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[54] APPARATUS FOR OXIDIZING A SPENT PULPING LIQUOR

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[52] **U.S. Cl.** ..... **23/284,** 23/252, 23/49, 23/253 A, 261/76, 259/4, 210/63, 162/31

[51] **Int. Cl.** **B01j 1/00,** D21c 11/14

[58] **Field of Search** ..... 23/284, 285, 252, 49, 253 A; 261/75, 76, 77, 116, DIG. 26; 259/4; 196/126, 127; 210/63; 162/31

[56] **References Cited**

UNITED STATES PATENTS

1,616,209	2/1927	Weisgerber	196/127 X
2,481,959	9/1949	Wahlin	261/116 X
3,178,260	4/1965	Tirado	23/49
3,207,572	9/1965	Saul	23/49

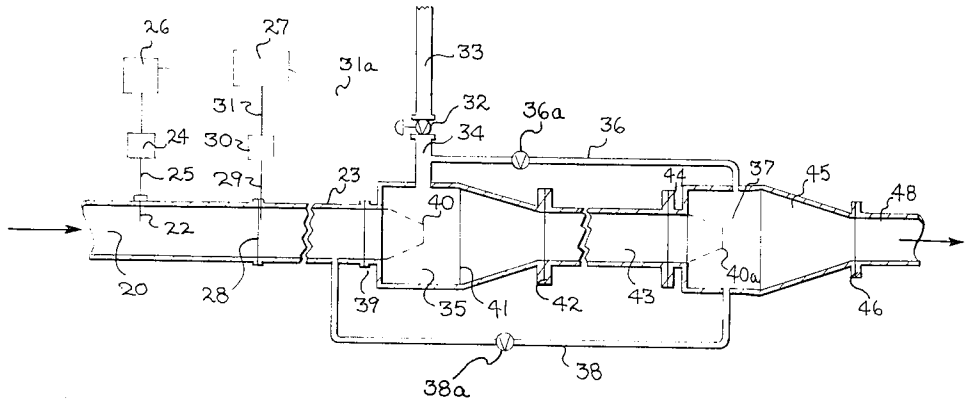
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[57] **ABSTRACT**

A dual stage oxidation apparatus having a first and a second oxidation chamber arranged so that the first chamber convergingly extends in a pipelike manner and discharges into the second chamber, an inlet conduit for supplying spent pulping liquor into the first chamber, an atomizing nozzle attached to the end of the inlet conduit for spraying the spent liquor into the first chamber, the first chamber converging from a large radius to a lesser radius and forming a conduit, a second atomizing nozzle attached to the converging conduit end formed from the first chamber and terminating in the second chamber for spraying the now partially oxidized spent liquor leaving the first chamber into the second camber, for essentially complete oxidation, an outlet formed by the converging of the second reaction chamber from a large radius to a lesser radius forming thereby the exit conduit, an externally mounted oxygen line supplying oxygen to both the first chamber and the second chamber, an externally mounted circulating conduit connecting the inlet spent liquor conduit with the second reaction chamber, detection means for measuring the liquid volume flow and detection means for measuring the sulfide concentration of the spent liquor with both means mounted on the inlet conduit and measuring the flow and sulfide concentration before the spent liquor enters into the first chamber, and said detection means governing the amount of oxygen supplied to both the first chamber and to the second for oxidizing the spent pulping liquor.

