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(54) A process for concentrating a black liquor and an apparatus therefor.

(57) A process and an apparatus are disclosed for concentrating an alkaline waste liquor which is discharged from a step of alkaline cooking wood fiber in order to recover cooking chemicals, characterized in that CO_2 gas and/or gas containing CO_2 gas is added to said waste liquor as a viscosity lowering agent, as a boiling point lowering agent and/or as a solidification promoter before and/or during said concentration.

Croydon Printing Company Ltd.

A PROCESS FOR CONCENTRATING A BLACK LIQUOR AND AN APPARATUS THEREFOR

The present invention is directed to an improved method and apparatus in the production of wood pulp for concentrating alkaline waste liquor discharged from cooking process of wood fiber (referred to as black liquor hereafter) from which liquor cooking chemicals are recovered.

In the production of wood pulp, particularly of chemical pulp, the Kraft cooking process (hereinafter referred to as the KP) which uses sodium hydroxide and sodium sulfide as major cooking chemicals (referred to as the KP process hereafter) has been the main process for producing chemical pulp, owing to the high quality of the pulp produced, and the advantages of its cooking chemicals recovery system, which has been established.

In recent years, it has been confirmed that an alkaline cooking process (hereinafter referred to as an AP process) substantially using sodium hydroxide as a main cooking chemical gives almost the same level of yield and quality of pulp as are obtainable in the KP process by additionally using an anthraquinone cooking aid. Moreover, in this process, no sulfur compound like sodium sulfide is used as a cooking chemical, and therefore the process is seen as a production process of chemical pulps which generates no sour smell substance from the cooking process which is in contrast with the KP process.

As the method of recovering chemicals in the AP process, it is possible to employ a direct causticizing process by ferric oxide wherein the black liquor is blended with ferric oxide and subjected to combustion to produce sodium ferrite, which is then hydrolyzed to recover sodium hydroxide as a cooking chemical. This method is known to be advantageous in terms of energy efficiency because it requires no calcination by lime kiln and its process is simplified as compared with a causticizing method using calcium hydroxide as is employed in the KP process.

It is possible to use entirely the same production apparatus in the AP process as in the conventional KP process and it also has the aforementioned advantages, so that it is anticipated to provide an excellent production process of chemical pulp. However, it has problems in practical use, one of which is that the viscosity of the AP black liquor is ten times as high as that of the KP black liquor, as shown in Fig. 1, even if the concentrations of the solid contents in the black liquor (hereinafter referred to as the black liquor concentration) are at the same level. The alkaline sulfite process has been noted as a process of producing chemical pulp in higher yields and with higher brightness than the KP process, when anthraquinone and the like is added to the cooking additives.

A step of concentrating the black liquor is a very important step before the recovery boiler which recovers the chemicals and the heat energy produced by the combustion of organic materials contained in the black liquor.

The black liquor discharged from the process normally has a very low concentration of 10 - 20%. It is necessary to concentrate the black liquor to a concentration of greater than about 50%, normally 60 - 70%, because a high concentration of the black liquor is effective for the recovery and re-use of the heat energy produced by the combustion.

When a ton of pulp is produced, 1.5 - 2 tons of black liquor solids are normally discharged. In order to concentrate the black liquor from 15% to 50%, 9 - 12 tons of water per ton of pulp must be evaporated from the black liquor. A great deal of evaporation energy is needed in order to evaporate this water from the black liquor. Thus the step of concentrating the black liquor involves multiple-effect evaporator wherein steam which has been used once in the concentration of the black liquor is re-used in another evaporator.

However, it is known that as the concentration of the black liquor increases, its vapor pressure drops and its boiling point sharply increases. It has problems in practical use, one of which is that the viscosity of the AP black liquor is ten times as high as that of the KP black liquor, even if the black liquor concentration are at the same level. High viscosity of the black liquor indicates that its fluidity has deteriorated and the concentration efficiency of the black liquor in an evaporator is lowered. It also lowers the efficiency of transporting the black liquor into a combustion furnace and deteriorates sprayability from a burner in the furnace, so that the combustibility of the black liquor will be lowered.

Dropping the vapor pressure of the black liquor and sharply increasing the boiling point of the black liquor has the effect of making the water content in the black liquor less volatile. The highly concentrated black liquor is further concentrated by adding a large amount of heat energy thereto, so that the vapor pressure thereof is increased and the temperature thereof is risen to its boiling point.

The key to the present invention is the discovery of the fact that an addition of CO_2 gas to the black liquor reduces its boiling point and viscosity, makes its solidification easier, and improves its ability to be concentrated.

The method of adding CO_2 gas to KP black liquor mainly used in chemical process has been utilized in the prior art only for specific purposes such as the separation of lignin or silica. If CO_2 gas is added to KP black liquor, it becomes acidic by absorbing the CO_2 gas, and generates toxic hydrogen sulfide which has a bad smell. The hydrogen sulfide also present corrosion problems for the apparatus. Thus no attempt has been made toward the purpose of the present invention.

The prior techniques of enhancing the ability of KP black liquor to be concentrated are as follows:

(A) Increasing the area of the heating surface of the evaporator;

(B) Increasing the heat conductivity of the heating surface of the evaporator;

(C) Increasing the temperature of the black liquor; and

(D) Reducing the viscosity of the black liquor.

If the area of the heating surface is increased, the amount of evaporated black liquor is also increased. This means an enlargement of the size of the apparatus for concentrating the black liquor. This enlargement has no merit as regards energy costs, but leads to an increase in the cost of the apparatus.

If the heat conductivity of the heating surface of the evaporator is increased, the heat transfer speed on the surface is increased, whereby the concentration rate is also increased. In practice, it is necessary to directly contact the black liquor with metal surfaces on the heating surface, and prevent the attachment of scale, which reduces the heat conductivity of the heating surface, to the heating surface. Specifically, the heat conductivity has been recovered by removing the silica or alumina which causes scaling from the black liquor, or by removing such scaling by washing with dilute black liquor, warm water, or acidic water. It is possible as a method of this type to change the shape of the heating surface so that scale is less likely to deposit on the surface. The purpose of such a method is to maintain the initial heat conductivity rather than to positively enhance the ability of the black liquor to be concentrated.

If the temperature of the black liquor is increased, its vapor pressure is naturally increased, but a great deal of evaporation energy is needed for increasing this pressure, and this method has no merit as regards energy.

The improvement in the ability of the black liquor by reducing its viscosity is known in the art. See, for instance "Kraft Pulp and Non-wood Fiber Pulp" in the Complete Technical Book of Production of Pulp and Paper (volume 3, page 145) edition (1967) by The Japanese Technical Association of the Pulp and Paper Industry. The method incorporated therein by reference is directed to the use of a low concentration of black liquor, to increase the temperature of the black liquor, or add a surface active agent to the black liquor as a method of reducing the viscosity of the black liquor.

A method of adding such a surface active agent to the black liquor as a viscosity-reducing agent is disclosed in Japanese Laid-open Patent Publication No. 228094/84. According to this method, the viscosity is reduced by only 1/2 - 1/3, compared with black liquor to which no surface active agent is added. This method has no advantage concerning the reduction of the boiling point and the making of the solidification easier.

US Patent No. 2,997,466 and Tappi 62 (11), 108, (1979) refer to the separation of lignin.

The increase in the concentration of the black liquor is accompanied by a great rise in the boiling point of the black liquor. As a result, the ability of the black liquor to be concentrated becomes worse, and a large amount of heat energy is needed to further concentrate the black liquor. The purpose of the present invention is to solve this problem.

The present invention provides

(A) a process for concentrating an alkaline waste liquor substantially free of a sulfur compound, which is discharged from a step of alkaline cooking wood fiber and/or the subsequent step of bleaching said fiber, in order to recover cooking chemicals and/or bleaching chemicals from said waste liquor,

characterized in that CO_2 gas and/or gas containing CO_2 gas is added to said black liquor as a viscosity lowering agent, as a boiling point lowering agent and/or as a solidification promoter before and/or during said concentration which may consist of one or more stages, and

(B) a process for concentrating an alkaline waste liquor containing a sulfur compound or sulfur compounds, which is discharged from a step of alkaline cooking wood fiber in order to recover cooking chemicals from said waste liquor,

characterized in that CO_2 gas and/or gas containing CO_2 gas is added to said black liquor as a viscosity lowering agent, as a boiling point lowering agent, as a solidification promoter and/or as a corrosion inhibitor, said addition being after a step of oxidizing said waste liquor and before and/or during said concentration.

Furthermore, the present invention provides

(C) an apparatus for concentrating the black liquor substantially free of a sulfur compound, comprising vacuum evaporators and means for absorbing CO_2 gas and/or gas containing CO_2 gas into said black liquor, said means being positioned prior to and/or in said vacuum evaporators, and

(D) an apparatus for concentrating the black liquor containing a sulfur compound or sulfur compounds, comprising vacuum evaporators and means for absorbing CO_2 gas and/or gas containing CO_2 gas into said black liquor, said absorption means being positioned prior to and/or in said vacuum evaporators and subsequent to means for oxidizing said black liquor.

Fig. 1 illustrates variations in the viscosity of the black liquor with the corresponding concentration thereof.

Fig. 2 illustrates variations in average particle diameter of the black liquor with the corresponding pH thereof.

Fig. 3 illustrates variations in the viscosity of the black liquor with the corresponding pH thereof.

Fig. 4 illustrates variations in the boiling point of the black liquor with the corresponding concentration thereof.

Fig. 5 illustrates variations in the boiling point with the corresponding concentration of AP cooking liquor.

Fig. 6 illustrates variations in the boiling point with the corresponding concentration of KP cooking liquor.

Fig. 7 illustrates variations in the concentration velocity of AP black liquor with the corresponding concentration thereof.

Fig. 8 illustates variations in the concentration velocity of KP black liquor with the corresponding concentration thereof.

Figs. 9 through 22 illustrate typical embodiments of CO_2 gas absorption means used in the present invention.

Figs. 23 and 24 are examples of the present invention.

Fig. 25 is a flow sheet of the prior art.

In Figs. 23 through 25, the KP process needs an oxidation means but the AP process does not need such means.

This liquor may contain black liquor discharged from a step of cooking wood fibers using (1) sodium hydroxide (soda process), (2) sodium hydroxide and sodium sulfide (sulfidity of 1 - 100%, particularly 5 - 35% i.e. from low sulfidity Kraft process to Alkafide process) and/or (3) sodium sulfite, sodium carbonate and sodium hydroxide (Alkaline Sulfite process) as the main cooking chemicals, together with anthraquinone, derivatives thereof, anthracene derivatives, aliphatic or aromatic amines, or aliphatic alcohols, either solely or in combination, as a cooking aid.

Addition of CO_2 gas to the AP black liquor causes no problem but if CO_2 gas is added to KP black liquor which as just been discharged from a wood fiber cooking step, the pH of this liquor is reduced and hydrogen sulfide is generated by the reaction of the sulfur compounds therein and the CO_2 gas. It is necessary according to the present invention to oxidize the KP black liquor before the addition of CO_2 gas to the liquor, so as to prevent the generation of toxic hydrogen sulfide gases which create had smells and corrode the apparatus. Such oxidation of the KP black liquor has generally been carried out in the art for the purpose of preventing bad smells and increasing the sulfur recovery efficiency.

However, the prior art does not provide the improved method of the present invention for efficiently concentrating black liquor, which comprises the addition of CO_2 gas to the black liquor as a boiling-point-reducing agent, viscosity-reducing agent, solidification promoter of the black liquor and aniti-corrosive agent for apparatus, after the step of oxidizing the black liquor.

There is a negative method of contacting a CO_2-containing gas with KP black liquor in a cascade evaporator, but this method is not often used currently. This method comprises contacting the exhaust gas from the recovery boiler with the concentrated black liquor which has just been treated by the concentrating apparatus, to further concentrate the black liquor, whereby the heat energy contained in the exhaust gas is efficiently utilized. This method may negatively imply a partial contact and reaction between the KP black liquor and the CO_2 gas contained in the exhaust gas of the recovery boiler, because the gas inevitably contains CO_2 gas generated by the combustion of the organic materials in the black liquor. However, it is in no way intended that a positive reaction of the KP black liquor with the CO_2 gas contained in the exhaust gas occurs, but that such contact is controlled by maintaining the pH at 13.0 - 12.5 so that the generation of hydrogen sulfide by the reaction with CO_2 gas can be avoided.

The step of adding CO_2 gas to the KP black liquor according to the present invention comes after the black liquor oxidation step subsequent to the KP-cooking step. However, even if the addition is carried out simultaneously with the oxidation, a similar effect can be obtained. Therefore, the present invention is not limited to the claimed method. However, in this case it is necessary to have the black liquor react with oxygen in preference to the CO_2 gas. This preferential reaction is put into practice by making the concentration of O_2 gas in the mixture of O_2 and CO_2 gases greater than that of the CO_2 gas. However, the system of adding CO_2 gas to the black liquor after the oxidation step is recommended from the standpoint of preventing the generation of hydrogen sulfide.

The oxidation degree of the oxidized KP black liquor according to the present invention is preferably 70 - 100%, more preferably 90 - 100%. A higher oxidation degree is desirable from the standpoint of preventing the generation of hydrogen sulfide and improving the ability of the black liquor to be concentrated.

An oxidation degree of 70 - 100% is attainable by using a prior-art oxidation step. Paper mills adopting the present invention may need not only the prior-art air oxidation step, but also another oxidation processing conducted by a gas containing a high concentration of O_2 such as adsorption, membrane separation, or low-temperature processing. Moreover, not only the prior-art oxidation of dilute black liquor but also the O_2-oxidation of concentrated black liquor may be needed.

According to the present invention, when CO_2 gas is added to the black liquor, an improvement in its ability to be concentrated is expected within a pH range of 8.5 - 12.5, preferably 10.0 - 12.0, particularly less than or equal to 9.0 in black liquor obtained from some kinds of tree such as eucalyptus.

