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G. H. TOMLINSON ET AL

2,406,867

METHOD OF TREATING LIGNOCELLULOSIC MATERIAL

Filed Dec. 31, 1943

4 Sheets-Sheet 2

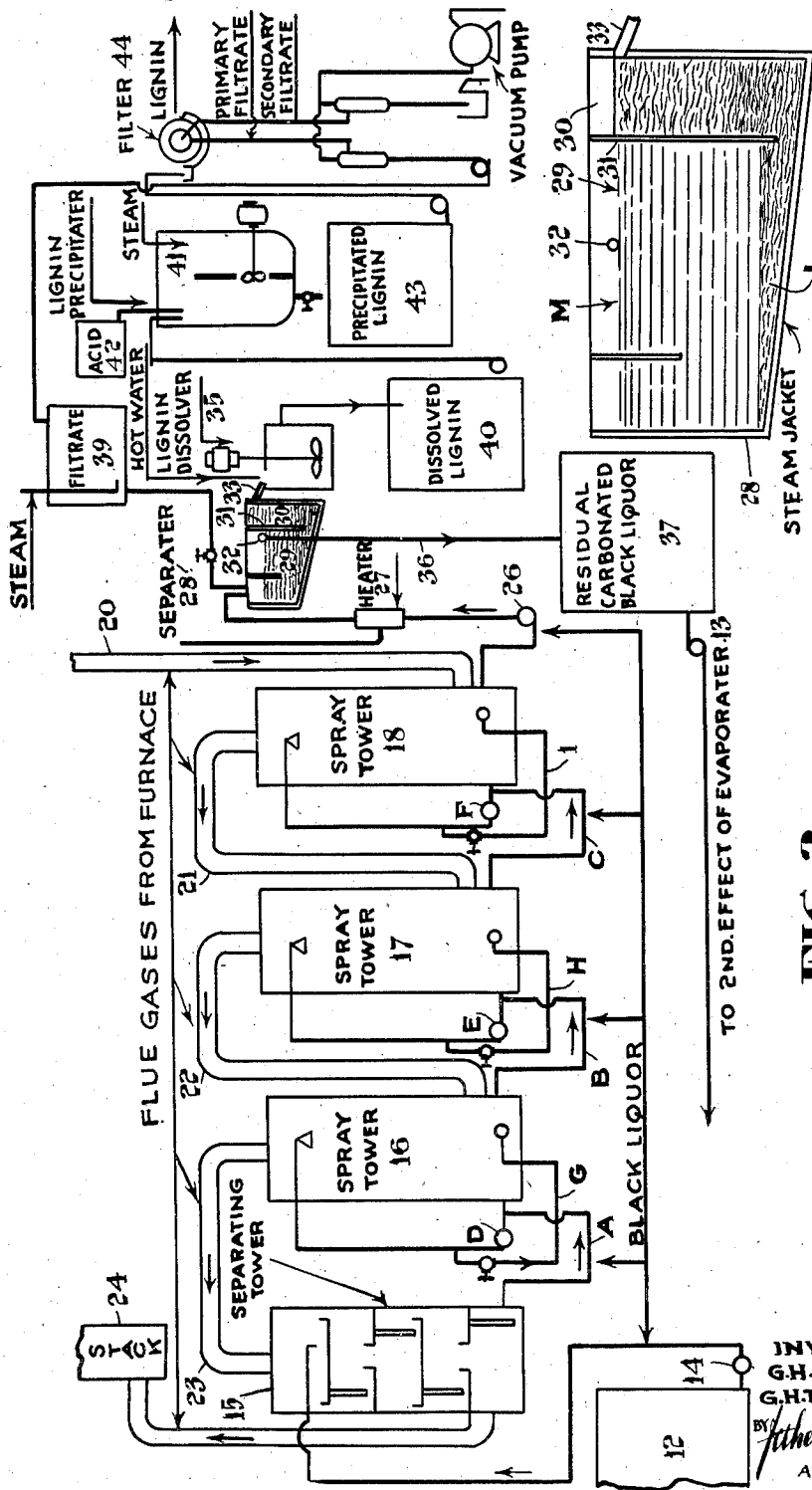


FIG. 2

FIG. 3

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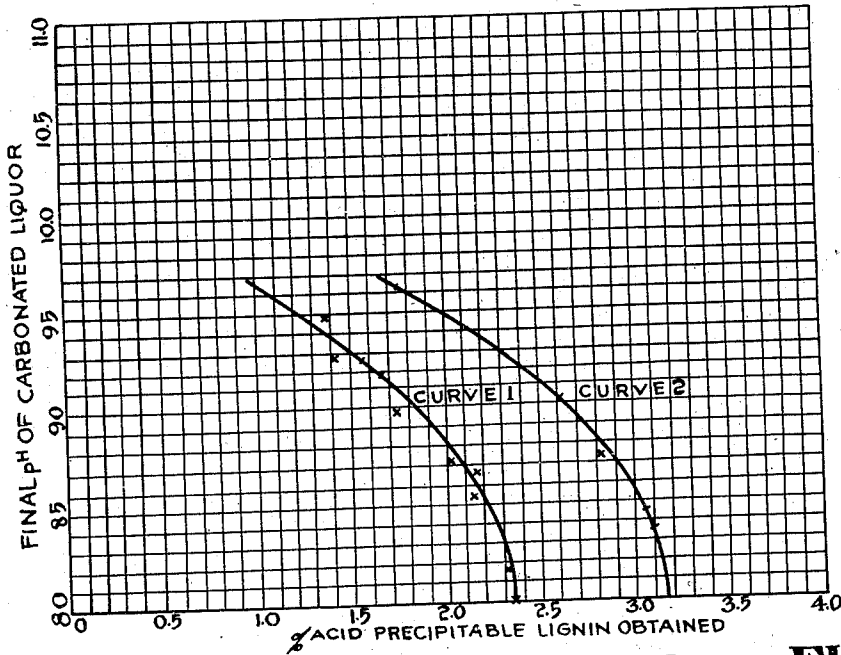