2 Claims, 4 Drawing Figures



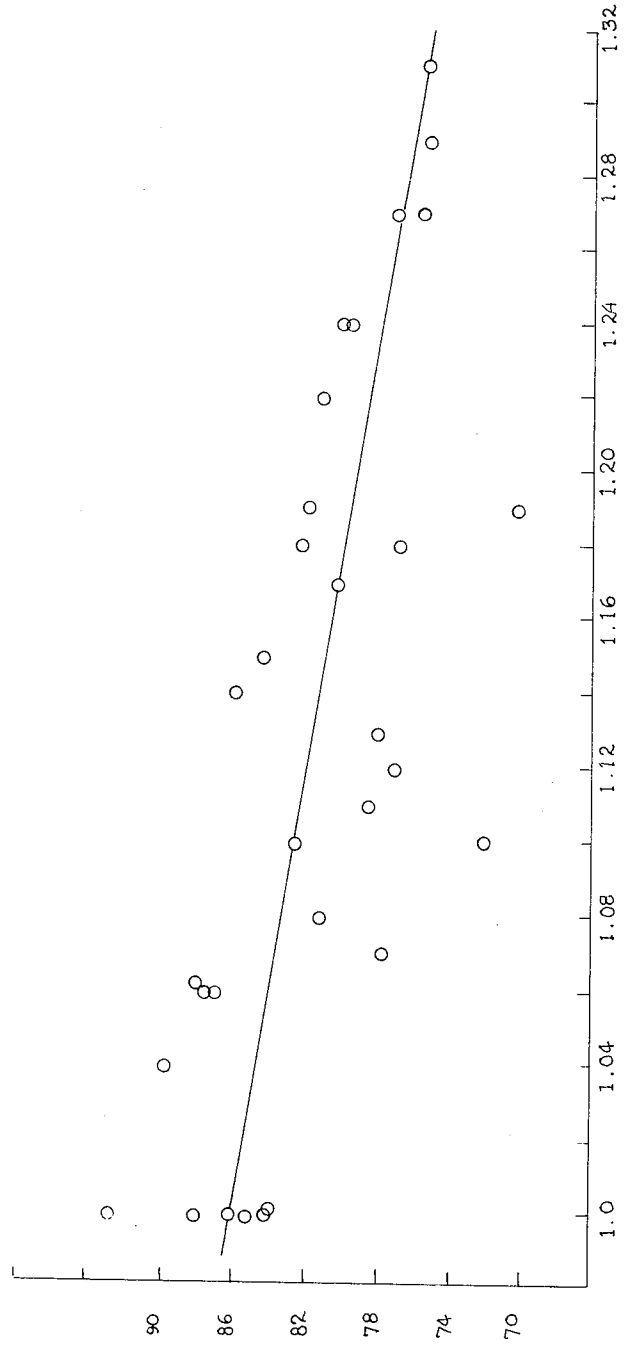


FIG. 1

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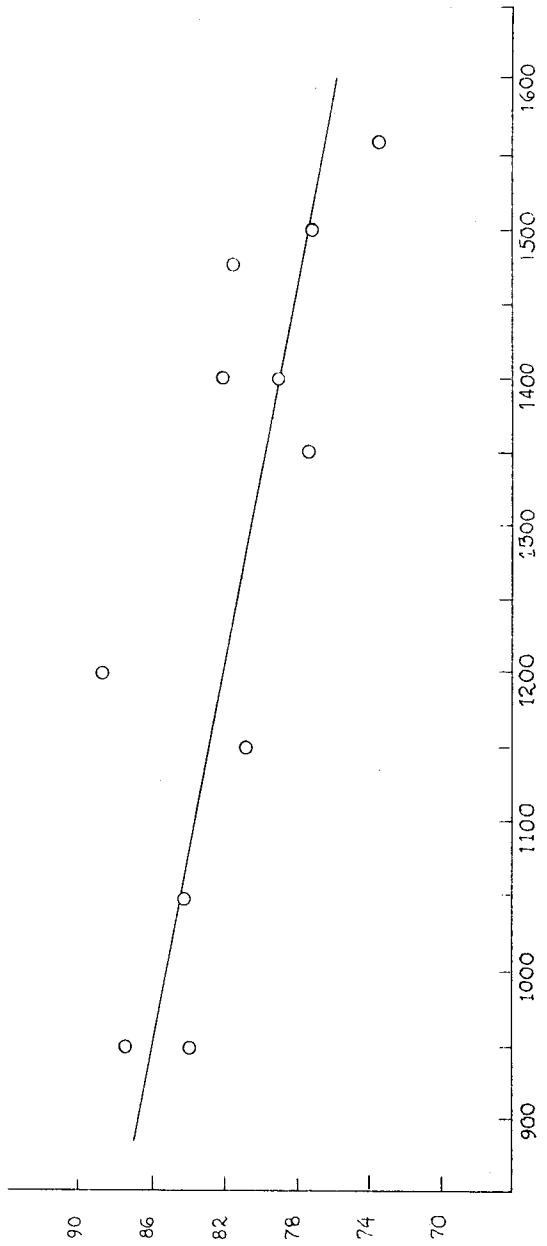


