An Investigation in the Recovery of Sodium Bisulphite Cooking Liquor.

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INTRODUCTION

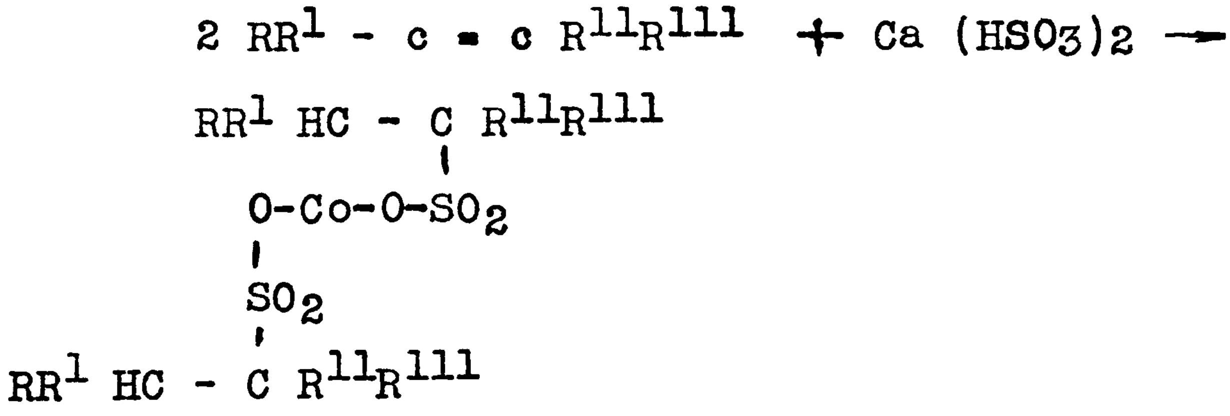
As an introduction to this work, it is pertinent to include a short discussion of the nature and the action of some of the more common acid and neutral cooking liquors on wood. The nature of the action of calcium bisulphite liquor is outlined in particular and a comparison between it and the other cooking liquors is made. The possible advantages to be derived from the use of sodium bisulphite cooking liquor instead of the other industrially used cooking liquors is mentioned. Providing a method of recovery can be developed, the industrial importance of sodium bisulphite cooking liquor is apparent, and therefore work along the nature of this investigation is worthy of consideration both from a scientific and economic viewpoint.

The use of liquors of a sulphite or bisulphite nature either acid or neutral, as the cooking medium in the preparation of wood pulp may be regarded as a modern process. Due to the lack of knowledge of the structure of cellulose the study of the action of cooking liquors on wood has been greatly retarded but during the past twenty years considerable progress has been made. The nature of the action of cooking liquors on wood is now regarded as being of a physical as well as a chemical action.

The specific action of either sulphite or bisulphite liquors is regarded as similar. The differences noted in the products obtained by cooking the same wood with acid liquors containing as base either calcium, magnesium or sodium are explained by different reaction rates of the acids used and local catalytic effects of the base under observation. The differences in the nature of the raw pulp obtained from sulphite liquor using as base calcium, magnesium or sodium is outlined in the discussion of these liquors.

The general mechanism of the cooking of wood with sulphite or bisulphite liquors may be better understood from a study of the action of calcium bisulphite cooking liquor. This is the more common process and the action of the liquor on wood has received considerable investigation. During the past few years, Hägglund and many other investigators have made important contributions to the knowledge of the cooking process. According to Hägglund (23) the sulphite or bisulphite is added to the lignin-carbohydrate complex, forming an insoluble compound which, during the cooking process is hydrolyzed into lignin sulphonic acid and carbohydrates. The soluble sulphonic acid is a stronger acid than the sulphurous acid of the cooking liquor, and it reacts with the base to form a lignin sulphonic salt. The carbohydrates are hydrolyzed to soluble sugars. The speed with which the latter reaction takes place depends upon the temperature, the acid concentration, and the pressure, the temperature being by far the most important factor.

The work of Mitchell and Yorston (34) indicates this action to be one of the addition of the bisulphite to an ethylenic linkage which may be written as:



$$2\ RR^1 - c = c\ R^{11}R^{111} + Ca\,(HSO_3)_2 \rightarrow$$

$$\begin{array}{l} RR^1\ HC - C\ R^{11}R^{111} \\ \qquad\quad | \\ \quad O{-}Co{-}O{-}SO_2 \\ \quad | \\ \quad SO_2 \\ \quad | \\ RR^1\ HC - C\ R^{11}R^{111} \end{array}$$

They also state that the sulphur content of well cooked wood when calculated on a percentage basis agrees with the above structure or a small amount less which might show that there is a small fraction of lignin remaining in the pulp.

Water may be looked upon as a very active reagent under the conditions employed in the cooking process. Since water comprises the main bulk of the liquor, its effect must be considered. The role of water in cooking wood has been studied by Aronovsky and Gortner (1). It was shown that cooking with water at different temperatures for varying lengths of time, has a profound effect upon the various constituents of the wood. Pentoses and pentosens are rapidly destroyed, resulting in the production of appreciable quantities of furfural; lignin although apparently the most stable constituent, undergoes partial depolymerization and the celluloses are broken down to water soluble constituents and to gaseous products. About 37 percent of the total cellulose and 46 percent of the alpha cellulose was destroyed in twelve hour cooks at 186 degrees C. At longer times and higher temperatures the rate of destruction of the alpha cellulose was faster than that of the total cellulose to hydro celluloses.

The Action of Calcium Base Liquors:

The importance of the impregnation of the wood chips during the cooking stage with the base cannot be too greatly stressed. Miller and Swanson (31) state that if insufficient base is present, the ligno-sulphonic acid reacts on the unaltered lignin to form a resin-like product which is very hard to remove. The ligno-sulphonic acid also increases the hydrogen ion concentration and results in dark cooks which are difficult to bleach, the yield is lowered and the fibre is of poor quality. To ensure impregnation of the base, a cooking schedule is followed which enables the diffusion of the calcium bisulphite into the intercellular spaces. The rate of the diffusion varies directly with the temperature and the concentration gradient in the wood itself. Thus a high concentration of the base in the acid is important, giving better yields, less screenings and a shorter penetration period. These observations are confirmed by the work of Gishler and Maass.(20) With calcium the concentration of the base in the acid is limited, as at high concentrations the calcium precipitates out of the liquor in the form of gypsum or calcium sulphate, depositing on the digester lining, the tubing of indirect liquor heaters when used, and on the fibres themselves, the latter resulting in harsh and transparent fibres.

It is the usual mill practice to refer to the strength of the cooking liquor as % total, % free and % combined. The total is the dissolved sulphur dioxide, sulphurous acid and bisulphite; the combined is one half of the bisulphite; and the free is the difference between the total and the combined all calculated as sulphur dioxide on a percent by weight basis. This nomenclature will be used throughout this thesis.

The usual combined carried in calcium base liquors is from 1 to 1.2%, as this amount usually gives a better product providing that care is taken to ensure rapid penetration of the liquor. Miller and Swanson (32) showed that the maximum combined that could be carried using calcium as the base was about 1.6%. Percent combined in calcium base liquors above this value gave no increase in yield.

It is worth noticing that no methods have been suggested for the recovery of the base. Calcium salts as limestone, are sufficiently cheap that complicated chemical recovery processes for the base are not needed. However, with recent legislation in some countries regarding the disposal of the digester waste liquor, some methods are being employed to make use of this by-product liquor.

The Action of Magnesium Base Liquors:

The use of either magnesium bisulphite or sodium monosulphite and bisulphite rather than calcium bisulphite in combination with sulphurous acid in the cooking of wood, necessitates the establishment of some means of chemical recovery of the base. Magnesium or sodium base salts are too expensive and thus prohibits their use without the recovery of the base. Besides the recovery of the base, there is also recovered the heating value derived from the burning of the carbonaceous matter in the liquor, and it is hoped to obtain enough heat from this source to supply most of the steam used in cooking.

In addition to the recovery of the heating value of the waste liquor, the use of magnesium bisulphite liquor in conjunction with sulphurous acid permits the use of higher concentrations of the base, as the liquor is more stable due to the greater solubility of the sulphite and sulphate, resulting in better penetration of the liquor into the wood. Magnesium base liquors seems to possess better penetrating power for the same change in concentrations than calcium liquors. The encrusting matter when formed is milder and is more easily washed out of the pulp giving a product which is softer and whiter than calcium base liquors. The fibres are easier to bleach than those of calcium base liquors and due to the higher combined carried gives better fibre strength but necessitates a higher cooking temperature to give the same cooking cycle. The rate of reaction follows closely that of calcium liquors and reaches a maximum at a combined of 3%. The other qualities of the pulp derived from the liquor such as strength, yield and opacity are still under investigation but are said to be equal to, if not superior to, pulp obtained from calcium base liquors.

The Action of Ammonium Base Liquors:

It has been found quite feasible, on a laboratory scale, to produce excellent pulps by using ammonium bisulphite as the base instead of calcium bisulphite. The ammonia is easily recovered due to its volatility but recovery costs are high due to the large amount of liquor which must be evaporated or distilled. The use of ammonium base liquors gives shorter cooks at higher temperatures than employed using calcium base liquor and a better product is derived. The use of ammonia also permits better control as to the type of fibre obtained and it is stated that pulp may be obtained resembling anything from the easily bleached calcium bisulphite pulp to kraft pulp. Other advantages are freedom from encrustants, uniform fibre length and small percentage of screenings due to better penetration. Houghton (27) reports higher alpha cellulose and mullen test than with calcium liquors. Hepher and Jahn (25) on cooking White Fir report high yield and a more rigid removal of lignin, while the cooking of Douglas Fir gave low yields.

The Action of Sodium Base Liquors:

The use of sodium bisulphite cooking liquors possesses even to a greater extent the advantageous properties of magnesium base liquors. Advantages as to fibre strength are still in dispute but it is agreed that whiter fibres are obtained by the use of sodium base liquors than are obtained from either magnesium or calcium base cooking liquors. Experimental work by Hägglund (23) and others lead one to expect much better yields with lower lignin content, while that of Cable (11) gave the same yield but much better strength, flexibility, opacity and other qualities of fibre using sodium base liquor than that obtained from calcium bisulphite liquor.

Considerable work has been done on the use of sodium sulphite liquor. This liquor is weakly alkaline or nearly neutral. Cross (17) found that the hydrolytic action of neutral salts was weaker than the sulphurous ion and required a higher cooking temperature. The work of Brot and Herschel (14) on cooking cereal straw with sodium sulphite showed that the yield decreased to a minimum at 4% solution and then increased, which signifies that sodium sulphite, because hydrolysis is suppressed, inhibits the erosive action on the fibre and exercises a protective action. The fibres are lighter in colour than those obtained by sodium hydroxide cooks and have strength representative of kraft. The cooking process is free from noxious odours and unlined iron digesters may be used.

Rawlings and Staidl (37) from their investigations in the cooking of aspen sawdust with sodium sulphite liquor, obtained a more complete removal of the lignin and they also concluded that the action on pulp in the presence of free acids or alkali is of a hydrolytic nature. Johnsen (28) confirmed their findings as to higher yield, the bleaching quality of the pulp, and the quality of the fibre. Statements of Johnsen and those of Miller and Swanson (33) suggest the use of sodium sulphite liquor in the cooking of resinous woods such as southern pine. Brauns (10) also suggests the possibility of the sulphite pulping of Canadian Jack Pine using a sodium sulphite liquor and employing the same operating conditions as used in the calcium bisulphite process.

The use of sodium sulphite alone and in combination with sodium hydroxide has been successful in the commercial Keebra process, where the liquor after re-use is either discarded or is recovered in conjunction with a sodium hydroxide pulping process.