The pH is determined at a concentration of 40% and a temperature of 80°C; and, unless otherwise specified, the pH determined hereafter depends on this condition.

When the pH of the black liquor is more than 12.5, the reduction in its boiling point is not sufficient to concentrate the liquor. On the other hand, when the pH of the liquor is less than 8,5, its viscosity is increased, and this makes its ability to be concentrated worse.

Reducing the pH of the liquor to an excessively low level means an addition of excess CO_2 gas. A long time is necessary for this addition, and the excess gas is removed from the liquor by evaporation in the concentration step.

The range of the concentration of the black liquor to which CO_2 gas is added is not specifically limited. At whatever stage the CO_2 gas is added, the ability to be concentrated is improved after that addition. However, the higher concentration of the liquor to which the CO_2 gas is added, the less the amount of liquor to be treated. When CO_2 gas is added to liquor of an excessively high concentration, its viscosity is increased. Thus the addition of CO_2 gas to the liquor becomes less efficient owing to the poor capacity of the liquor to absorb CO_2 gas. The lower the concentration of the black liquor to which the CO_2 gas is added, the more the amount of liquor which can be treated. However, the capacity of the liquor to absorb CO_2

gas is increased by its low viscosity. When CO_2 gas is added to oxidized black liquor, the concentration of the liquor is normally 20 - 75%, preferably 40 - 65%.

The temperature at which the CO_2 gas is added to the black liquor is not also particularly limited. Normally, the lower the temperature of the black liquor, the greater the absorption velocity of the gas by the liquid. However, the viscosity of the black liquor is higher at low temperatures, and the diffusion velocity of the CO_2 gas into the black liquor is reduced. On the other hand, the higher the temperature, the lower the absorption velocity. However, the viscosity of the black liquor is lower at high temperatures and the diffusion velocity of the CO_2 gas is increased. Methods conducted with the temperature of the black liquor high or low have their merits and demerits. Selection of one of the two methods is left to the pulp mills adopting the present invention. The temperature of the oxidized black liquor to which CO_2 gas is added may be 20 - 100°C, preferably 40 - 90°C.

The use of the present invention is limited to wood fibers, but is also applicable to non-wood fibers.

According to the present invention, only CO_2 gas is used as a viscosity reducing agent and the like but nitric acid, oxalic acid and/or material which exhibits acidity when dissolved in water and the like can be used, bringing about similar advantages.

As shown in Fig. 1, when CO_2 gas is added to AP black liquor or oxidized KP black liquor, the viscosity thereof is reduced so that it is less than that of oxidized KP black liquor or AP black liquor which have not been treated with CO_2 gas in concentrations of greater than about 67%.

Part of the lignin in the black liquor agglomerates and is dispersed therein by the reduction of the pH of the black liquor, as finely-divided particles. Thus a high-molecular aqueous solution of the lignin is thought to be changed to an emulsion thereof. This is why the viscosity of the black liquor with added CO_2 gas is reduced by more than that of the black liquor to which no CO_2 gas is added.

Fig. 2 shows variations in the average particle diameter of the black liquor with added CO_2 gas, together with the corresponding pH thereof. Solid particles of such a diameter are acted on by the Brownian motion in the liquid and the efficiently dispersed therein. Accordingly, it is assumed that, in black liquor with added CO_2 gas, the part of the lignin which has agglomerated is sufficient to form an emulsion.

As can be seen from Fig. 2, when the pH of the black liquor is reduced, the average particle diameter of the agglomerated lignin becomes small. In general, the smaller the diameter of particles in an emulsion, the higher its viscosity. It can be easily understood from Fig. 3 that the viscosity of the black liquor with added CO_2 gas is increased at a pH of less than 9.5, because of the viscosity properties of the emulsion.

The boiling point of the black liquor is greatly reduced by adding CO_2 gas to the liquor. As shown in Fig. 4, the boiling point of the black liquor prepared by cooking Douglas fir is reduced, by 18 - 20°C, from 126°C (the boiling point of untreated black liquor) to 106 - 108°C (the boiling point of black liquor with CO_2 gas added) at atmospheric pressure and a concentration of 80%.

Fig. 6 is a graph of boiling point versus the concentration of solid content, for (1) an aqueous solution of a mixture of sodium hydroxide and sodium sulfide, which is used in KP cooking, (2) an aqueous solution of mixture of sodium hydroxide and sodium thiosulfate which is obtained by oxidizing the mixture of (1), and (3) an aqueous solution of a mixture of sodium carbonate and sodium thiosulfate which is obtained by adding CO_2 gas to the mixture of (2). As can be seen from Fig. 6, the boiling point of mixture (3) is much lower than those of mixtures (2) and (1). This is the reason why the boiling point of the black liquor is reduced by the addition of CO_2 gas.

Fig. 5 illustrates the boiling point under atmospheric pressure of sodium hydroxide which is used in the AP cooking, and of sodium carbonate prepared by adding CO_2 gas to sodium hydroxide.

It is assumed that when the boiling point of the black liquor is reduced, its vapor pressure is increased accordingly.

Fig. 7 shows the concentration velocity of the oxidized KP black liquor, which is 1.2 - 1.6 times larger than that of untreated oxidized black liquor. This confirms that the ability to be concentrated has been improved by the present invention.

Fig. 8 shows that the concentration velocity of the AP black liquor to which CO_2 gas has been added is 1.4 - 5.5 times larger than that of untreated black liquor.

The black liquor concentrated by the process of the present invention is less sticky than the black liquor concentrated by the prior process. The black liquor which is completely concentrated by the process of the present invention is very brittle and easily grindable and its capacity to absorb moisture is greatly reduced. This makes the preparation of a 100% solidified black liquor easier, and its combustion energy is effectively usable when it is burnt by a recovery boiler.

The highly-concentrated KP black liquor according to the present invention has a very low corrosivity with respect to the apparatus of the system. The reason therefor can be easily understood by experiments set forth below, conducted with respect to KP black liquor from which organic materials have been removed. When a test peace of stainless steel (SUS-316) which has a metallic luster surface is immersed at 120°C for 100 hours in aqueous solution of (1) a mixture of sodium hydroxide and sodium sulfide having a sulfidity of 25%, (2) a mixture of sodium hydroxide and sodium thiosulfate (i.e. a mixture obtained by oxidizing mixture (1)), the surface turns from liver brown to brown, and a dark green precipitate is formed. On the other hand, the metallic luster surface of the stainless steel was maintained unchanged when immersed at 120°C for 100 hours in an aqueous solution of a mixture of sodium carbonate and sodium thiosulfate, obtained by adding CO_2 gas to the mixture of (2).

Presumably alkali corrosion occurred on the stainless steel (SUS-316) immersed in mixtures (1) and (2) because they are strongly alkaline and have a high boiling point. On the other hand, such corrosion is less likely to occur on the stainless steel immersed in the aqueous solution of the mixture of sodium carbonate and sodium thiosulfate produced in accordance with the present invention, because it is less strongly alkaline and lower temperature than the above mixtures.

The moisture absorption properties of the black liquor concentrated by the method of the present invention is greatly reduced. This is probably because the mixture of sodium carbonate and sodium thiosulfate is less likely to absorb moisture from that air than mixture (1) which is deliquescent. Thus this method is very effective for keeping such a solidified black liquor in storage, and preventing moisture on combustion.

The following specific examples taken with reference to the drawings are further illustrative of the nature of the present invention; but it is understood that the invention is not limited thereto.

<u>Examples 1 through 10, Comparative Examples 1 through 3 and Reference Examples 1 through 3</u>

AP black liquor obtained by AP-cooking of Douglas fir was concentrated to 40% and then CO_2 gas was added to the AP black liquor with heating and stirring at 80°C. The pH, viscosity (concentration of 80% at 80°C) and boiling point (under atmospheric pressure) of the black liquor are shown in Table 1 as Examples 1 through 5. The results obtained with oxidized KP black liquor of Douglas fir to which CO_2 gas was added are shown as Examples 6 through 10. The comparative examples 1 through 3 show similar results with respect to untreated AP black liquor, a KP black liquor and an oxidized KP black liquor. The reference examples 1 through 3 show cases where nitric acid or oxalic acid is added to an AP black liquor, and where CO_2 gas is added to a non-oxidized KP black liquor. The viscosity of the liquor was determined by a flow tester.

Table 1

	Example No.	Black liquor	acidic substance	pH 80°C 40%	Viscosity of black liquor (cps) 80°C, 80%	b.p. (°C) 80% 1 atm
Process according to this invention	1	AP	CO_2 gas	12.5	4.0×10^5	106
	2	AP	CO_2 gas	11.5	5.6×10^4	106
	3	AP	CO_2 gas	11.0	2.1×10^4	106
	4	AP	CO_2 gas	9.5	2.5×10^5	106
	5	AP	CO_2 gas	9.0	8.6×10^5	106
	6	Oxidized KP	CO_2 gas	12.5	3.4×10^4	108
	7	Oxidized KP	CO_2 gas	11.5	3.2×10^4	108
	8	Oxidized KP	CO_2 gas	11.0	2.4×10^4	108
	9	Oxidized KP	CO_2 gas	9.5	5.0×10^4	108
	10	Oxidized KP	CO_2 gas	9.0	8.0×10^4	108
Prior art	Comp. Ex. 1	AP	No addition	13.9	4.0×10^6	127
	Comp. Ex. 2	KP	No addition	13.4	9.5×10^4	126
	Comp. Ex. 3	Oxidized KP	No addition	13.4	9.5×10^4	121
	Ref. Ex. 1	AP	Nitric acid	11.0	1.2×10^4	110
	Ref. Ex. 2	AP	Oxalic acid	10.8	2.7×10^4	106
	Ref. Ex. 3	KP	CO_2 gas	10.7	7.1×10^4	118

Table 1

	Example No.	Additive	pH 80°C 40%	Viscosity of black liquor (cps) 80°C, 75%	b.p. (°C) 80% 1 atm
Present invention	11	CO_2 gas	9.0	5.4×10^4	106
Prior art	Comp. Ex. 4	No addition	10.4	2.3×10^6	111

Table 1

	Example No.	Black liquor	Acidic substance	pH		Viscosity of black liquor (cps) 80°C, 85%
				80°C 40%	20°C 40%	
Process of this invention	Ex. 12	O_2-alkali	CO_2 gas	10.0	10.9	5.8×10^4
Conventional process	Comp. Ex. 5	O_2-alkali	No addition	10.3	11.2	1.4×10^5

Table 2

Chemicals (Corresponding to black liquor of 65%	SS41 corrosiveness (mm/yr)	SUS316 corrosiveness (mm/yr)
Sodium hydorixde + Sodium sulfide	1.7×10^{-4}	1.5×10^{-4}
Sodium hydroxide + Sodium thiosulfate	1.6×10^{-5}	4.8×10^{-5}
Sodium carbonate + Sodium thiosulfate	4.8×10^{-6}	1.4×10^{-6}

Example 11 and Comparative Examples 4 and 5

The results with respect to AP black liquor obtained from eucalyptus conducted by the same procedures as Examples 1 through 5 and comparative Example 1 are shown in Table 1.

Example 12 and Comparative Example 6

The results conducted by the same procedures as Examples 1 through 5 are shown in Table 1 with respect to O_2-alkali bleached waste liquor of KP pulp of spruce, which was concentrated to 40%.

Examples 13 and 14 and Comparative Examples 7 and 8

CO_2 gas was added to the AP black liquors and oxidized KP black liquors used in Examples 1 through 10 and Comparative Examples 1 through 3 and the pH of the black liquors was thereby adjusted to 11.0 and 10.5, respectively. The relationship between viscosity and concentration of the black liquor at $80^{\circ}C$ is shown in Fig. 1 which contains as controls the results obtained with untreated AP black liquor and oxidized KP black liquor.

Example 15

Fig. 2 illustrates variations in the average diameter of the agglomerated particles used in Examples 1 through 5 with the corresponding pH thereof. The diameters were determined by a Coulter counter.

Fig. 3 illustrates variations in the viscosity of the black liquor used in Examples 1 through 5 (concentration: 80%; temperature: $80^{\circ}C$), to which CO_2 gas was added, with the corresponding pH thereof.

Examples 16 and 17, Comparative Examples 9 and 10 and Reference Examples 4 through 9

Fig. 4 illustrates the relationship between the boiling point and the concentration of the black liquors under atmospheric pressure. The black liquors were prepared by adding CO_2 gas to the AP black liquor and the oxidized KP black liquor used in Comparative Examples 1 through 3 and the pH were thereby adjusted to 11.0 and 10.5, respectively. Fig. 4 shows as controls the boiling points of untreated AP black liquor and of oxidized KP black liquor with the corresponding concentration thereof.

Fig. 5 illustrates as a reference the relationship between the boiling point under atmospheric pressure of sodium carbonate prepared by adding CO_2 gas to sodium hydroxide used in AP cooking, and the concentration of the solid content.

The boiling point at atmospheric pressure was determined for (1) an aqueous solution of a mixture of sodium hydride and sodium sulfide having a sulfidity of 25%, which is used in KP cooking, (2) an aqueous solution of a mixture of sodium hydroxide and sodium thiosulfate, which is obtained by oxidizing mixture (1), and (3) an aqueous solution of a mixture of sodium carbonate and sodium thiosulfate, which is obtained by adding CO_2 gas to mixture (2). The relationship between such boiling point and the concentration of solid content is shown in Fig. 6.

Examples 18 and 19, and Comparative Examples 11 through 13

Fig. 7 illustrates the concentration velocity of the black liquor prepared by adding CO_2 gas to the AP black liquor used in Examples 1 through 5 until the pH of the AP black liquor became 11.0. The concentration velocity of untreated AP black liquor is also shown in Fig. 7 as a control.

Fig. 8 illustrates the concentration velocity of the KP black liquor prepared by adding CO_2 gas to the oxidized KP black liquor used in Examples 6 through 10 until the KP black liquor was adjusted to have a pH of 10.5. The concentration velocity of KP black liquor without added CO_2 and oxidized KP black liquor is also shown in Fig. 8. The concentration was carried out by using a rotary vacuum evaporator under a pressure of -550mmHg (AP black liquor) and of -600mmHg (KP black liquor), and at 80°C. The concentration velocity was calculated by the reduction of water of the concentrated black liquor.

