaving the SO_2 tower at **37** having a composition, on a dry basis, of approximately 14% to 17% carbon dioxide, 4.5% to 5% oxygen, and 78.5% to 81% nitrogen at a temperature of approximately 170° to 174° F. Satisfactory results have been obtained with sulphited liquor leaving the SO_2 tower at **39** having a specific gravity of 1.220 at 145° F. and a composition, in terms of equivalents of sodium per liter, of:

Na_2SO_3	1.20
Na_2CO_3 and $NaHCO_3$	3.00
$Na_2S_2O_3$	0.16
Na_2SO_4	0.40
Total	4.76

Carbonation and stripping steps

The clarified leach liquor described above in the clarifying or settling tank **27** is introduced through pipe line **40** to counter-current carbonation and stripping apparatus where it is reacted with gases rich in carbon dioxide so that substantially all the sodium sulphide present in the leach liquor is carbonated or converted into sodium carbonate and/or sodium bicarbonate by carbon dioxide in the furnace flue gas. The gases, during this carbonation step, strip off and carry away in the form of hydrogen sulphide and sulphur originally present as sodium sulphide in the leach liquor.

Apparatus for accomplishing these carbonation and hydrogen sulphide stripping steps may vary widely in its construction and design. As one form of apparatus embodying and for practicing this invention, four gas-liquid counter-current absorption towers are shown in Fig. 2 at **41**, **42**, **43**, and **44**. Suitable apparatus that is designed to effect and promote the chemical reaction of a gaseous phase with a liquid phase, such as a column or tower packed with well known materials as pieces of coke, carbon rings, or wooden slats which furnish an open structure and large surface area, or a so-called "bubble-plate" column, or a series of splash chambers, may be used. Because, however, of its simplicity of construction and operation and because of its ability to handle relatively large volumes of gases at low pressures and correspondingly low pumping requirements, a series of cylindrical towers filled with a packing well known to chemical engineers as "Raschig" rings has been found satisfactory, although it will be understood that a single tower or a greater or lesser number may be used depending upon various operating conditions such as quantity of liquid and gas through-put, convenience of placement in plant design, etc. Satisfactory results have been obtained according to this invention with the towers **41–44** being each approximately 50 feet high, two feet in diameter, and packed with two-inch Raschig rings for the processing according to this invention of approximately 350 pounds per hour of total sodium compounds in leach solutions of the approximate compositions stated when operating under the preferred conditions described. For satisfactorily efficient removal of sulphide with a desirably limited volume of gas, the towers are operated in a counter-current fashion so that leach solution being treated comes into contact last with gases very low in or free of hydrogen sulphide, while the last contact of gases is with a solution which is high in sulphide content.

Thus the leach solution from settling tank **27** is introduced by pipe **40** into the top of the first tower **41** at **50** and proceeds downwardly through that tower to the outlet **51**, thence to the inlet **52** at the top of tower **42**, downwardly through that tower to the outlet **53**, and so on until the carbonated leach solution finally emerges from the bottom of the last tower **44** at the outlet **54** thereof to be introduced into the SO_2 tower at **38** as hereinbefore described. When entering the top of tower **41**, the leach solution has substantial quantities of sodium sulphide as noted above. Upon leaving the last tower **44**, the carbonated leach solution is substantially free of sulphide and is composed almost entirely of sodium carbonate and bicarbonate. The sulphide originally present in the leach solution before carbonation is stripped out by the carbon dioxide gases as hydrogen sulphide which is returned to the furnace as hereinafter described to be converted to sulphur dioxide for reuse in the process.