The use of sodium base liquors is advocated on the basis of higher yields, better quality of pulp, and the possibility of using species of woods that are not suitable for the present calcium bisulphite process. The process is capable of yielding a very strong pulp suitable for various purposes but the problem of recovering the sodium base has apparently not been satisfactorily solved except in mills where a combination of this process with a modified sodium hydroxide pulping process has been found practicable.

LITERATURE REVIEW

Due to the similarity in the action on wood and the general mechanism of the recovery of waste liquors from cooks using sodium sulphite and sodium bisulphite cooking liquors, it is desirable to review the literature on the use of both liquors.

The Action and Recovery of Sodium Sulphite Cooking Liquors:

As early as 1880 reference is found to the use of sodium in a neutral form and with or without the combination of sulphurous acid. Cross and Bevan (16) list Cross's invention of 1880 in their classification of the chemical processes for disintegrating wood. They state that the hydrolyzing action of neutral sodium sulphite is more feeble than that of bisulphites and requires a higher temperature, viz 160 degrees to 180 degrees C, for successful pulping of wood, adding that in the presence of ligno-cellulose undergoing decomposition, the sulphite is dissociated, - the base going to the acid group and the acid sulphite to the aldehyde groups of the cellulose.

By the use of sodium sulphite Schact (40) claims an increase of 15 to 25% in yield over that obtained with the use of calcium bisulphite liquor. The liquor is prepared by nearly saturating the crude recovered soda solution with sulphur dioxide and then causticizing the residual carbonates. The liquor consists therefore of a mixture of sodium sulphite, sodium thiosulphate and sodium hydroxide. Sodium hydroxide is necessary to a certain extent in order to deal with the silica and alumina of the raw materials and it should not exceed the proportions required for this purpose.

C. A. Braun (9) proposes the use of sodium thiosulphate together with sodium sulphide. He claims a process for making semi cellulose from highly lignified plants such as wood. He also proposes the use of some sodium hydroxide in addition to the mixture of sulphide and sulphur. There are some actual chemical data in connection with the use of neutral sodium sulphide for the delignification which shows that it reacts somewhat differently from the other delignifying agents. This work was done by Rawlings and Staidl (37) and has been reviewed by Hawley and Wise (22). It is shown that when cooking wood under constant temperature and time conditions but varying the sodium sulphite content from 12.8 to 128.9% based on the weight of the wood, the cellulose remains high and nearly constant but that the lignin is reduced from 21.83% in the original wood to 9% with low concentrations of sulphiteto finally 5.2% with the higher concentrations. When an attempt was made to remove more lignin by raising the temperature, the cellulose was rapidly attacked and finally the cellulose yields are lower than those of the soda process, although the more severe cooking with sodium sulphide never gave less than 3% residue of lignin.

Very good work of a similar nature on the cooking of wood with sodium sulphite under varying conditions of concentration and temperature was done by Aronovsky and Gortner (2). Their work was carried out on aspen sawdust, and they include in their report the method of analysis and show the effect of the cooking liquor on the organic matter throughout the cook and the distribution of the salts formed. They found that the sodium thiosulphate content of the waste liquor was small, as was also the content of sodium sulphate and sodium sulphide and that the concentration of the latter two chemicals decreased directly with the cooking time, till frequently there was no sodium sulphide in the waste liquor.

The recovery of sodium sulphite from spent sulphite liquors has been studied by Pierre A. Barbou (3). In one of his patents he specifies the treatment of the spent liquors with sulphuric acid. Calcium bisulphite is added to the sodium sulphate obtained and then treated with sodium hydroxide or sodium carbonate. The organic substances are precipitated by the addition of the sulphuric acid and are separated and destructively distilled. The spent liquor may be aerated before treatment with the sulphuric acid in order to oxidize the unchanged sulphite. The second method suggested is the treatment of the spent liquors with an alkaline earth base such as calcium. Calcium sulphite is precipitated. The liquor is then treated with a calcium bisulphite liquor prepared from the calcium sulphite previously obtained and the insoluble organic compounds of calcium are precipitated and may be distilled. A mixture of sodium sulphite and bisulphite remain in solution. The solution is neutralized with sodium hydroxide.

George A. Richter (38) of the Brown Corporation has been investigating the use of sodium sulphite and the recovery of the waste liquor on a commercial scale. The nature of his work was reviewed from the reports in the Chemical Abstracts. The waste liquor is smelted in a reducing atmosphere and dissolved in water and carbonated, the sodium sulphide being converted to sodium carbonate. The carbonated solution is treated with a water solution of an oxidizing agent such as chlorine water and the unconverted sodium sulphide is oxidized to sodium sulphite or sodium sulphate. The solution is then acidulated with sulphur dioxide to form a fresh liquor.

This same general scheme is also proposed by Walter F. Hoffman (26).

The Keebra Process:

Since 1920 the use of sodium sulphite both alone and in combination with sodium hydroxide has been given an added impetus through the efforts of Bradley and McKeefe (6). For the application of the process woods are divided into three classes: the hardwoods; softwoods carrying little resin; and softwoods containing more resin, and the process is modified in accordance with this classification.

For hardwoods the cooking liquor used contains neutral sodium sulphite alone. For the second class, softwoods containing a small amount of resin, a moderate amount of sodium hydroxide is used with the sodium sulphite; while for those of the third class where the woods contain much resin, a greater amount of sodium hydroxide is used together with sodium sulphite. Sodium hydroxide is recommended to be used after the wood has been subjected to the action of neutral sodium sulphite alone. By this process it is claimed that is is not only possible to pulp a mixture of woods of like character satisfactorily but materially higher yields are obtained than is customarily obtained by other methods. Instead of 38 to 45% of the weight of the wood being obtained as pulp which is customary by the other methods, by this process there is obtained from old poplar wood 61%; new poplar 67%; birch 60% and hemlock 50%.

While the sodium content of the residual liquor can be recovered for re-use, it is possible to use the blow liquor over again with the addition of a further amount of sodium sulphite. It is stated that the same cooking liquor has been used for as many as five successive charges. The quantity of sodium sulphide to be used in the case of hardwoods is from 35 to 45% based on the weight of the wood, pressures used from 110 to 140 pounds per square inch and the cooking time from four to six hours.

The waste liquor from the digester usually contains sodium sulphide in low concentrations which is converted to sodium thiosulphate in the usual recovery process. Sodium thiosulphate has injurious effects on the fibre although Clark (14) states that up to 5% of the total soda as sodium thiosulphate may be used. This figure is questioned by Drewson (19), who states that sodium thiosulphate should be avoided altogether.

Chidester and Billington (12) also point out that mixtures of sodium monosulphite and bisulphite produce inferior pulps of low yields and that monosulphite liquors alone produced the highest strength but low yields.

Other difficulties pointed out in the recovery of the waste liquor are the sulphuric acid attack on the evaporators, the corrosion of the condensation equipment and vacuum pumps due to sulphides and the sulphur compounds recovered in the fused salts varied as to quality and activity.

An indication of the methods of recovery proposed by Bradley and McKeefe can be found in the abstracts (7) of the patents which they have filed, and articles (8) that they have written. The process provides for the following steps in the recovery of the spent liquor from sodium sulphite cooks.

(a) passing the spent liquor through hot furnace gases thereby evaporating water, cooling the gases and recovering a portion of the oxy-sulphur constituents carried by the gases.

(b) introducing into the furnace organic matter and sodium-oxy-sulphur compounds that were contained in the spent liquor, burning the organic matter to produce heat, recovering soda and sulphur as sodium carbonate and sodium sulphide and producing hot furnace gases that carry oxy-sulphur constituents including sulphur dioxide.

(c) Dissolving the solid residue to produce an alkali solution containing the recovered sodium carbonate and sodium sulphide.

(d) treating this alkali solution with solid sodium bicarbonate obtained in step (h) in amount sufficient to convert the sodium sulphide to sodium carbonate.

(e) removing the hydrogen sulphide from solution,

(f) burning the hydrogen sulphide to sulphur dioxide.

(g) sulphiting the solution resulting from (d) and (e) at a temperature of 60 degrees C. to produce sodium sulphide and sodium bicarbonate in solution.

(h) separating the precipitated sodium bicarbonate from solution.

(i) recovering the sulphur dioxide produced from (f) and the sulphur dioxide carried by the furnace gases after (a) and combining it with sodium carbonate contained in the liquor resulting from (d) and (e).

(j) using the recovered sulphur dioxide in the form of sodium sulphide cooking liquor to digest cellulosic raw materials.

The Action and Recovery of Sodium Bisulphite Cooking Liquors:

The first reference to the use of sodium bisulphite in the pulping of wood is given by C. Keller (29) as early as 1871 or 1872. Keller reports that it gave a somewhat hard product which could be rubbed in a mortar to a fiber measurably whiter in colour than given by other common pulping agents. V. B. Drewson and L. F. Dorenfeldt (18) in an Austrian patent covered the preparation of sodium bisulphite by the addition of sodium sulphite to calcium bisulphite solution. The precipitated calcium sulphate could, it was suggested, be used as a paper filler.

Clifford (15) has conducted a series of experiments and states that cooks using sodium base liquors will bleach easier and give a better quality of pulp. Thus, for spruce chips using calcium base liquor, the bleach requirements are 14 to 16% while for the same wood using sodium base liquor would require 8% bleach.

Eric Hägglund and Fritz Hedborg (24) state that a good yield of sulphite pulp with satisfactory strength may be obtained from quick growing pine using a cook in two stages with sodium bisulphite and sulphurous acid. However, with slow growing woods with a large amount of resin and pronounced heartwood the same process will give a very dark cook. Hägglund (23) also states that in cooking wood with sodium bisulphite, lowering the acidity increases the time of cooking. He states that using sodium bisulphite cooking liquor, a white pulp is obtained with a yield of 60% based on the initial weight of the wood as compared to 55% yield containing 7 to 8% lignin using calcium base liquors under the same cooking conditions.

In an article by Myron W. Black (5) on the use of the sodium bisulphite process, he suggests the following advantages to be derived from the liquor; the use of wood of a more resinous nature, the disposal of waste liquors, and the recovery of a part of the steam requirements of the mill. He states that sodium bisulphite as a cooking liquor is being used commercially in Norway and gives a translation of an article on the recovery of the waste liquor by Gustef Haglund (5).
The process of digestion is carried out in two separate stages.
(1) ordinary treatment with sulphite or bisulphite which does not contain any excess sulphur dioxide. The bisulphite combines with the lignin without any disintegration.
(2) the quantity of sulphur dioxide required for disintegration is added in the form of waste liquor from a previous digestion.

The waste liquor is evaporated to the desired consistency, incinerated and purged from sulphides and sodium thiosulphate by a special process. The saline mixture thus obtained consists of mainly sodium sulphate, sodium carbonate and sodium sulphite which have to be converted into bisulphite and sulphite.

The saline mixture recovered from the regeneration of the liquor is dissolved in water and the proper quantity of finely crushed limestone is added. After this the resulting suspension is pumped through a battery of several towers or reaction chambers placed along side of each other. Here it encounters a current of sulphur dioxide gas, through the action of which the limestone and sodium sulphate are converted into sodium bisulphite and gypsum or sodium sulphate which is later precipitated. Sodium carbonate and sulphite are simultaneously converted into sodium bisulphite. After separation from the gypsum, the liquor is ready for use.

General Articles on the Conversion and Recovery of Sodium Sulphide:

One of the difficulties encountered in the recovery of waste cooking liquors from either a sodium sulphite or sodium bisulphite pulping process is the formation of sodium sulphide and a partial conversion of the sodium sulphide to sodium thiosulphate in later stages of recovery of the waste liquor. The action of sodium sulphide on wood has received some investigation, but its effect in connection with the pulping of wood by sodium bisulphite liquor has not been reported.

