

Studies on the Carbonation of Black Liquor for Lignin Precipitation and its Subsequent Separation

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INTRODUCTION

A critical assessment of black liquor regeneration process, made in an earlier communication¹, indicated feasibility of developing a simplified soda recovery method based on organic removal by lignin precipitation²⁻³ and by electro-dialytic fractionation of black liquor constituents⁴⁻⁵⁻⁶. Apart from its inapplicability to smaller capacity plant, due to uneconomical operation, conventional soda recovery process is confronted with the hard fact, that, only fifty per cent of the cellulosic raw material is utilized, other half being burnt out during incineration stage of the standard soda recovery method.

There has been criticism of the conventional soda recovery process because of the complete destruction of the potentially available organic chemicals in black liquor, and consistent attempts⁷⁻⁸⁻⁹⁻¹⁰⁻¹¹ were made from time to time, to eliminate incineration stage for the recovery of cooking chemicals along with organic chemicals. Up till now, all such efforts were unsuccessful on commercial scale, and also detailed plant data are not available, since such processes are covered by patent rights. As a first step for the development of a simplified soda recovery process, eliminating hazardous incineration stage, an attempt has been made in this present work, to study the feasibility of removing ligno-organic constituents from alkaline black liquor by carbonation, so as to render it causticizable for the conversion into active alkali form, after organic precipitation and filtration.

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Experimental investigations were carried out to study the feasibility of removing ligno-organic constituents from alkaline black liquor by carbonation; and to render it suitable for causticization, for the conversion of soda compounds into caustic form.

Influencing process parameters during carbonation, i.e., degree of turbulence, temperature, pressure, time and the final pH, were studied and optimum conditions evaluated. Pressure carbonation at 4.5 Kg/cm² followed by coacervation-flocculation treatment with acetone, was found to have pronounced effect on the removal of ligno-organic precipitate, obtained as a stable lyophilic colloid.

Carbonation under atmospheric pressure were carried out in a 1.5 litre capacity pyrex glass reactor having provisions for sample collection, thermometer pocket, agitation through mercury seal, gas introduction line through a sparger and heating arrangement. Pressure carbonation work was done in an electrically heated 18 litre capacity S. S. autoclave having liquor recirculation arrangement through a heat exchanger, heated by electrical load.

It is observed, that, black liquor, precipitation phenomenon and its response to coagulation-coacervation-flocculation treatment for lignin separation, is correlated intimately with the morphological characteristics of the cellulosic raw material with respect to lignin content and its distribution within the cellular layers and the middle lamella.

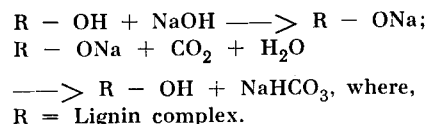
THEORETICAL CONSIDERATION

Lignin complex is the only organic constituent in black liquor, which is insoluble in water, while other organic matter present as carbohydrate degradation products, are water soluble.

Othmer¹² reported that for the complete dissolution of lignin complex, present as phenolates in b.l., four moles of caustic soda are required per monomer unit of lignin of molecular weight of about 840, containing one phenolic hydroxyl group. When pH of the b.l., is appreciably below 11.5, or when there is appreciably less than four equivalents of caustic soda per unit of lignin, such solution shows increased viscosities, and the solubility of lignin become more sensitive to the presence of other salts. With only one equivalent of caustic soda, alkali lignin remains insoluble in hot solution of sodium salts of black liquor.

Therefore, the major organic complex, lignates, which is very soluble in b.l.,

because of its high alkalinity, comes out as a precipitate, when alkalinity of the liquor is reduced by lowering its pH by acidification. For the conversion of soda compounds into carbonate form, which could be recovered as caustic soda by causticization, and for the prevention of over acidification, carbon-di-oxide may be conveniently used as the acidifying agent for lignin precipitation, resulted from the combined effect of salting out phenomena, and hydrolysis of lignin phenolates, according to the following scheme¹³.



PLAN OF THE WORK AND EXPERIMENTAL SET UP

Based on the removal of lignin and associated organic matter from soda black liquor by acid precipitation, it was proposed to remove organic matter,

by subjecting it to the following treatments:

- i) Carbonation of b.l., under atmospheric and elevated pressure for the hydrolytic decomposition of lignin phenolates as precipitate along with associated organics.
- ii) Separation of the colloidal lignin precipitate after carbonation, by coagulation and centrifugation, or by coacervation — flocculation treatment.

During b.l. carbonation, it was decided to study the following process parameters, so that optimum process conditions could be established:

- a) Temperature during b.l. carbonation
- b) Time of carbonation
- c) Concentration of black liquor as t.d.s., per cent
- d) Final pH of the carbonated black liquor
- e) Degree of turbulence in terms of agitator r.p.m., and carbon-di-oxide gas velocity.

It was also decided to study the effect of aging of black liquor on the degree of lignin precipitation, during carbonation investigations. The study of aging effect was thought to be important, not so much as a plant variable, where one has little control over the age of black liquor supplied, but from the question of laboratory technique.

Firstly, it was important to know whether a black liquor sample could be kept unchanged in case it became necessary to repeat an experiment, and secondly laboratory concentration is a tedious and time-consuming separation, resulting in laboratory-concentrated b.l., being days old.