A number of chemical reactions take place during these interchanges between the gas and the leach solution in the column. In the first portion of the columns where the fresh leach solution is meeting gases which have already passed most of the way through the column, carbon dioxide and some hydrogen sulphide are absorbed relatively rapidly by the descending leach solution until any sodium hydroxide present is converted to sodium carbonate or sodium sulphide. Essentially all the sodium sulphide originally present in the leach solution is then converted to sodium hydrosulphide and a portion of the sodium carbonate is converted to sodium bicarbonate. These reactions are suggested as follows:

$$2NaOH+CO_2 \longrightarrow Na_2CO_3+H_2O$$
$$2NaOH+H_2S \longrightarrow Na_2S+2H_2O$$
$$2Na_2S+CO_2+H_2O \longrightarrow 2NaHS+Na_2CO_3$$
$$Na_2S+H_2S \longrightarrow 2NaHS$$
$$Na_2CO_3+CO_2+H_2O \longrightarrow 2NaHCO_3$$
$$Na_2CO_3+H_2S \longrightarrow NaHCO_3+NaHS$$
$$NaHCO_3+Na_2S \longrightarrow NaHS+Na_2CO_3$$

As these reactions progress and as the sulphide-containing leach solution moves through the carbonation towers, there occurs a decrease in the pH of the solution, a decrease in the rates of absorption of the gases and, in particular, an increase in the partial pressure or escaping tendency of hydrogen sulphide from the solution. Thus, a point is reached after a fairly short contact of the untreated leach solution with effluent gases rich in hydrogen sulphide where carbon dioxide absorption into solution continues while hydrogen sulphide is simultaneously given up to the rising gases. This major stage of the carbonation and stripping operation, which occurs over most of the extent of the columns, may be conveniently represented as follows:

$$2NaHS+CO_2+H_2O \longrightarrow Na_2CO_3+2H_2S$$

Additionally there may be some further increase in the proportion of bicarbonate in the solution as suggested by the reactions:

$$NaHS+CO_2+H_2O \longrightarrow NaHCO_3+H_2S$$
$$Na_2CO_3+CO_2+H_2O \longrightarrow 2NaHCO_3$$

It should be noted that the normal and expected theoretical equilibrium conditions and their effects on rate of exchange or reaction for either the absorption of carbon dioxide or the stripping of hydrogen sulphide separately are altered in interdependent fashion as the solution and gases pass through the described apparatus by reason of the continuously varying concentrations of these two components in both the liquid and gaseous phases within the

towers. Such interdependent variations and interrelation of the equilibrium conditions and rates of exchange may be determined within the necessary requirements of operational accuracy by simple measurements of small scale trials, should it be desired to construct some modification of the carbonation and stripping apparatus described above for accomplishing this controlled carbonation and hydrogen sulphide stripping step of the process of this invention.

Satisfactory results have been obtained with the compositions noted above according to this invention by introducing gases leaving the SO_2 tower at **37** into the bottom of tower **44** at **60** at a flow rate of approximately 650 pounds per hour of wet gases containing about 2.3 pound-moles per hour or 4.6 equivalents per hour of carbon dioxide. Such gases proceed upwardly through tower **44** to emerge at the outlet **61** at the top thereof and proceed thence to the inlet **62** of tower **43** and so in counter-current fashion as indicated in Fig. 2. A leach liquor having the above composition is discharged from tower **41** having a specific gravity of 1.205 at 146° F. and the following composition as equivalents of sodium per liter:

Na_2CO_3	2.53
$NaHCO_3$	0.61
NaHS	1.59
$Na_2S_2O_3$	0.12
Na_2SO_3	0.01
Na_2SO_4	0.38
Total	5.24

Carbonated leach liquor leaving the outlet **54** of tower **44** has a specific gravity of 1.225 at 143° F. and the following composition in terms of equivalents of sodium per liter:

Na_2CO_3	3.69
$NaHCO_3$	0.85
NaHS	0.03
$Na_2S_2O_3$	0.12
Na_2SO_3	0.02
Na_2SO_4	0.38
Total	5.09

It has been discovered that the equilibrium conditions within the counter-current carbonation and stripping towers are such as to favor, under the operating conditions described, the reabsorption of hydrogen sulphide in the top portion of tower **41**—i. e., that portion of the stripping step in which the sulphide-rich or exiting stripping gases contact the sulphide-rich or entering leach solution. Therefore, in order to increase hydrogen sulphide concentration in gases recycled through the furnace and reduce recycled gas volume, only a portion of the stripping gases passes through this top section of the first tower. As noted in Fig. 2, all stripping gases enter tower **41** at the gas inlet **65** thereof, but a substantial portion of these gases is removed from tower **41** almost immediately at the gas outlet **66** thereof for recycling through the furnace **20**—i. e., without contacting a substantial portion of solution in the tower. A portion only of the gases admitted to tower **41** contacts the leach liquor therein and passes upwardly through the tower to be exhausted to the atmosphere through a stack **67**.