FIG. 5

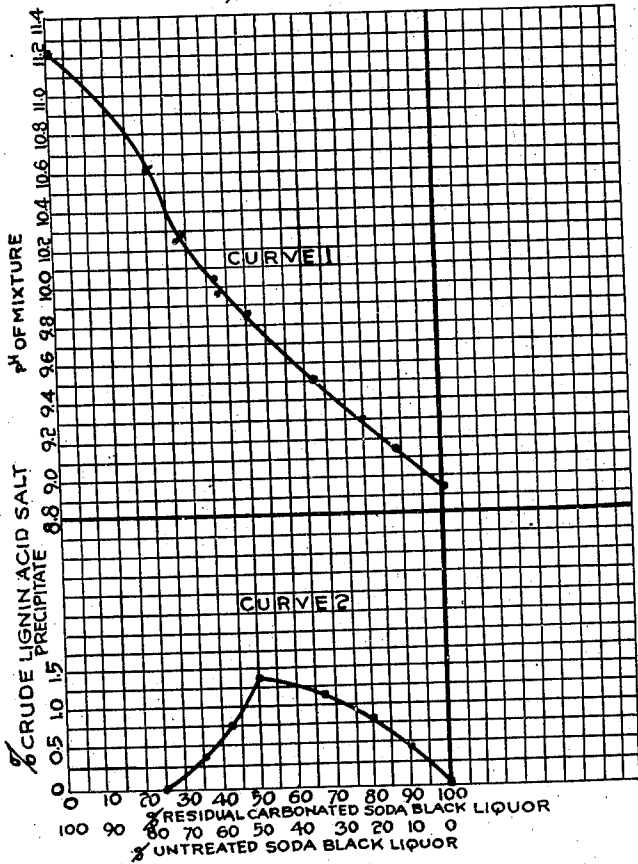


FIG. 4

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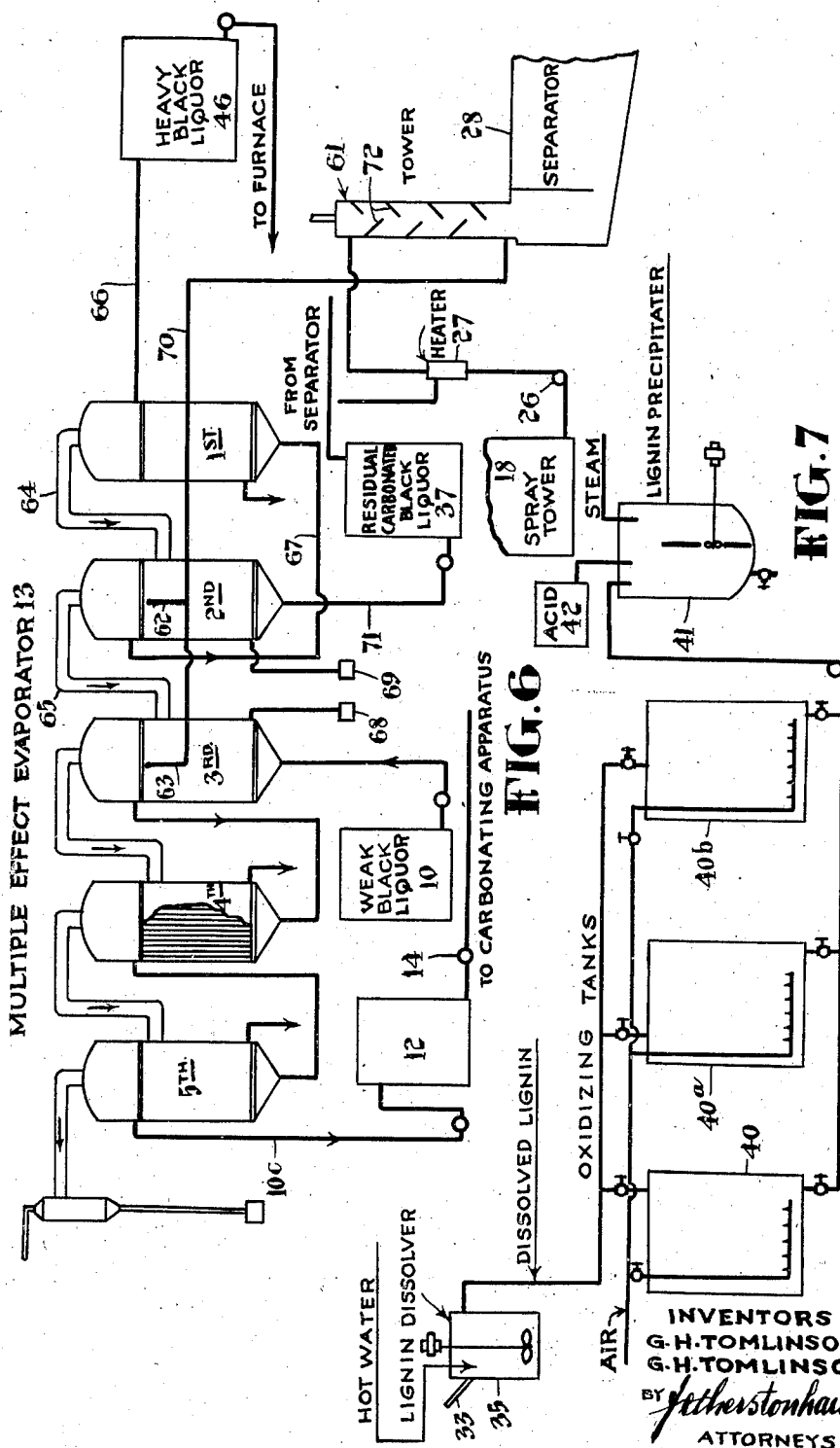


FIG. 7

FIG. 6

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# UNITED STATES PATENT OFFICE

2,406,867

## METHOD OF TREATING LIGNOCELLULOSIC MATERIAL

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18 Claims. (Cl. 260—124)

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The present invention relates in general to improvements in the manufacture of pulp by the digestion of cellulose fibrous material in an alkaline solution, such, for example, as by the sulfate and the soda processes and more particularly to an improved cyclic system for recovering chemical products and heat from the residual pulp liquor in a process of this character.

The general object of our invention is the provision of an improved cyclic process of treating the residual pulp liquor in a system of the character described to recover the sodium salts in a form permitting their economic reuse in the pulping process, heat in economic quantities, and also isolating and recovering new types of lignin products, including an essentially non-oxidized type.

The various features and novelty which characterize our invention are pointed out with particularity in the claims annexed to and forming a part of this specification. For a better understanding of the invention, its operating advantages and the specific objects attained by its use, reference should be made to the accompanying drawings and descriptive matter, in which we have illustrated and described a preferred embodiment of our invention.

Figures 1-2 collectively constitute a flow diagram of a cyclic alkaline pulp residual liquor recovery system embodying our invention.

Fig. 3 is an enlarged view of a separator included in said system.

Fig. 4 is a curve diagram illustrating the effect of adding residual carbonated black liquor to varying quantities of untreated residual black liquor.

Fig. 5 is a curve diagram illustrating the effect of the pH of carbonated black liquor on the yield of lignin extracted therefrom.

Fig. 6 is a flow diagram of a cyclic system for utilizing carbon dioxide in the carbonation of alkaline pulp residual liquor.

Fig. 7 is a flow diagram of a system for producing an oxidized lignin.

In conducting alkaline pulp processes, the cyclic processing of the residual so-called black liquor for the recovery of the sodium salts and its generation of heat is, of course, old. Such sys-

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tems normally consist of the following successive steps:

1. Separating the black liquor from the pulp;
2. Evaporating the black liquor in multiple effect evaporators;
3. Burning the concentrated liquor in a suitably designed furnace and utilizing the heat thus generated for the production of steam;
4. Drawing off from the furnace the sodium salts in a molten condition and dissolving these salts in water;
5. Causticizing the solution obtained in step 4 with lime and allowing the solids to settle;
6. Drawing off the clarified and causticized solution for use in another cooking cycle.

All of these steps are established on the most extensive commercial scale.

In addition to sodium salts, the black liquor contains a mixture of complex organic substances which are derived from the wood during its digestion and it is these substances which represent the fuel value of the concentrated liquor and which can be burned for the generation of steam. The isolation and identification of the organic components contained in the black liquor is attended with many difficulties and, consequently, little exact knowledge exists regarding the composition of these components. It is known, however, that when black liquor is acidified a ligneous material is precipitated from the solution and various processes have been devised for thus isolating this material from the various other substances which are present. The product obtained in this way, however, normally comes down in a gelatinous or gummy condition, making it extremely difficult to handle by usual methods. The process which we have discovered overcomes these handling difficulties, provides for the efficient recovery of the sodium salts and heat, and results in the production of new and valuable types of lignin product.