The procedure to be used would be to carbonate a b.l., within a hour of the cook and then repeat the carbonation experiment after keeping it for a certain period of storage.

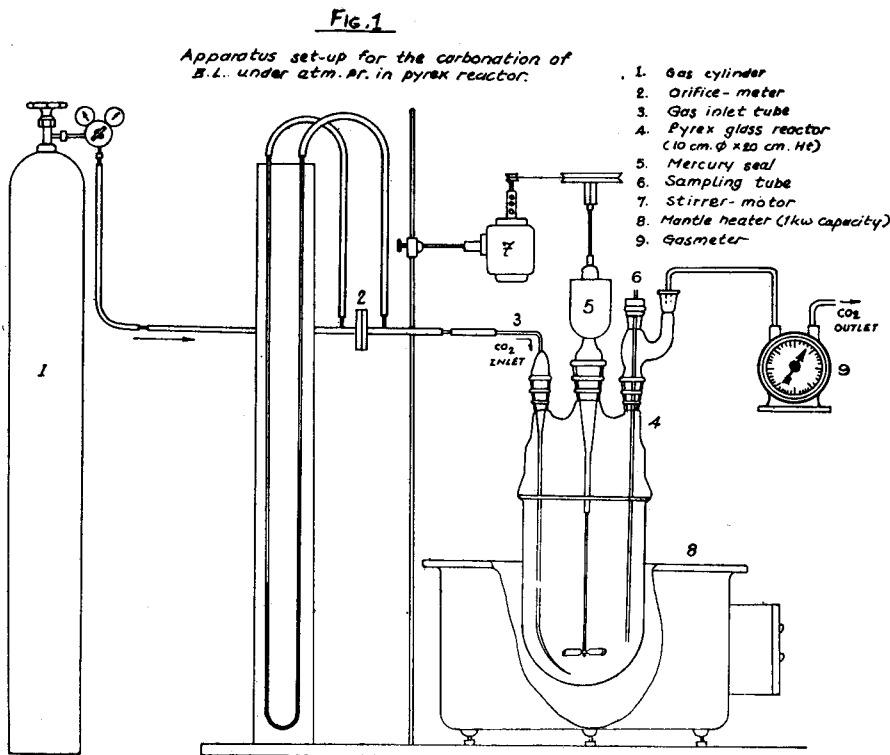
In order to find out the effect of b.l., oxidation on the degree of lignin precipitation, to simulate industrial condition, in case where the flue gas could be used as the cheap source of carbon-di-oxide for black liquor carbonation, it was decided to use oxidised b.l., for one carbonation experiment.

Oxidized b.l., was obtained by passing oxygen gas to b.l., kept in a pyrex reactor. Oxidation of b.l., was carried out for the two hours at 80°C under constant agitation, according to the procedure, reported in a previous communication¹⁴.

The experimental set-up for black liquor carbonation under atmospheric condition is shown in Fig. 1.

provided for the stirrer and the 1 KW mantle heater respectively.

For every batch experiment, 500 ml., of black liquor was taken in the pyrex reactor. Before the start of the experiment, °Be and temperature of the b.l., was determined accurately and converted to 20°C. From the °Be value at 20°C, the corresponding t.d.s., concentration, organo-soda, total soda content



The apparatus consisted of a 1.5 litre capacity pyrex reactor fitted with agitator through mercury seal, thermometer pocket, sample collection tube line, and an inlet tube-line with nozzle for the introduction of gas.

The carbon-di-oxide gas from the cylinder was passed through an orifice meter, fitted with manometer, to gas inlet line and bubbled out through a nozzle near the bottom of the reactor. The gas flow was regulated by means of a pressure regulating valve, and the flow rate was determined by the calibrated manometer.

The stirring r.p.m., and the temperature of the liquid, was adjusted and maintained constant by means of the continuously variable auto-transformers,

(as Na₂O), total organic and lignin content of black liquor were evaluated from the correlation graphs, as per the procedure outlined in the reference no. 15.

When the particular temperature was reached, carbon-di-oxide gas from the cylinder was passed inside the pyrex reactor, containing b.l., through the calibrated orifice meter. The proper rate of gas introduction was controlled by adjusting the manometer reading, while r.p.m., of the agitator and the temperature of the reacting liquor was controlled by the auto-transformers.

At an interval of half-an-hour, carbonated b.l., sample was taken out from the collection tube line, and analysed for its pH value, in a pH meter (ELICO make, model No. LI — 10), NaOH and Na₂CO₃ contents by the differen-

tial conductometric titration procedure, in a conductometric — titration bridge of Philips make, model 9500. Colloidal lignin precipitate, obtained after carbonation, was separated as far as possible by coagulation, decantation and centrifugation.

For analysis, 25 ml. of carbonated black liquor was taken out, coagulated by heating it to about 80°C, followed by sudden cooling by putting it inside an ice box. The top layer after coagulation was diluted four times with distilled water and then subjected to centrifugation for half-an-hour, the bottom layer being added to the reaction vessel, for undergoing carbonation reaction along with the main bulk. The centrifuged liquor was then analyzed for organo soda content, total organic and lignin constituent.

From this analytical information, lowering of pH value, per cent removal of organic and lignin matter, and hydrolytic decomposition of organo soda into carbonate form, were estimated and recorded.