Reference Example 4

The corrosiveness of steel of various kinds was determined by contacting the steels for 100 hours at 120°C with (1) an aqueous solution of a mixture of sodium hydride and sodium sulfide having a sulfidity of 25%, which is used in KP cooking, (2) an aqueous solution of a mixture of sodium hydroxide and sodium thiosulfate, which is obtained by oxidizing mixture (1), and (3) an aqueous solution of a mixture of sodium carbonate and sodium thiosulfate, which is obtained by adding CO_2 gas to mixture (2) (Table 2).

The foregoing Examples relate to the introduction of CO_2 gas to the black liquor and the contact-reaction therebetween, but the material introduced to the liquor is not limited to CO_2 gas. Exhaust gas containing CO_2 gas from the black liquor recovery boiler, or from burnt organic materials from another system, may be introduced into the black liquor, effectively causing a contact reaction therebetween.

One of the merits of the present invention is to use the combustion exhaust gas of a recovery boiler or of another system which is not otherwise useful. Thus, the present invention saves money by using such a source.

The CO_2 in the exhaust gas can also be used after it is concentrated by an adsorption process or membrane separation process. In this case, the volume of a gas containing CO_2 gas introduced into the black liquor can be reduced, and the capacity of the black liquor to absorb CO_2 gas is increased.

The CO_2 gas-absorbing apparatus according to the present invention is set forth below in detail.

Vapor-liquid contacting apparatuses or gas-absorbing apparatuses of various types can be used in the present invention, such as a known wetted-wall column (Fig. 9), a packed tower (Fig. 10), bubble-cap tower (Fig. 11), perforated-plate tower (Fig. 12), spray tower (Fig. 13), scrubber (Fig. 14), foam-mixing tank, cyclone-spray scrubber (Fig. 15), floatator used as a de-inking apparatus in the pulp and paper industries, Swemack cell (Fig. 16), vertical floatator, or aeration apparatus for air or oxygen used in the activated sludge process. These apparatuses make it possible to have the oxidized KP black liquor absorb CO_2 gas by providing it with CO_2 gas and/or a gas containing CO_2.

It is also possible to use a premixer (Fig. 17) as a gas-liquid contact apparatus for the present invention; this is generally used for chlorinating pulp in a medium concentration of chlorine. In this case, black liquor is introduced thereinto instead of a pulp slurry, and flue gas is introduced instead of chlorine and/or chlorine dioxide.

A static mixer (Fig. 18), injection feeder (Fig. 19), a steam ejector, or a mechanical stirring aeration apparatus (Fig. 20) using CO_2 gas and/or CO_2-containing gas are also usable as the gas-liquid contact apparatus for the present invention.

The foregoing various types of CO_2 gas-absorbing apparatus can be used alone or in combination. An oxidizing apparatus (Fig. 21(a) or (b)) for black liquor can also be used as a CO_2 gas-absorbing apparatus for oxidized dilute black liquor, using CO_2 gas and/or CO_2-containing gas instead of air or oxygen for the oxidation.

It is also desirable to use an apparatus in which CO_2 gas and/or CO_2-containing gas is sucked into a mixing tank containing the oxidized black liquor, or in which the oxidized black liquor is sprayed into a tank containing CO_2 gas and/or CO_2-containing gas under at least atmospheric pressure.

When the combustion exhaust gas of the black liquor and the like is used as a gas source, foaming problems can be eliminated by the use of a wetted-wall tower of a multiple-tubular construction. It is also possible to control the gas-absorption performance by cooling the tube from the outside thereof, and such a CO_2 gas-absorption apparatus also has the merit that pressure losses on the gas side can be maintained at a comparatively low level. A packed tower, bubble cap tower, and/or perforated plate tower can also be used for the practice of the present invention, and it is desirable to provide a defoaming installation and a gas temperature-reducing installation which washes the exhaust gas with water.

It is further possible to use a Venturi scrubber, from the viewpoint of gas absorption performance, even although the pressure losses on the gas side are great, and it is difficult to control foaming. When such a CO_2-absorbing operation is conducted, it is sufficient to circulate the black liquor in the CO_2 gas-absorption apparatus with a pump, and draw it out while reducing its pH to 9.5 - 12.5, preferably 10.0 - 12.0, compared with the pH 12.6 - 13.8 of the black liquor at the inlet.

A packed tower, perforated-plate tower or the like employing as a gas source the combustion exhaust gas of the KP black liquor are preferably usable as the CO_2 gas-absorption apparatus for KP black liquor of a relatively high concentration. In such towers, the gas-liquid contact is efficiently conducted. It is desirable to wash the exhaust gas with water beforehand and reduce its temperature to a lower level in order to avoid any problems that may be caused by the concentration of the black liquor, which concentration is conducted by adding the exhaust gas to the black liquor. On the other hand, when a wetted-wall tower is used for this purpose, its gas-absorption performance is greatly decreased by the increase of the liquuid temperature. It is also preferable to use a Venturi scrubber, from the viewpoint of promoting the gas-liquid contact. In this case, the pressure losses on the gas side are large, but few problems are cuased, even if the black liquor is concentrated by exhaust gas.

Furthermore, it is possible to use a cascade evaporator (Fig. 22(a)),which is conventionally employed in the art as a contact-reaction apparatus, in which black liquor of a medium concentration contacts the exhaust gas from a boiler. However, the CO_2 gas-absorption performance of this conventional apparatus is not recommended for use, because the apparatus of this type was designed only for the purpose of concentrating black liquor, and avoiding the contact-reaction of the CO_2 gas with the black liquor as much as possible. Thus, it is necessary to increase the speed of the drums and the number of the drums in order to bring the CO_2 gas in the exhaust gas into contact with the black liquor. A disc evaporator (FIG.22(B)) which is conventionally employed can also be used.

It is possible to use an apparatus which contacts a highly-concentrated black liquor with the exhaust gas of a boiler, in which the boiler exhaust gas is introduced from above and/or below the surface of the black liquor, in a black liquor tank of a disc evaporator conducting concentration by a rotary disc of an indirectly-heated type. In this apparatus, the degree of contact of the CO_2 gas with the black liquor, as well as the ability of the black liquor to be concentrated, can be promoted by providing a scraper near the surface of the rotary disc to scrape off the black liquor attached to the surface of the disc. It is also possible to use an apparatus which provides a gas-liquid contact between black liquor of a medium concentration and exhaust gas from a boiler, this apparatus is also applicable to liquor of a high concentration, or the use an apparatus having a pressure-resistant structure so that it can provide a gas-liquid contact at a high temperature. These gas-liquid contact apparatuses can be used alone or in combination, and may also be used as a black liquor concentration apparatus.

When CO_2 gas has been added to the black liquor, its boiling point is reduced by 1 - 20°C from that of black liquor which has not been treated with CO_2. The elevation of the boiling point of the black liquor can be maintained to within an extremely small range, so that it is possible to greatly enlarge the effective available temperature difference, compared with the total temperature difference in such a concentration apparatus. This not only realizes an improvement in the ability of the black liquor to be concentrated, the miniaturization of the concentrating apparatus and a reduction in cost, but it also makes possible the concentration of the black liquor to a high level, and cause an increase in the quantity of heat recovered from the combustion of the black liquor.

According to the method of the present invention, since the viscosity of the liquor is reduced, its fluidity is improved, and the motive power of the concentration apparatus is reduced. The ability of the liquor to be concentrated is also further improved.

Transport by pipe becomes easier owing to the improved fluidity, and this is expected to reduce the power load on the pumps transferring the black liquor through piping. If such a load is constant, it is assumed to be possible to transport black liquor of a higher concentration.

Moreover, owing to the improved fluidity i.e. the improved ability of the black liquor to be injected into a combustion furnace, it is expected to be possible to inject black liquor of a higher concentration. This indicates a decrease in the water content of the black liquor taken into the recovery furnace. The amount of water to be evaporated in the recovery furnace is thus reduced. The latent heat of evaporation is not totally used, and thus is considered to be available as effective heat energy. Since the KP black liquor concentrated by the method of the present invention is less corrosive with respect to the concentrating apparatus, maintenance thereof becomes easier.

Claims:

1. A process for concentrating an alkaline waste liquor substantially free of a sulfur compound, which is discharged from a step of alkaline cooking wood fiber and/or the subsequent step of bleaching said fiber, in order to recover cooking chemicals and/or bleaching chemicals from said waste liquor,

characterized in that CO_2 gas and/or gas containing CO_2 gas is added to said waste liquor as a viscosity lowering agent, as a boiling point lowering agent and/or as a solidification promoter before and/or during said concentration.

2. A process according to Claim 1, wherein said step of alkaline cooking wood fiber is carried out by soda process.

3. A process according to Claim 1, wherein said subsequent step of bleaching said fiber is carried out by oxygen bleaching, hydrogen peroxide bleaching and/or ozone bleaching, and/or the subsequent step of alkaline extraction.

4. A method according to Claim 1, wherein the source of said CO_2-containing gas is selected solely or in combination from exhaust gases from a recovery boiler burning said concentrated black liquor, a boiler burning materials containing organic compounds other than said black liquor, a combustion furnace, an incinerator, and/or a reaction furnace.

5. A method according to Claim 1, wherein said CO_2-containing gas is a exhaust gas in which CO_2 gas contained in said exhaust gas is concentrated.

6. An apparatus for concentrating the waste liquor of Claim 1, comprising vacuum evaporators and means for absorbing CO_2 gas and/or gas containing CO_2 gas into said waste liquor, said means being positioned prior to and/or in said vacuum evaporators.

7. The apparatus according to Claim 6, wherein said absorbing means is selected alone or in combination from a wetted-wall tower, a packed tower, a perforated plate tower, a bubble cap tower, a Venturi scrubber, a stirring tank,

and/or a pressurized tank containing CO_2 gas or a gas containing CO_2 gas.

8. An apparatus according to Claim 6, wherein said concentrating apparatus is an indirectly-heated type of disc evaporator provided with a scraper to scrape off said black liquor attached to heating surfaces of said apparatus.

9. A process for concentrating an alkaline waste liquor containing a sulfur compound or sulfur compounds, which is discharged from a step of alkaline cooking wood fiber in order to recover cooking chemicals from said waste liquor,

characterized in that CO_2 gas and/or gas containing CO_2 gas is added to said waste liquor as a viscosity lowering agent, as a boiling point lowering agent, as a solidification promoter and/or as a corrosion inhibitor, said addition being after a step of oxidizing said waste liquor and before and/or during said concentration.

10. A process according to Claim 9, wherein said step of alkaline cooking wood fiber is carried out by Kraft process and/or alkaline sulfite process, solely or in combination.

11. A process according to Claim 9, wherein said subsequent step of bleaching said fiber is carried out by oxygen bleaching, hydrogen peroxide bleaching and/or ozone bleaching, and/or the subsequent step of alkaline extraction.

12. A process according to Claim 9, wherein the source of said CO_2-containing gas is selected solely or in combination from exhaust gases from a recovery boiler burning said concentrated black liquor, a boiler burning materials containing organic compounds other than said black liquor, a combustion furnace, an incinerator, and/or a reaction furnace.

13. A process according to Claim 9, wherein said CO_2-containing gas is a exhaust gas in which CO_2 gas contained in said exhaust gas is concentrated.

14. An apparatus for concentrating the waste liquor of Claim 9, comprising vacuum evaporators and means for absorbing CO_2 gas and/or gas containing CO_2 gas into said waste liquor, said absorption means being positioned prior to

and/or in said vacuum evaporators and subsequent to means for oxidizing said black liquor.

15. The apparatus according to Claim 14, wherein said absorbing means is selected alone or in combination from a wetted-wall tower, a packed tower, a perforated plate tower, a bubble cap tower, a Venturi scrubber, a stirring tank, and/or a pressurized tank containing CO_2 gas or a gas containing CO_2 gas.

16. An apparatus according to Claim 14, wherein said concentrating apparatus is an indirectly-heated type of disc evaporator provided with a scraper to scrape off said black liquor attached to heating surfaces of said apparatus.