FIG. 2

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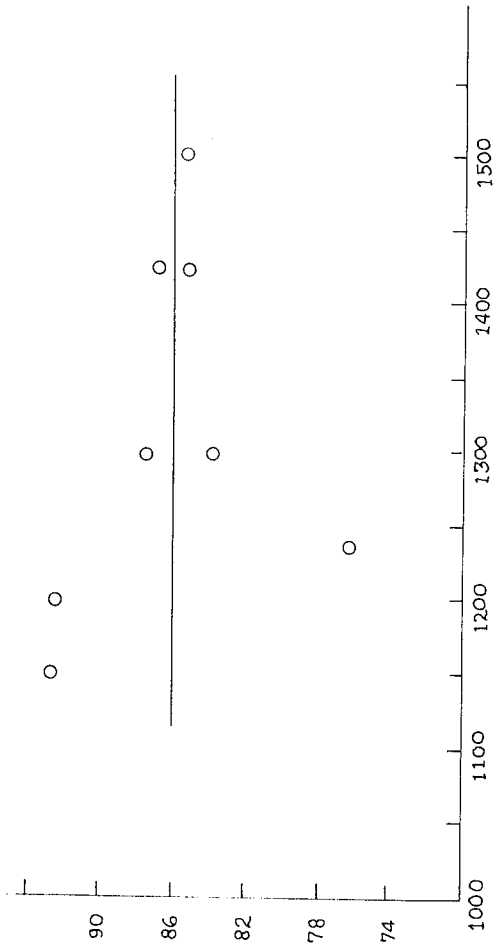


FIG. 3

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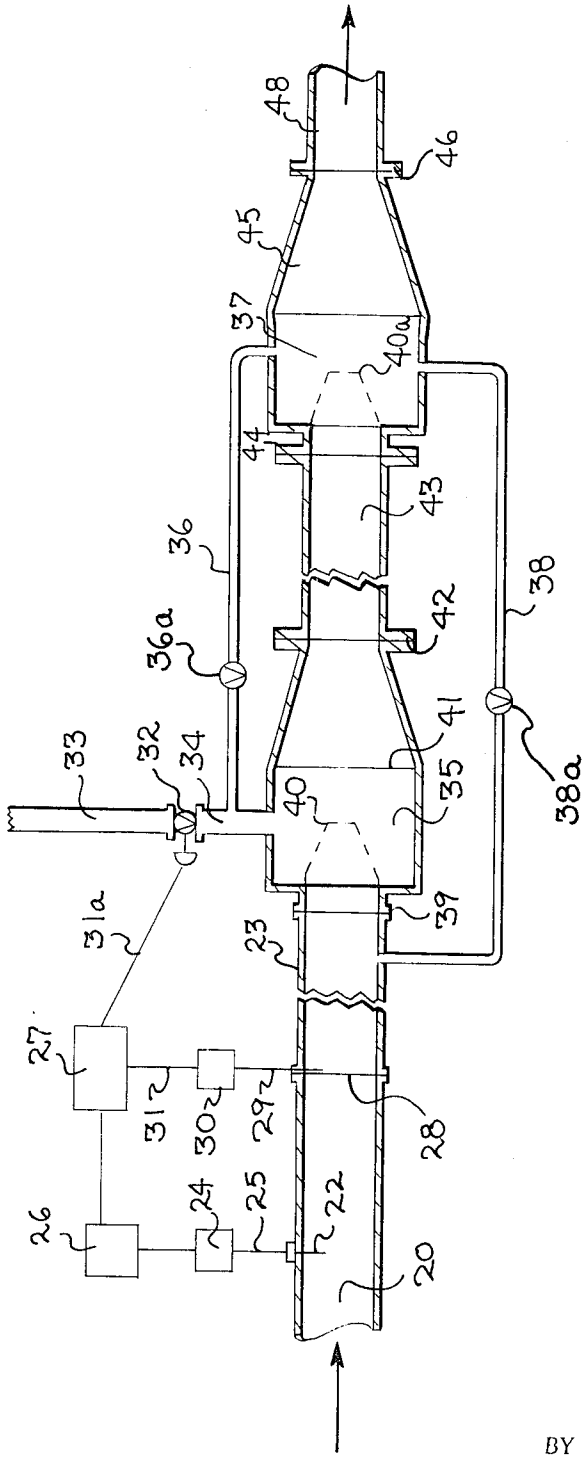