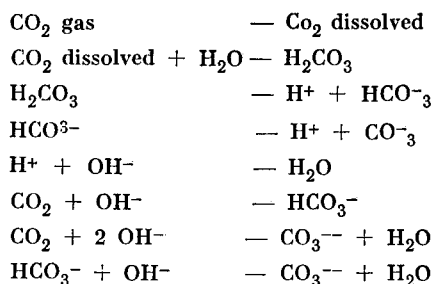
RESULTS AND DISCUSSIONS

During carbonation process, the lignin matter together with its associated organic substances, comes out as precipitate through the combined effect of the following:

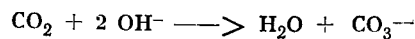
- i) Salting out phenomena at lower alkalinity¹⁶
- ii) Flocculation of colloids by acidification¹⁷
- iii) Hydrolytic decomposition of soda lignin which renders lignin complex insoluble at lower pH value¹³

Thus it may be assumed that all factors for the precipitation of lignin are dependent on the lowering of black liquor pH by carbon dioxide gas. Carbonation of black liquor by carbon-dioxide gas could be characterised as a problem of absorption followed by chemical reaction. However, unlike a simple gas pure liquid system (like sulfur-dioxide-water system) the liquid phase is complicated by the multiplicity of black liquor soda components and as such is not amenable to the usual technique of handling problems involving a gas and a pure liquid. Moreover, the chemical kinetics and, in fact, the ac-

tual chemistry of the absorption reaction between carbon-di-oxide gas and caustic soda are not well understood¹⁷. It has been reported¹⁸ that absorption process of carbon-di-oxide gas in caustic soda solution follows the following pattern:



The ionic reactions are believed to be very rapid, but the rates of the other reactions, which are not all independent, are not well known. Various assumptions are made by different researchers as to which of these reactions may be controlling. It seems probable that the over-all reaction is:



and that it goes directly in the presence of free caustic soda, and that the rate of reaction is very rapid. Because of the complications of the reaction between carbon-di-oxide gas and black liquor, containing different soda compounds i.e., free NaOH, Na₂CO₃, NaHCO₃ and organo soda plus small amounts of silicates, resinsates, attempt was not made in the present work to study the reaction mechanism of black liquor carbonation process.

Efforts were made in the present work to correlate the results of black liquor carbonation, with the different influencing process parameters so as to arrive at the optimum carbonation condition.

The first effect of b.l., carbonation results in the neutralization of caustic soda by carbonic acid, which is followed by the reactions between sodium silicates and carbonic acid, whereby silica comes out as a flocculating precipitate of silicic acid. Because of these neutralizing reactions, alkalinity of the liquor drops down, and pH is lowered considerably below 10.0. As soon as the pH goes below 10.0, lignin with associated organic matter, makes its appearance as a colloidal precipitate, and the precipitation process is continued up to saturation of carbon-di-oxide gas absorption.

Relative efficiency of carbonation process (with respect to the removal of organic matter in black liquor) may be measured in terms of lowering rate of pH with respect to carbonation time, which control the precipitation process by b.l., acidification with carbon-di-oxide gas.

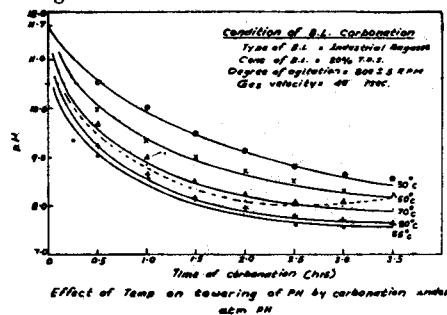
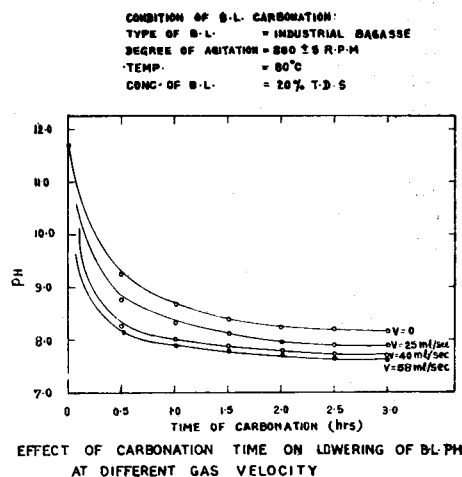
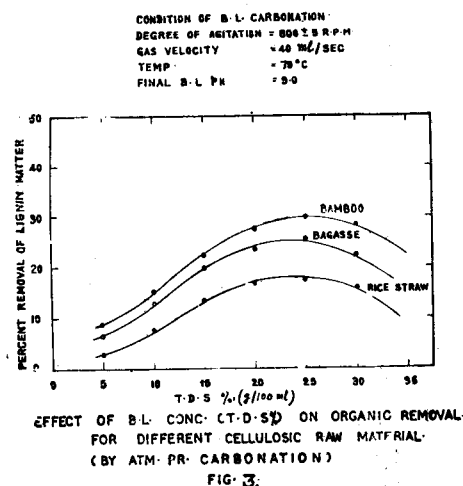


Fig. 2



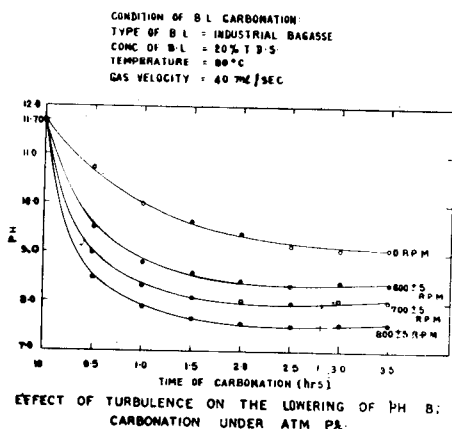


Fig. 5

Effects of carbonation temperature, b.l., concentration (t.d.s. per cent), gas velocity and the degree of turbulence, are evaluated in terms of lowering rate of black liquor pH, and are depicted in figures 2, 3, 4 and 5 respectively.