In our co-pending application Serial No. 455,148 filed Aug. 17, 1942, of which the present application represents a continuation in part, we disclosed a process for the separation of a lignin from black liquor by treating the black liquor with flue gas containing carbon dioxide, as for example, by circulating the black liquor through a spray tower in countercurrent contact

with the gases until the pH of the black liquor has been reduced to about 8.5. This reduction in alkalinity together with the salting-out effect of the inorganic contents of the liquor, results in the separation of a portion of the lignins contained therein. During this operation, the temperature of the black liquor is maintained below 45° C. in order to avoid premature coagulation and settling of the lignin. Following this, the black liquor is then heated to a temperature of about 90° C., which brings about the separation of the lignin in the form of a viscous liquid, which can be readily removed in a condition relatively uncontaminated with the aqueous solution in which it was originally dissolved. Following this separation the aqueous solution containing the sodium salts, together with the residual organic matter, can then be subjected to the recovery processing customarily employed in alkaline pulping.

It should be pointed out that by this method of treatment the temperature is purposely carried to such a point that the lignin becomes a viscous liquid i. e., melts rather than stopping at that point where it coagulates as a solid and may be filtered off. Such a coagulated precipitate would be somewhat gelatinous and bulky in nature and considerable quantities of the supernatant liquor would be occluded therein, thus necessitating considerable further washing and purification. It has been found that by carrying out the separation after the lignin material has been formed into the liquid state where it is in melted condition, the interface between lignin and liquor is reduced to a minimum, and the lignin carries only such relatively small amounts of water and other materials as may be soluble therein when in equilibrium with the liquor. If it be desired to further reduce the quantity of the impurities contained by virtue of this equilibrium, this may be accomplished by agitating the separated lignin with an amount of hot water sufficiently small so that the bulk of the lignin will not dissolve therein (say one part water to two parts lignin), allowing the mixture to separate and separating the further purified lignin therefrom. The aqueous layer, which contains that portion of the lignin which redissolved as well as the impurities, may then be added back to a fresh portion of the heated carbonated black liquor, whereupon the dissolved lignin salts reprecipitate by virtue of the high concentration of sodium salts and is recovered with the main portion of the separable lignin contained therein. By this method the yield of lignin is maintained but its purity is enhanced, and this without significantly increasing the quantity of water which must be evaporated from the residual black liquor in the recovery system. It will also be seen that this method of liquid-liquid separation lends itself to simplified continuous operation since continuous decanting equipment can be used, avoiding the necessity of filter-pressing, such as would be required were the separation carried out on the bulky and gelatinous precipitate obtained at lower temperature. The lignin material obtained by this liquid separation from carbonated black liquor is readily dispersed in hot water.

As an explanation for the course of the reactions which occur when black liquor is acidified, it would appear that the lignin contains two types of acidic groups of differing degrees of acidity such, for example, as phenolic hydroxyl and carboxylic groups, the former being liberated from the sodium salt by carbon dioxide and the latter

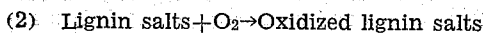
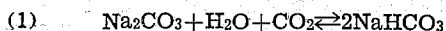
by mineral acid at somewhat lower pH. The lignin contained in the black liquor may therefore be present in the form of a di-sodium type lignin salt, this salt reacting with acid to yield either a sodium hydrogen type lignin salt, a di-hydrogen type lignin acid or a mixture, depending upon the degree of acidification. The product obtained on carbonation, which is insoluble in the carbonated black liquor but is readily dissolved in hot water, may be considered to be essentially the sodium hydrogen type lignin salt. The water insoluble product obtained when the solution of the above is further acidified with the mineral acid, may be considered to be the di-hydrogen type lignin acid. In the descriptions which follow in this specification we will use the term "lignin salt" when referring to the lignin product present in the original black liquor, the term "lignin acid salt" when referring to the lignin product isolated by carbonation, and the term "acid-precipitated lignin" when referring to the water insoluble lignin product obtained by precipitation with mineral acid.

The present invention, among other things, provides an improved continuous process for carrying out the operations previously described, as a part of the cyclic process normally employed for the recovery of chemicals and heat from the black liquor. Moreover, the carbonation reaction is carried out in such a manner that the total time in which the liquor and flue gas are in contact is so reduced that only a negligible quantity of the oxygen normally contained as an impurity in such gas can react with the lignin. The lignin acid salt thus separated is dissolved in water from which it is precipitated at elevated temperature with mineral acid to yield a purified water insoluble essentially non-oxidized acid-precipitated lignin which when filtered and dried yields a powder.

We have found that non-oxidized acid-precipitated lignin is characterized by a lower fusion point than an oxidized or partially oxidized acid-precipitated lignin when the latter is obtained from the same liquor by slower methods of flue gas carbonation. We have also found that the non-oxidized and oxidized acid-precipitated lignins can be distinguished by their behaviour when precipitated with acid at approximately 80° C. from an aqueous solution of the lignin acid salt. If precipitated cold both give a gelatinous type product which is extremely difficult to filter and which, on drying, shrinks to give a dense resinous product which must be pulverized or ground to yield a powder. If precipitated at 80° C. the non-oxidized acid-precipitated lignin filters readily and dries, with little shrinkage, to give a product showing little adhesion of one particle to the next, thus yielding a powder, without the necessity for grinding. The behaviour of the oxidized acid-precipitated lignin at 80° C. is similar to the behaviour of that obtained at low temperatures, and depending on the degree of oxidation, it is necessary to heat to considerably higher temperature, say 95° C., to obtain a product showing similar behaviour to that obtained with the non-oxidized acid-precipitated lignin at 80° C. If strongly oxidized, it may still show the gelatinous properties described above, even when heated to the boiling point of the mixture.

Having discovered that the lignin salts present in the black liquor react with oxygen and that under certain conditions of flue gas carbonation this secondary reaction of the lignin salts with the small amount of oxygen contained as an im-

purity in the gas will result in an oxidized product having physical characteristics markedly different from those of the unoxidized acid-precipitated lignin, we now find that this oxidation reaction can be controlled and to all practical purposes be eliminated. This may be done by carrying out the carbonation reaction under conditions whereby at a given time the ratio of the liquor surface, contacting the gas, to liquor volume is great, and new liquor surfaces are repeatedly formed. These conditions can be satisfactorily met by carrying out the reaction in a spray tower system, utilizing efficient spray nozzles and a high rate of recirculation. This can be explained by a study of the reactions and physical conditions involved. The reaction of carbon dioxide with sodium carbonate (which in turn controls the precipitation of the lignin acid salt) can be represented by reaction 1 and that of oxygen with lignin salts by reaction 2:



Reaction 1, where the carbon dioxide reacts with the ionized inorganic sodium carbonate, is relatively rapid, while reaction 2, where the oxygen reacts with the organic lignin salts, is relatively slow. However, in a heterogeneous two-phase reaction between a gas and liquid the rate of the chemical reaction is not necessarily the controlling factor, and in the case of flue gas carbonation, diffusion rates are believed to normally control the overall absorption rate. Thus as carbon dioxide is absorbed by the solution at the liquid interface it is rapidly depleted by reaction according to reaction 1 and will not penetrate as such to any appreciable distance into the body of the fluid. After the initial relatively rapid interface reaction takes place the absorption becomes dependent on slow diffusional changes such as intermigration of carbonate towards the surface and bicarbonate into the body of the fluid. However, if the liquor entering into reaction is dispersed in small droplets, the ratio of interface area to liquor volume is great, this condition resulting in a rapid reaction of carbon dioxide, and by recirculating the liquor with the formation of new surfaces the absorption time for carbonating a given volume of liquor to given pH can be reduced from a period requiring many hours to a matter of a few minutes.