FIG. 1

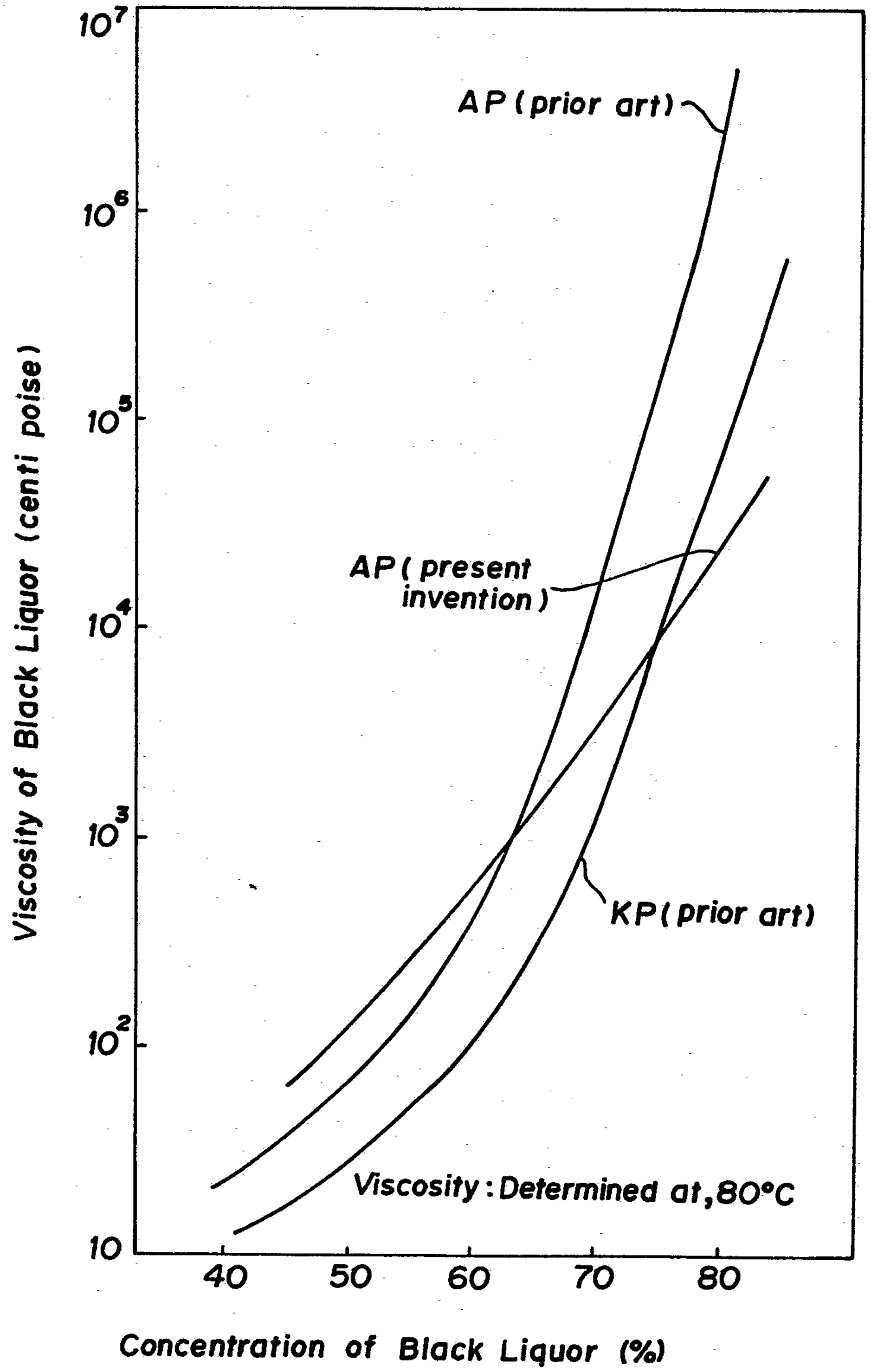

10^7
10^6
10^5
10^4
10^3
10^2
10
40
50
60
70
80
Viscosity of Black Liquor (centi poise)
Concentration of Black Liquor (%)
AP (prior art)
AP (present invention)
KP (prior art)
Viscosity : Determined at, 80°C

FIG. 2

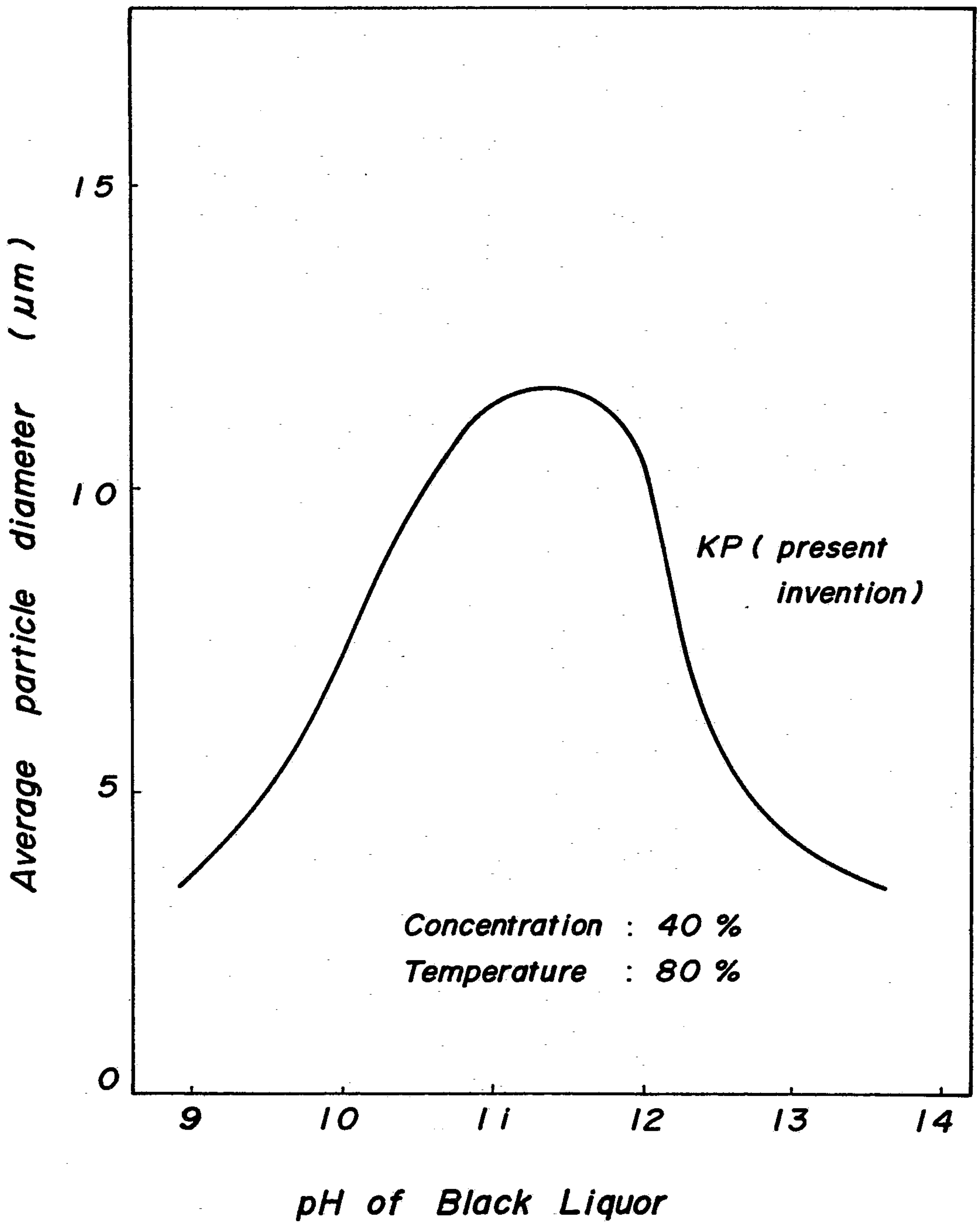
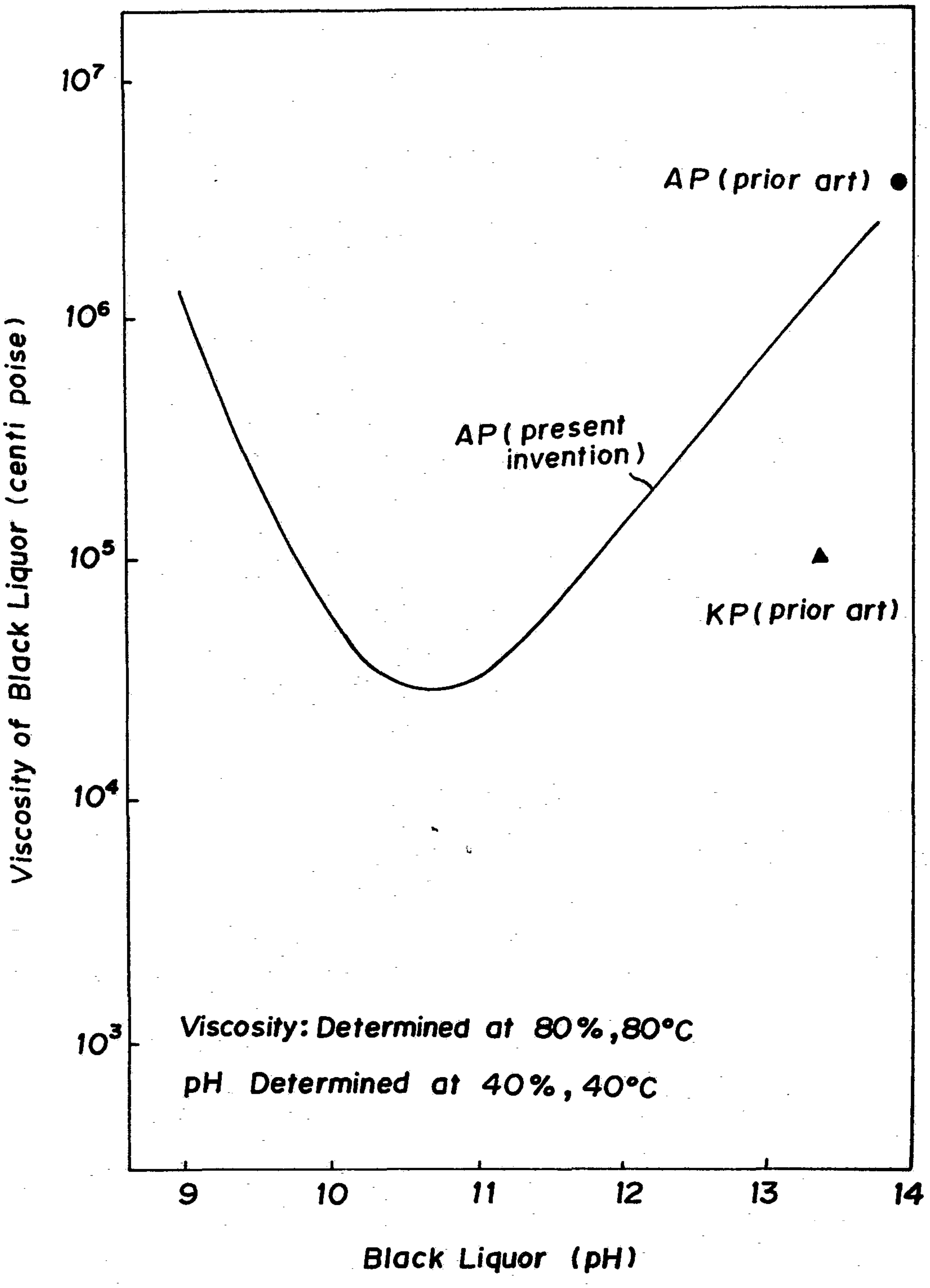

Average particle diameter (μm)
15
10
5
0
9
10
11
12
13
14
pH of Black Liquor
KP (present invention)
Concentration : 40 %
Temperature : 80 %

FIG. 3



Viscosity of Black Liquor (centi poise)
10^7
10^6
10^5
10^4
10^3
AP (prior art) ●
AP (present invention)
▲
KP (prior art)
Viscosity: Determined at 80%, 80°C
pH Determined at 40%, 40°C
9
10
11
12
13
14
Black Liquor (pH)

F I G. 4

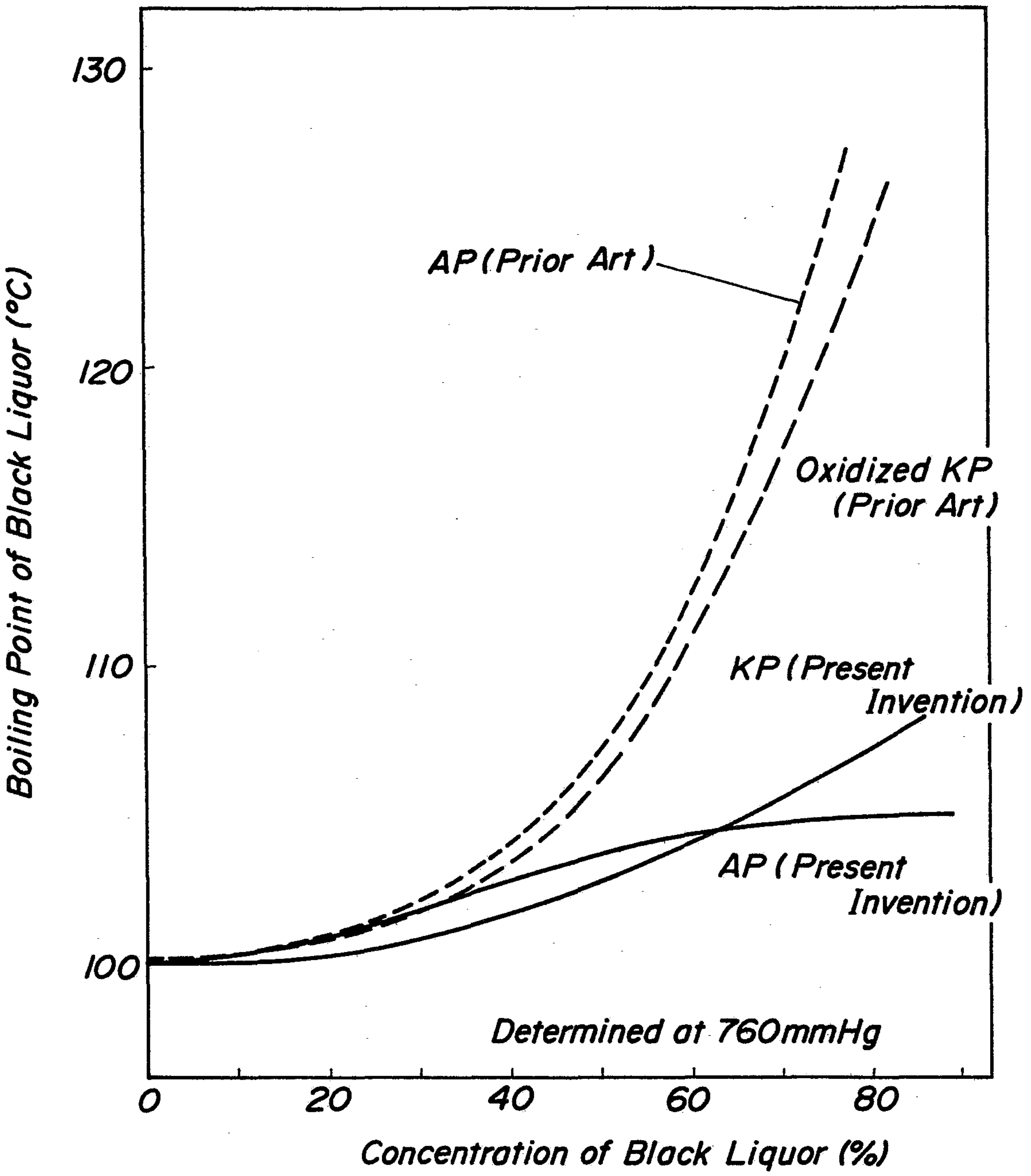

130
120
110
100
Boiling Point of Black Liquor (°C)
AP (Prior Art)
Oxidized KP (Prior Art)
KP (Present Invention)
AP (Present Invention)
Determined at 760mmHg
0
20
40
60
80
Concentration of Black Liquor (%)