Fig. 2 states that the lowering rate of pH during black liquor carbonation is influenced considerably by the temperature upto 80°C. After 80°C the curve shows a downward slope indicating that higher temperature is unsuitable for lignin precipitation by carbonation process.

Since lowering rate of black liquor pH is predominantly controlled by the rate of absorption of carbon-di-oxide gas by free caustic soda, its temperature dependence follows as a natural sequence. In majority of the investigations on the absorption rate of carbon-di-oxide gas in NaOH or KOH solutions, it has been stated, that the rate of diffusion in the liquid phase determines the over-all rate of absorption. Temperature gives pronounced effect on the diffusivities and viscosities of liquid (which lowers considerably liquid film coefficient), and the combined effect of these variables is quantitatively similar to the effect of temperature on the rate of chemical reaction, which to a large extent affects the over-all rate of CO₂ gas absorption in caustic soda solution. Thus over-all mass transfer coefficient (KGa) of CO₂ gas in caustic soda solution is increased considerably at higher temperature, and consequently it affects significantly on the lowering rate of black liquor pH, con-

trolled by the speed of absorption rate of CO₂ gas in free NaOH present in black liquor.

At higher temperature, solubility of carbon-di-oxide gas in the reaction product (i.e., carbonate and bicarbonate) drops down considerably, thereby increasing the equilibrium partial pressure rapidly. It has been stated, that, increasing absorption temperature from 16°C to 100°C, a tenfold increase in the CO₂ partial pressure is achieved¹³.

As soon as carbon-di-oxide gas comes in contact with the gas-liquid interface, it gets absorbed and interface layer becomes saturated, and depleted with gas by reacting with free caustic soda, and sodium-bi-carbonate content of black liquor at a fast rate. After the rapid interfacial reaction, the absorption becomes dependent on slow diffusional changes, such as, migration of carbonate in the main body of the fluid.

However, if the interfacial saturated zone is replaced with fresh liquor by means of dispersion or agitation, rate of gas absorption rate is increased considerably, which results in the rapid increase on the lowering rate of black liquor pH.

This supposition is confirmed by referring to Fig. 5 which shows significant effect of turbulence (measured in terms of agitation r.p.m.) on the decreasing rate of black liquor pH.

The precipitation efficiency during carbonation process, measured in terms of per cent removal of ligno-organic matter, is dependent to a large extent on the morphological characteristics of the cellulosic raw material with particular reference to lignin content and its distribution within the middle lamella and the cellular layers. This is reflected in the experimental results presented in figure 3, showing per cent removal of ligno-organic matter from three different cellulosic raw material (Rice straw, bagasse and bamboo), under similar conditions of black liquor carbonation.

The dependence of final pH of the carbonated black liquor, on the precipitation efficiency, is indicated in figures 6 and 7.

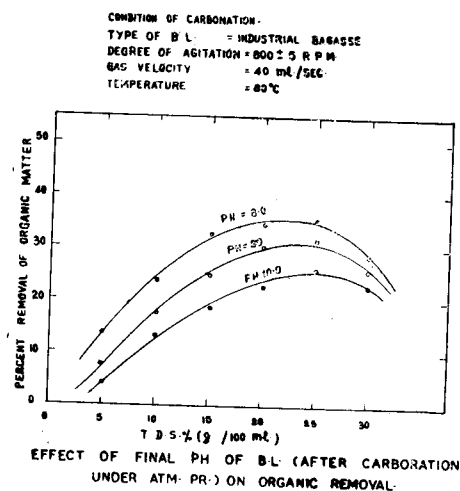


Fig. 6

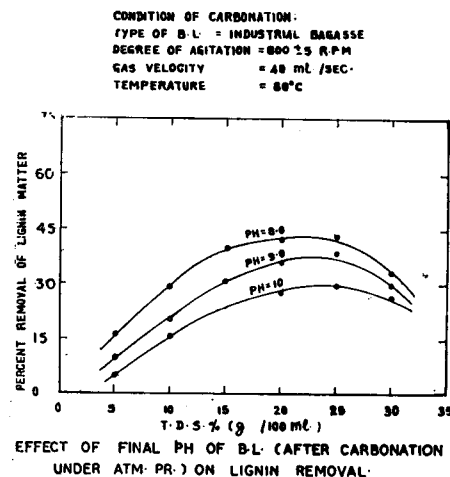


Fig. 7

The effect of aging and black liquor oxidation on the per cent removal of organic matter by carbonation, are presented in figures 8 and 9.