In an article by J. H. Ross (39) it is stated that it is a generally accepted view that whereas the addition of sodium sulphide to a solution of sodium hydroxide causes a more rapid pulping of coniferous woods, the substitution of sodium sulphide for more than a certain proportion leads to a diminution in the rate of cooking but that this is only true if the cooking conditions are kept along the lines of commercial practise. Thus, the use of sodium sulphide in cooking is limited to narrow undefined limits for a fixed operating condition. Dr. Ross also states that the addition of sodium sulphide to sodium hydroxide cooking liquor causes a vast increase in its delignifying power and that sodium sulphide exerts a protective action on the carbohydrates formed during cooking.

The physical chemistry of the reactions of oxidation of sodium hydrosulphide, sodium sulphide, sodium thiosulphate, and sodium sulphite, giving the order of the reaction and a discussion of the same is given in an untranslated Russian article by S. A. Shehukarev and E. M. Kireeva - Tuzulakhva (42).

A method of converting sodium sulphide to sodium carbonate in the recovery of sodium base liquors is given in an article by P. S. Billington, C. H. Chidester, and C. E. Curran (4). The method consists in the evaporation and burning of the spent liquors followed by a treatment with sodium bicarbonate, to convert the sulphide formed in the burning to sodium carbonate which can be used for the preparation of fresh cooking liquor. The article includes a suggested method of application of the process as presented together with a theoretical chemical balance on the various stages.

Resumé and Necessity for Further Investigation:

The investigations reported of the use of sodium bisulphite liquor for cooking wood in the manufacture of pulp show that a better yield of a whiter pulp with a lower bleach consumption may be obtained than is customary by the calcium bisulphite process. In addition, certain woods such as Canadian Jack Pine and other resinous woods are known to give a very satisfactory pulp, using sodium as the base in the cooking liquor, which fail to give a good pulp by the sulphite process in which calcium is used as the base. The strength of the fibre obtained from sodium bisulphite cooks is as good or better than that obtained from calcium bisulphite cooks.

The problem of the recovery of the sodium base from the waste liquor is necessary before the process will be commercially feasible and as yet no satisfactory recovery method has been established. It is apparent that in any recovery process that is found to be feasible the waste liquor will be evaporated and ashed to a smelt. Thus the problem of the disposal of the waste liquor from the pulping operation will be solved, and also the production of a large portion of the steam requirement of the mill will be possible.

Methods suggested for the recovery of the base from sodium bisulphite liquor are incomplete but indicate the recovery of the sodium in conjunction with a modified sodium hydroxide cooking process, or by the formation of a carbonate and subsequent recovery. Both of these methods are indirect and troublesome and as such make the sodium bisulphite cooking process impracticable. The recovery process proposed by Gustef Haglund (5) has not been satisfactorily accomplished and is still under investigation.

The use of sodium bisulphite liquor in the cooking of wood has certain advantages over other cooking processes being used, and as such investigations in the recovery of the waste liquor are important both from a scientific and economic viewpoint. Before any recovery process may be suggested it is necessary to determine the inorganic constituents present in the waste liquor during various stages of a general recovery scheme. Reports of this nature are not given in the literature, and as a result, further investigation with this object in view should be made, with the subsequent establishment of a process to recover the waste sodium bisulphite cooking liquor.

STATEMENT OF THE PROBLEM

The proposed field of this investigation was to determine the main inorganic constituents present in the waste sodium bisulphite cooking liquor during the various stages of a standard method of recovery rather than to develop any actual recovery process. It is necessary to determine the various constituents present in the waste liquor and the changes which might be expected during evaporation, ashing and smelting of the waste liquor before proposing any recovery scheme. As technical methods of analyses for the inorganic constituents present in a sodium base liquor suggested in the literature are still under examination, it is the purpose of this investigation to develop a satisfactory method of analysis of the liquor as well as to determine quantitatively the inorganic constituents present.

The proposed general method of recovery is similar to that used in the soda or kraft pulping process and is illustrated in figure 1. Briefly the process consists in the evaporation of the waste liquor from the cooking process to 50% solids, and the absorption of the gases consisting mainly of sulphur dioxide in a sodium hydroxide absorption tower. The strong black liquor obtained is ashed in a high temperature pyrex tube furnace under various oxidation and reduction atmospheres and the gases derived are absorbed in the sodium hydroxide tower mentioned above. The sodium hydroxide is converted to sodium bisulphite by the action of the sulphur dioxide recovered and additional sulphur dioxide. The sodium bisulphite thus derived is added to the sodium bisulphite recovered directly from the waste liquor and is used as fresh cooking liquor. The black ash obtained from the ashing stage is smelted in crucibles in an electric furnace and the smelt obtained is analyzed.

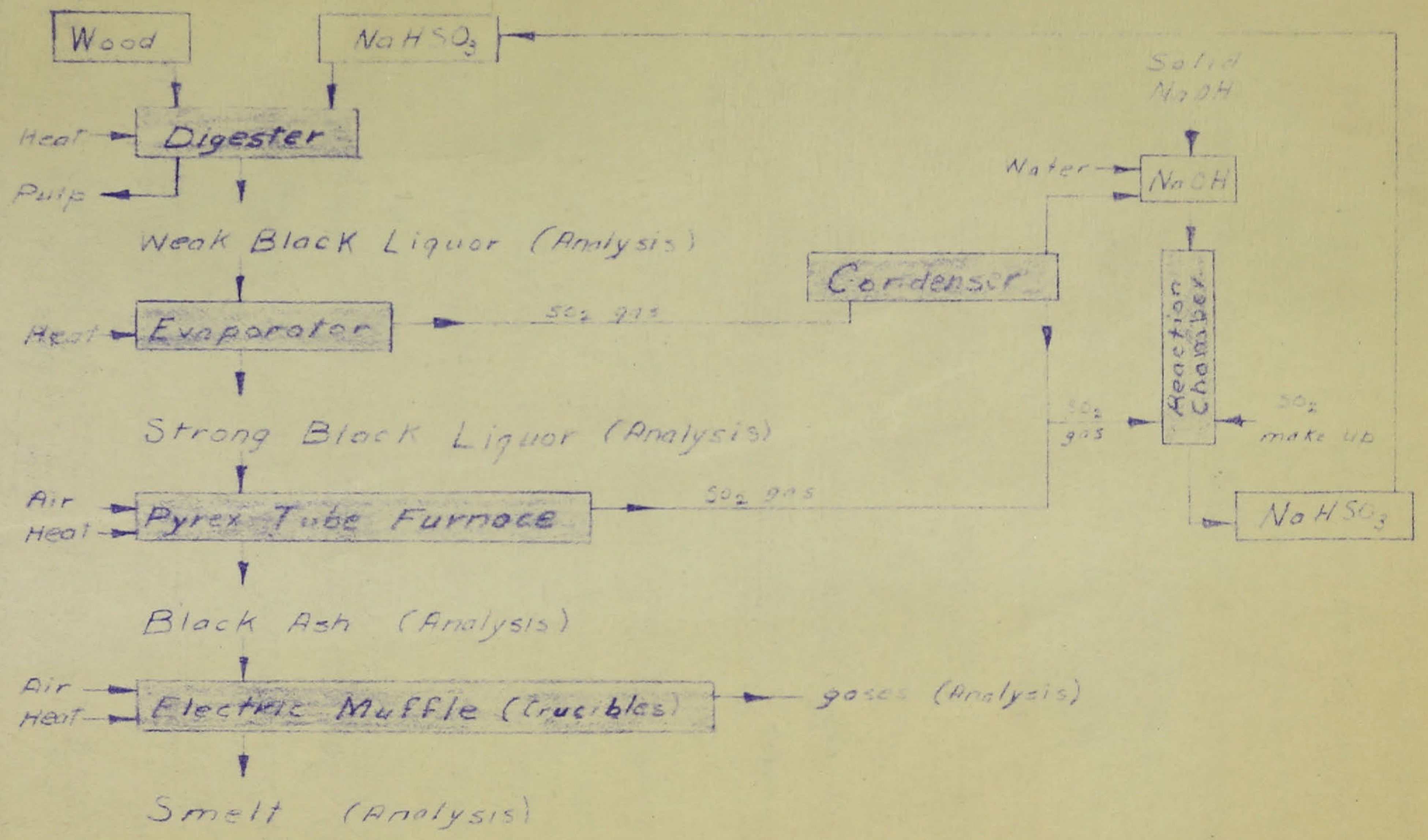


Figure 1: Flow Sheet illustrating a general method of Recovery of $NaHSO_3$ Waste Liquor

EXPERIMENTAL WORK

The Nature of the Investigation:

As the initial work necessitated the development of a method of analysis, it was decided to use a liquor which could be easily obtained and which would resemble the sodium bisulphite waste liquor as to properties and chemical constituents. Calcium bisulphite waste liquor to which sodium sulphide had been added, was first used in the evaporation stage, and analyses were made of the liquor before and after evaporation of 50% of the water content of the liquor. This was followed with the use of sodium hydroxide waste pulping liquor which had been saturated with sulphur dioxide gas. Various methods of analysis were attempted of the liquor before and after evaporation but due to the difficulties encountered, and the nature of the product on evaporation it was decided to use sodium bisulphite waste liquor.

Sodium bisulphite waste liquor was obtained from a number of cooks made on spruce chips using sodium bisulphite cooking liquor. Four books in all were made, the liquor was collected separately and the raw pulp obtained was discarded. Various methods of analysis of the waste liquor were attempted and compared as to efficiency and ease of analysis. The strong waste liquor obtained from the evaporation stage was ashed in a pyrex tube furnace and an analysis was made on the ash obtained. The temperature at which the strong liquor could be ashed and also the smelting temperature of the ash was roughly determined.

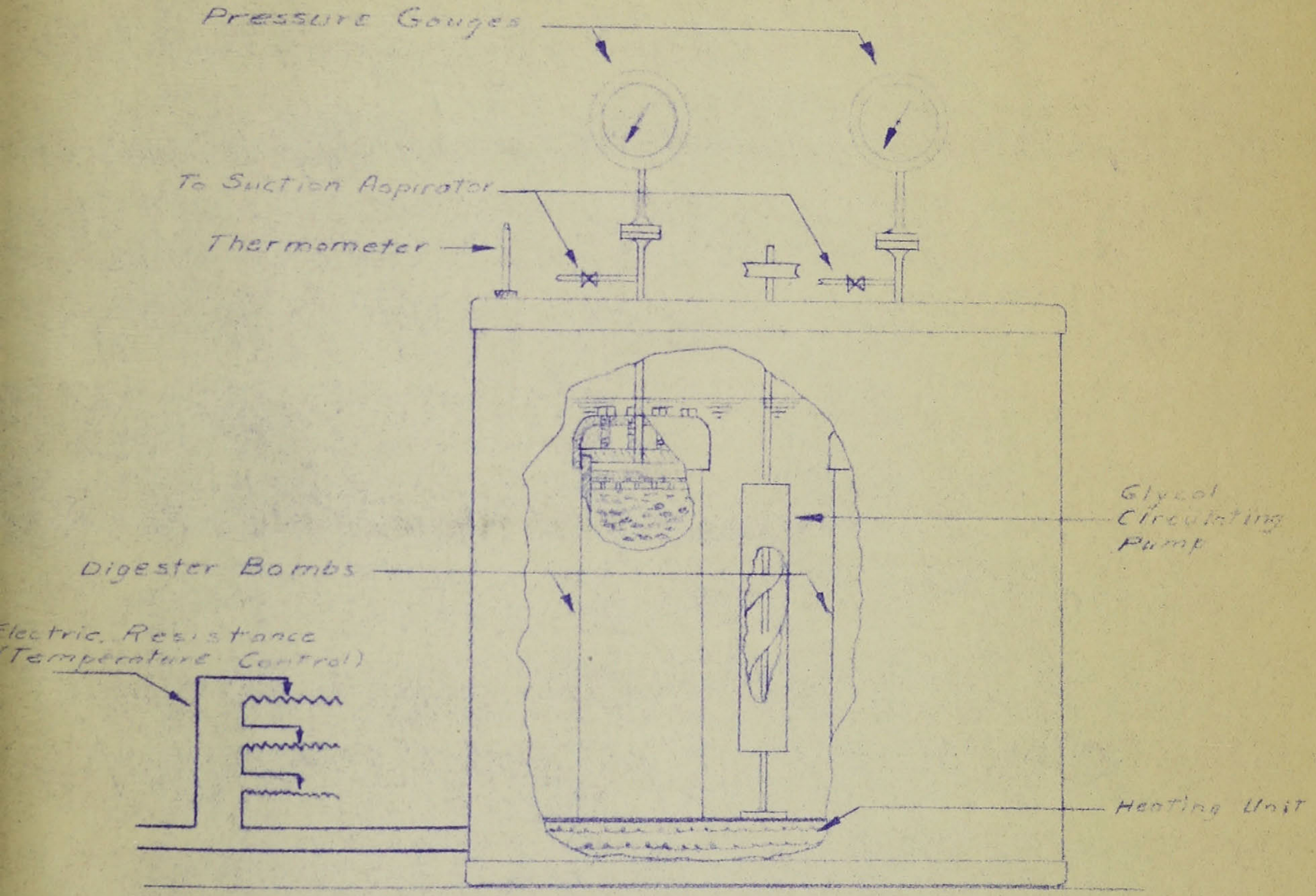


Figure 2: The Cooking Equipment
(Forest Products Laboratory)