This splitting of the gas flow in the top section or first tower is controlled so that substantially all of the hydrogen sulphide contained in gases which pass through tower **41** is reabsorbed by the leach solution in that tower so that the remaining gases in tower **41** are discharged to the atmosphere at **67** without air pollution and without appreciable loss of hydrogen sulphide from the system. By splitting the gas flow at the top section or first tower, according to this invention, essentially complete removal of sulphide is effected and only a portion of the carbonation and stripping gases needs to be returned to the furnace as hereinafter described for recombustion therein. That is, the gases containing hydrogen sulphide to be recycled through the furnace are removed from the carbonation tower at **66** at the point in the carbonation reaction where hydrogen sulphide concentration in the gases is greatest.

The carbonated leach solution emerging from the bottom of tower **44** is introduced into the SO_2 tower, as noted above, where the sodium carbonate therein is converted to sodium sulphite, and the thus sulphited solution leaves the SO_2 tower at **39** and is introduced through pipe **70** to a finished liquor storage tank **71** from which the finished liquor is withdrawn as desired for reuse as a fresh cooking liquor for introduction into the digester **10** in the pulp cooking step of the process. The sulphite concentration in this finished liquor may be enhanced in known manner as desired—e. g., by the addition of sulphur dioxide from a sulphur burner—to bring the recovered finished liquor up to the desired composition for a fresh cooking liquor.

H_2S *recycling steps*

That portion of the gases emerging from outlet **66** in tower **41** rich in hydrogen sulphide is recycled through the upper or oxidizing portion of the furnace combustion chamber **21**, as indicated in Fig. 2, where the hydrogen sulphide is substantially all oxidized to sulphur dioxide which is admixed in the flue gases to be absorbed with other sulphur dioxide in the flue gases in the SO_2 tower **35**. Satisfactory results have been obtained with gases emerging from outlet **66** at tower **41**, to be recycled through the furnace, containing, on a dry basis, approximately 10.5% to 13.5% hydrogen sulfide, 7.5% to 9.5% carbon dioxide, and 79% to 80% oxygen and nitrogen. The gases released to the atmosphere through stack **67** from the top of tower **41**, in the treatment of the foregoing example according to this invention, were found to contain no hydrogen sulphide by odor, by lead acetate test, or by Tutwiler test, and represented approximately 30% to 40% of the total gases introduced into the carbonation and sulphide stripping step, about 60% to 70% of the total gases being returned to the furnace as noted above.

Gas flow and distribution

It is preferred to keep the gas volume utilized in the carbonation and stripping steps as low as possible for operating convenience in the towers as well as to maintain at a practical minimum the volume of gas to be recycled to the furnace. The minimum amount of gas necessary to accomplish satisfactorily the carbonation and sulphide stripping desired depends, of course, on such considerations as temperature of operation, concentration of sodium sulphide in the leach solution, and the concentration of carbon dioxide in the gas used. As noted above, it is preferred to utilize but a limited excess of air in the combustion step for the purpose, among others, of maintaining the carbon dioxide concentration in the flue gases as high as possible. According to this invention a further control is exercised in that a portion only of the flue gases is utilized in the carbonation and stripping steps.

For example, the total effluent flue gases from the furnace are passed, as noted above, through the SO_2 tower **35** for the removal of sulphur dioxide. Gases leaving tower **35** at the outlet **37** pass through a blower **75** and thence to a discharge stack **76**. A portion only of these discharged gases, however, is taken off at **77**, and it is this diverted portion which is introduced into tower **44** at the gas inlet **60** to be utilized in the carbonation and stripping step. For the compositions and operating conditions herein described, a volume of flue gases corresponding to approximately 10% to 20% of the total flue

gases produced by the furnace in the combustion step has been found satisfactory for use in the carbonation and stripping step. It has been found that, if a gas volume substantially in excess of 5% to 25% of the original total flue gases is recycled through the furnace from the gas outlet **66** in tower **41**, it may upset furnace operation.