FIG. 4

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APPARATUS FOR OXIDIZING A SPENT PULPING LIQUOR

BACKGROUND OF THE INVENTION

This invention relates to an apparatus for the oxidation of a spent or weak/or strong black liquor produced in the pulping of wood. More particularly, the present invention pertains to a multi-stage tubular reactor by which the oxidation with molecular oxygen of the spent or weak/or strong black liquor, produced, for example, in a kraft pulping process, is efficiently and economically performed without any undesireable foam formation and without the concentrated accumulation of inactive sulfate type compounds. Specifically, the subject invention concerns the direct and intimate oxidation of weak/or strong black liquor in a two-stage tubular reactor and wherein the liquor originated in a kraft pulping process using southern pine, or in any other wood species suitable for pulping.

The oxidation of a spent or black pulping liquor produced in the conventional art known kraft pulping processes has been heretobefore carried out by employing air as the oxidizing agent. In the prior art, oxidation is also being carried out on spent liquors produced from hardwoods on both the weak liquor, that is a spent liquor containing about 12 to 16 percent solids and on strong spent liquors, that is, liquors containing 30 to 36 percent solids. Generally, in the pulping installations employing the cooking of southern pine, there are only a few installations wherein the oxidation of a strong black liquor is practiced with air. Also, as far as is known, there does not appear to be any practice of the oxidation of the weak liquor due to excessive foaming. The oxidation of a spent liquor produced from a southern pine often is accompanied by a most objectionable characteristic, that is, the formation of excessive amounts of foam. Different methods of air oxidation have been suggested by the prior art for controlling the foam; however, the methods have not received universal acceptance and the attempts have generally led to the fact of uncontrolled foam formation and attempts to use the foam in a better economical way. In view of this prior art discussion, the fact seemingly remains that the presently employed processes for the oxidation air of weak black liquor is not very feasible at this time. It has been suggested by those versed in the art that a solution to this problem may reside in the employment of molecular oxygen for the oxidation of black liquor, especially the oxidation of a kraft weak black liquor from a kraft process using southern pine. However, the subject suggestion has not found acceptance in the pulping art because of the lack of a suitable means for effecting the oxidation.

Accordingly, it is a purpose of the present invention to provide an economical and more simple apparatus that is easy to operate for overcoming the difficulties associated with the prior art.

Another purpose of this invention is to provide an apparatus for the oxidation of a spent pulping liquor with molecular oxygen.

Still another object of the invention is to make available to the prior art a multi-stage reactor, in which design, the better utilization of the principles of mass transfer and chemical reaction for regulating the oxidation of black liquor are successfully utilized.

Yet still another object of the invention is to provide a novel apparatus which while performing the oxidation of the spent liquor does not generate foam and objectionable gaseous emissions as they are generated and released at the oxidation tower of systems practicing the prior art.

A further purpose of the invention is to make available an apparatus which eliminates the possibility of cooling the treated spent liquor by storage time or the effect of air flow.

Yet another object of the invention is to effect an oxidation reactor in which the temperature of the spent liquor is increased 10° to 15° F. in the first stage, thereby promoting better efficiency in the second stage of the reactor and generally helping in the operation of the evaporators used in conventional recovery systems.

The invention also consists of the novel construction and arrangement of the parts and combination of parts hereinafter more fully set forth in the following detailed drawings, detailed specification and the accompanying claims.

SUMMARY OF THE INVENTION

The invention concerns a two stage device for the molecular oxidation of a spent pulping liquor, mainly a black liquor. The two-stage device consists essentially of two reaction chambers connected one into the other as a series. In using the device, the spent liquor is first atomized and turbulently mixed and intimately contacted with molecular oxygen to oxidize a high percentage of the spent liquor. The first oxidation stage occurs in the first reaction chamber. Next, the just oxygen treated liquor is again atomized, that is, for a second time, and again turbulently mixed and intimately contacted with molecular oxygen to further oxidize any unoxidized spent liquor remaining from the first oxidation in the first stage of the reactor. The second oxidation occurs in the second reaction chamber of the two-stage device.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 graphically indicates how the efficiency of oxygen utilization linearlly decreases as the ratio of oxygen injected into initial sulfide content increases above the stoichiometric ratio of 1.00.