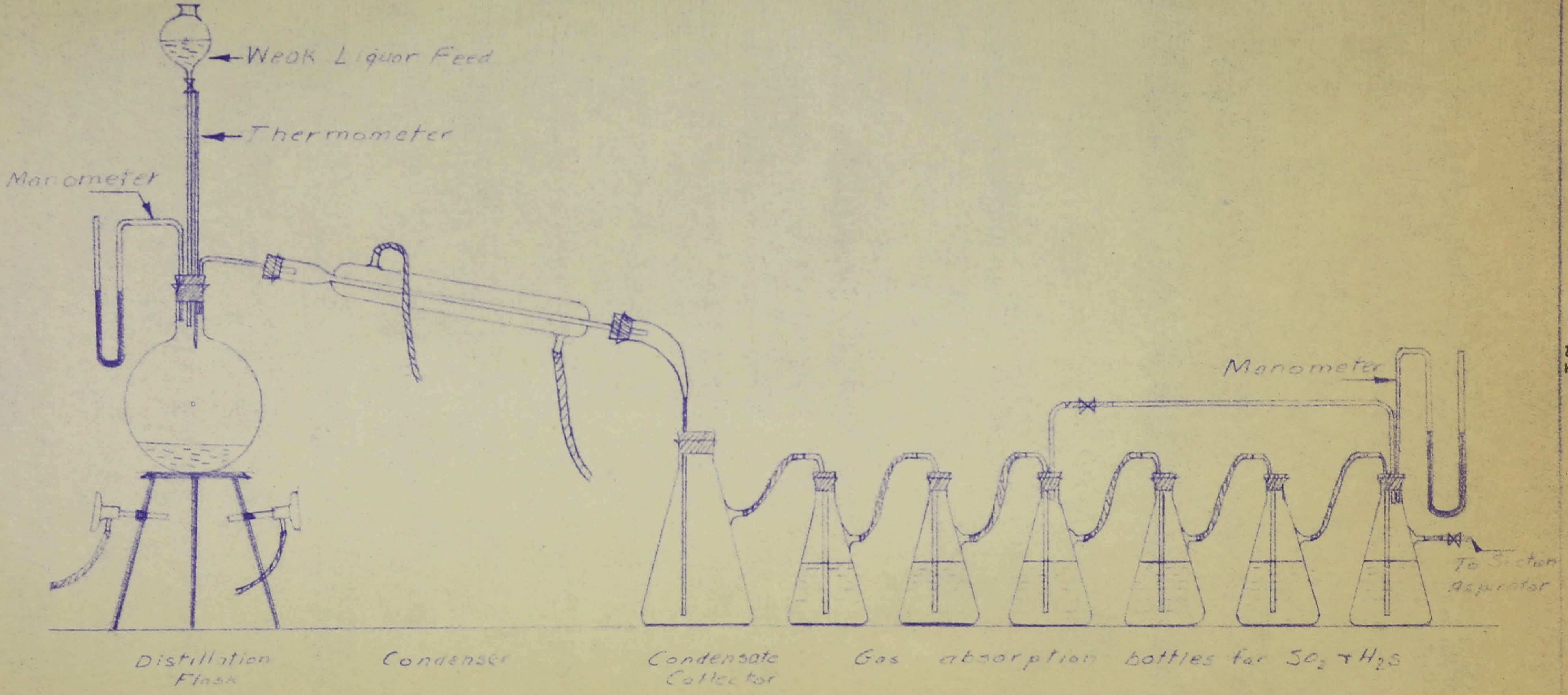


Figure 3: The Evaporating Apparatus and Equipment.

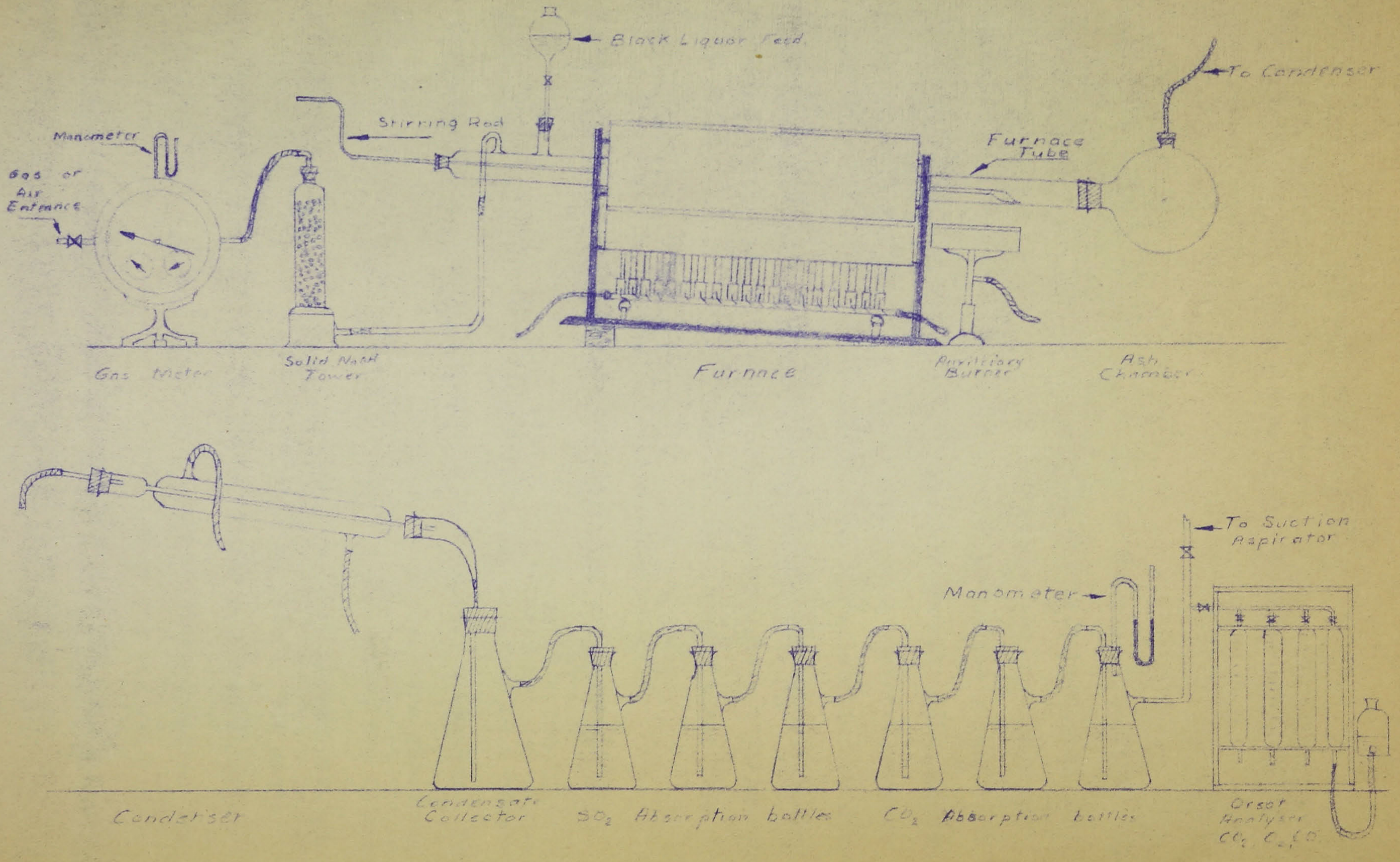


Figure 4: The Combustion Furnace and Equipment.

APPARATUS AND EQUIPMENT

The following is a description of the apparatus used during this investigation:

1. The cooking equipment - figure 2.

The small stainless steel digesters in the Forest Products Laboratory were used to cook the wood in the preparation of the sodium bisulphite waste liquor. There are two digesters of about three litre capacity in a common diethylene glycol bath which is heated by an electrical heating element. The temperature of the cook was observed by means of a standard mercury thermometer immersed in the glycol, and was controlled by means of a resistance coil in series with the heating element. The pressure was observed on a standard pressure gauge attached to each digester, and was controlled by relieving the gas from each digester.

2. The evaporating apparatus and equipment - figure 3.

The evaporation of the liquor was carried out in a two litre distillation flask, the temperature being observed on a mercury thermometer, and the pressure read on a mercury manometer. The heat was obtained from two open Bunsen burners. The gases and water were first passed through a Liebig condenser, the condensate collected, and the uncondensed gases then passed through a series of absorption bottles containing water. The gases which contained mostly sulphur dioxide and hydrogen sulphide were absorbed in the water. The vacuum maintained during the evaporation was obtained from an aspirator and was applied to the sixth absorption bottle as illustrated. The vacuum applied was limited by the rate of the bubbling of the gas in the absorption bottles.

3. The combustion furnace and equipment - figure 4.
The furnace proper was made of high temperature pyrex glass tubing, one and a quarter inches in diameter and five feet long. The centre portion for about three feet of length was heated by a group of open burner flames from a combustion furnace, with additional auxiliary open flames as illustrated. The furnace was so arranged that it was air sealed with openings at one end for continuous feed for air or gas for combustion, and for an agitator-rod for breaking up the ash; and at the other end was an outlet for the products of combustion. The seal between the furnace proper and the ash chamber was made with asbestos fibre putty. The air or gas for combustion was measured by means of a standard gasometer. Between the gasometer and the furnace was placed in series a tower filled with solid sodium hydroxide to protect the vanes of the gasometer from sulphur dioxide fumes in case the gases of combustion backed up the furnace.

The ash could be either left in the furnace or pushed into the glass collecting chamber. The latter was also heated to drive off any products which might condense. The gases passed through a Liebig condenser, the condensate being collected in a flask, thence in series through three absorption flasks containing 0.1 N iodine solution for the absorption of sulphur dioxide gas, followed by three flasks containing 0.1 N sodium hydroxide for the absorption of carbon dioxide. The residual gases were intermittently analysed for carbon dioxide and oxygen by means of a standard Orsat gas analyser. Suction was applied to the apparatus as illustrated by means of an aspirator, to draw the gases through the equipment. The pressure at the furnace and at the end of the absorption flasks were read by means of a water and mercury manometer.

ANALYTICAL METHODS

A. Analysis of gases.

The following analytical methods of analysis for the quantitative determination of the gases derived from the evaporation and ashing of the waste liquor were used in this work and are an adaptation of methods outlined by Scott (41) and Lunge and Ambler (30).

1. (a) Determination of hydrogen sulphide and sulphur dioxide absorbed in the condensate from the evaporation and the ashing stage.

There are no simple methods to accurately determine the amount of hydrogen sulphide and sulphur dioxide in the presence of one another and the following method which was used in the determination of these gases appeared more satisfactory than the other methods attempted.