FIG. 5

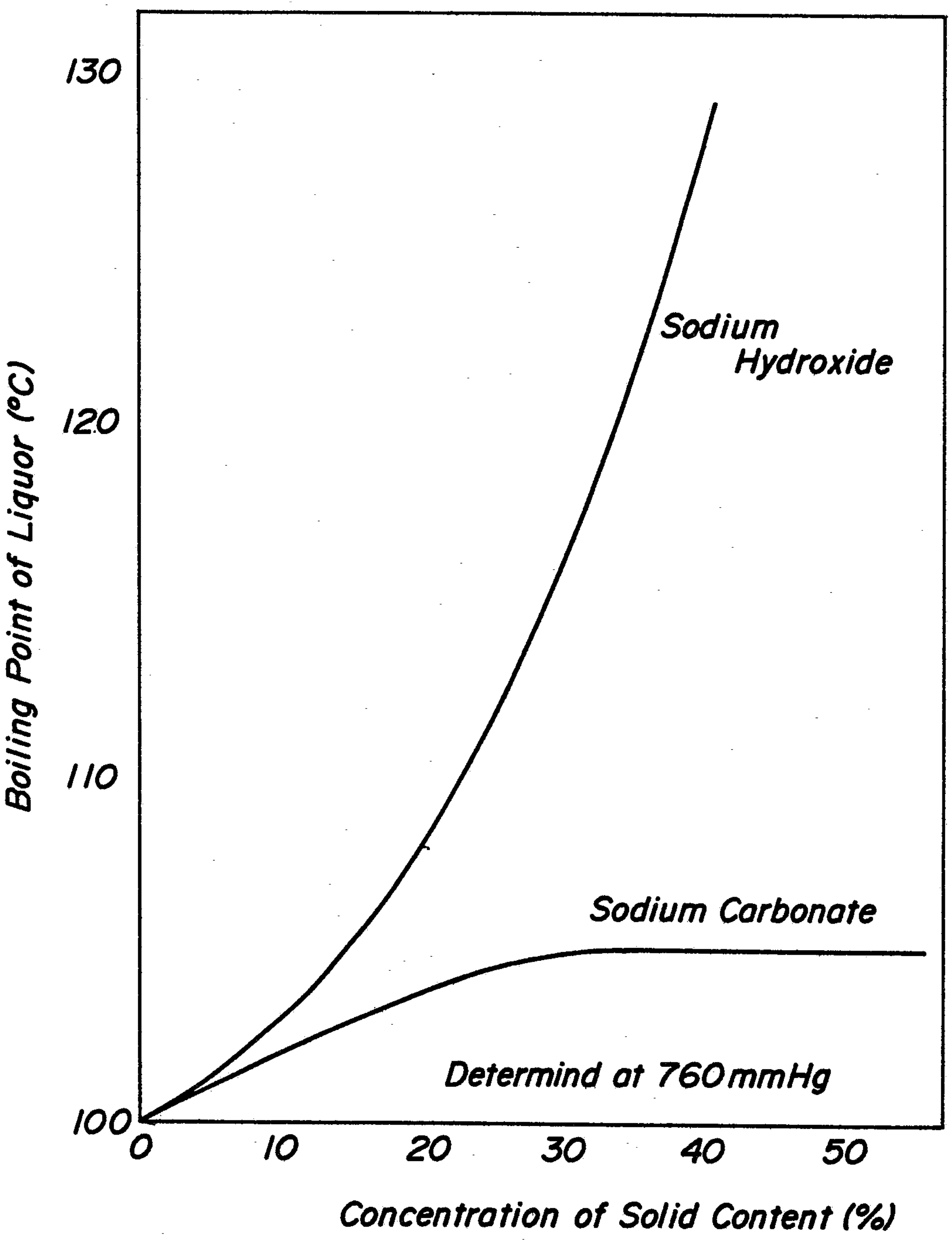

130
120
110
100
Boiling Point of Liquor (°C)
0
10
20
30
40
50
Concentration of Solid Content (%)
Sodium Hydroxide
Sodium Carbonate
Determind at 760mmHg

FIG. 6

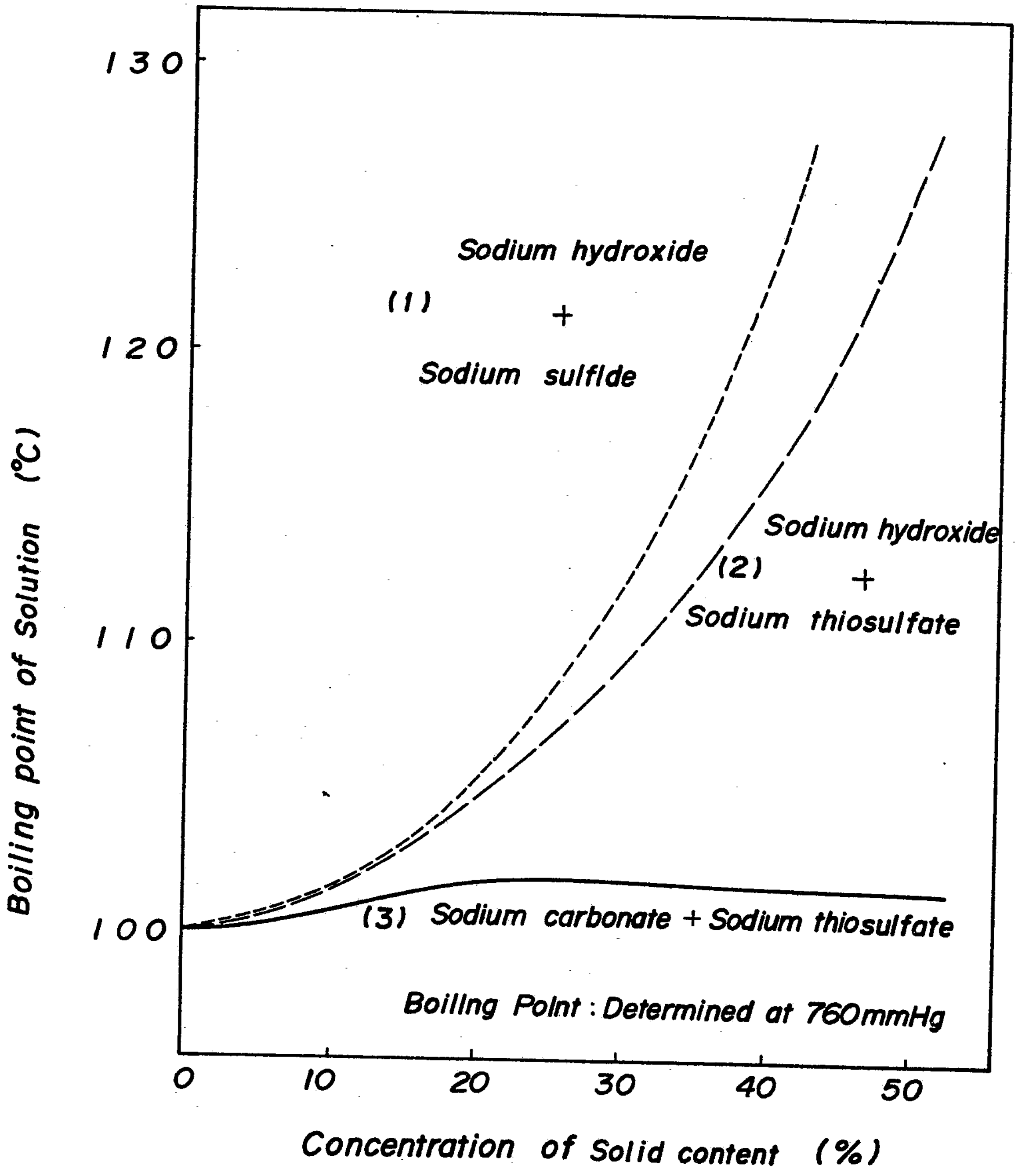

130
120
110
100
Boiling point of Solution (°C)
Sodium hydroxide
(1) +
Sodium sulfide
Sodium hydroxide
(2) +
Sodium thiosulfate
(3) Sodium carbonate + Sodium thiosulfate
Boiling Point : Determined at 760mmHg
0
10
20
30
40
50
Concentration of Solid content (%)

FIG. 7

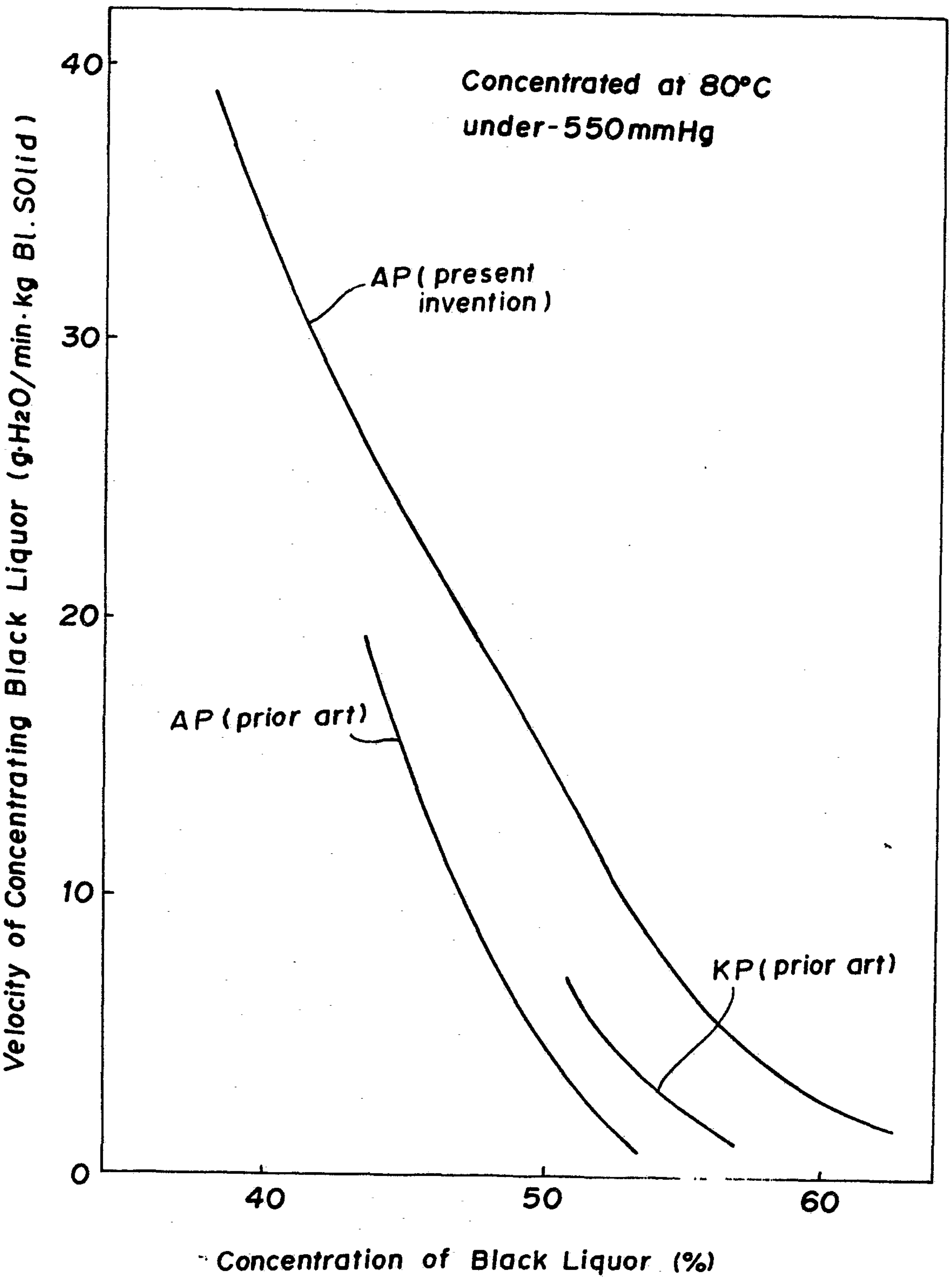

Concentrated at 80°C
under-550mmHg
AP (present invention)
AP (prior art)
KP (prior art)
Velocity of Concentrating Black Liquor (g·H2O/min·kg Bl. Solid)
0
10
20
30
40
40
50
60
Concentration of Black Liquor (%)