Thus, according to this invention, the sulphur dioxide in the flue gases is removed therefrom at the tower **35**; thereafter a portion only of the remaining gas rich in carbon dioxide is split off at **77** to be used in the carbonation step; and finally only a portion of this gas is recycled into the furnace, the remainder being exhausted at **67**. Thus the gas volumes at each step of the process are kept within operational limits and are such as to force the various equilibria to the desired point, while yet, by the constant and controlled splitting of gas flow, substantially complete recovery is effected and the dumping of sulphurous waste products or the exhaustion of obnoxious hydrogen sulphide gas is substantially avoided.

It has been found that satisfactory results are obtained if the carbonation and hydrogen sulphide stripping steps of a process embodying this invention are performed at a somewhat elevated temperature in order to introduce favorable equilibrium conditions and desirably high rates of absorption of carbon dioxide by the sulphide-rich leach solution. For example, too low a temperature in the carbonation step may result in a precipitation therein of sodium bicarbonate. If a higher temperature is provided by introducing steam into the gas flow, too high a temperature may mean the introduction of too much steam which, apparently, acts as a diluent of the desired gaseous carbon dioxide concentration. A higher temperature, however, favorably affects the partial pressure of hydrogen sulphide. Satisfactory results have been obtained according to this invention with operating temperatures in the carbonation step maintained within the range of 120° F. to 200° F., with 160° F. to 170° F. being preferred. In this connection, in the examples above noted, satisfactory results have been obtained with the leach solution having a temperature of approximately 114° F. upon introduction thereof into the top of tower **41**, with the portion of the flue gases introduced into the bottom of tower **44** having a temperature of approximately 170° to 174° F. In the same example, the temperature of the gases withdraw from tower **41** at **66** ranged from 152° to 158° F., while the temperature of gases exhausted from the top of tower **41** through stack **67** was approximately 104° to 108° F.

Also, in order to force the carbonation and stripping equilibria to a satisfactory point, it has been found desirable to maintain a high concentration of sodium salts in the leach solution introduced into tower **41**. This is accomplished according to this invention by limiting the amount of water utilized in dissolving the molten furnace product in solution tank **26**. Satisfactory results have been obtained where the total sodium concentration in the leach solution is in excess of approximately 2 Normal, but total sodium concentrations within the range of 4 to 6 Normal are preferred, the desirable upper limit being set by the solubility limits of the compounds present during the carbonation and stripping steps. It has also been noted that the rate of hydrogen sulphide stripping increases with increasing bicarbonate concentration and, in the temperature range indicated, approaches satisfactory rates of stripping with bicarbonate concentrations from approximately 0.2 to 1 Normal.

Satisfactory control of the split flow of gas referred to above depends upon a number of factors. The proportion of flue gases (from which sulphur dioxide has been removed) which are taken off at **77** for utilization in the carbonation steps is determined to a large extent by the amount of carbon dioxide necessary to effect substantially complete carbonation and stripping. This amount may vary from a volume of gas containing a quantity of carbon dioxide from approximately ½ to 3 times the chemical equivalent of total sodium salts present in the leach solution to be carbonated, although satisfactory results have been achieved by using a volume of gas which will introduce into tower **44** an amount of carbon dioxide corresponding to approximately one to two times the chemical equivalent of total sodium salts present in the leach solution introduced to the top of tower **41**. For the compositions and operating conditions described above, a volume of flue gases corresponding to approximately 10% to 20% of the total flue gases produced in the combustion step has been found satisfactory.

According to this invention, in order conveniently to regulate and control the split flow of gases noted above in the top section or first tower **41** an adjusting valve or damper **80** is provided at the stack **67** and another adjusting valve or damper **81** is provided at the gas outlet **66**. The control is maintained by first closing the valve **80** until no hydrogen sulphide is exhausted to the atmosphere from the top of tower **41**. That is, hydrogen sulphide emerging from the stack **67** indicates that too much gas is flowing through tower **41** for the leach liquor in the upper portion of the tower to reabsorb all the hydrogen sulphide contained in the gases flowing out of stack **67**.