Hydrogen sulphide:

To an aliquot of the undiluted condensate run in from a burette an amount of ammoniacal silver nitrate solution as close to the saturation point as can be estimated. Mix the contents of the beaker rather vigorously for 2 or 3 seconds. This causes the black silver sulphide to separate in thick lumps from the clear solution. Add another drop of the silver nitrate solution from the burette. If this forms a heavy precipitate where the drop comes in contact with the solution, add a few more drops, give the beaker a shake, and repeat the additions until only a faint cloud appears in the clear solution. The last drop necessary to complete the precipitation forms only a faint cloud in a clear solution.

Ammoniacal silver nitrate solution - Dissolve 87.07 grams of pure silver nitrate in water.

Then add 250 ccs of concentrated ammonium hydroxide and dilute to 1 litre. 1 cc of this solution is equivalent to 0.0087 grams of hydrogen sulphide.

Sulphur dioxide.

Pipette 25 ccs of the condensate into a beaker, add 100 ccs of distilled water and titrate with 0.1 N iodine, using starch indicator to determine the end point. 1 cc of 0.1 N iodine is equivalent to 0.0032 grams of sulphur dioxide.

(b) Determination of hydrogen sulphide and sulphur dioxide absorbed in the water in the absorption system of the evaporation stage.

A similar analytical method as outlined above was used in determining the hydrogen sulphide and sulphur dioxide absorbed in the water in each of the bottles used in the absorption train of the evaporation stage.

2. Determination of sulphur dioxide from the ashing stage.

The sulphur dioxide unabsorbed in the condensate is absorbed in three absorption bottles in series containing 0.1 N iodine. On completion of a run, an aliquot sample of each bottle is back titrated with 0.1 N sodium thiosulphate using starch indicator. The sulphur dioxide absorbed is calculated from the iodine neutralized. 1 cc of 0.1 N iodine is equivalent to 0.0032 grams of sulphur dioxide.

3. Determination of carbon dioxide from the ashing stage.

The gases from the furnace after passing through the condenser and the three absorption bottles containing 0.1 N iodine for absorption of the sulphur dioxide, pass through three absorption bottles in series containing 0.1 N sodium hydroxide for the absorption of the carbon dioxide gas. On completion of the run an aliquot sample of each bottle is back titrated with 0.1 N hydrogen chloride using phenolphthalein as indicator. The carbon dioxide absorbed is calculated from the sodium hydroxide neutralized. 1 cc of 0.1 N Sodium hydroxide is equivalent to 0.0440 grams of carbon dioxide using phenolphthalein as indicator.

4. Determination of the residual gases from the ashing stage after determination of the hydrogen sulphide, sulphur dioxide and carbon dioxide content.

The gases from the furnace after removal of the condensate containing absorbed sulphur dioxide and hydrogen sulphide, and the absorption of the residual sulphur dioxide and the carbon dioxide, go to an aspirator. Between the last absorption bottle and the aspirator and in parallel with the latter is an Orsat gas analyser. Samples of the gas are drawn off intermittently and a volumetric analysis made for any unabsorbed carbon dioxide, oxygen and carbon monoxide. The carbon dioxide remaining in the gas as well as any unabsorbed sulphur dioxide and hydrogen sulphide, are absorbed in a 50% solution of potassium hydroxide. The oxygen is absorbed in an alkaline solution of pyrogallic acid and the carbon monoxide in a solution of ammonium chloride and cuprous chloride. The nitrogen is determined by difference and the quantitative content of the gases for a given run are calculated on a nitrogen basis, as the amount of air going to the furnace is measured by means of the gasometer.

B. Analysis of the strength of sodium bisulphite cooking liquor.

The strength of the cooking liquor is expressed in the industrial nomenclature of % total, % free, and % combined. As outlined previously, the % total is the sulphur dioxide, sulphurous acid and the bisulphite; the % combined is one half of the bisulphite; and the % free is the difference between the % total and the % combined, all calculated on a sulphur dioxide basis as percent by weight. The analysis of the strength of the liquor was made using the method of determination outlined by G. V. Palmrose (35).

The method outlined by Palmrose is as follows: To a 250 ccs erlenmeyer flask containing 75 ccs of distilled water, add 2 to 4 drops of methyl-red indicator solution and 2 ccs of starch-potassium iodide solution. Pipette 2 ccs of the sample into the flask and titrate with 0.125 N potassium iodide solution. Avoid shaking the flask until the colour begins to appear. The % total is 0.2 times the ccs of 0.125 N potassium iodide used in the titration. One drop of 0.125 N sodium thiosulphate solution is added to decolourize the blue of the starch, and the same sample is titrated with 0.125 N sodium hydroxide solution. The titration is complete at the point at which one drop of the sodium hydroxide solution turns the sample an orange or yellow colour. The apparent % free is 0.2 times the ccs of 0.125 N sodium hydroxide. The % Combined is obtained by difference between the % total and the % free.

C. Analytical methods of analysis used in the determination of the inorganic constituents in the waste liquor before and after evaporation.

Analysis of calcium bisulphite waste liquor by A. M. Partansky and H. K. Benson (36).

The following analytical method, which was attempted to determine some of the constituents present in the treated calcium bisulphite waste liquor, was adapted from the method of Partansky and Benson. A complete analysis as outlined by them was not attempted on this liquor and only the procedure as followed is outlined.

Total Solids:

Accurately pipette a 25 ccs sample of the waste liquor into a tared 50 ccs porcelain crucible and place in a 105°C oven for twelve hours. Cool in a desiccator and weigh. Report as grams per litre and % by weight. Save the sample for further analysis.

Residue on ignition (as sulphate):

Ignite thoroughly the sulphite waste liquor solids obtained from the above determination with a good Mecker burner for about fifteen to thirty minutes, cool; moisten with a little water; and add carefully 1.5 to 2 ccs of concentrated sulphuric acid (an excess) and evaporate to dryness on a hot plate under a hood. After the white fumes of sulphur trioxide cease, ignite on a Mecker burner for five minutes, cool in a desiccator, and weigh as residue on ignition. Report as grams per litre and percent.

Total Sulphur:

The total sulphur is determined by the method of Pollock and Partansky. Place from 1.5 to 2 ccs of the sulphite waste liquor diluted to 5 ccs with water in a 25 ccs porcelain crucible, add 1 cc of concentrated sodium hydroxide solution and

5 to 7 ccs of saturated potassium permanganate solution. Take up the colourless residue with hot water and filter into a 600 cc beaker, washing thoroughly, dilute the filtrate to 400 ccs, adjust the acidity and precipitate the sulphates with barium chloride in the usual way. Report as grams of sulphur per litre. Calculation - 1 gram of barium sulphate = 0.13736 grams of sulphur.

Organic matter and potassium permanganate:

Pipette 10 ccs of 0.1 N potassium permanganate solution and 1 cc of saturated sodium hydroxide solution, add 5 ccs of the waste liquor diluted to 1000 ccs, and bring the volume to 110 ccs. Boil the solution for thirty minutes on a water bath. After digestion of the sample add 25 ccs of Timmerman-Reinhardt solution, and back titrate with 0.1 N potassium permanganate solution. The difference between the value obtained and a titration on the solution without any waste liquor is the ccs of 0.1 N potassium permanganate solution consumed. Report as grams of oxygen consumed per litre of waste liquor. Calculation - 1 cc of 0.1 N potassium permanganate = 0.8 milligrams of oxygen.

The Timmerman-Reinhardt solution is prepared bydissolving 67 grams of $MnSO_4 \cdot 4H_2O$ in water, add 138 ccs of 85% phosphoric acid, 130 ccs of 98% sulphuric acid, 10 ccs of 0.1 N ferrous sulphate solution, and carefully dilute to 1 litre.

General analysis of black liquor by Francis J. Cirves (13).

The following procedure based on the method of Cirves, was attempted on the treated calcium bisulphite waste liquor and the treated sodium hydroxide waste liquor to determine the inorganic constituents present. The method of analysis as outlined by Cirves is suggested for use on sodium sulphate waste liquor. Where the calculations have not been made directly to grams per litre of the original substance, sodium hydroxide equivalents have been made in order to obtain comparable evaluations.

Partial alkalinity:

The partial alkalinity, namely the NaOH, 1/2 NA_2S, and 1/2 Na_2CO_3 value is determined by titrating a 10 ccs aliquot diluted with 100 ccs. of distilled water, with standard hydrochloric acid using phelolphthalein as indicator. A sufficient amount of the original solution is made up for subsequent determinations by dissolving 100 ccs of the waste liquor with distilled water and filling to the mark on a 500 ccs volumetric flask.

20 x ccs x 0.5N HCl = partial alkalinity.

Total alkalinity:

A similar aliquot titrated with hydrochloric acid using methyl orange as indicator gives an estimate of the alkalinity caused by the NaOH, Na_2S, Na_2CO_3 , 1/2 Na_2SO_3, Na_2SiO_3, sodium oleate, sodium resins, sodium tannin, and sodium lignin content.

20 x ccs x 0.5 N HCl = total alkalinity.

Active alkalinity:

The active alkalinity caused by NaOH, and 1/2 Na_2S is obtained by precipitating a 100 ccs sample of black liquor with 200 ccs of 20% barium chloride solution and diluting with distilled water to the mark on a 500 ccs volumetric flask. A 50 ccs aliquot of the supernatant liquid or filtrate is titrated with standard HCl using phelolphthalein as indicator.

4 x ccs x 0.5 N HCl = active alkalinity.

Sodium carbonate:

2 x (partial alkalinity - active alkalinity) = Na_2CO_3 equivalent.

Total iodine value:

To determine the total iodine value caused by the Na_2S, Na_2SO_3, and $Na_2S_2O_3$ titrate a 25 ccs sample of the liquor prepared for partial alkalinity, diluted with 100 ccs of distilled water and acidified with acetic acid, with standard iodine solution using a starch solution as indicator.

8 x ccs x 0.1N iodine = total iodine equivalent.

Partial iodine value:

To determine the Na_2S and $Na_2S_2O_3$ present titrate a 25 ccs aliquot of the liquor prepared for active alkalinity with standard iodine solution using starch solution as indicator.

8 x ccs x 0.1 N iodine - partial iodine value = Na_2SO_3 equivalent.

Sodium sulphite:

Total iodine value - partial iodine value $\overset{x}{=}$ Na_2SO_3 equivalent.

Sodium thiosulphate:

A 100 ccs aliquot of the liquor prepared for active alkalinity is treated with 25 ccs of 5% zinc chloride solution to precipitate the sodium sulphide. A 25 ccs aliquot of the filtrate is acidified with acetic acid and titrated with iodine solution.

10 x ccs x 0.1 N iodine = sodium thiosulphate equivalent.

Sodium sulphide:

Partial iodine value - sodium thiosulphate = sodium sulphide equivalent.

Sodium hydroxide:

Active alkalinity - 0.5x (sodium sulphide) = sodium hydroxide in grams per litre.

Total solids:

A 25 ccs sample of the black liquor is precipitated in a tared platinum evaporating dish and evaporated to dryness at 105 degrees C.

40 x weight of residue = total solids in grams per litre.

Ash:

The residue in the platinum dish is subjected to a red heat until all the carbonaceous matter has been driven off.

40 x weight of the ash = ash in grams per litre.

Combustible organic matter:

Total solids - ash = combustible organic matter in grams per litre.

Sodium chloride:

Neutralize the ash which has been obtained above with a pinch of sodium carbonate and titrate with silver nitrate solution using potassium chromate solution as indicator.

2.34 x ccs x 0.1 N $AgNO_3$ = Sodium chloride in grams per litre.

Silica:

A duplicate sample of the ash as obtained above is treated with a few ccs of concentrated hydrochloric acid, evaporate to dryness, and dilute with 25 ccs of distilled water. The residue is filtered and ignited in a tared crucible.