With the oxidation reaction the situation is quite different. Reaction 2 is relatively slow and therefore the oxygen is able to diffuse through the body of liquid tending to reach an equilibrium condition within the liquid dependent only on the temperature of the liquid and on the oxygen partial pressure in the gas. Thus the chemical oxidation will proceed not only at the interface but also for a considerable distance therefrom. If the primary carbon dioxide absorption is carried out by bubbling the gas through the liquid, or by spraying the liquid in large drops through the gas at low rate of recirculation in relation to the volume of liquor being handled, the carbonation, which in this case depends largely on diffusion, is slow, and an appreciable quantity of oxygen in the flue gas will simultaneously diffuse into the liquor where it will react with the lignin salts. However, if the carbon dioxide absorption is carried out rapidly, as a result of large surface area, by the method already described, no equivalent increase in the rate of oxidation can take place, and in fact the lignin acid salt obtained by this method shows properties similar to those of the

lignin acid salt obtained by carbonation with pure carbon dioxide.

Although rapid carbonation could also be obtained in absorption equipment of the packed tower type, this is considered less suitable for the present purpose since the relatively slow liquor velocities over the packing surfaces are not always sufficient to prevent the precipitating lignin acid salt from settling and clogging the tower. If the alternative method of carbonation is used in which the flue gas is bubbled through the liquor, rapid carbonation requires a large volume of gas relative to the volume of the liquor at given time, the gas being dispersed as fine bubbles and these conditions, where the liquor forms the continuous film, result in a foam which is difficult, if not impossible to contain. For these reasons spray tower carbonation is at present considered the most suitable method.

If for any purpose, as for example, the production of an acid-precipitated lignin of higher melting point, an oxidized or partially oxidized acid-precipitated lignin should be desired, we have found that in place of oxidizing the lignin salts simultaneously with the carbonation, this can be effected as a separate step and under conditions more favourable for controlling the degree of oxidation. This can be accomplished by oxidizing a concentrated aqueous solution of the lignin acid salt, as for example by bubbling air through the solution.

An important feature of the present invention lies in the fact that it also provides for the continuous recovery of the inorganic sodium salts and heat values in the liquor. In operating a system for the recovery of lignin, we have found that if only a portion of the black liquor is carbonated for the separation of the lignin acid salt, difficulties arise when, following separation, the residual portion is mixed with liquor which has not been carbonated. In such a case the residual carbonated liquor, which may have a pH ranging between pH 7.8 and pH 9.8, when added to the liquor which has not been carbonated, results in a mixture having a pH lower than that of the uncarbonated liquor, this in turn resulting in a further precipitation of lignin acid salt. The extent of this secondary and undesirable precipitation will, of course, depend not only on the concentration of the liquor used but upon the pH of the carbonated liquor and also upon the ratio of the carbonated liquor to that which has not been carbonated. By way of illustration of the effect of such addition of a residual carbonated liquor to varying quantities of the original untreated black liquor, reference is made to Fig. 4. The black liquor (pH 11.22), which was obtained by the soda process from aspen wood, had been carbonated to pH 8.93, and following the separation of the lignin acid salt, it had a pH of 8.96 and a s. g. of 1.135 (21.6% total solids). In Fig. 4, curve 1 shows the pH obtained with varying ratios of the two liquors, while curve 2 shows the quantity (moisture-free basis) of crude lignin acid salt thrown down from the uncarbonated liquor as a result of this reduction in pH. It can be seen that in the case illustrated any quantity of residual carbonated black liquor in excess of 25% will give a pH of less than 10.6, thus causing undesirable precipitation when the two liquors are mixed. It will be understood that were the initial carbonation carried further, to say pH 8.0, the pH at any given ratio of the mixed liquors would be lower and a greater quantity of lignin acid salt would thus precipitate out. Even

a comparatively small amount of lignin acid salt precipitated under these conditions may clog pipelines and also seriously impair evaporator efficiency because of its tendency to collect on the heating surfaces. Consequently, any system which is dependent upon the batch processing of a portion of the black liquor and subsequent mixing of this liquor with liquor which has not been carbonated, for the purpose of recovering the inorganic sodium salts and heat from the residual carbonated liquor, is restricted in its application to certain limited ratios.

In order to avoid this undesirable secondary precipitation, our process provides for the carbonation of the entire quantity of black liquor produced, by means of a continuous process, so designed that the amount of lignin acid salt isolated can be selectively controlled. The amount of lignin acid salt precipitated from the black liquor increases as the pH is lowered. The equilibrium pH value that may be attained in the liquor under any particular circumstance is fixed by a relationship which depends on the normality of the sodium in the form of caustic soda and alkaline salts, the concentration of carbon dioxide in the carbonating atmosphere and the reaction temperature, but in practice it is usually not economically practical to carry the carbonation to this stage. The final pH that will be reached in a given absorption system will depend on the surface area of liquor exposed to the carbonating gas, the time of treatment, and of course on the reaction temperature and the carbon dioxide content of the flue gas. In a spray tower system the ratio of liquor surface area to liquor volume is great, and if the volume of liquor in flight at given time be increased by increasing the rate of recirculation, the pH will be lowered and vice versa. By thus adjusting the pH of the liquor the quantity of precipitated lignin acid salt can be controlled.

By way of illustration of the effect of the pH of the carbonated liquor on the yield of lignin product obtained, reference is made to Fig. 5. Black liquor obtained by the soda process from aspen wood was carbonated at 70° C. to definite pH, the resultant carbonated liquor heated to 85° C., and the viscous liquid layer of lignin acid salt thus obtained separated by decantation. The crude lignin acid salt was dissolved in hot water and precipitated with sulfuric acid at 95° C. by reducing the pH to 3.0. The moisture-free weight of acid-precipitated lignin obtained on filtration is expressed in Fig. 5 as a percentage of the weight of the initial black liquor, this value being plotted against carbonation pH. Curve 1, Fig. 5, shows this relationship for a black liquor of s. g. 1.102 (17.3% solids) as normally obtained from the pulp washers while curve 2 is for the same liquor after partial evaporation to s. g. 1.140 (23.5% solids). Thus, knowing the rate of production of black liquor of given s. g., the correct pH may be selected to obtain the desired quantity of lignin product. The pH of the carbonated liquor can then be readily adjusted by increasing or decreasing the amount of liquor recirculated in the carbonating towers.