With valve **80** closed sufficiently that the gases exhausted through stack **67** contain substantially no hydrogen sulphide, valve **81** in outlet **66** is opened until analysis shows the carbonated solution emerging from outlet **54** of tower **44** contains substantially no sulphide. That is, controlling valve **81** controls the entire gaseous through-put through the carbonation steps. If there is not sufficient gaseous through-put, there will not be complete carbonation and some sodium sulphide will emerge from the outlet **54**.

Thus the adjustment of valves **80** and **81** provides a simple control for gas distribution in the carbonation steps, as well as controlling the proportion of total flue gases diverted from the stack at **77** and introduced into the carbonation steps. At the same time, such control system permits avoiding a large gaseous excess through-put and keeps the total gas volume as low as possible consistent with satisfactorily complete recovery as noted above.

For a further understanding of the theoretical considerations relating to the control of carbonation gas, reference is made to Figs. 3 and 4. It will be noted that Fig. 3 graphically indicates the carbon dioxide distribution in a process embodying and for practicing this invention under satisfactory operating conditions. The curves of Fig. 3 are drawn plotting moles of CO_2 in the total carbonation gases for 100 moles of active chemical against the mole per cent of sodium sulphide as percentage of active chemicals in the leach liquor. The curves depict the carbon dioxide distribution with active chemical (i. e., the sum of sodium sulphide and sodium carbonate in the leach liquor) at a concentration of 5 Normal total sodium, an operating temperature of approximately 160° to 170° F., a total absolute pressure of about 1 atmosphere, and a flue gas composition of about 16% carbon dioxide on a dry basis or 10 mole percent on a wet basis. Under such conditions the equilibrium partial pressure relationships in the carbonation step may be stated as follows:

$$\underset{H_2S}{\text{Molar percentage}} \simeq \frac{10\,(NaHS)\,(NaHCO_3)}{(Na_2CO_3)}$$

$$\underset{CO_2}{\text{Molar percentage}} \leq \frac{6\,(NaHCO_3)^2}{(Na_2CO_3)}$$

Thus an increase in leach liquor concentration, an increase in temperature, or a decrease in carbon dioxide concentration will decrease the quantity of carbon dioxide required by decreasing the conversion of carbonate to bicarbonate. Thus, the quantity of carbon dioxide shown in Fig. 3 between the stoichiometric curve A and curve B represents, generally speaking, the car-

bon dioxide used to convert a portion of the carbonate to bicarbonate. The portion of Fig. 3 between curves B and C represents the carbon dioxide returned to the furnace with that portion of the flue gas containing hydrogen sulphide recycled from outlet **66** in tower **41**. The portion of Fig. 3 between curves C and D represents the carbon dioxide entering the top section or first tower **41** at the gas inlet **65** and may generally be considered an excess to provide proper so-called driving force in the carbonation steps. Thus, curve D represents the total carbon dioxide required, with negligible absorption of carbon dioxide in tower **41**, for the satisfactory operation described of a process according to this invention. Actually, some absorption of CO_2 in tower **41** may occur, and this amount may vary broadly depending on the compositions, size of the tower, etc.

Fig. 4 represents a graphic indication of the minimum fraction of total carbonation gases to be returned to the furnace from outlet **66** when operating with a minimum gas volume. The curve shows moles of CO_2 in the total gases passing through the carbonation step for 100 moles of active chemical plotted against mole percent of sodium sulphide as percentage of active chemicals in the leach liquor, and reflects essentially the operating conditions achieved by regulating gas through-put as described above through the control of valves **80** and **81**. It will be understood, of course, that the data in Figs. 3 and 4 is primarily illustrative and, when operating with very high flow rates or towers of restricted size, such values may not be achieved. That is, with lower rates and very large towers, equilibrium conditions are approached. As liquor rates are increased or tower sizes reduced, however, the relative proportions of gas to liquor, for both total gas flow as well as that portion returned to the furnace must be increased. For many operating conditions, therefore, actual operating flow rates may be from 50% to 100% greater than the minimum values noted in Figs. 3 and 4.