FIG. 2 depicts how the efficiency of the oxygen utilization decreases with a decrease in retention time in the reactor for a ratio of oxygen to sulfide ranging between 1.05 to 1.15.

FIG. 3 illustrates how the oxygen efficiency remains constant at different retention time since the ratio oxygen injected to sulfide content is below the stoichiometric value of 1.0, generally 0.75 to 0.85. These graphs, depicting the interpretation of data collected at a mill, indicate the employment of a controlled operation in which time, oxygen injected and sulfide content are utilized to achieve better oxygen efficiency and oxidation.

FIG. 4 is an elevational view of the reaction apparatus with injection means and control means for performing the subject matter of the present invention.

DETAILED DESCRIPTION OF THE DISCLOSURE

In attaining the features, advantages and purposes of the invention it has now been found that a simple, efficient and relatively inexpensive tubular chemical oxidation reactor can be made available to the art for performing the purpose of the invention. In addition to the novel apparatus, the use of existing pipeline in a pulping facility can be used for connecting the pulping area with the weak liquor storage tanks or the pipeline connecting the weak liquor storage tanks with the evaporators, or the pipelines connecting the strong liquor tanks to the direct contact evaporator or the multiple effect evaporator can, if desired, be used as a functional part of the apparatus. Thus, the pipeline can be used according to its diameter and liquor flow as an integral part of the tubular reactor. These features, coupled with the reactor can reach efficient utilization of oxygen levels above 95 percent. For the apparatus object of this invention an equation indicates the necessary design value. This equation is expressed as:

$C_f = C_i e^{-kL/v}$ in which C_f and C_i are the desired final and initial sulfide concentration of the liquor, v the velocity flow in the reactor, k the rate constant equal to 5.7 min.$^{-1}$ and e Naperian base logarithm, and L is the length of pipeline required between the first and second reactor stages. This equation permits designing the unit according to existing or new conditions at any mill.

In the oxidation of black liquor with molecular oxygen, or O_2, the rate of oxidation is governed by the combined effect of oxygen absorption and the chemical reaction rate. The chemical reaction rate is first order with relation to both oxygen and sulfide concentration according to the equation:

$$d C_s^{=} / d_t = -k_1 Co_2 C_s^{=}$$

where $d\ C_s$ is the differential of the concentration of sulfide; with respect to time, k_1 is the chemical reaction rate constant; Co_2 and C_s are the concentration of the oxygen and sulfide in the reaction zone. Oxygen absorption in most of the cases tested by experiments has shown to be liquid flow controlling, thus the rate of oxygen transfer $d\ Mo_2$ is defined according to the equation:

$$d\ Mo_2/d = k_2\ (Co_2\ (e) - (Co_2)$$

where $d\ Mo_2$ is the mass transfer differential of oxygen with respect to time; and e denotes the equilibrium concentration of oxygen in the liquor surface, and k_2 is the mass transfer rate constant. A combined expression for both the effects is given by the equation:

$$\frac{dC_s^{=}}{d_t} = -\frac{k_1 k_2 Po_2 C_s^{=}}{k_1 C_s + k_2 H}$$

where H is Henry's constant and Po_2 is the partial pressure of oxygen in liquor. The other members of the equation are defined above. If the chemical reaction rate is high as it is for high temperatures and pressures above atmospheric conditions with a high concentration of sulfide, at the beginning of the oxidation process, the overall reaction rate is zero order with respect to sulfide and controlled by oxygen transfer. As oxidation progresses, the concentration of sulfides decreases and the equation becomes first order with respect to sulfide; for example,

$$\frac{dC_s^{=}}{d_t} = -\frac{k_1 Po_2 C_s^{=}}{H}$$

Thus, a change in rate orders of the reaction suggest the convenience of a two-stage reactor in which in both stages a rapid absorption of oxygen is promoted and an increase in final constant rate value is provoked. In this manner in the second stage a fraction of both the oxygen and black liquor are again mixed with the bulk of the reacting liquor.