It will be understood that carbonation can be effected with gases containing carbon dioxide regardless of the source. For carbonating the black liquor, however, we prefer to use flue gas, such for example, as that obtained from black liquor recovery furnaces, such gas normally containing about 12% to 17% carbon dioxide and 6% to 2% oxygen. When carbonating with

these gases it is impractical to lower the pH of the liquor essentially below the range of 9.0 to 8.8. If, however, a higher yield of lignin acid salt is desired than can be thus obtained, we have found that the carbonation can be carried further by utilizing a carbon dioxide free of non-condensable gases liberated from the liquor in a subsequent stage of our cyclic process. When the residual carbonated black liquor, that is, the liquor obtained immediately following the separation of the lignin acid salt, is evaporated, carbon dioxide originating from the sodium bicarbonate is disengaged with the steam. When employing multiple effect evaporation, this carbon dioxide must be purged from the heating chambers in which the carbon dioxide may otherwise accumulate, and the mixture of carbon dioxide and steam thus purged can be employed for further carbonating and heating the flue gas carbonated liquor passing to the lignin separator. By employing this feature it can be seen that a portion of the carbon dioxide required for carbonating the black liquor can be recycled to advantage either to obtain an additional yield of lignin acid salt or, if this latter is not required, to permit of a somewhat higher pH being carried in the primary flue gas carbonating stage.

In carbonating the liquor, we have now found that when the liquor is carbonated while in motion, as for example, in a spray tower such as will later be described at temperatures not exceeding about 75° C., the lignin acid salt is precipitated in finely divided form and, under these conditions has little, if any, tendency to settle or accumulate in the carbonating equipment. By operating in a higher temperature range, say, approximately 70° C., the carbonating reaction is accelerated and dilution of the residual black liquor resulting from condensation of the moisture contained in the flue gas is minimized. At slightly higher temperatures, say 80° C., the lignin acid salt begins to melt and may settle rapidly, forming a viscous liquid mass. In operating our system, we therefore maintain the temperature conditions during the carbonation below the temperature at which melting occurs and then, after removing the liquor from the carbonating system, quickly raise the temperature of the liquor to a temperature above 80° C., as for example 90° C., and then settle and separate the viscous liquid lignin acid salt from the residual black liquor. As a result of this procedure, it therefore becomes possible to provide a continuous separator from which liquid lignin acid salt is withdrawn at one point and residual black liquor is withdrawn at another.

The lignin acid salt which is isolated in this way and at this stage of the process is soluble in water and still contaminated with black liquor impurities. In addition to its use as described below, it may also be utilized in accordance with the process described in our co-pending application No. 455,148.

By subjecting this type of lignin material to a further process, it is transformed into a water-insoluble non-gelatinous type which, when filtered and dried, yields a purified acid precipitated lignin directly in powder form.

The black liquor impurities can be partially removed by subjecting the liquid lignin acid salt to a treatment with a small amount of hot water, as previously mentioned, and, if desired, such a step can be employed preceding the purification process now to be described. According to the present invention, the liquid lignin acid salt is dis-

solved in hot water either following or in the absence of a step involving its washing with water and the solution is made up preferably to a concentration of between 10% and 25% total solids, and a temperature of 80° C. or somewhat higher in order to maintain a suitably low viscosity. Acid, preferably sulfuric acid, is then added slowly, with agitation, in such an amount that the pH of the solution is adjusted to a pH of about 3, although for many purposes when treating a non-oxidized lignin a pH of about 5 may be used. By following such treatment, and maintaining a sufficiently low viscosity to give such thorough agitation as to allow an intimate dispersal of the reactants, the lignin is precipitated with a particle size of approximately 2 to 15 microns and the formation of larger particles or grit is avoided. Depending on the temperature employed during precipitation and degree of oxidation, it may be found desirable to raise the temperature of the final mixture to 95° or even higher, thus facilitating filtration of the lignin, although with non-oxidized lignin a maximum temperature of about 80° C. may be used. When this technique is followed, the filtered and washed acid-precipitated lignin can be dried to yield a powder.

Acid-precipitated lignin obtained by the described procedure can be added to a pulp furnish in any desired proportion, either in the form of a thick paste as obtained directly from the filter or after it has been dried to a powder, and we have found that such a mixture can then be made into a lignin-enriched and moldable paper by running the mixture over a standard paper machine. Alternatively the slurry containing the acid-precipitated lignin as it comes from the lignin precipitator can be mixed with pulp in the desired proportion and the mixture can then be washed by passing it over a rotary vacuum filter to provide a paper making furnish. We have found that almost perfect retention of the lignin in the paper can be obtained, providing a small percentage of a colloid, such for example as a solution of glue, and a small percentage of alum, both in the proportions of about one-half percent, are introduced into the stock prior to running the stock onto the paper machine wire. On adding the colloid and alum, flocculation occurs and the lignin apparently attaches itself to the fibres, this attraction being of such an order that the desired retention is effected. When making such a paper we preferably use an acid-precipitated lignin having a particle size within the general range indicated above. We have also found that an acid-precipitated lignin made in accordance with our invention and having such particle size will, when in a paste form, normally exhibit either thixotropic or dilatant properties, or sometimes a combination of both, depending on the water content.

By conducting the acid precipitation at a relatively high lignin concentration, the subsequent continuous filtering of the material on a rotary vacuum filter is facilitated. The filtrate, containing sodium sulfate together with excess sulfuric acid, can also be utilized, adding it back to the carbonated black liquor immediately prior to separation of the lignin acid salt. By following this procedure, the loss of inorganic sodium salts and such lignin as may be suspended in the filtrate is minimized. As a result of this procedure, the carbonated black liquor also undergoes a slight reduction of pH, resulting in a corresponding precipitation of additional lignin acid salt.

In our cyclic system, wood chips from chip

bin 1 and alkaline cooking liquor from cooking liquor storage tank 2 are supplied to digester 3 which is heated by means of steam. When the cooking operation is completed, the contents of the digester may be discharged into a blow tank 4 from which the gases are vented to condenser 6 and the pulp and the liquor may then be dropped into a suitable stock chest 5 and from there passed to a pulp washing system such as rotary pulp washers 7 and 8. Hot water is delivered to the pulp washer 8 as indicated and the filtrate from the washer 8 is delivered to pulp washer 7 to serve as washing liquor therein. The filtrate from the second washer 8 is also employed as indicated at 8a to ensure correct consistency of the pulp going to that washer. The filtrate of the first washer 7 is sent to a degassing tank 9 from which a portion is returned to the stock box of the first washer 7 and another portion to the stock chest 5 to increase the fluidity of the pulp and thus facilitate its delivery to the pulp washers. The residual liquor in the degassing tank 9 is passed to the weak black liquor storage tank 10. The pulp leaving pulp washer 8 and from which the black liquor has been substantially removed, then passes into a stock system, which may consist of stock tanks, knotters, riffles and screens and paper-making equipment, but with these operations we are not particularly concerned in connection with the present application.

From the weak black liquor storage tank 10 the liquor may be sent through line 10a directly to tank 12 and from thence through the liquor carbonating and lignin recovering equipment illustrated in Figure 2 before being evaporated in the conventional manner in evaporator 13 from which it would then pass to tank 46. In place of this, however, we may partially evaporate the liquor as a preliminary step, since by following this procedure the volume of the liquor to be handled in the processes for the isolation of lignin is reduced, thus making for a saving in power and steam, and also, the liquor has less tendency to foam at the higher concentration. Consequently, in place of sending the weak black liquor from the storage tank 10 directly to the tank 12, the liquor may be passed through the intermediate stages of a multiple effect evaporator, such as the five-stage evaporator 13. In this case, the liquor, normally having a temperature of about 60° to 70° C. as it comes from the washers, is introduced into the third evaporating effect via lines 10a and 10b. From the third effect it passes successively through the fourth and fifth effects, the fifth effect being the high vacuum unit, leaving the fifth effect at a temperature of about 50° C. and at a concentration of between 20% and 30% total solids. The liquor on leaving the fifth effect is then passed through line 10c to tank 12.