53.1 x wt. of residue = Na_2SiO_3 equivalent.

Analysis of sodium sulphate waste liquor by R. C. Griffin (21):

The analytical method of analysis of sodium base sulphate waste liquor as outlined by Griffin was found to be the most satisfactory for both the treated sodium hydroxide waste liquor and the sodium bisulphite waste liquor. Griffin's procedure was followed as outlined except in the determination of the sodium sulphide content by the volumetric zinc solution method, as this method was unsatisfactory due to the poor end points obtained.

The following is an outline of the method followed in the analysis of the sodium base waste liquor both before and after the evaporation stage and including the alternate procedure used in the determination of the sodium sulphide content.

Specific gravity:

Determine the specific gravity at 15.5°C with the Westphal balance.

Total solids:

Weigh out 100 grams of the waste liquor and dilute to one litre with water using a volumetric flask. Mix thoroughly and pipette into a weighed platinum dish 25 ccs of the diluted liquor. Evaporate on a steam bath and then dry to a constant weight at 105 degrees C.

Ash:

Ignite the above residue until the carbon is burned off. Cool in a desiccator and weigh.

Silica:

Moisten the ash above obtained with concentrated hydrochloric acid, add a few ccs of water, evaporate to dryness on a steam bath, bake at least one hour at 120 to 140 degrees C, take up with dilute hydrochloric acid, heat to boiling, filter through a quantitative filter, wash with hot water, ignite strongly in a platinum dish and weigh as SiO_2.

Sodium sulphate:

Pipette 25 ccs of the original sample into a beaker, add about 100 ccs of distilled water, make slightly acid with HCl and heat to boiling. Add 10 ccs of hot barium chloride solution slowly, drop by drop, boil for 0.5 hours, filter and wash with hot water. Ignite in a weighed platinum crucible. On account of the organic matter present some of the $BaSO4$ is likely to be reduced to BaS. Moisten the precipitate in the crucible with a few drops of dilute sulphuric acid. Again ignite, cool and weigh as $BaSO_4$.

Calculate to Na_2SO4 and also to Na_2O.

$BaSO_4$x 0.6086 = Na_2SO4

$BaSO_4$x 0.2656 = Na_2O

Total sodium:

To an aliquot of the original solution corresponding to 5 grams of the sample, add an excess of HCl, evaporate to dryness and ignite to a dull red heat. All the sodium salts except the sulphate are decomposed to NaCl. The temperature must be kept low to avoid volatilization of the latter. Leach out the residue with hot water and filter. Cool and titrate the NaCl with 0.1 N $AgNO_3$ in the usual way, using Na_2CrO_4as an indicator. It is necessary to leach the residue thoroughly with small portions of hot water and to remove all the platinum from the dish. For accurate work it is desirable to filter and ignite the residue on the filter paper gently in a platinum dish and again leach with water. The leaching should be continued until the filtrate gives no reaction with silver nitrate. Calculate the titration to Na_2O.

1 cc of 0.1 N $AgNO_3$ = 0.0031 grams of sodium chloride.

The sum of the Na_2O thus found and the Na_2O found present as sulphate gives the total sodium as Na_2O.

Sodium sulphide:

Volumetric zinc solution method: -

Solutions. Standard zinc solution - Dissolve 16.75 grams of pure 30 mesh zinc in a small excess of nitric acid. Add sufficient ammonium hydroxide to redissolve all the precipitate formed and then 50 ccs excess. Dilute to 2000 ccs.

Ammoniacal nickel sulphate indicator - Make an approximately 10% solution of nickel ammonium sulphate and add a slight excess of ammonium hydroxide.

Titration. From the solution previously prepared for total solids, pipette out 100 ccs (equivalent to 10 grams of the original liquor). Dilute to about 250 ccs in a beaker with distilled water and run in from a burette the standard zinc solution. The end-point is reached when a drop of the nickel sulphate indicator tested on a white spot plate no longer forms a black precipitate. From the number of ccs of zinc solution required, calculate the amount of sodium sulphide.

1 cc of zinc solution = 0.0100 grams of sodium sulphide.

Silver nitrate method:-

This procedure is adapted from Griffin's (21) method for the quantitative determination of sodium sulphide present in sodium sulphate cooking liquor. Pipette 25 ccs of the liquor into a dry beaker of about 300 ccs capacity. Do not dilute with water. Run in from a burette an amount of ammoniacal silver nitrate solution as close to the saturation point as can be estimated. This can be done from a preliminary titration. Then shake the contents of the beaker rather vigorously for 2 or 3 seconds. This causes the black silver sulphide to separate in thick lumps from the clear solution. Add another drop of the silver nitrate solution from the burette. If this forms a heavy precipitate where the drop comes in contact with the solution, add a few more drops, give the beaker a shake, and repeat the additions until only a faint cloud appears in the clear solution. The last drop necessary to complete the precipitation forms only a faint cloud in the clear solution. If then another drop is run in after shaking, instead of forming a faint dark cloud, it will remain as a clear colourless spot surrounded by the faintly distributed precipitate in the pale brownish solution.

Ammoniacal silver nitrate solution is prepared by dissolving 87.07 grams of pure silver nitrate in water. Then add 250 ccs of concentrated ammonium hydroxide and dilute to one litre. 1 cc of this solution is equivalent to 0.02 grams of sodium sulphide.

Total available alkalinity:

An estimate of the alkalinity caused by the NaOH, Na_2S, Na_2CO_3, and 1/2 Na_2SO_3.

Evaporate 25 ccs of the original sample to dryness in a platinum dish, ash over a Tirill burner. It is unnecessary to burn off all the carbon. Leach out the soluble salts with hot distilled water as in the determination of the total sodium above. Cool the filtrate and titrate with 0.5 N HCl and methyl orange. Calculate the titration to Na_2O and also to NaOH. This gives the alkalinity available for recovery.

1 cc of 0.5 N HCl = 0.01550 grams Na_2O

= 0.0200 grams NaOH.

Free Caustic Soda:

The alkalinity due to NaOH is determined by subtracting the alkalinity due to 0.5 Na_2S from the active alkalinity caused by NaOH and 0.5 Na_2S, determined as follows:

Pipette 50 ccs of the waste liquor (calculate the weight from its specific gravity) into a 500 ccs volumetric flask and add 50 ccs of 10% barium chloride solution. Shake and dilute to the mark with distilled water, freshly boiled and free from carbon dioxide. Let settle until clear. Pipette 50 ccs of the clear supernatant liquor (equal to 10 ccs of the original) into a beaker and titrate with 0.1 N HCl and phenolphthalein. Calculate to NaOH.

1 cc of 0.1 N HCl = 0.004001 grams of sodium hydroxide.

The above determination is corrected for Na_2S according to the reaction: $Na_2S + HCl = NaSH + NaCl$. Hence 1 cc of 0.1 N HCl = 0.007806 grams Na_2S. To apply the correction, calculate the weight of the Na_2S which would be present in the amount of the liquor taken for the titration and divide by 0.007806. This will give the number of ccs of 0.1 N HCl required by the Na_2S. Subtract this from the titration and calculate the difference to NaOH.

Sodium carbonate:

(The following determination which is an adaption of the method outlined by Cirves, was used as it appeared to be a more accurate method of analysis). The partial alkalinity, namely the NaOH, 1/2 Na_2S, and 1/2 Na_2CO_3 value is determined by titrating a 10 ccs aliquot diluted with 100 ccs of distilled water with standard HCl using phenolphthalein as indicator. The equivalent active alkalinity due to the NaOH and 1/2 Na_2S, as determined as outlined under free caustic soda, is subtracted. The sodium carbonate content is equal to twice the difference between the equivalent titration due to the partial alkalinity and the active alkalinity as determined above.

1 cc of 0.5 N HCl = 0.02650 grams Na_2CO_3.

Total alkalinity:

Pipette 25 ccs of the original liquor into a white casserole and add 200 ccs of water. Titrate with 0.5 N HCl and methyl orange. This titration gives the alkalinity due to Na_2CO_3, NaOH, Na_2S, 1/2 Na_2SO_3, Na_2SiO_3, sodium oleate, sodium resins, sodium tannin, and sodium lignin content. Calculate the titration as Na_2O and also as NaOH.

1 cc of 0.5 N acid = 0.01550 grams Na_2O.

= 0.02000 grams NaOH.

Sodium Silicate:

The sodium silicate may be approximately calculated by multiplying the amount of SiO_2 by 2.03. This is for the formula Na_2SiO_3.

D. Analytical method of quantitative analysis used in the determination of the inorganic constituents after ashing of sodium bisulphite waste liquor.

The following procedure is outlined by Griffin (21) for the analysis of sodium sulphate waste liquor ash.

Carbon:

To 40 grams of the finely ground sample in a large beaker, add about 500 ccs of water and boil gently for about one hour. Filter through a filter paper, previously dried and weighed in a weighing bottle, collecting the filtrate in a litre volumetric flask; wash thoroughly with hot water, dry at 100 degrees C, and weigh in the same bottle as carbon and insoluble matter. Then ignite in a platinum crucible until the carbon is completely burned off. Cool in a desiccator and weigh the insoluble matter. Report the loss in weight as carbon.

Sodium silicate:

(The following procedure is outlined by Griffin (21) in the determination of silica present in sodium sulphate waste liquor).

Moisten the ash above obtained with concentrated HCl, warm, add a few ccs of water, evaporate to dryness on a steam bath, bake at least one hour at 120 to 140 degrees C, take up with dilute HCl, heat to boiling, filter through a quantitative filter, wash with hot water, ignite strongly in a platinum dish and weigh as SiO_2. The sodium silicate may be approximately calculated by multiplying the amount of SiO_2 by 2.03. This is for the formula Na_2SiO_3.

Caustic Soda:

Cool the filtrate from the above determination to room temperature, dilute to one litre and mix thoroughly. Call this solution "A". Pipette 50 ccs of the solution (equivalent to 2 grams) into a 250 ccs volumetric flask and precipitate the carbonates with a slight excess of neutral barium chloride solution. Dilute to the mark with freshly boiled and cooled water. Shake thoroughly; let settle, pipette out 100 ccs of the clear liquid (equivalent to 0.8 grams of the original sample) and titrate with 0.1 N HCl and methyl orange. From this titration subtract 0.49 ccs for each percentage of sodium sulphide (as determined below). Calculate the difference to NaOH.

1 cc of 0.1 N HCl = 0.004 grams of sodium hydroxide.

Sodium sulphite:

To 80 ccs of recently boiled water in a flask add 25 ccs of solution "A" (equivalent to 1 gram of the sample). Acidify with acetic acid and titrate at once with 0.1 N iodine using starch as an indicator. Calculate the titration to Na_2S.

1 cc of 0.1 N iodine = 0.0039 grams of sodium sulphide.

Sodium carbonate:

Pipette 25 ccs of solution "A" into a flask. Dilute to about 100 ccs with water and titrate with 0.5 N HCl and methyl orange. Subtract from the titration the amount of 0.5 N HCl equivalent to the sodium hydroxide and the sodium sulphide (i.e. 0.25 of the number of ccs of 0.1 N HCl required by the titration under caustic soda) and calculate the difference to Na_2CO_3.

1 cc of 0.5 N HCl = 0.0265 grams of sodium carbonate.

Salt:

Pipette 25 ccs of solution "A" into a small flask, make slightly acid with dilute nitric acid and boil to expel any hydrogen sulphide. Filter and wash the residue. Cool the filtrate, add an excess of powdered $CaCO_3$ and about 1 cc of chromate indicator solution, and titrate with 0.1 N $AgNO_3$ solution until a reddish colour appears and remains after stirring. Calculate to NaCl.

1 cc of 0.1 N $AgNO_3$ = 0.005845 grams of salt.