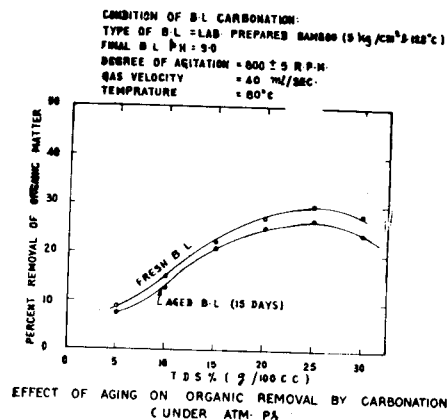


Fig. 8

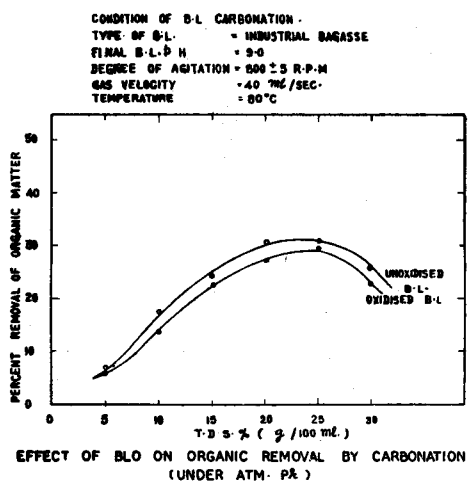


Fig. 9

It is observed, that, due to black liquor oxidation, per cent removal of organic matter is decreased from 30.5 per cent to 27.0 per cent at 20 per cent t.d.s., concentration of black liquor.

Effect of aging represents a slight reduction of organic matter removal from 27.0 to 25.50 per cent.

The results of these two variables, aging and black liquor oxidation, on lignin precipitation from b.l., by carbonation indicated that some kind of physico-chemical changes might have undergone within the organic constituents, the exact mechanism of which could be visualized. Tomlinson¹⁹ observed a type of chemical modification to lignin matter by black liquor oxidation, whereby filterability and coagulation capacity of the lignin precipitate (obtained after carbonation) is adversely affected due to its finer and gelatinous nature.

Kleinert¹⁷ after thorough investigations on lignin preparation from kraft black liquor by acidification, remarked, that during pulping process, free radicals are formed through the break-down of the lignin, a part of which is trapped by the resultant lignin fraction. Although relatively stable, these trapped free radicals are visualized to undergo slowly secondary reactions, such as recombinations, propagation, and in presence of air, probably also formation of peroxyl radicals, initiating various oxidation reactions. These post-degradation reactions of the lignin, could possibly explain the changes of the lignin properties observed during storage and

oxidation, resulting in the variation of the per cent removal of organic matter from the carbonated black liquor, obtained after oxidation and aging.

Investigations carried out on the separation of organic precipitate from the carbonated black liquor (under atmospheric as well as pressure condition) by filtration, coagulation, and centrifugation, indicate, that the lignin with associated organic substance, comes out as a stable lyophilic colloidal precipitate, which offers extraordinary resistance to its removal by the said treatment. Due to the protective shell, called a hydrated water layer around each colloids, it could not be agglomerated effectively through coalescence and coagulation with other colloids in the suspension during coagulation and centrifugation treatment. Furthermore, it is reported, that, a surface charge or zeta potential is associated with each solvated colloidal particle due to tendency of the large ionizable organic polymers to collect a diffuse layer, or cloud, of ions. By electrophoresis studies on lignin fraction, it has been reported²⁰ that the alkali lignin has a electrophoretic mobility of

$$-12.8 \times 10^{-5} \text{ cm}^2 \cdot \text{v}^{-1} \cdot \text{sec}^{-1}.$$

Since solvating force of water is the principal stabilizing factor of the colloidal lignin precipitate against environmental physico-chemical influences, the first step toward effective separation of the colloidal lignin precipitate from the carbonated black liquor, would be to destroy this protective shell by adding coacervating agent to the system which should be a poor solvent for the lignin colloids, and highly miscible with water.

Several coacervants, including, methanol, ethanol, formaldehyde and acetone, were tried with the object to determine the most suitable for coacervating carbonated black liquor. Black liquor carbonation experiments carried out under atmospheric conditions, led to the following observations :

- Pronounced effect of turbulence, and interfacial surface area on the lowering rate of black liquor pH, whereby precipitation time is considerably decreased.
- Requirement of comparatively higher carbonation time to reach equilibrium precipitation condition, if carbonation is carried out in reac-

tion vessel under atmospheric pressure.