FIG. 8

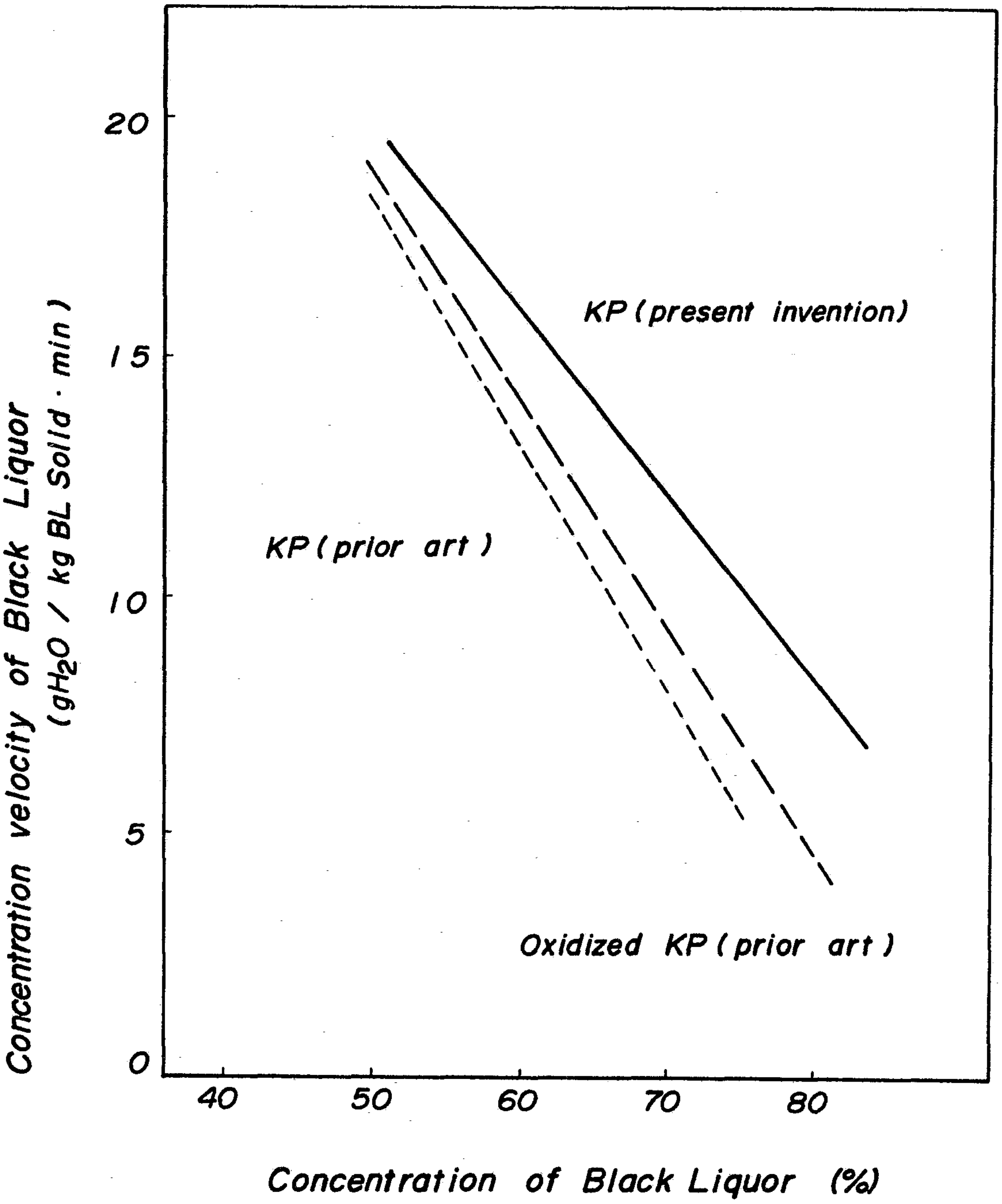

Concentration velocity of Black Liquor
(gH2O / kg BL Solid · min)
20
15
10
5
0
40
50
60
70
80
Concentration of Black Liquor (%)
KP (present invention)
KP (prior art)
Oxidized KP (prior art)