The feasibility of the above was carried out experimentally on a single stage tubular reactor and a two stage reactor. The trials were conducted in a southern kraft mill where for the first time weak black liquor was oxidized satisfactorily for several weeks at flow rates ranging from 850 to 1,550 gallons per minute. In Table 1 is set forth the black liquor oxidation in a tubular reactor which shows the effects of the ratio of O_2/S in terms of oxidation efficiency expressed in percent. The column Na_2S indicates the concentration of the Na_2S in the spent liquor; the phrase "oxygen injected" is the amount of oxygen mixed with the spent liquor, with the oxygen efficiency of the oxidation expressed in percent, and, in the final column is set forth the flow of the spent black liquor in gallons per minute.

TABLE I

Lb. mole/hr.				
Initial Na_2S	Oxygen injected	$O_2/S^{=}$ ratio	Oxygen efficiency (percent)	Flow gpm
81.2	79.59	0.98	93.2	1,200
75.0	77.80	1.04	89.5	1,215
72.8	81.18	1.11	78.5	1,150
99.0	99.50	1.0	85.0	1,395
93.0	99.32	1.07	77.7	1,355
82.0	98.49	1.19	70.7	1,395
86.0	101.81	1.18	82.4	1,355
87.2	106.74	1.22	81.0	1,395
97.6	109.03	1.12	77.0	1,495
99.5	107.18	1.08	81.2	1,480
94.8	107.24	1.13	76.8	1,355
94.5	120.49	1.27	77.2	1,355
93.6	120.49	1.29	75.0	1,355
91.8	120.55	1.31	75.0	1,355
89.8	114.47	1.27	75.5	1,355
90.5	112.04	1.24	79.8	1,375
92.0	109.90	1.19	81.9	1,395
94.4	103.35	1.10	72.0	1,395
99.0	108.89	1.10	82.1	1,395
101.0	115.45	1.14	85.8	1,525
107.5	119.20	1.11	73.6	1,560
103.5	122.34	1.18	75.5	1,560
63.4	67.47	1.07	69.0	895
68.2	84.34	1.24	79.5	895
76.5	87.96	1.15	84.4	950
104.3	111.46	1.06	87.5	1,495
92.0	92.75	1.0	83.8	1,055
68.6	73.07	1.06	87.5	950
79.0	84.30	1.07	75.5	895
73.0	85.55	1.17	80.2	895
124.2	124.10	1.00	85.8	1,670
117.8	115.67	0.99	87.3	1,525

The data set forth in FIG. **1** indicates how the efficiency of oxygen utilization decreases when the ratio of oxygen injected into initial sulfide content increases above the value 1.00. The numbers along the X-axis represent the ratio of oxygen injected into initial sulfide content in black liquor. The numbers along the Y-axis represent the stoichiometric efficiency of oxygen utilization. The results were obtained in a single stage tubular reactor. The results plotted in FIG. **2**, indicate that when the ratio of oxygen to sulfide ranges between 1.05 to 1.15 the efficiency of oxygen utilization decreases with a decrease in retention time in the two-stage reactor, because time is also needed to complete the reaction. This fact seemingly suggests that the chemical reaction is controlling since time is needed to complete a reaction that stoichiometrically should otherwise occur. Also, the increase in turbulence by decreasing the retention time does not appear to improve the completeness of the reaction, as there is need, besides diffusing the oxygen in the liquid, to give adequate time. In FIG. **2**, the X-axis represents flow in the tubular reactor in gallons per minute for the ratio of $O_2/S^{=}$ between 1.05 and 1.15. The Y-axis is as with FIG. **1**. The presence of two rates of conversion is further demonstrated in FIG. **3**. In FIG. **3**, the oxygen to sulfide ratio are below the stoichiometric value of 1.00; that is, at 0.75 to 0.85, indicating that theoretically all sulfides cannot be oxidized for lack of enough oxygen. The efficiency of oxygen utilization remains practically constant, at different velocities, because the remaining concentration of sulfide, not oxidized, has not reached a value low enough to induce the first order reaction as the controlling one. In FIG. **3**, the X-axis represents the flow of the spent liquor in the two-stage reactor in gallons per minute and the Y-axis, the oxygen utilization efficiency, as in FIGS. **1** and **2**, for a ratio of $O_2/S^{=}$ between 0.75 and 0.85. This evidence seemingly indicates the soundness for a dual step reactor, and desireability for turbulent diffusion and oxygen mass transfer, and of the apparatus design as set forth in the use of the nozzle, the reactor and the like.