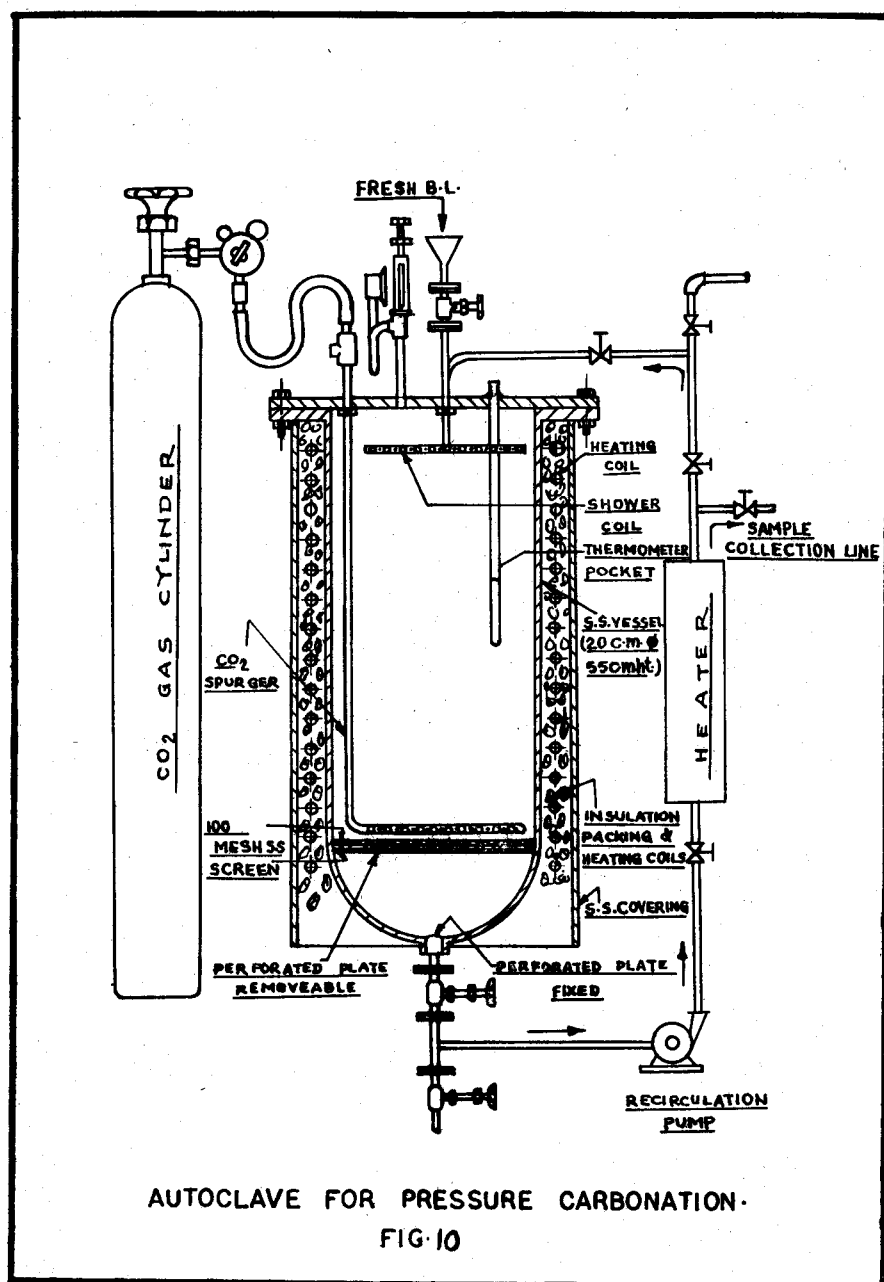
- Extraordinary difficulties in the removal of organic precipitate by filtration, coagulation, or centrifugation and also by coacervating treatment, thereby lowering considerably the per cent removal of organic and lignin matter, from the 'modified' b.l., i.e., carbonated b.l.
- Yield of lignin precipitate from the hydrolytic decomposition of soda-lignin complex is comparatively low.

The interaction between dissolved lignin and carbonic acid for the hydrolytic decomposition of alkali lignin, may be assumed to be a function of the concentration of carbon-di-oxide in the black liquor, and the speed of saturation of b.l., with respect to carbon-di-oxide gas, which in turn are expected to be increased under elevated pressure. In order to carry out black liquor carbonation reaction, efficiently under elevated pressure, an autoclave was designed, fabricated and installed.

It consisted of an electrically heated 18 litre (Fig. 10) capacity s. s. vessel (30 cm. \varnothing x 60 cm. height) with 0.5 mm. false bottom welded to the body. One detachable gas spurger (20 cm. \varnothing) having 0.1 mm perforations was fitted at the bottom for the introduction of CO_2 gas under pressure. For creating better turbulence and intimate gas-liquid contact, the liquor was forced through a centrifugal pump (with s.s. impeller) and recirculated through another removable spurger ring (20 cm \varnothing) fixed at the top of the vessel. Provision was made to re-heat the recirculated liquor with the help of a heat exchanger, electrically heated by 1 KW. capacity resistance wire, before it entered the autoclave.

Just beneath the gas-spurger, one perforated S.S. plate (having 1 mm holes) fixed with two 100 mesh S.S. screen (one at the top and the other at the bottom of the plate), was placed and kept in position for protecting the perforated false bottom, and the centrifugal pump from being clogged up, due to precipitates of organic matter, and silicic acid precipitates.

Effect of carbonation pressure, concentration of black liquor, and operating



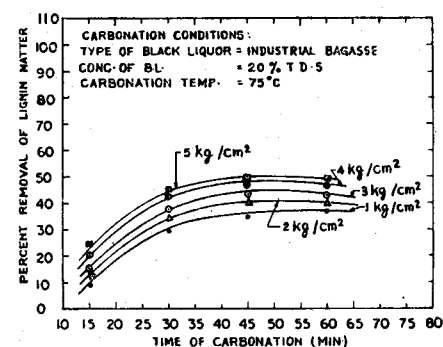
temperature on the per cent removal of organic and lignin matter by carbonation under pressure, are depicted in Figures 12, 13 and 14 respectively.

Effect of coacervation treatment, after carbonation of black liquor, by different coacervants are presented in figure 11.

Ethanol gives better results compared to methanol, while formaldehyde proves to be the poorest as a coacervating agent for the colloidal lignin precipitate studied in the present investigations.