FIG. 9

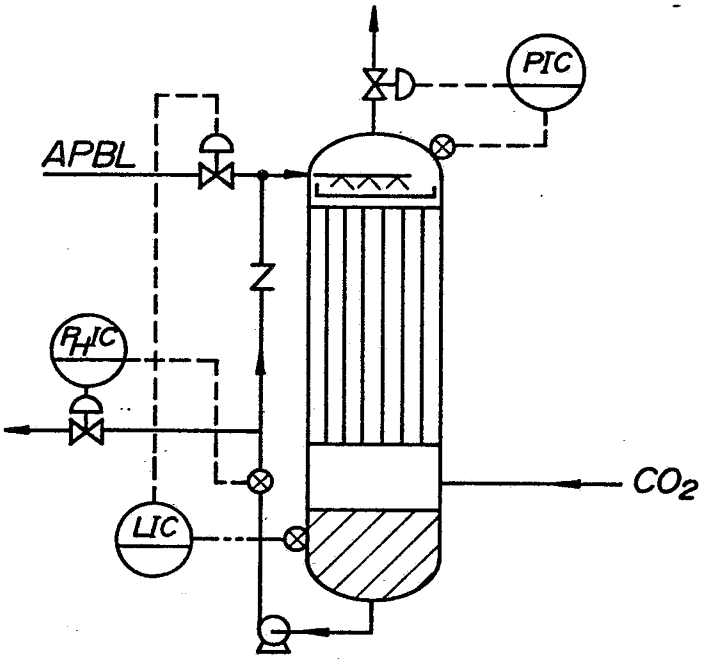


FIG. 10

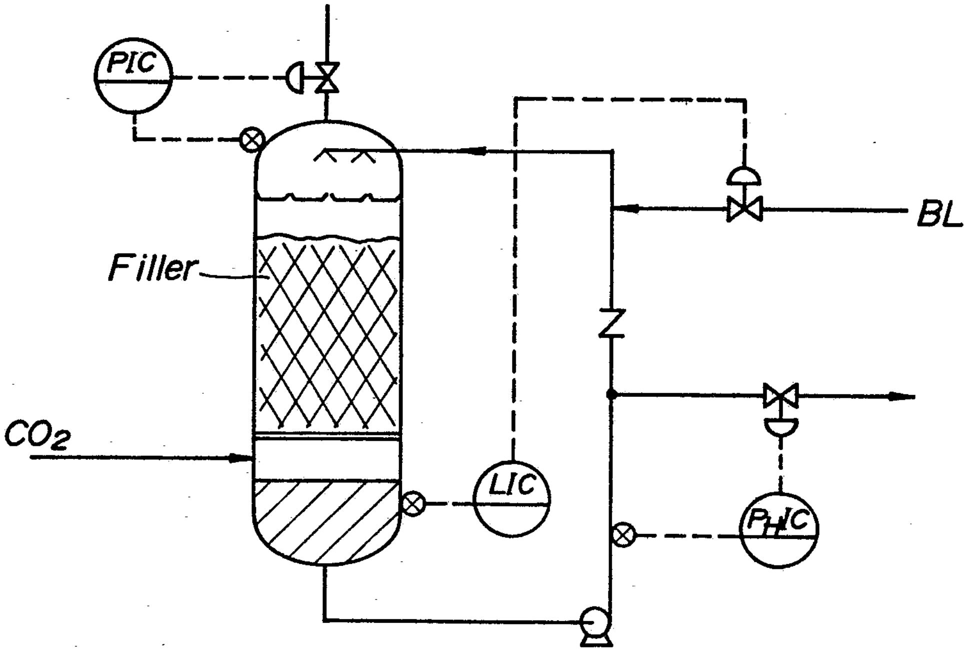


FIG. 11

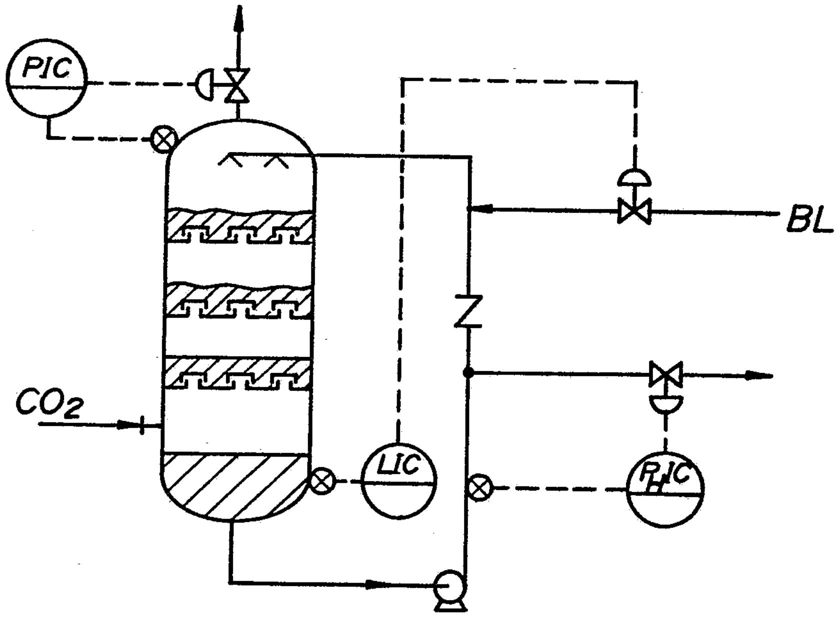


FIG. 12

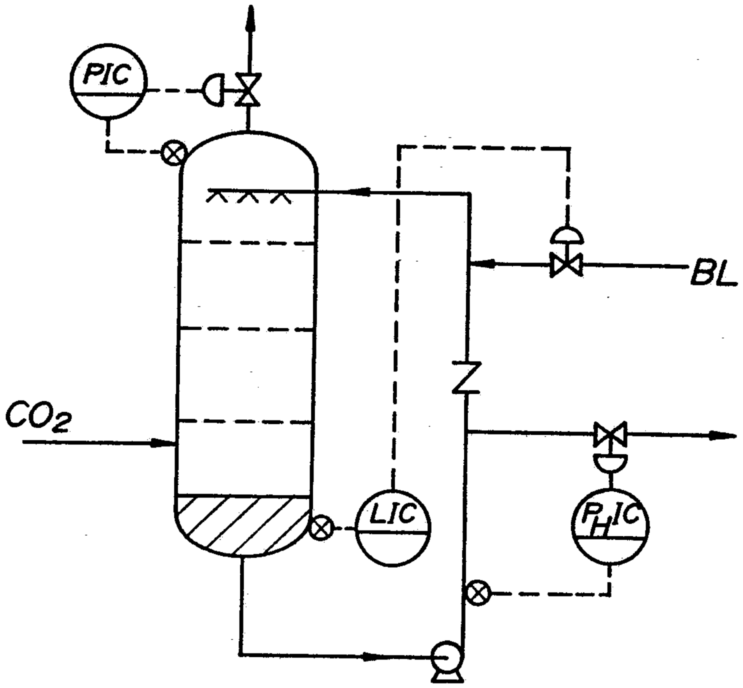


FIG. 13

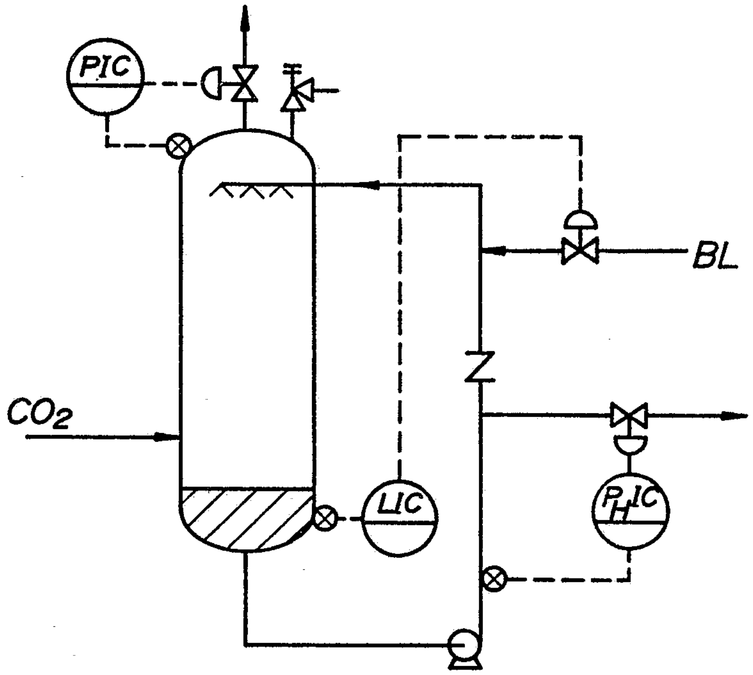

PIC
BL
CO2
LIC
PHIC

FIG. 14

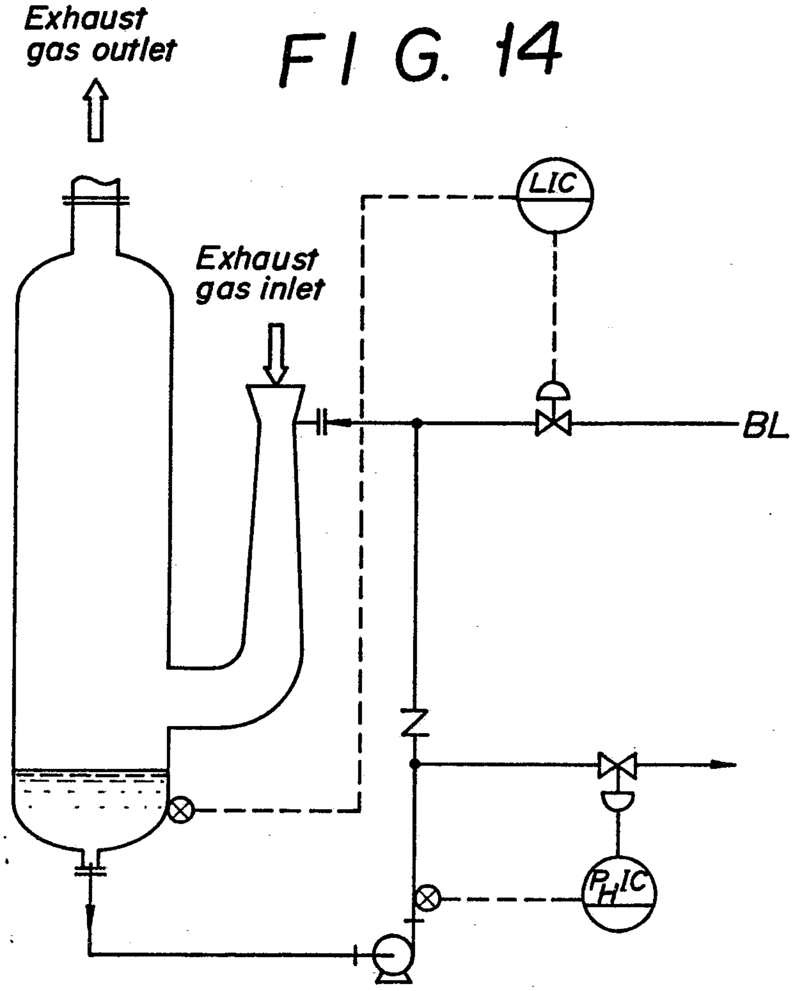

Exhaust gas outlet
Exhaust gas inlet
LIC
BL
PHIC

FIG. 15

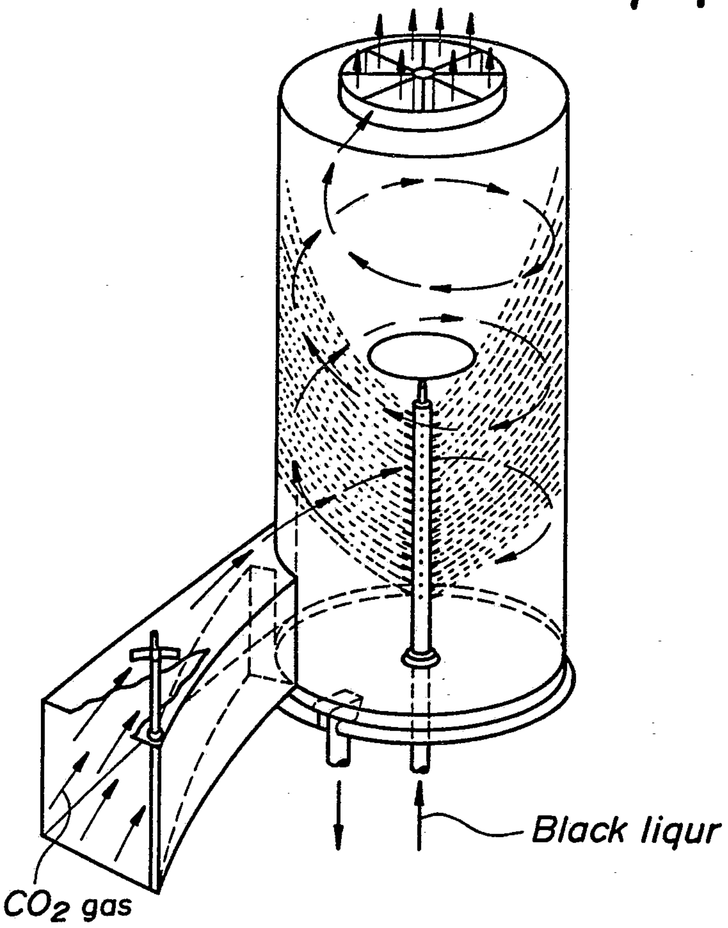


FIG. 16(a)

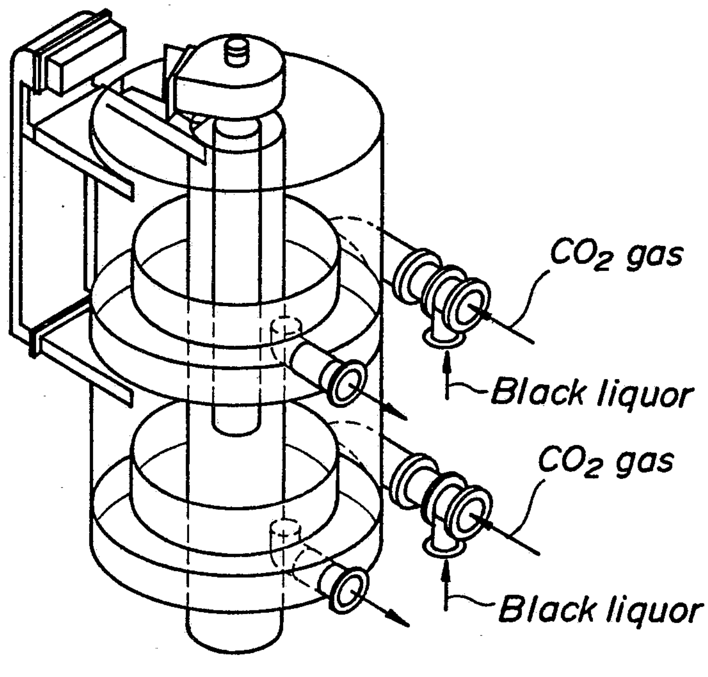


FIG. 16(b)

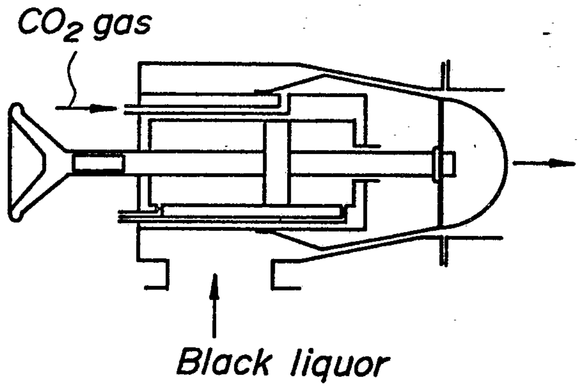


FIG. 17

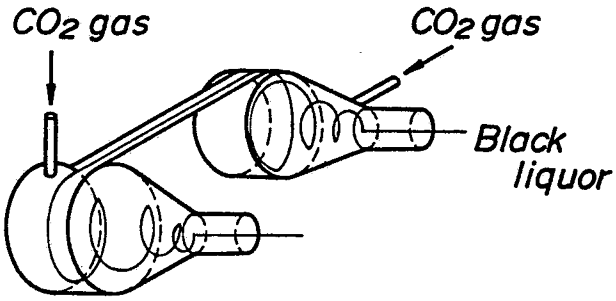


FIG. 18

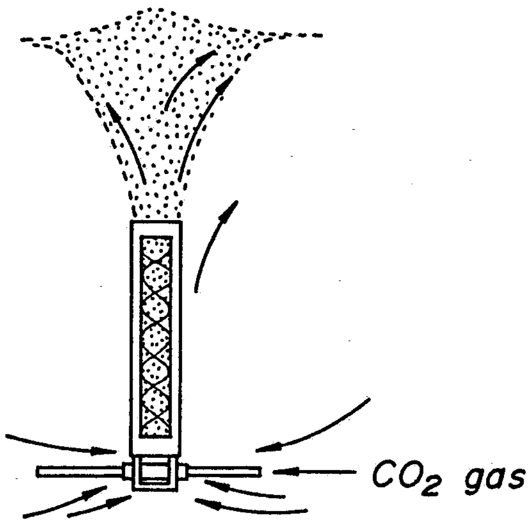


FIG. 19

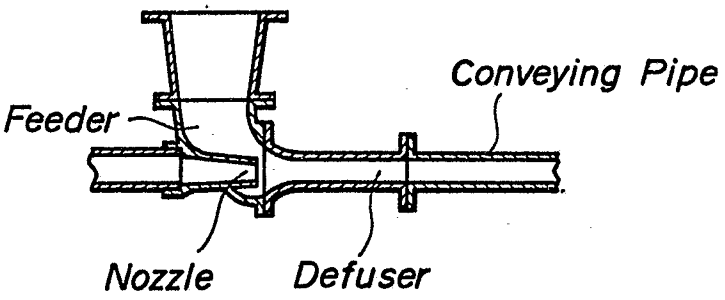


FIG. 20(a)

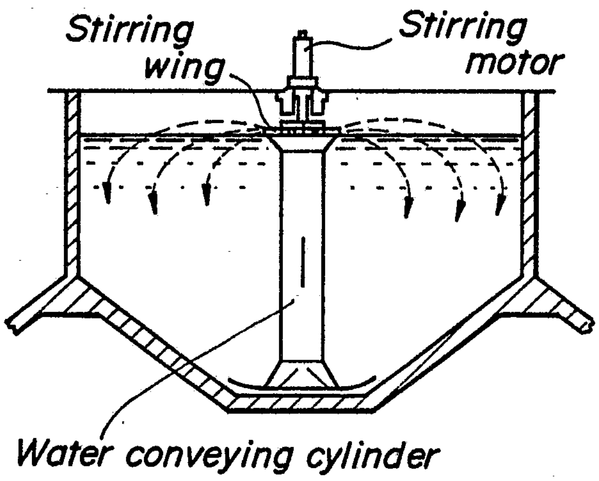


FIG. 20(b)

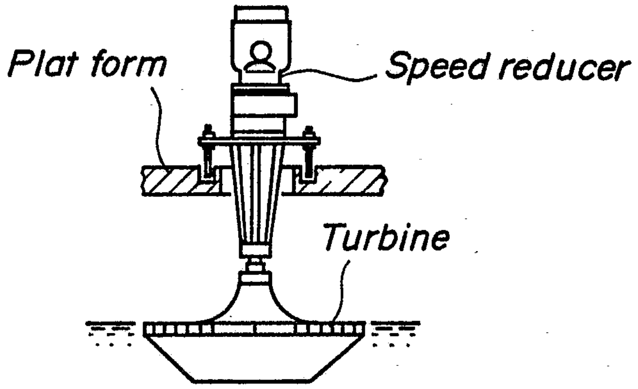


FIG. 21(a)

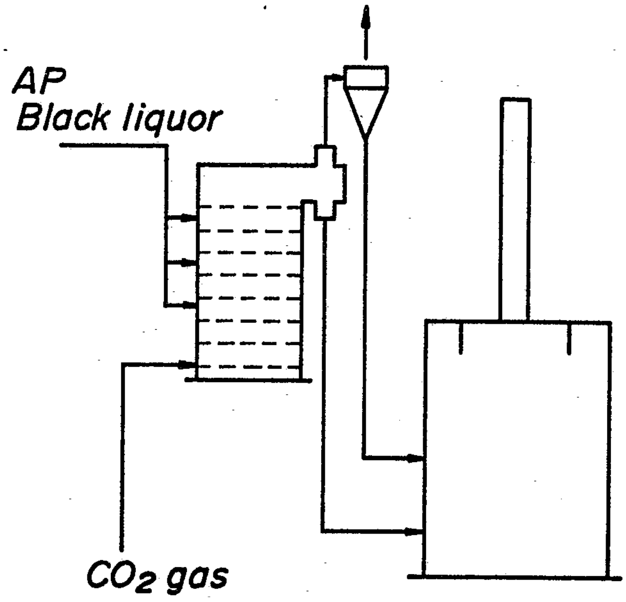


FIG. 21(b)

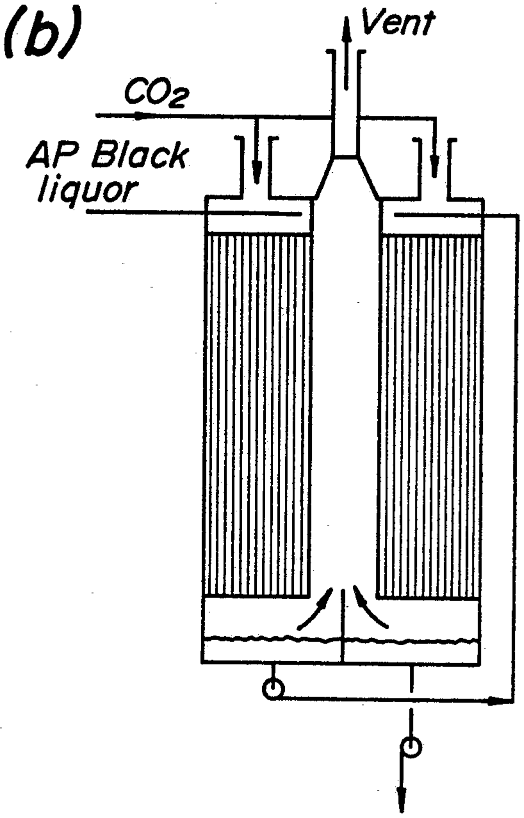


FIG. 22 (a)

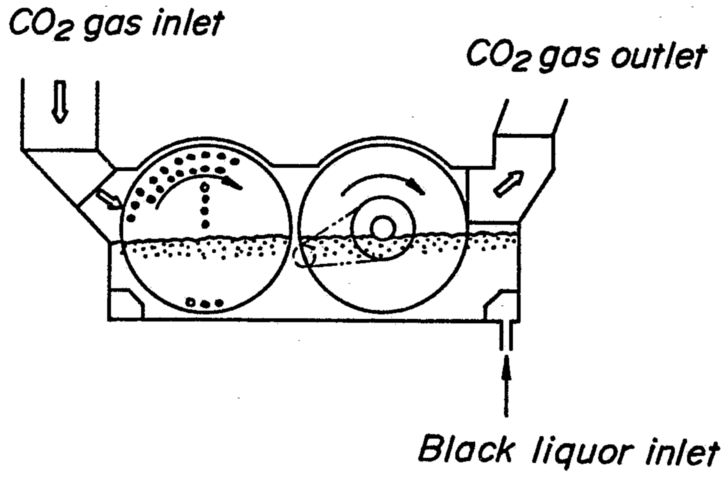


Fig. 22-(b)