Referring now to drawing FIG. **4** in detail, wherein a two-stage reactor is depicted for use of oxygen absorption and chemical reaction in the oxidation of black liquor. In FIG. **4**, a pipeline **20** which is connected to source of spent liquor to be treated (not shown) and also connects to the first stage of a reactor **35** where the essentially bulk oxidation of the spent liquor occurs. The black liquor flow in pipeline **20** passes an oxidation-reduction-potential (ORP) cell or sulfide electrode **22** suitably mounted in the wall **23** of feed pipeline **20**. The pipeline **20** is made of stainless steel or any other duct or conduit material that does not chemically react or is adversely affected by the spent black liquor. The described cell **22** is commercially available from Beckman Instrument Co., of Fullerton, California, and it protrudes into the black liquor wherein, in operation, it relays a current signal through line **25** to an ORP Beckman 900 analyzer, for determining the sulfide content as ascertained by analyzer **24**. The analyzer **24** provides essentially for a sulfide concentration signal, which is relayed to a primary control **26** which, in turn, is connected to a secondary controller or control **27**. The primary control **26** is the first cascade of a two pen cascade controller made by Honeywell Manufacturing Co., of Philadelphia, Pennsylvania, and sold under the commercial designation S-320-1 and No. 32631. The secondary controller **27** is an integral part of the control station **27** which contains the primary controller. The secondary controller **27** is designed to interpret a signal which measures the flow of liquor in pipeline **20**. The flow of liquor is ascertained by an orifice meter **28** which is pneumatically connected through lines **29** to a pressure differential cell **30**. This cell is commercially available and it is manufactured by Honeywell Manufacturing Co. and made available as S-292-3, No. 29212. The pressure differential cell **30**, in turn, is connected to a transducer, which converts the pneumatic signal to

a current signal to be supplied through electrical line **31** to the secondary controller **27**. The secondary controller **27** is connected through an electrical line **31***a* to a conventional control valve **32** such as a double-seated, diaphragm, cage in line type, which is part of an oxygen feedline **33**. Thus, in operation thus far, spent liquor flows in pipeline **20** past cell **22** which measures the amount of sulfide in the spent liquor while the flow rate of the spent liquor in the pipeline **20** is also being measured by an orifice meter **28**. The two data are evaluated by the signals sent to the primary and secondary controllers **26** and **27** which send a command signal to valve **32** through line **31***a* for letting a now predetermined amount of oxygen enter into the system by a tee pipe **34** which permits some of the oxygen to enter the first stage reactor **35** and also permits some of the oxygen to travel in a conduit or pipe **36** suitably equipped with an in line gate valve **36***a* to a second stage reactor **37**. The first stage reactor **35** is connected to the second stage reactor **37** by a pipeline **43**, and pipeline **20** extends into a flange **39** and enters the first stage reactor shortly thereafter. The pipeline narrows and terminates with a nozzle **40** attached thereto for atomizing the spent liquor in the first stage reactor **35**. The first stage reactor **35** has a joint **41** for converging into a flange **42** which leads into a pipe section **43** through a flange **44** and into second stage reactor **37**. The length of the pipeline **43** is determined by use of the equation previously indicated. Second stage reactor **37** is constructed in a manner similar to first stage reactor **35** by having a converging section leading into a flange **46** and then into a pipe **48** for transporting oxidized black liquor to storage tanks, not shown. The second stage reactor **37** is also externally connected to inlet pipeline **20** through a circulating conduit **38** suitably equipped with an inline gate valve **38***a*. The circulating conduit **38** circulates the spent liquor to aid in the oxidation of the spent liquor. In operation, the pressure in pipeline **20** forces the liquor into conduit **38** for circulation into reactor **37**.