Sodium sulphate:

To 500 ccs of solution "A" add an excess of HCl, boil to expel carbon dioxide, and precipitate while boiling with a slight excess of barium chloride, added drop by drop. Boil for 5 minutes, let stand overnight protected from SO_3 fumes, filter, wash thoroughly with hot water, dry, ignite in a weighed platinum crucible, cool in a desiccator, and weigh as $BaSO_4$. Calculate to Na_2SO_4.

$BaSO_4$ x 0.6086 = sodium sulphate.

RESULTS

A. Evaporation and analysis of treated calcium bisulphite waste liquor.

The preliminary work in this investigation was to develop a complete scheme of analysis for the quantitative determination of the inorganic substances present in the sodium bisulphite waste cooking liquor in order to follow quantitatively the changes produced during the various stages of a standard recovery method. With this end in view, calcium bisulphite waste liquor, to which was added 25 grams of sodium sulphide hydrate per litre of solution, was used for the initial experimental work.

The initial liquor was a clear brown colour with tiny black particles suspended in it, and on the evaporation of about 50% of the water content of the liquor, the liquor turned very dark and became more viscous. The condensate collected during the evaporation was clear and free from turbidity and the walls of the apparatus remained clean.

The adopted methods, as outlined under analytical methods, of analysis of waste cooking liquor by Partansky and Benson, and also that of Cirves were attempted on the liquor both before and after the evaporation stage. The gases given off during the evaporation were also analysed as outlined under analytical methods. A complete material balance on the constituents present in the liquor during the evaporation stage was not attempted, as the main purpose of this work was to study the analytical procedures suggested. The results of an analysis of the treated calcium bisulphite liquor before and after evaporation by the Partansky and Benson method, and a material balance is given in Table I.

The Cirves method of analysis for the determination of the constituents present in the waste liquor either before or after the evaporation stage, was not satisfactory due to the dark colour of the liquor. This method depends upon the use of indicators and as a result poor end points were obtained and it was difficult to duplicate results.

TABLE I

A typical analysis (Partansky and Benson Method) of treated calcium bisulphite waste liquor before and after evaporation.

	Weak Liquor		Strong Liquor		Strong Liquor
	Grams Per Litre	%	Grams per Litre	%	Grams per litre of original Liquor
Total Solids	88.0	8.3	225.0	19.6	72
Residue on ignition (as sulphate)	16.01	1.5	43.49	3.8	14.56
Total sulphur (as sulphur)	9.62	0.9	20.9	1.8	7.02
Oxygen demand	84		196.7		66
Total weight	1059		1148		

Material balance on the evaporation stage.

Liquor charged:				
400 ccs Sp. gr. - 1.059			423.6 grams	
Recovered:				
Strong Liquor - 134 ccs sp. gr. 1.148	154 grams	36.3%		
Condensate	266	62.9		
Sulphur dioxide	1.87	0.4		
Hydrogen Sulphide	0.01	0.0		
			421.9 grams	99.6%
Unaccounted:			1.7 grams	0.4%
			423.6 grams	100.0%

B. Evaporation and analysis of treated sodium hydroxide waste liquor.

As the calcium bisulphite liquor used was low in sodium base compounds, it was decided to use a liquor which more nearly represented the type of liquor under investigation. For this reason it was decided to use sodium hydroxide waste digester blow liquor which was saturated with sulphur dioxide gas and to which 25 grams of sodium sulphide hydrate was added per litre of liquor.

Three evaporation runs and analyses were made on this liquor with the view of obtaining material balances on the constituents of the liquor. The evaporations were all carried out under an approximate vacuum of 15 cm of mercury and the observed boiling point of the liquor was 93 to 94 degrees C. Under these conditions it took approximately forty-five minutes to evaporate 400 ccs of the liquor from the initial specific gravity of 1.163 to 1.346. The initial liquor after treatment with sulphur dioxide and sodium sulphide had a brown greenish cast and fine dark particles which settled out on standing were observed. On evaporation the liquor turned quite dark and a stringy black tarry mass settled out.

The condensate collected was clear in appearance but on titration with standard iodine solution for the determination of the sulphur dioxide content, as outlined in the method of analysis, a white precipitate which turned brown and then white again was formed in the condensate and no end point was observed using starch indicator solution. The water in the absorption bottles was analysed for sulphur dioxide and hydrogen sulphide as outlined under analytical methods. Although no measurable amount of hydrogen sulphide was present in the water, a strong mercaptan odour existed throughout the evaporation.

The method of analysis of waste liquor by Cirves as outlined under analytical methods, was attempted on the waste liquor both before and after evaporation, but due to the dark nature of the liquor, it was impossible to establish satisfactory end points. The method of analysis adapted from Griffin's analytical method of analysis of sulphate waste liquor, as outlined under analytical methods, was used to analyse both the weak and concentrated waste liquor.

A typical analysis of the liquor before and after evaporation together with a material balance on the evaporation stage is given in Table II and III. It is noticed that the sum of the inorganic materials analysed and the total inorganic material determined as such do not check. This is possibly due to improper ashing to determine the inorganic constituents and also to the small portion of the liquor taken as a basis for analysis. It is also noticed that there is a large discrepancy between the organic matter before and after evaporation. This discrepancy is largely due to the solids of apparently an organic nature, which separated out during the evaporation and which were not analysed along with the strong waste liquor.

TABLE II

A typical material balance on the treated sodium hydroxide waste liquor before and after evaporation.

Liquor charged:				
	400 ccs	sp. gr. - 1.163	468 grams	
Recovered:				
	Strong Liquor			
	146 ccs	sp. gr. - 1.346	197.2 grams	42.2%
	Condensate		245	52.6
	Precipitated matter		23	4.6
	Sulphur dioxide		1.4	0.2
	Hydrogen sulphide		0.0	0.0
			466.6 grams	99.6%
Unaccounted:			1.4 grams	0.4%
			468 grams	100.0%

TABLE III

A typical analysis (Griffin method) of treated sodium hydroxide waste liquor before and after evaporation.

	Weak Liquor		Strong Liquor		Strong Liquor
	Grams per Litre	%	Grams per Litre	%	Grams per litre of original liquor
Inorganic and organic	185.	15.9	803.	59.7	118
Inorganic	74.	6.4	434.	32.2	63.8
Organic	111.	9.5	369.	27.5	54.2
Na_2SiO_3	4.16	0.4	29.4	2.2	4.18
Na_2SO_4	9.62	0.8	198.0	14.7	29.1
Na_2S	35.2	3.0	0.0	0.0	0.0
Na_2CO_3	25.7	2.2	134.5	10.0	19.7
Total sodium as Na_2O	82.5	7.1	319.	23.7	61.4
Na_2O (equivalent of Na_2SO_4)	4.18	0.4	86.8	6.4	12.8
Na_2O (equivalent of Na_2S)	28.0	2.3	0.0	0.0	0.0
Na_2O (available alkalinity)	70.6	6.1	89.5	6.7	13.2
Specific gravity	1.163		1.346		

C. Investigations using sodium bisulphite waste liquor.

It was decided to prepare and use sodium bisulphite waste liquor to continue the investigation, after accomplishing the preliminary work as outlined. The disadvantage of using treated calcium bisulphite waste liquor was its low content of sodium compounds, while that of the treated sodium hydroxide waste liquor was due to the solid matter which separated out during the evaporation.

1. Preparation of sodium bisulphite cooking liquor.

The waste liquor used in this investigation was obtained by cooking spruce chips with sodium bisulphite cooking liquor. The strength of the liquor desired for the pulping process was % total of 6.0, % free of 4.75 and a % combined of 1.25 ; determined by the method G. V. Palmrose as outlined under analytical methods of analysis.

The liquor was prepared by dissolving 93 grams of sodium bisulphite per litre of water and absorbing sulphur dioxide gas in the solution until the required strength of the acid was obtained. For the first series of cooks, the strength of the sodium bisulphite cooking liquor used was % total of 7.35, % free of 6.12 and a % combined of 1.23; while for the second series of cooks the % total was 6.34, % free 5.04, and the % combined 1.30.

2. Preparation of waste liquor:

The waste sodium bisulphite cooking liquor was obtained by cooking spruce chips approximately one half inch square and an eighth of an inch thick, in the small experimental digesters in the Forest Products Laboratory. As each digester yields a litre of waste liquor and as two cooks were made at the same time, sufficient liquor was obtained from two series of cooks. Each digester was charged with 400 grams of spruce chips and 1800 grams of sodium bisulphite cooking liquor.

For the first series of cooks the maximum temperature used was 140 degrees C and was reached at the seventh hour, the temperature being gradually raised, taking three hours to reach 100 degrees C. The pressure started to rise after the first hour and gradually rose to a maximum at 80 pounds per square inch gauge at the seventh hour. The total cooking time was ten hours, the pressure being relieved during the last half hour. The raw pulp obtained was well cooked and free from uncooked bits of wood. This characteristic was possibly due to the long penetration or soaking time of forty-five hours used. No strength or quality tests were made on the raw pulp but the cooked chips were white in colour. The waste liquor obtained was clear and light brown in colour.

The second series of cooks was practically a repetition of the first series. The penetration time was thirteen hours. The temperature and pressure were raised more rapidly, reaching the maximum of 140 degrees C and 80 pounds per square inch gauge at the end of the fifth hour. The total cooking time was ten hours, the pressure being relieved during the last half hour. The raw pulp and the waste liquor obtained from this series had the same general appearance as that obtained from the first series of cooks. The raw pulp was again discarded, and the waste liquor collected separately from that obtained from the previous cooks.

3. Evaporation and analysis of sodium bisulphite waste liquor.

Four evaporation runs were made on this liquor all under the same conditions, namely evaporation of 400 ccs of the waste liquor under a vacuum of 12 to 13 cm of mercury at which the observed temperature of boiling was 95 to 96 degrees C. Material balances on the evaporation stage for runs 7 and 8 are given in tables IV and V. The liquor on evaporation changed from a light brown to a brown green colour with fine black particles suspended in it, which settled out on standing. No precipitate was formed during the evaporation and the condensate collected was free from turbidity. The gases given off were absorbed in water and the latter was analysed for sulphur dioxide and hydrogen sulphide as outlined under analytical methods of analysis of gases.

The constituents present in the waste liquor before and after evaporation of about 50% of the water content of the liquor, were determined using the method of analysis adapted from Griffin's analysis of sulphate waste liquor as outlined under analytical methods of analysis. The results of the analysis of weak liquor used in evaporation runs 7 and 8 is given in table VI while the analysis of the concentrated liquor from evaporation runs 7 and 8 and a misture of 8, 9, and 10 is given in table VII.

TABLE IV

Material balances on the evaporation of sodium bisulphite waste liquor.

Run #7

Liquor charged:					
400 ccs	sp.gr. - 1.051			421 grams	
Recovered:					
Strong liquor -					
140 ccs	sp.gr. 1.134	159 grams	37.8%		
Condensate		255	60.6		
Sulphur dioxide		1.72	0.4		
Hydrogen sulphide		0.001	0.0		
				415.7 grams	98.8%
Unaccounted				5.3 grams	1.2%
				421.0 grams	100.0%

Run #8

Liquor charged:					
400 ccs	Sp.gr. - 1.054			423 grams	
Recovered:					
Strong liquor -					
85 ccs	sp.gr. 1.191	101 grams	23.9%		
Condensate		308	72.8		
Sulphur dioxide		1.7	0.4		
Hydrogen sulphide		0.002	0.0		
				410.7 grams	97.1%
Unaccounted				12.3 grams	2.9%
				423.0 grams	100.0%

TABLE V

Material balance on constituents present in sodium bisulphite waste liquor during evaporation.

Basis: Grams per 400 ccs of weak liquor.