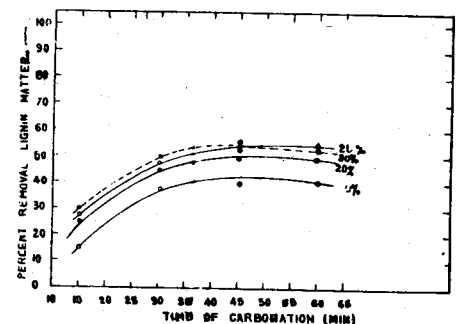
It appears, that formaldehyde on first being mixed with the carbonated black liquor, it produces an unstable colloidal system, which after a short interval of time, reacts with the system, destroying both the coacervant and the process of coacervation.

Acetone gives best performance as a coacervating agent for the separation of lignin precipitate from the carbonated black liquor. A dosage of 6 mp. of acetone per 100 ml. of carbonated b.l., of 20 per cent t.d.s., concentration (g/100



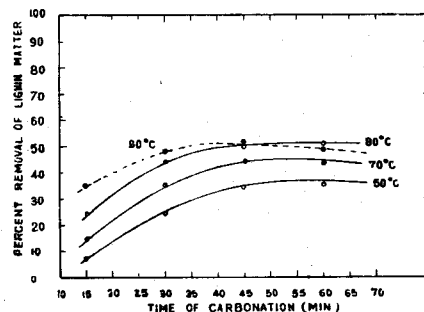
EFFECT OF PRESSURE ON THE REMOVAL OF LIGNIN MATTER BY CARBONATION.

CONDITION OF B.L. CARBONATION
TYPE OF B.L. = INDUSTRIAL BAGASSE
PRESSURE OF CARBONATION = 4.5 kg/cm²
TEMP " " = 80°C
FINAL PH = 8.00



EFFECT OF B.L. CONG. (T.D.S.) ON LIGNIN REMOVAL BY PA CARBONATION.

CONDITION OF B.L. CARBONATION:
TYPE OF B.L. = INDUSTRIAL BAGASSE
PRESSURE OF CARBONATION = 4.5 kg/cm²
CONC. OF B.L. = 20% T.D.S.
FINAL PH = 8.0



EFFECT OF OPERATING TEMP ON LIGNIN REMOVAL BY PA CARBONATION

ml), removes over 75 per cent lignin matter, while ethanol, methanol and formaldehyde gives lignin removal of 41, 35, and 27 per cent respectively, under similar conditions (fig. 11).

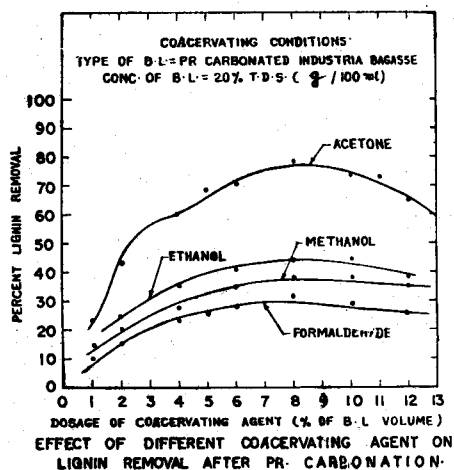


Fig. 11

With the increase of the dosage of coacervating agent above a certain point, lignin separation drops down significantly, which is evident in figure 11, representing the effect of acetone dosage on the per cent removal of lignin matter. It is seen from the said figure, that 5 per cent dosage (volume basis) could remove 72 per cent lignin matter, and it is dropped down to 68 per cent lignin matter, with a dosage of 12 per cent, under similar conditions of coacervation — flocculation treatment. It reflects peptonizing effect of the coacervating agent, at higher dosage, on the lignin-organic matter, whereby a certain quantity goes into stable suspension.

This fact, together with the lowering effect of soda recovery (as free NaOH + Na₂CO₃ expressed as Na₂O) at higher dosage of coacervation — flocculation treatment (figure 15), dictates an optimum dosage to be used for the removal of lignin matter from carbonated black liquor.

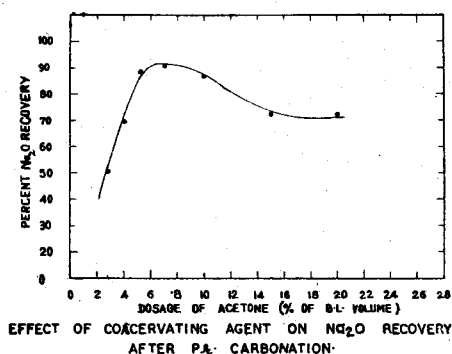


Fig. 15

Since pH of the black liquor controls the precipitation efficiency with respect ligno-organic removal from carbonated b.l., a certain quantity of fresh black liquor could be mixed with the 'modified' b.l., (carbonated to pH of 8.0) for the separation of lignin from b.l., without carbonation.

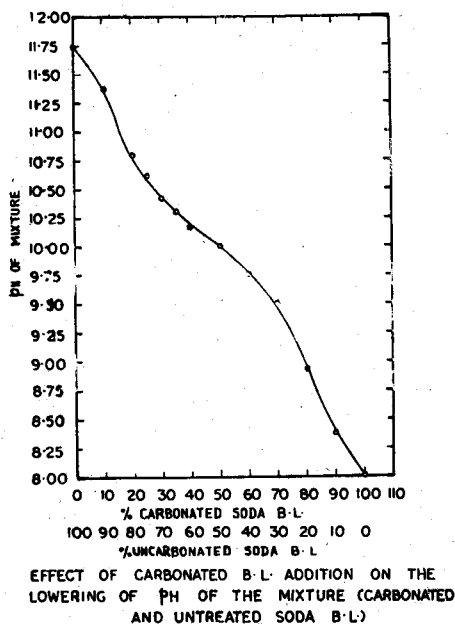


Fig. 16

This is evident in figure 16, which presents the effect of black liquor mixing in terms of lowering of the pH of the resultant mixture i.e., fresh and carbonated black liquor. It is seen that fresh b.l., upto 20 per cent could be mixed giving a resultant pH of the mixture to 8.85, whereby approximately 38 per cent of the total lignin content of fresh b.l., is precipitated out (vide figures 6 & 7) without carbonation.

All these coacervation experiments were carried out by adding different dosage of coacervating agent to 100 ml. of carbonated b.l., at 20 per cent t.d.s., concentration, taken in a measuring cylinder. Approximately 1.5 g. calcium hydroxide was added to the system as an aid to flocculation after coacervation treatment. The mixture of carbonated b.l., coacervating agent and calcium hydroxide was mixed slowly for 10 minutes with the help of a stirring rod, and then allowed quiescence sedimentation for half an hour. The lignin concentration of the superatant de-lignified liquor was estimated after removing acetone by distillation.

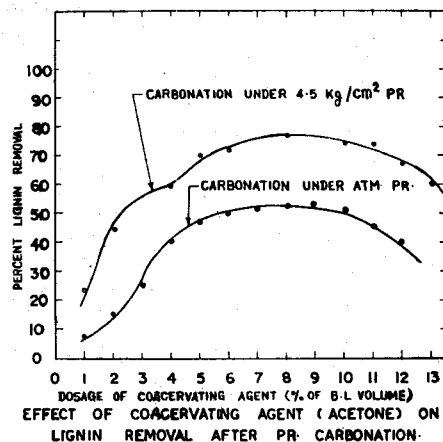


Fig. 17

Carbonation of black liquor under pressure renders it better suited for coacervation treatment (compared to atmospheric pressure carbonated liquor) with regards to the removal of lignin matter. This could be seen in figure 17, which presents per cent removal of lignin matter against different dosage of coacervating agent. It is seen, that, approximately 75 per cent lignin is separated from pressure carbonated liquor, compared to 50 per cent lignin removal from the other one, under similar conditions of coacervation treatment. Coacervation treatment improves lignin separation significantly, as per figure 18.

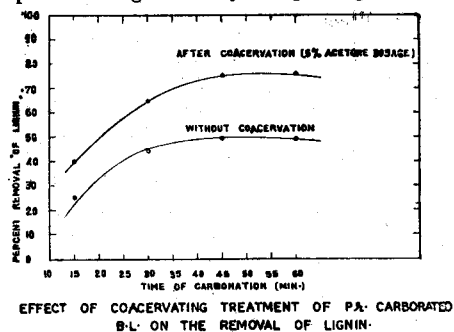


Fig. 18

An examination of the experimental analytical figures of the carbonated b.l., under atmospheric pressure, indicates, that, out of the total amount of organo-soda, approximately 10.5 per cent is hydrolysed during carbonation process, yielding equivalent amount of sodium carbonate.

It is also observed, that, out of the total quantity of organic matter removed by carbonation, approximately 70 to 75

per cent belongs to lignin matter, while the remaining portion of 25 to 30 per cent is basically non-ligneous in nature. The non-lignin part of the black liquor precipitate may be assumed to be mostly carbohydrate degradation products, which come out as a co-precipitate along with lignin, during carbonation process. Simultaneous co-precipitation of lignin and hemi-cellulosic product during black liquor acidification by carbon-di-oxide gas may be due to strong chemical linkages between lignin and hemi-cellulose²¹, which could be existed already in the cellulosic raw material, or they were formed during pulping reactions.

Based on the black liquor carbonation investigations, the following conclusions are made :

- 1) Precipitation efficiency, calculated on the basis of per cent removal of ligno-organic matter from the carbonated b.l., with respect to carbonation time, is improved significantly due to pressure effect, upto 5 kg./cm².
- 2) Higher concentration of black liquor, above 20 per cent t.d.s., concentration, does not affect b.l., precipitation phenomenon quantitatively.
- 3) Black liquor carbonation produces ligno-organic precipitate in the form of highly stable lyophilic colloid, offering extraordinary resistance to its separation by coagulation — centrifugation and sedimentation treatment.
- 4) Lignin matter may be separated effectively from the carbonated b.l., by means of coacervation flocculation treatment, followed by quiescence sedimentation, acetone providing a good coacervating agent.

The optimum carbonation process conditions may be evaluated as follows :

- i) Carbonation pressure
— 4.5 Kg/cm²
- ii) Carbonation temperature
— 80°C
- iii) Black liquor concentration
— 15 to 20 per cent t.d.s.

iv) Carbonation time
— 45 minutes.

- 5) The precipitation efficiency during carbonation process is dependent on the morphological characteristics of cellulosic raw material, with particular reference to lignin content and its distribution within cellulose matrix and the middle lamella.

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