In actual operation, the tubular reactor is operated at a high Reynolds number, above 500,000 to guarantee turbulent conditions in the reactor. The relative dimensions of a typical reactor are for example, as follows; the nozzle diameter is 0.5 times the pipeline diameter, the reaction chamber, for example, **35**, has a diameter 1.8 times the pipeline diameter, the length of reaction chamber is 5.5 times the pipeline diameter, the length of the converging zone is 3 times the pipeline diameter. The diameter of the oxygen line **36** and spent liquor lines **43** to the second stage reactor are 0.33 times the respective diameters of the incoming oxygen pipelines **33** and the incoming liquor pipeline **20** which latter line has a diameter of any predetermined size, for example, according to the installation of 4, 6, 8 and 10 inches, etc. Of course, these dimensions are by way of example, and they can be varied by those skilled in the art as larger multi-stage reactors or smaller multi-stage reactors can be constructed in the light of the present broad disclosure. The oxygen absorption process and the subsequent chemical reaction takes place in the reactor in three phases. In the first phase, oxygen molecules are transferred to the liquid black liquor surface. The liquid interphase has a definite thickness, usually a few molecules. Next, the second phase, oxygen must pass through this layer by diffusion. Finally, in the third phase, oxygen diffuses into the bulk of the spent liquor and the oxidation reaction takes place. The speed of the phases can be increased by turbulence. In the first stage, a fraction of the black liquor, that is, 80 to 90 percent of the total flow in incoming pipeline **20**, is atomized at nozzle **40** at a high Reynolds number above 500,000. The necessary oxygen is injected at **34** for oxidation, about 1.05 times the required stoichiometric amount used. Intimate mixing and diffusion of the spent liquor takes place in chamber **35**, with oxidation taking place therein and in tubular section **43**. Section **43** leads to the second reactor where the remaining fraction of unoxidized liquor is introduced and atomized by nozzle **40***a*. Oxygen, for the oxidation of the remaining liquor is introduced by line **36**. The mixing again takes place in the second stage reactor **37**, and the liquor passes out in pipe **48**. The process can be run on a limited quantity of liquor or on a continuous basis.

The present invention may be embodied in other forms without departing from the spirit or essential attributes thereof and, accordingly, such embodiments as would be obvious to those versed in the present art in the light of this application are indicated as within the scope of the invention.

What is claimed is:

1. A two-stage oxidation apparatus for the oxidation of sodium sulfide and mercaptide in spent black pulping liquor, the apparatus comprising a first oxidation reaction chamber in series with a second oxidation reaction chamber, a liquid inlet conduit extending into and terminating in the first chamber, means for supplying the black pulping liquor from the inlet conduit into and through the first reaction chamber, a nozzle integrally fixed to the end of the inlet conduit terminating in the first chamber, the first chamber converging inwardly and forming directly into a second fluid transport conduit that terminates in the second reaction chamber, the second transport conduit being a tubular reactor and having a substantial tubular section in the end that terminates in the second reaction chamber, a nozzle integrally fixed to the end of the second fluid transport conduit, the second chamber converging inwardly and extending outwardly into an outlet flow conduit from the second chamber, an external oxygen supply conduit for molecular oxygen divisibly connected to both the first and second chamber, means for controlling the amount of molecular oxygen delivered to the first and second reactors flowing through the external oxygen supply conduit, the means for controlling the oxygen responsive to the sulfide content of the black liquor and the flow rate thereof in the inlet conduit that extends into the first reaction chamber, an externally mounted fluid circulating conduit connecting the inlet feed conduit before it enters the first reaction chamber with the second chamber for supplying the second chamber with some black liquor that has not been oxidized, and wherein said apparatus is used for efficient oxidation of the spent black pulping liquor at relatively low temperatures and pressures.

2. An oxidation apparatus for the oxidation of sodium sulfide and mercaptide and spent black pulping liquor, the apparatus comprising an oxidation reaction chamber, a liquid inlet conduit extending into and terminating in the reaction chamber, means for supplying black liquor from the inlet conduit into and through the reaction chamber, an oxygen supply conduit connected to the reaction chamber, means for supplying molecular oxygen through the oxygen supply conduit into the reaction chamber, a tubular reactor at the exit end of the reaction chamber, the tubular reactor having a length according to the following equation: $C_f = C_i e^{-kL/v}$ where C_f is the final sulfide concentration of the oxidized black liquor, C_i is the initial sulfide concentration of the black liquor, e is the Naparian base logarithm, v is the velocity of flow in gallons per minute of the liquor in the tubular reactor, and L is the length in feet of the tubular reactor, and control means for controlling the amount of molecular oxygen to the reaction chamber through the oxygen supply conduit, the control means responsive to the sulfide content of the black liquor and the flow thereof in the inlet conduit.

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