In view of the above considerations, the gas outlet **66** in tower **41** is located substantially at a point in tower **41** where the hydrogen sulphide concentration in the gas removed for recycling through the furnace approaches a maximum value in order to reduce as much as practicable the total volume of recycling gases. Such volume reduction or maintaining high sulphide concentration, is aided to a considerable degree by the reabsorption of hydrogen sulphide in tower **41** and the resulting exhaustion through stack **67** of a portion of the total gas throughput containing substantially no hydrogen sulphide and primarily gases which it is not desired to recycle through the furnace. Accordingly, since there may be some absorption of carbon dioxide in the upper portion of tower **41** and since such absorption of carbon dioxide may diminish the amount of hydrogen sulphide which is reabsorbed by the leach liquor in the upper portions of tower **41**, the gas outlet **66** is located in tower **41** at a point where the sulphide concentration of gases diverted through outlet **66** will approach a maximum and also where absorption of carbon dioxide above outlet **66** is minimized and the absorption of hydrogen sulphide enhanced in order to increase the volume of non-sulphide gases exhausted through stack **76** while maintaining maximum hydrogen sulphide absorption in tower **41** and maximum sulphide concentration in the gases diverted from tower **41** at outlet **66**.

If it is desired to utilize this invention in connection with pulp cooking steps using a cooking liquor containing sodium acid sulphite instead of sodium sulphite, the absorption of sulphur dioxide by the carbonated leach solution at tower **35** and/or the introduction of additional sulphur dioxide is controlled so that sufficient gas is absorbed into the solution to convert substantially all the carbonates therein to sodium acid sulphite instead of to a mixture of sodium sulphite and sodium bicarbonate as with a neutral sulphite pulp cooking liquor. Spent liquors from such acid sulphite cooking steps are then treated substantially as described above for conversion to a sulphide solution, carbonation, etc., for recovery therefrom of sodium and sulphur compounds according to this invention.

Additional quantities of sulphur dioxide are added to the liquor either during its passage through tower **35** or thereafter to adjust the sulphite and sulphur dioxide compositions of the sulphited liquor for reuse as a fresh cooking liquor for neutral or acid sulphite digesting steps as desired and to replenish in the system inevitable sulphur losses. Such additional sulphur dioxide may be derived in known manner from a sulphur burner or from sulphur dioxide contained in the so-called "blow-off" encountered in practicing an acid sulphite cooking or digestion step. Inevitable sodium loss may satisfactorily be replenished in the system by the addition of sodium carbonate as a neutralizing agent in the spent liquor storage tank **13** prior to concentration of the spent liquor as described or similar additions to the carbonated solution, or may be replenished, along with sulphur losses, by introducing sodium sulphur compounds into other steps of the process, e. g., adding sodium sulphate into the furnace combustion chamber **21** or fresh sodium sulphide to the leach liquor in tank **27**.

While the methods and forms of appartus herein described constitute preferred embodiments of the invention, it is to be understood that the invention is not limited to these precise methods and forms of apparatus, and that changes may be made therein without departing from the scope of the invention which is defined in the appended claims.

What is claimed is:

1. In recovery apparatus of the character described for recovery of heat and chemicals from pulp manufacturing spent cooking liquors, the combination which comprises a recovery furnace for combustion of said spent liquor, a scrubbing tower for removing sulphur dioxide from effluent gases from said furnace, means for exhausting to the atmosphere a limited portion of said gases flowing out of said scrubbing tower, means for dissolving molten furnace products from said furnace, countercurrent carbonation tower means for reacting another limited portion of said effluent gases from said scrubbing tower with said solution of said molten furnace products, a gas take-off in said carbonation tower means intermediate the ends thereof for returning directly to said furnace a limited portion of said gases flowing through said carbonation tower means, and a gas exhaust at one end of said carbonation tower means for exhausting to the atmosphere another limited portion of said gases flowing through said carbonation tower means.