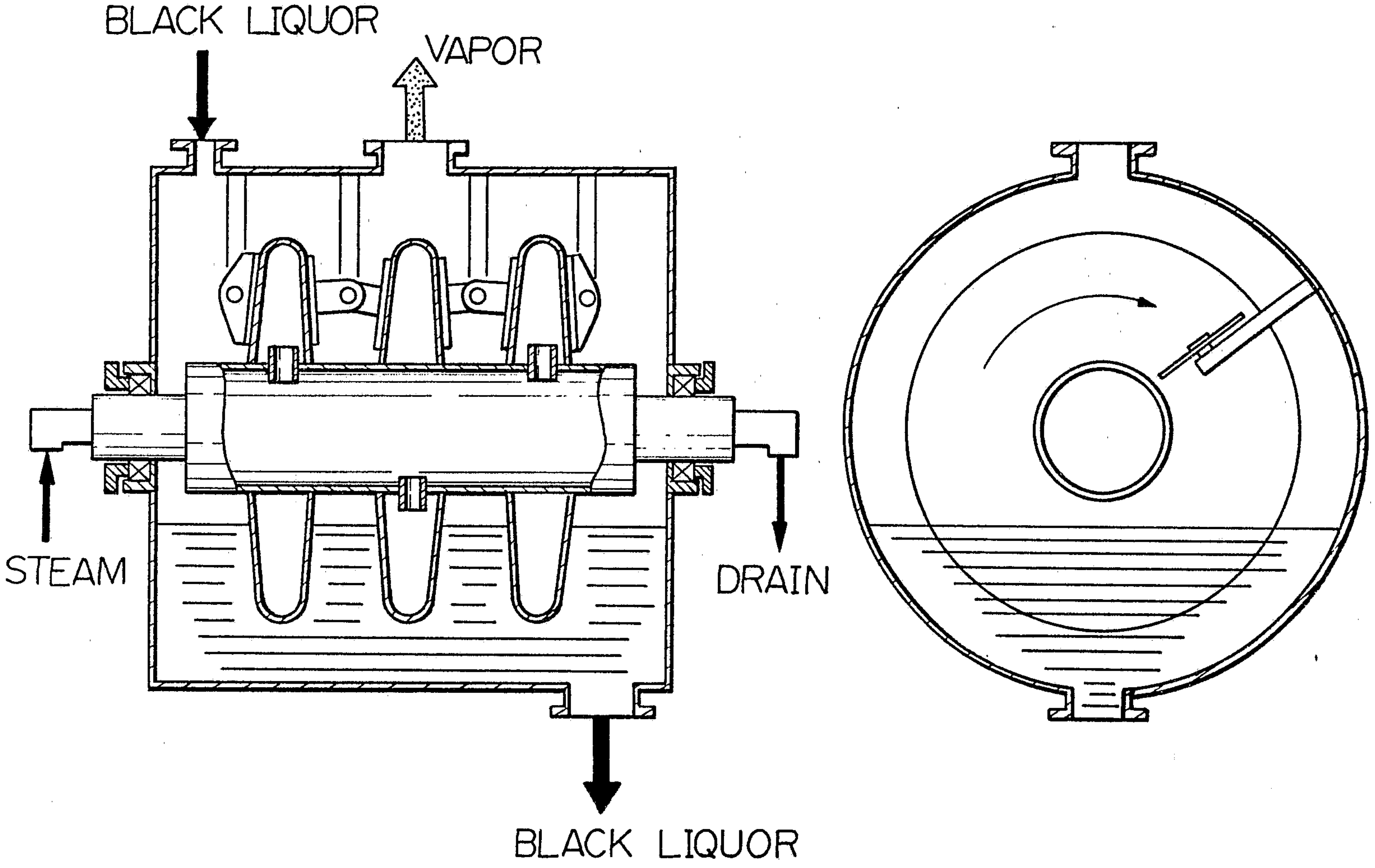


FIG. 23

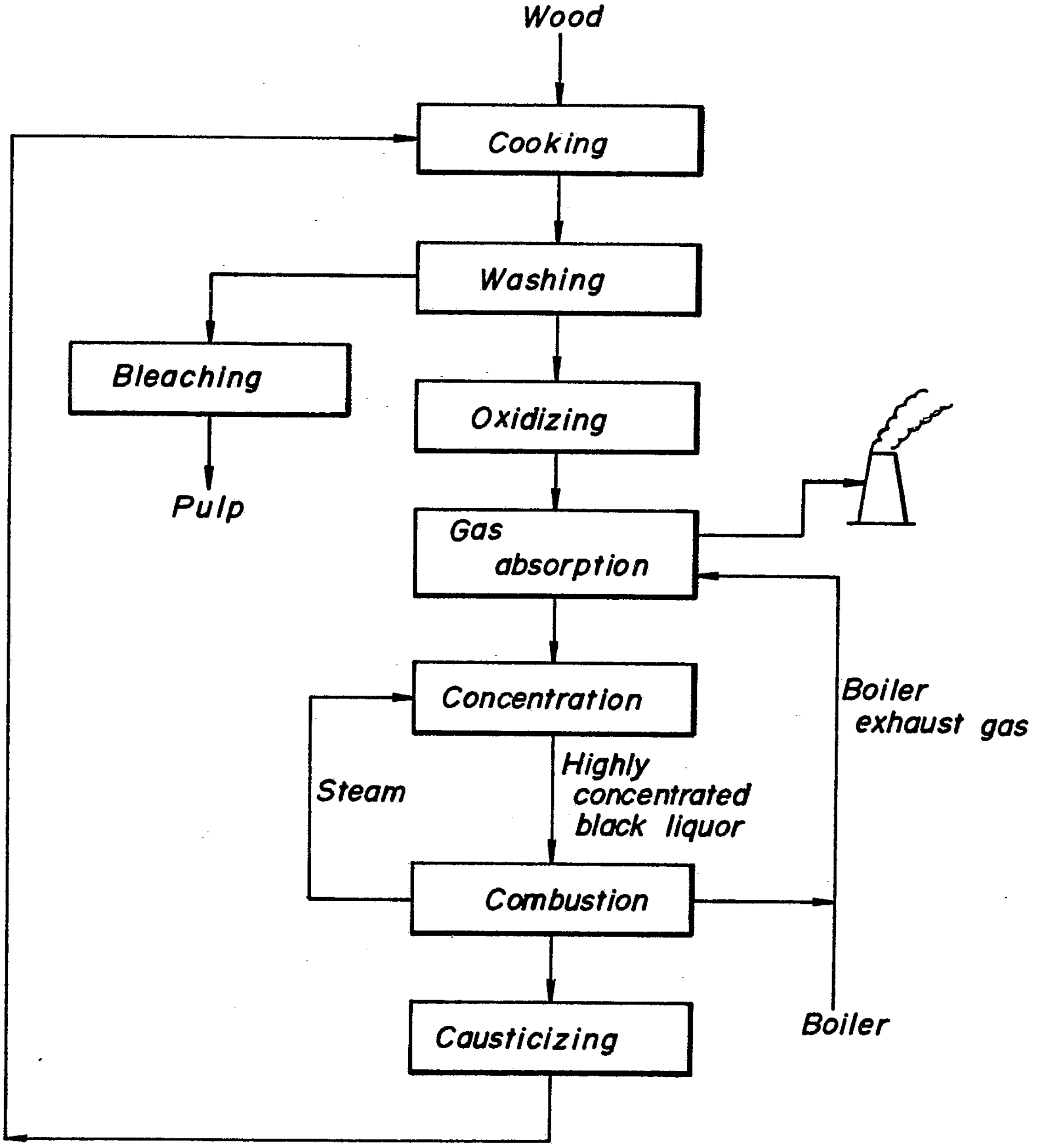

Wood
Cooking
Washing
Bleaching
Pulp
Oxidizing
Gas absorption
Concentration
Steam
Highly concentrated black liquor
Combustion
Causticizing
Boiler exhaust gas
Boiler

FIG. 24

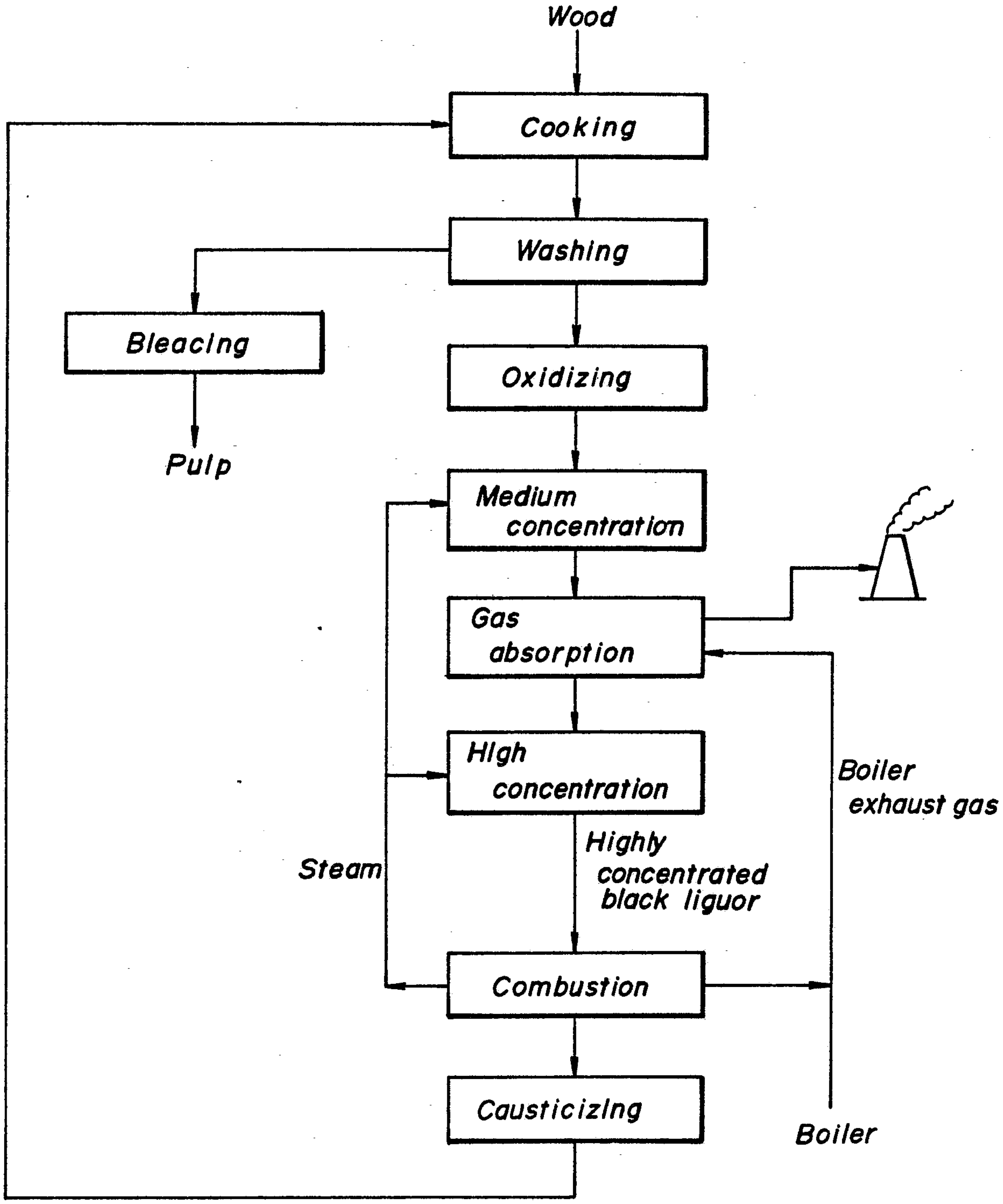
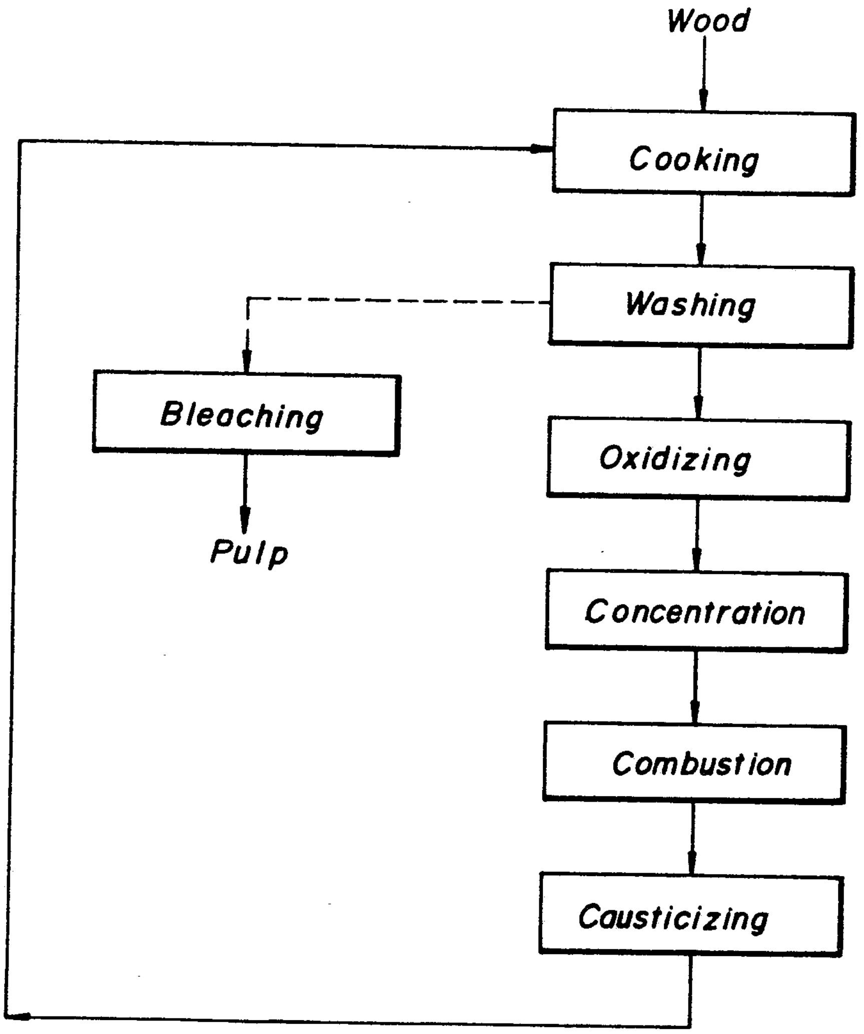

Wood
Cooking
Washing
Bleacing
Pulp
Oxidizing
Medium concentration
Gas absorption
High concentration
Highly concentrated black liguor
Steam
Combustion
Causticizing
Boiler exhaust gas
Boiler

FIG. 25


Wood
Cooking
Washing
Bleaching
Pulp
Oxidizing
Concentration
Combustion
Causticizing