From tank 12 the liquor is pumped continuously by pump 14 to the top of separating tower 15 which may be constructed with trays over which the liquor cascades in its passage from the top to the bottom. From the bottom of tower 15 the liquor is transferred by means of overflow connection A to the bottom of spray tower 16 through which it is circulated by means of pump d. In like manner it is transferred successively to spray towers 17 and 18 by means of overflow connections B and C respectively, being circulated in the towers by means of pumps E and F respectively. The gas is admitted through duct 20 to tower 18 from which it passes to the other

towers in countercurrent relationship to the liquor as indicated at 21, 22 and 23. By providing excess capacity in the pumps D, E and F, provision is made at the towers 16, 17 and 18 for recirculating a substantially larger volume of liquor through the sprays than that entering tower 16 from tower 15. By-pass connections G, H and I, each provided with a suitable control valve, provide a means for controlling the quantity recirculated through the sprays. The flue gases leaving the top of tower 16 are passed into the top of tower 15, where they then impinge against the surface of the liquor contained in the trays while passing through this tower from top to bottom. By thus impinging the gases against the liquor surfaces, the loss of foam and black liquor spray particles which may be carried in the gases is minimized. After passing through tower 15, as described, the gases may then be passed to a stack 24.

The liquor in its passage through towers 15, 16, 17 and 18 is carbonated and the lignin acid salt is precipitated. Coagulation of the lignin acid salt into particles of a size to cause trouble through settling out or otherwise clogging the apparatus is avoided by maintaining the temperature at about 70° C.

The carbonated liquor is withdrawn continuously from tower 18 by means of pump 26 and passed through the heater 27, where its temperature is raised to a temperature above 80° C. and preferably between 85° and 100° C., to be then delivered into the continuous separator 28. Separator 28 may consist of a steam jacketed tank divided into two main compartments 29 and 30 by means of baffle 31, which extends from the top of the tank to within a short distance of the bottom in such a way that the two compartments 29 and 30 are completely separated one from the other in the upper zone of the tank but are in communication in the bottom zone. An overflow outlet 32 is provided in the upper zone of compartment 29, and a similar overflow outlet 33 is provided in the upper zone of compartment 30. Upon entering the separator 28 the precipitated lignin acid salt carried in the hot liquor coagulates and settles to the bottom of the tank as a viscous liquid layer L. When the level of the liquid lignin acid salt layer L rises above the bottom of baffle 31 the aqueous layer M accumulating in compartment 29 is automatically prevented from passing into compartment 30. Consequently, when this condition is once established, and further quantities of the liquid lignin acid salt settle to the bottom of the separator, the lignin is forced up into compartment 30 on account of the hydrostatic pressure exerted by the aqueous layer accumulating in compartment 29 until it reaches the outlet 33 through which it then overflows. Similarly, the aqueous component confined to and accumulating in compartment 29 will overflow on reaching the outlet 32. The liquid lignin acid salt overflowing from compartment 30 through overflow outlet 33 passes into the lignin dissolver 35 and the aqueous liquor overflowing from compartment 29 passes through connection 36 into the residual carbonated black liquor storage tank 37.

In the dissolver 35 the viscous liquid lignin acid salt is mixed with hot water, is dissolved, and passes to the dissolved-lignin storage tank 40 from whence it is pumped to lignin precipitator 41.

Acid, preferably sulfuric acid, is supplied to precipitator 41 from acid tank 42 in a quantity

such that the pH of the contents of the precipitator will be lowered to a pH of something less than 4, preferably of a pH of about 3, for the purpose of precipitating the lignin from its aqueous solution. The acid should be added slowly and may have a concentration of about 10%. If the temperature of the mixture during the precipitation of the lignin has been below a temperature of 90° to 95° C., the temperature may be increased into that range by the introduction of steam before finishing the batch. The charge may be then dropped into the precipitated-lignin storage tank 43. From tank 43 the mixture may then be pumped to the rotary vacuum filter 44, where the acid-precipitated lignin is separated and washed. The primary filtrate, containing some inorganic sodium salts, excess sulfuric acid and such acid-precipitated lignin as may pass through the filter when the cake first forms may be sent to the filtrate tank 39, from whence it may be delivered to the separator as indicated, the secondary filtrate being sent to the sewer. The acid-precipitated lignin coming from the filter 44 may, if desired, be further purified by mixing it with water and then passing the mixture over a second rotary vacuum filter. In place of vacuum filters, centrifugal hydro extractors may be employed for these operations if so desired. The thus separated and purified acid-precipitated lignin can then be used either in the pasty condition in which it comes from the filter, or it may be dried by passing it through a suitable dryer to yield a fine powder.

From tank 37 the aqueous liquor is returned into the equipment shown in Fig. 1, being pumped to the second effect of evaporator 13 for further concentration, and may pass successively through the second and first effects into the heavy black liquor storage tank 46. From tank 46 it may then be pumped to the spray chamber 47 before being introduced into the furnace 48 to be burned in the conventional manner. The gases of combustion may pass successively through the boiler 49 air heater 50 and spray chamber 47 into pipe 20 which leads into the bottom of spray tower 18, (Fig. 2), heat contained in these gases being utilized for the generation of steam in the boiler 49 and thus furnishing steam required for the various process operations. The gases are cooled in their passage through the spray chamber 47 to a temperature of about 250° F., a temperature suitable for use in tower 18. The concentration of the liquor is increased in the spray chamber 47 by contact with the gases passing therethrough.

The smelted inorganic sodium salts pass from furnace 48 through spout 52 into dissolving tank 53 where they are dissolved yielding the so-called green liquor. The green liquor is pumped to causticizing tank 54 and there mixed with lime from bin 55, the resulting mixture being passed through reaction tanks 56 and 57 into the white liquor clarifier 58 from whence the clarified liquor is decanted into storage tank 59. The lime sludge which settles in clarifier 58 may be pumped to a rotary vacuum filter 60 and washed with water before being calcined for reuse or otherwise disposed of. The filtrate from filter 60 may be returned to dissolving tank 53 for use in dissolving the smelted sodium salts. The clarified white liquor is pumped from storage tank 59 to the cooking liquor storage tank 2, thus completing the cycle.

When it is desired to utilize that feature of our process which involves the recovery for cyclic

reuse of carbon dioxide from the residual carbonated liquor, this can be accomplished by employing a suitable stripping column through which the residual carbonated liquor would be passed prior to entering evaporator 13. We prefer, however, when using this feature, to carry out the carbonation with a partially concentrated liquor, and in that case a method such as that separately illustrated for purposes of simplicity in Figure 6 may be used. The residual carbonated black liquor from tank 37 passes to the multiple effect evaporator 13 through pipeline 71, entering the heating section of the second effect. Carbon dioxide resulting from the sodium bicarbonate, and steam, are evolved from the liquor, these gases passing under pressure through pipe 65 to the steam chamber of the third effect, where the weak black liquor undergoes initial evaporation. The liquor further evaporated in the second effect passes through line 67 to the first effect where the final evaporation, as carried out in the multiple effect evaporator 13, is completed, the evaporated liquor passing through line 66 to heavy black liquor tank 46 while steam and lesser quantities of carbon dioxide evolved from the liquor pass under pressure through line 64 to the steam chamber in the second effect. The steam that is thus passed to the steam chambers of the second and third effects is partially condensed as a result of heat interchange with the liquor through the tubes, the condensate leaving the system through traps 69 and 68 respectively. To prevent the accumulation of the non-condensable carbon dioxide a purge gas consisting of this, with a portion of steam, is taken from the steam chambers of the second and third effects through purge lines 62 and 63 respectively, thence passing to tower 61 through pipe line 70. Tower 61 may be fitted with slightly inclined baffles 72 to promote condensation of steam and absorption of carbon dioxide by the flue gas carbonated liquor coming from spray tower 18 by means of pump 26 and being passed through tower 61 countercurrently to the gases entering through pipeline 70. Tower 61 may be mounted over separator 28 as shown. The heated and further carbonated liquor, having a temperature of over 80° C., drops into separator 28, where separation of the lignin acid salt from the liquor is effected in the manner previously described.