2. In recovery apparatus of the character described for recovery of heat and chemicals from pulp manufacturing spent cooking liquors, the combination which comprises a recovery furnace for combustion of said spent liquor and having distinct oxidation and reduction zones therein, a scrubbing tower for removing sulphur dioxide from effluent gases from said furnace oxidation zone, means for exhausting to the atmosphere a limited portion of said gases flowing out of said scrubbing tower, means for dissolving molten furnace products from said furnace reduction zone, countercurrent carbonation tower means for reacting another limited portion of said effluent gases from said scrubbing tower with said solution of said molten furnace products, a gas take-off in said carbonation tower means intermediate the ends thereof for returning directly to said furnace oxidation zone a limited portion of said gases flowing through said carbonation tower means, and a gas exhaust at one end of said carbonation tower means for exhausting to the atmosphere another limited portion of said gases flowing through said carbonation tower means.

3. In recovery apparatus of the character described for recovery of heat and chemicals from pulp manufacturing spent cooking liquors, the combination which

comprises a recovery furnace for combustion of said spent liquor and having distinct oxidation and reduction zones therein, a scrubbing tower for removing sulphur dioxide from effluent gases from said furnace oxidation zone, means for exhausting to the atmosphere a limited portion of said gases flowing out of said scrubbing tower, means for dissolving molten furnace products from said furnace reduction zone, countercurrent carbonation tower means for reacting another limited portion of said effluent gases from said scrubbing tower with said solution of said molten furnace products producing hydrogen sulphide as a product of said reaction, a gas take-off in said carbonation tower means intermediate the ends thereof for returning directly to said furnace oxidation zone a limited portion of said gases flowing through said carbonation tower means, said gas take-off being disposed on said carbonation tower means in the upper portion therof at the point of substantially maximum concentration of hydrogen sulphide in said gases, and a gas exhaust at one end of said carbonation tower means for exhausting to the atmosphere another limited portion of said gases flowing through said carbonation tower means.

4. In recovery apparatus of the character described for recovery of heat and chemicals from pulp manufacturing spent cooking liquors, the combination which comprises a recovery furnace for combustion of said spent liquor, a scrubbing tower for removing sulphur dioxide from effluent gases from said furnace, means for exhausting to the atmosphere a limited portion of said gases flowing out of said scrubbing tower, means for dissolving molten furnace products from said furnace, counter current carbonation tower means for reacting another limited portion of said effluent gases from said scrubbing tower with said solution of said molten furnace products, from said dissolving means, a gas take-off in the upper portion of said carbonation tower means and intermediate the ends thereof for returning directly to said furnace a limited portion of said gases flowing through said carbonation tower means, a gas exhaust at one end of said carbonation tower means for exhausting to the atmosphere another limited portion of said gases flowing through said carbonation tower means, and adjustable means for controlling the proportioning of said limited gas portions including first adjusting means at said gas exhaust for controlling the quantity of gases exhausted thereby and second adjusting means at said gas take-off for controlling the total gas through-put of said carbonation tower means.

5. In a recovery plant of the character described for recovery of heat and chemicals from pulp manufacturing spent cooking liquor, the carbonation and stripping apparatus which comprises in combination countercurrent reaction tower means, packing means therein for maintaining direct reacting contact between a gaseous phase and a liquid phase in said tower means, means for introducing a liquid phase into one end of said tower means for continuous flow therethrough, means for introducing a gaseous phase into the opposite end of said tower means for continuous countercurrent flow therethrough in the opposite direction to said liquid phase flow, a gas exhaust at the same end of said tower means as said liquid phase introducing means for exhausting a portion of said gaseous phase after flowing through substantially the full extent of said tower means, and a gas take-off in said tower means intermediate the ends thereof for withdrawing other portions of said gaseous phase not exhausted at said gas exhaust after said other portions have flowed through a substantial partial extent of said tower means.