Run Number	7		8	
	Charged	Recovered	Charged	Recovered
Inorganic and organic	40.4	42.5	42.5	35.3
Inorganic	6.6	9.2	7.1	7.4
Organic	33.8	33.3	35.4	27.9
Na_2SiO_3	0.39	0.39	0.35	0.29
Na_2SO_4	5.12	4.82	4.96	3.61
Na_2S	0.34	0.89	0.37	1.76
NaOH	3.12	2.54	3.15	1.85
SO_2		1.72		1.70
H_2S		.001		.002
Total sodium as Na_2O	2.45	3.12	2.55	3.05
Na_2O (equivalent of Na_2SO_4)	2.24	2.09	2.12	1.57
Na_2O (equivalent of Na_2S)	0.27	0.98	0.30	1.40
Na_2O (available alkalinity)	2.42	1.96	2.50	1.51
Specific gravity	1.051	1.134	1.054	1.191

TABLE VII

Analysis (Griffin Method) of concentrated sodium bisulphite waste liquor from evaporation runs 7 and 8 and a mixture of 8, 9 and 10.

Run number	7		8		8, 9 and 10	
	Grams per Litre	%	Grams per Litre	%	Grams per Litre	%
Inorganic and organic	303.	26.6	416.	34.9	505.	41.8
Inorganic	65.5	5.8	87.3	7.4	106.	8.7
Organic	237.5	20.8	328.7	27.5	399.	33.1
Na_2SiO_3	2.68	0.2	3.37	0.3	2.28	0.2
Na_2SO_4	34.4	3.0	42.7	3.6	52.0	4.3
Na_2S	8.2	0.7	20.8	1.7	20.7	1.7
NaOH	18.1	1.6	23.0	1.9	20.7	1.7
Total sodium as Na_2O	22.3	2.0	36.0	3.0	37.4	3.1
Na_2O (equiv.of Na_2SO_4)	14.9	1.3	18.6	1.6	22.7	1.9
Na_2O (equiv.of Na_2S)	6.53	0.5	16.5	1.4	16.5	1.4
Na_2O (available alkalinity)	14.0	1.2	17.8	1.5	16.05	1.3
Specific gravity	1.134		1.191		1.205	

4. Ashing and analysis of sodium bisulphite waste liquor.

It was decided that a continuous furnace would be more satisfactory than a batch system for the preliminary investigations in the ashing of the concentrated sodium bisulphite waste liquor. The furnace proper was built of high temperature pyrex glass tubing so as to observe the stage of burning and to note that the liquor would be uniformly ashed without being carried to a smelted or fused condition.

The continuous ashing of the liquor was used so that the residual gases of combustion after the absorption of the sulphur dioxide and carbon dioxide, could be intermittently analysed by the use of an Orsat gas analysis apparatus. If the batch system had been used it would have required a complicated absorption apparatus to quantitatively absorb the sulphur dioxide, carbon dioxide, carbon monoxide and oxygen, so as to determine the amount of each produced. It was decided unwise to build such equipment until the amount of the latter two constituents had been roughly determined.

A description of the furnace and auxiliary equipment is given under the discussion of apparatus. The first furnace was made from pyrex tubing having a softening point in the neighbourhood of 550 degrees C. A run was attempted but the tubing became badly distorted and broke while heating up to the required ashing temperature. Insufficient liquor was ashed in this first run for analysis and no material balance was made. A black tarry substance condensed on the cooling and absorption section of the equipment and over the surface of the absorption water, particularly in the condenser, condensate collector and the first absorption bottle.

The second furnace was made of pyrex glass tube having a softening point in the neighbourhood of 650 degrees C, and was supported at several points on asbestos covered saddles. This furnace was more satisfactory but at the high temperature needed for complete ashing, the tubing became badly distorted. The furnace was run for forty-five minutes during which interval 17 ccs of concentrated liquor from the mixture of runs 8, 9 and 10, was ashed. The furnace was cooled and broken so as to remove the ash, the latter was then ashed by the method adapted from Griffin's (21) method of analysis of sulphate process black ash as outlined under analytical methods.

During this second ashing run it was noticed that the condenser walls became covered with a white precipitate which was unanalysed; and also that the apparatus with the exception of the ash collecting chamber was free from the tarry substance observed during the previous run. This latter might be due to the higher combustion temperature used giving a more complete combustion of the volatile constituents. 1.248 cubic feet of air was used during the combustion, and the Orsat analysis of the residual gas after the absorption of the sulphur dioxide and carbon dioxide at several intervals during the combustion remained approximately constant at 4.0% carbon monoxide, 5.7% oxygen and no carbon dioxide.

A material balance on the ashing stage and an analysis of the ash from the second run is given in tables VIII and IX. It was impossible to recover all the ash from the furnace as some of it was fused with the glass walls and agitator. The percentage carbon is high showing incomplete combustion of all the liquor, as is also the percent of insoluble matter found. This latter was likely due to small particles of glass included in the sample of the ash analysed. The percent sodium sulphide present is surprisingly low.

TABLE VIII

Material balance on the ashing of sodium bisulphite waste liquor.

Run #2

Charged:				
Concentrated liquor -				
17 ccs sp.gr. 1.205	20.5 grams			
Nitrogen	0.078			
Oxygen	0.023			
			20.601 grams	
Recovered:				
Ash	1.78 grams	8.7%		
Condensate	12.0	58.4		
Nitrogen	0.078	0.1		
Oxygen	0.006	0.0		
Carbon dioxide	1.64	8.0		
Sulphur dioxide	0.624	3.0		
Carbon monoxide	0.004	0.0		
			16.132 grams	78.3%
Unaccounted			4.469 grams	21.7%
			20.601 grams	100.0%

TABLE IX

Balance on constituents during the ashing of sodium bisulphite waste liquor and a percent analysis of the ash.

Run #2

Basis: 17 ccs of concentrated liquor.

Charged:			
Organic			6.78 grams
Inorganic			1.8
Na_2SiO_3	0.039		
Na_2SO_4	0.885		
Na_2S	0.554		
NaOH	0.354		
Total sodium as Na_2O	0.604		
Recovered:			
Ash			1.78 grams
Carbon	0.7158 grams	45.53%	
Insoluble matter	0.2367	15.10	
Na_2SO_4	0.298	18.96	
Na_2S	0.0007	0.05	
NaOH	0.0128	0.82	
Na_2CO_3	0.223	14.22	
NaCl	0.0835	5.32	
		100.0%	
Total sodium as Na_2O	0.361		1.57 grams
Unaccounted:			0.21 grams
			1.87 grams

5. Determination of the temperatures of ashing and smelting.

The temperature necessary for ashing and smelting of the concentrated sodium bisulphite waste liquor was determined as it seemed pertinent to obtain this data before suggesting any apparatus to be used to carry on the investigation in these stages. The temperature of ashing was determined by burning some of the liquor to an ash in an open platinum crucible heated by an open Bunsen flame. The crucible, flame and retort stand were surrounded by asbestos paper to prevent draughts. An iron-constantan pyrometer was used in the determination, the pyrometer ends being placed as close as possible to the ash in the crucible. The ashing temperature was determined to be in the neighbourhood of 650 degrees C.

The temperature of smelting of the waste liquor was determined on the same sample using a hotter flame. The smelting point was determined by observing the softening point of siliceous pyrometer cones placed in the neighbourhood of the platinum crucible. The observed temperature of smelting by this method was between 1200 and 1300 degrees C.

DISCUSSION OF THE RESULTS

Due to the elementary nature of this investigation, it is impossible to comment on the feasibility of the recovery of sodium bisulphite waste liquor. Various analytical procedures were attempted in the analyses of waste cooking liquor having both calcium and sodium as the base, and the methods and results obtained with these methods are outlined under experimental work.

The method adapted from Griffin's (21) procedure suggested for the analysis of sulphate waste liquor, as outlined under analytical methods, appeared the most satisfactory for the analysis of the inorganic constituents contained in the waste liquor having sodium as the base. The results obtained using this procedure are outlined and show that reproducable analysis may be obtained. The determination of hydrogen sulphide in the gases from the evaporation stage and ashing stage could be improved but no simple method of determining this gas in the presence of sulphur dioxide was found in the literature.

The evaporation data and analysis of the weak and concentrated sodium bisulphite waste liquor indicates the inorganic contents of these liquors. Insufficient work was done on the ashing of this liquor to draw any conclusions. The work, however, indicates that the sodium sulphide is quite low although this value might have been higher if the liquor had been more completely burned. Insufficient experimental work was done on the analysis of the ash obtained from the sodium bisulphite waste liquor to make any comments on the procedure of analysis used. However, the method adapted from Griffin's (21) analysis of sulphate black ash as outlined under analytical methods, appeared satisfactory and no particular difficulties were encountered during the analysis.

Unfortunately, no work on the smelting stage was done other than the determination of the temperature necessary for the smelting of the ash.

A flow diagram based on one litre of sodium bisulphite waste liquor is given in table X and indicates the results obtained during the evaporation and ashing of the sodium bisulphite waste liquor. Due to experimental trouble encountered in the ashing stage a poor material balance was obtained and resulted in considerable loss of apparently inorganic constituents.

TABLE X

A flow diagram based on one litre of sodium bisulphite waste liquor indicating the results obtained during the evaporation and ashing of the liquor.

Weak Waste Liquor:

1 litre	sp.gr. - 1.054		1054 grams
Water		944 grams	
Organic constituents		88	
Inorganic constituents -			
Na_2SO_4	12 grams		
Na_2S	1		
$NaOH$	8		
Na_2SiO_3	1		
	22	22	
		1054	1054 grams

Evaporation Stage:

Condensate	768 grams	
Sulphur dioxide	4	
Unaccounted	30	
Strong liquor	252	
	1054	1054 grams

TABLE X (CONTINUED)

Concentrated waste liquor:

211 cc	sp.gr. 1.191		252 grams
Water		162 grams	
Organic constituents		69.5	
Inorganic constituents			
Na_2SO_4	11.8		
Na_2S	0.9		
NaOH	7.0		
Na_2SiO_3	0.8		
	20.5	20.5	
		252	252 grams

Ashing Stage:

Condensate	147 grams	
Sulphur dioxide	8	
Carbon dioxide	20.5	
Unaccounted	54.5	
Ash	22	
	252	252 grams

Ash:

Carbon	10	
Insoluble matter	3.3	
Na_2SO_4	4.2	
Na_2S	10.1	
NaOH	0.2	
Na_2CO_3	3.1	
NaCl	1.1	
	22	22 grams

CONCLUSIONS

From the work already carried out by the various investigators on the use of sodium bisulphite cooking liquor for the pulping of wood, it may be concluded that this liquor has many advantageous properties over calcium bisulphite and other cooking liquors. The resulting raw pulp obtained is whiter in colour hence requiring less bleaching. Better strength and other advantageous properties of pulp may be derived by the use of the sodium bisulphite process than is obtained using the common calcium base cooking liquors. In addition woods of a resinous nature such as the Canadian Jack Pine may be satisfactorily pulped using sodium bisulphite cooking liquor.

Due to the high initial cost of the sodium base, it is necessary that some satisfactory means of chemical recovery of the base should be developed before the process can become commercially feasible. As yet no completely satisfactory method of recovery of the waste liquor has been established and research work of this nature is important both from a scientific and commercial view-point.

The purpose of this investigation was to quantitatively determine the main inorganic constituents present in the waste liquor and to quantitatively determine these constituents during the various stages of a standard recovery process. It was necessary to examine various methods of analysis suggested for the analysis of waste cooking liquors and from this work develop and adapt a method suitable for the analysis of the waste liquor during the stages of the recovery process proposed.

A satisfactory method of analysis of the waste liquor before and after evaporation for the inorganic constituents was established as well as a method of analysis of the ash obtained from burning the concentrated liquor. The ashing temperature of the liquor has been determined as well as the smelting temperature of the ash.

From this latter investigation, it is concluded that the furnace used for ashing must be made of stainless steel or some material that would withstand a temperature in the neighbourhood of 650 degrees C. It would be advantageous to study the effect on ashing of the liquor in both an oxidation and a reduction atmosphere. The smelting of the ash could possibly be done in the same furnace or in a high temperature crucible which could be heated in a closed electric muffle.

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