When the production of an oxidized or partially oxidized lignin is desired, this can be obtained, as previously mentioned, by bubbling air through a solution of the sodium lignin acid salt. For this purpose a system such as that illustrated in Figure 7 may be used. This consists of a plurality of dissolved lignin tanks corresponding to the tank 40 shown in Figure 3. In Figure 7 we have shown three such tanks, these being tanks 40, 40a and 40b, into each of which the dissolved lignin acid salt may be delivered from the lignin dissolver 35 and from each of which the solution may in turn be delivered to the lignin precipitator 41. The tanks 40, 40a and 40b are each provided with air connections by means of which air can be bubbled through solution contained in the tanks. The number and size of the dissolved lignin oxidizing tanks required will depend upon the degree of oxidation that may be desired. The degree of oxidation, however, will proceed to the same extent in any given period of time, providing the temperature and strength of the solution are the same and the air is being supplied at uniform rate. The re-

action with air progresses slowly, consuming hours in place of minutes, thus simplifying the control of the reaction.

Having thus described what we now conceive to be the preferred embodiments of this invention, it will be understood that various modifications may be resorted to within the scope and spirit of the invention as defined by the appended claims.

We claim:

1. The process of producing lignin material from black liquor comprising carbonating the same with oxygen and carbon dioxide-containing gases, controlling the reaction to accelerate the carbonation by providing continuously a large and constantly changing interface between liquid and gas, the area of liquid surface exposed at any time relative to liquor volume in the carbonating vessel and the speed with which said liquid surface is changed in contact with the gas during carbonation in such vessel being such that the desired carbonation reaction is completed before the relatively slower oxidation reaction has proceeded to an appreciable extent, and then, while the carbonated black liquor has a temperature above the melting point of the lignin material and the lignin material is present as a distinct flowable viscous liquid layer, flowing the said layer of lignin material from the liquor while the lignin material is in such flowable viscous condition, and producing a water insoluble lignin material by dissolving the thus isolated lignin material in hot water, acidifying the hot aqueous solution with concomitant agitation, the acidifying agent being a mineral acid and the acidification and agitation being continued until the solution has a pH below about pH 5 and the lignin is precipitated out as finely divided insoluble particles, and filtering the product.

2. A moldable product comprising a thermoplastic, water-insoluble lignin material of substantially non-oxidized character and having a particle size mainly between 2-15 microns, prepared by the process of claim 1.

3. The process of producing lignin material from black liquor comprising carbonating the same with oxygen and carbon dioxide-containing gases, controlling the reaction to accelerate the carbonation by providing continuously a large and constantly changing interface between liquid and gas, the area of liquid surface exposed at any time relative to liquor volume in the carbonating vessel and the speed with which said liquid surface is changed in contact with the gas during carbonation in such vessel being such that the desired carbonation reaction is completed before the relatively slower oxidation reaction has proceeded to an appreciable extent, separating the substantially non-oxidized lignin material from the liquor, dissolving, in hot water, the lignin material thus isolated from the carbonated black liquor, acidifying the hot aqueous solution with concomitant agitation, the acidifying agent being a mineral acid and the acidification and agitation being continued until the solution has a pH below about pH 5 and the lignin is precipitated out as finely divided insoluble particles, and filtering the product.

4. In the art of producing lignin material from carbonated black liquor having a temperature above the melting point of the lignin material and wherein the lignin material is present as a distinct flowable viscous liquid layer, the step

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of flowing the said layer of lignin material from the liquor while the lignin material is in such flowable viscous condition.

5. The process of producing lignin material from black liquor comprising carbonating the same with oxygen and carbon dioxide-containing gases, controlling the reaction to accelerate the carbonation by providing continuously a large and constantly changing interface between liquid and gas, the area of liquid surface exposed at any time relative to liquor volume in the carbonating vessel and the speed with which said liquid surface is changed in contact with the gas during carbonation in such vessel being such that the desired carbonation reaction is completed before the relatively slower oxidation reaction has proceeded to an appreciable extent, and then, while the carbonated black liquor has a temperature above the melting point of the lignin material and the lignin material is present as a distinct flowable viscous liquid layer, flowing the said layer of lignin material from the liquor while the lignin material is in such flowable viscous condition.

6. The process of producing a water insoluble lignin material comprising dissolving lignin material isolated from carbonated black liquor, acidifying the hot aqueous solution with concomitant agitation, the acidifying agent being a mineral acid and the acidification and agitation being continued until the solution has a pH below about pH 5 and the lignin is precipitated out as finely divided insoluble particles, and filtering the product.

7. In the art of producing lignin material from carbonated black liquor having a temperature above the melting point of the lignin material and wherein the lignin material is present as a distinct flowable viscous liquid layer, the steps of flowing the said layer of lignin material from the liquor while the lignin material is in such flowable viscous condition, and producing a water insoluble lignin material by dissolving the thus isolated lignin material in hot water and acidifying the hot aqueous solution with concomitant agitation, the acidifying agent being a mineral acid and the acidification and agitation being continued until the solution has a pH below about pH 5 and the lignin is precipitated out as finely divided insoluble particles, and filtering the product.

8. A process of producing a lignin material from alkaline pulp black liquor which comprises carbonating the liquor, heating the said carbonated liquor to a temperature above the melting point of the precipitated suspended lignin material, settling the lignin material as a distinct flowable viscous-liquid layer, separating the liquid layers by flowing the said layer of lignin material from the liquor while the lignin material is in such flowable viscous condition.

9. A process of producing a lignin material from alkaline pulp black liquor which comprises carbonating the liquor, heating the said carbonated liquor to a temperature above the melting point of the precipitated suspended lignin material, settling the lignin material as a distinct flowable viscous-liquid layer, separating the liquid layers by flowing the said layer of lignin material from the liquor while the lignin material is in such flowable viscous condition, and producing a water insoluble lignin material by dissolving the thus isolated lignin material in hot water, acidifying the hot aqueous solution with concomitant agitation, the acidifying agent

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being a mineral acid and the acidification and agitation being continued until the solution has a pH below about pH 5 and the lignin is precipitated out as finely divided insoluble particles, and filtering the product.

10. In the art of producing lignin material from carbonated black liquor having a temperature above the melting point of the lignin material and wherein the lignin material is present as a distinct flowable viscous liquid layer, the steps of flowing the said layer of lignin material from the liquor while the lignin material is in such flowable viscous condition, dissolving the separated lignin material in water and acidifying the resulting solution for precipitating out the lignin material as finely divided insoluble particles, and filtering the product.

11. A process of producing a lignin material from alkaline pulp black liquor which comprises carbonating the liquor, heating the said carbonated liquor to a temperature above the melting point of the precipitated suspended lignin material, settling the lignin material as a distinct flowable viscous-liquid layer, separating the liquid layers by flowing the said layer of lignin material from the liquor while the lignin material is in such flowable viscous condition, dissolving the separated lignin material in water and acidifying the resulting solution for precipitating out the lignin material as finely divided insoluble particles, and filtering the product.

12. A method of treating residual liquor resulting from the digestion of cellulosic fibrous material in an alkaline cooking liquor which comprises passing the residual liquor through a carbonating zone, a separating zone and an evaporating zone to a furnace in which the residual liquor is burned to yield a smelt adapted for use in the preparation of fresh cooking liquor, passing CO<sub>2</sub>-containing flue gases from said furnace to and through said carbonating zone, carbonating the liquor during its passage through the carbonating zone by contacting the liquor with the CO<sub>2</sub>-containing flue gases under such liquid gas contact and temperature conditions that the pH of the liquor is quickly reduced to a value at which a substantial amount of lignin is precipitated in a finely divided form and remains suspended in the liquor, heating the carbonated liquor, after it leaves the carbonating zone, to a temperature at which the previously precipitated finely divided lignin is melted to a viscous liquid, permitting said viscous liquid lignin to settle as a discrete layer in the separating zone and separating the lignin from the separating zone while the lignin is in the viscous liquefied state.

13. A method of treating residual liquor resulting from the digestion of cellulosic fibrous material in an alkaline cooking liquor which comprises passing the residual liquor through a carbonating zone, a heated separating zone and an evaporating zone to a furnace in which the residual liquor is burned to yield a smelt adapted to be used in the preparation of fresh cooking liquor, passing CO<sub>2</sub>-containing flue gases from the furnace to and through said carbonating zone, contacting the residual liquor and the CO<sub>2</sub>-containing flue gases with each other during their passage through the carbonating zone under such liquid gas contact and temperature conditions that the pH of the liquor is quickly lowered to a value at which a substantial amount of finely divided lignin is precipitated and remains suspended in the carbonated liquor, heating the carbonated liquor after it leaves the carbonating zone, to a

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temperature at which the previously precipitated finely divided lignin is melted to a viscous liquid, permitting said viscous liquid lignin to settle as a discrete layer in the heated separating zone and separating the lignin from the heated separating zone while the lignin is in the viscous liquefied state.

14. A continuous method of treating residual liquor resulting from the digestion of cellulosic fibrous material in an alkaline cooking liquor which comprises passing the total quantity of the residual liquor in continuous flow through a carbonating zone, a heating zone, a separating zone and an evaporating zone to a furnace in which the residual liquor is burned to yield a smelt adapted for use in the preparation of fresh cooking liquor, rapidly carbonating the liquor during its passage through the carbonating zone by contacting the liquor, while in a finely divided form, with CO<sub>2</sub>-containing flue gases supplied to the carbonating zone from said furnace, maintaining the temperature of the liquor, during its passage through the carbonating zone, at a temperature at which a substantial amount of finely divided lignin is precipitated and remains suspended in the liquor, heating the carbonated liquor during its passage through said heating zone to a temperature at which the previously precipitated finely divided lignin is melted to a viscous liquid which is permitted to settle as a discrete layer in the separating zone and continuously withdrawing the lignin from the separating zone while the lignin is in the viscous liquefied state.

15. A continuous method of treating residual liquor resulting from the digestion of cellulosic fibrous material in an alkaline cooking liquor which comprises passing the residual liquor in continuous flow through a series of liquor recirculating spray type carbonating towers in each of which the liquor is repeatedly sprayed downwardly in counter-current contact with an ascending current of CO<sub>2</sub>-containing flue gas so that the liquor is quickly carbonated to a pH value at which a substantial amount of lignin is precipitated, maintaining the temperature of the liquor, during its passage through the carbonating towers at a temperature close to but below the melting point of the lignin, continuously passing the liquor from the last of the carbonating towers to a separating zone and heating the liquor, after it leaves the carbonating towers, to a temperature at which the previously precipitated lignin melts to a viscous liquid, permitting said viscous liquid lignin to settle as a discrete layer in said separating zone, continuously withdrawing the viscous liquid lignin from the separating zone, passing the supernatant aqueous liquor from the separating zone through an evaporating zone to a furnace in which the liquor is burned to yield a smelt adapted for use in the preparation of fresh cooking liquor and continuously passing CO<sub>2</sub>-containing flue gases from the furnace to and through said carbonating towers.

16. A method of treating residual liquor resulting from the digestion of cellulosic fibrous material in an alkaline cooking liquor which comprises passing the residual liquor through a carbonating zone, a separating zone and an evapo-

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rating zone to a furnace in which the residual liquor is burned to yield a smelt adapted for use in the preparation of fresh cooking liquor, rapidly carbonating the liquor during its passage through the carbonating zone by contacting the liquor, while in a finely divided form, with CO<sub>2</sub>-containing flue gases supplied to the carbonating zone from said furnace, passing the liquor to the furnace in heat interchanging relation with the flue gases passing from the furnace to the carbonating zone to thereby cool said gases sufficiently to prevent heating of the liquor, during its passage through the carbonating zone, to a temperature above the melting point of the lignin contained therein, heating the liquor after it leaves the carbonating zone to a temperature at which the previously precipitated lignin is melted to a viscous liquid, permitting said viscous liquid lignin to settle as a discrete layer in the separating zone and separating the lignin from the separating zone while the lignin is in the viscous liquefied state.

17. In the art of producing lignin material by carbonating alkaline pulp black liquor and then separating precipitated lignin material from the carbonated liquor, the improvement which consists in passing the liquor through a primary carbonating zone and then through a secondary carbonating zone, carbonating the liquor with flue gases during its passage through the primary carbonating zone, further carbonating the liquor with relatively pure CO<sub>2</sub> during its passage through the secondary carbonating zone, separating the precipitated suspended lignin from the carbonated liquor after its passage through the secondary carbonating zone while the carbonated black liquor has a temperature above the melting point of the precipitated lignin material by settling the lignin material as a distinct flowable viscous liquid layer and flowing the said layer of lignin material in flowable viscous condition from the liquor, recovering CO<sub>2</sub> from the separated liquor, and delivering the recovered CO<sub>2</sub> to the secondary carbonating zone.

18. In the art of producing lignin material by carbonating alkaline pulp black liquor and then separating precipitated lignin material from the carbonated liquor, the improvement which consists in passing the liquor through a primary carbonating zone and then through a secondary carbonating zone, carbonating the liquor with flue gases during its passage through the primary carbonating zone, contacting the liquor with a mixture of steam and relatively pure CO<sub>2</sub> during its passage through the secondary carbonating zone, separating the precipitated lignin material from the carbonated liquor after its passage through the secondary carbonating zone while the carbonated black liquor has a temperature above the melting point of the precipitated lignin material by settling the lignin material as a distinct flowable viscous liquid layer and flowing the said layer of lignin material in flowable viscous condition from the liquor, heating the separated liquor to disengage therefrom a mixture of steam and relatively pure CO<sub>2</sub>, and delivering said mixture to the secondary carbonating zone.

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