6. In a recovery plant of the character described for recovery of heat and chemicals from pulp manufacturing spent cooking liquor, the carbonation and stripping apparatus which comprises in combination countercurrent reaction tower means, packing means therein for maintaining direct reacting contact between a gaseous phase and a liquid phase in said tower means, means for introducing a liquid phase into one end of said tower means for continuous flow therethrough, means for introducing a gaseous phase into the opposite end of said tower means for continuous countercurrent flow therethrough in the opposite direction to said liquid phase flow, a gas exhaust at the same end of said tower means as said liquid phase introducing means for exhausting a portion of said gaseous phase after flowing through substantially the full extent of said tower means, a gas take-off in said tower means intermediate the ends thereof for withdrawing other portions of said gaseous phase not exhausted at said gas exhaust after flowing through a substantial but partial extent of said tower means, and adjustable means for controlling the gaseous through-put flow in said tower means including an adjustable control at said gas exhaust for adjusting the quantity of gases exhausted thereby and another adjustable control at said gas take-off for adjusting the quantity of gases withdrawn from said tower means at said gas take-off.

7. In a recovery plant of the character described for recovering heat and chemicals from pulp manufacturing spent cooking liquors, sulphide carbonation and stripping apparatus adapted for a carbonation reaction of a gaseous phase containing carbon dioxide with a liquid phase containing sulphide for producing gases containing hydrogen sulphide and a solution of carbonate and bicarbonate, which comprises in combination countercurrent reaction tower means, packing means therein for maintaining direct reacting contact between said gaseous phase and said liquid phase, a liquid inlet for introducing said liquid phase into one end of said tower means for continuous flow therethrough in one direction, a gas inlet for introducing said gaseous phase into the opposite end of said tower means for continuous countercurrent flow therethrough in the opposite direction, said packing means and said countercurrent flow of said gaseous and liquid phases promoting said stripping and carbonation reaction with the concentration of hydrogen sulphide in said gaseous phase increasing to a maximum and then decreasing as said gaseous phase flows through said tower means, a gas exhaust at the same end of said tower means as said liquid inlet for exhausting a portion of said gaseous phase after flowing through substantially the full extent of said tower means, and a gas take-off in said tower means intermediate the ends thereof for withdrawing other portions of said gaseous phase not exhausted through said gas exhaust, said gas take-off being disposed on said tower means near said liquid inlet end thereof and at the point where the hydrogen sulphide concentration of portions of said gaseous phase withdrawn through said take-off is substantially at said maximum concentration.

8. In a recovery plant of the character described for recoveirng heat and chemicals from pulp manufacturing spent cooking liquors, sulphide carbonation and stripping apparatus adapted for a carbonation reaction of a gaseous phase containing carbon dioxide with a liquid phase containing sulphide for producing gases containing hydrogen sulphide and a solution of carbonate and bicarbonate, which comprises in combination countercurrent reaction tower means, packing means therein for maintaining direct reacting contact between said gaseous phase and said liquid phase, a liquid inlet for introducing said liquid phase into one end of said tower means for continuous flow therethrough in one direction, a gas inlet for introducing said gaseous phase into the opposite end of said tower means for continuous countercurrent flow therethrough in the opposite direction, said packing means and said countercurrent flow of said gaseous and liquid phases promoting said stripping and carbonation reaction with the concentration of hydrogen sulphide in said gaseous phase increasing to a maximum and then decreasing as said gaseous phase flows through said tower means, a gas exhaust at the same end of said tower means as said liquid inlet for exhausting a portion of said gaseous phase after flowing through substantially the full extent of said tower means, a gas take-off in said tower means inter-

mediate the ends thereof for withdrawing other portions of said gaseous phase not exhausted through said gas exhaust, said gas take-off being disposed on said tower means near said liquid inlet end thereof and at the point where the hydrogen sulphide concentration of portions of said gaseous phase withdrawn through said take-off is substantially at said maximum concentration, and adjustable means for controlling the gaseous through-put flow in said tower means including an adjustable control at said gas exhaust for adjusting the quantity of gas exhausted thereby and other adjustable control at said gas take-off for adjusting the quantity of gas withdrawn from said tower means at said take-off.

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1,864,619 Richter ---------- June 28, 1932

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

August 26, 1958

Patent No. 2,849,292

Philip E. Shick

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 7, line 43, for "and sulphur" read -- the sulphur --; column 15, line 35, after "products", strike out the comma.

Signed and sealed this 25th day of November 1958.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents