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[54] **PROCESS FOR DETERMINING ALKALI CONTENT IN ALKALINE PULPING LIQUOR BY A CALORIMETRIC MEASUREMENT OF THE HEAT OF PARTIAL NEUTRALIZATION OF THE PULPING LIQUOR**

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[58] **Field of Search** .... 162/49, 62; 73/15 R, 15 B, 73/61.1 R, 190 R, 190 H; 23/230 R, 253 R

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[57] **ABSTRACT**

A method is provided for determining the alkali content of alkaline pulping liquor such as sulphate pulping liquor, based on measuring calorimetrically the heat liberated by the pulping liquor when the pH of the liquor is brought to within the range from about 9.5 to about 12.5 by addition of an acid-reacting buffer.

21 Claims, 4 Drawing Figures

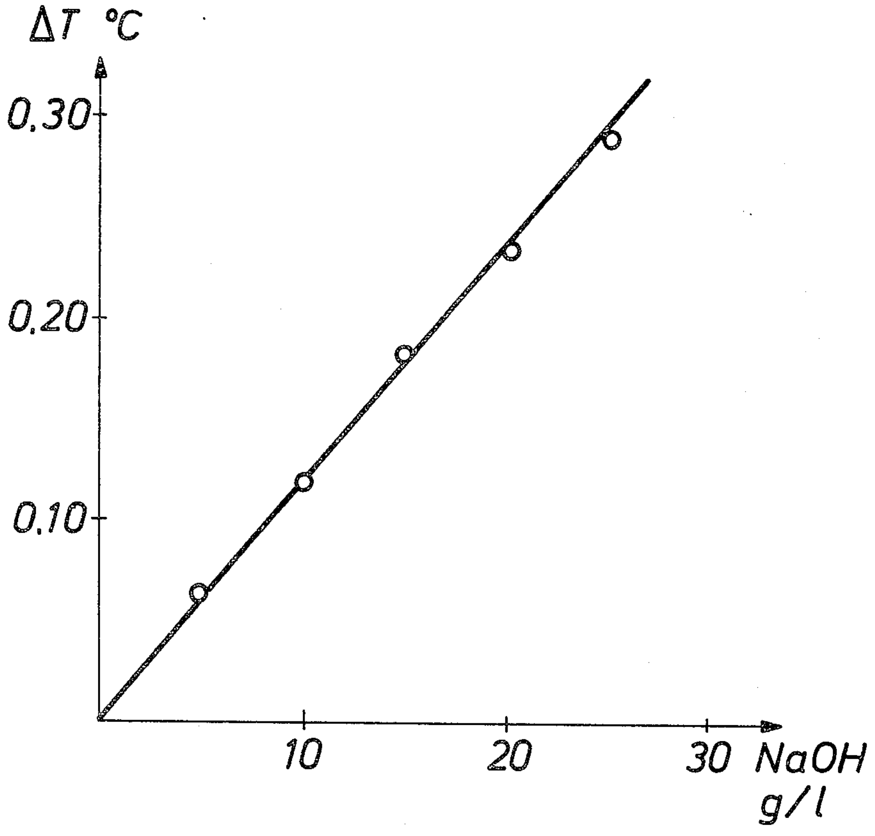


Fig. 1

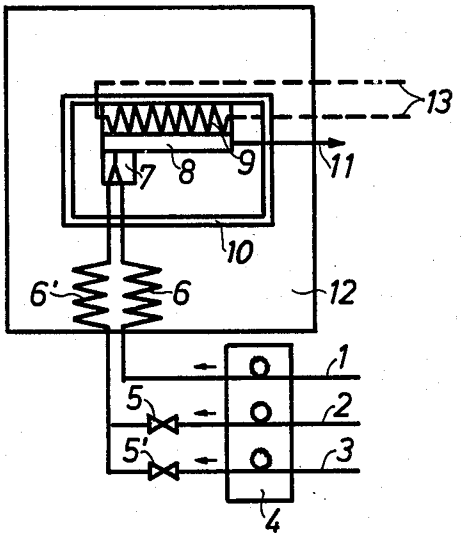


Fig. 2

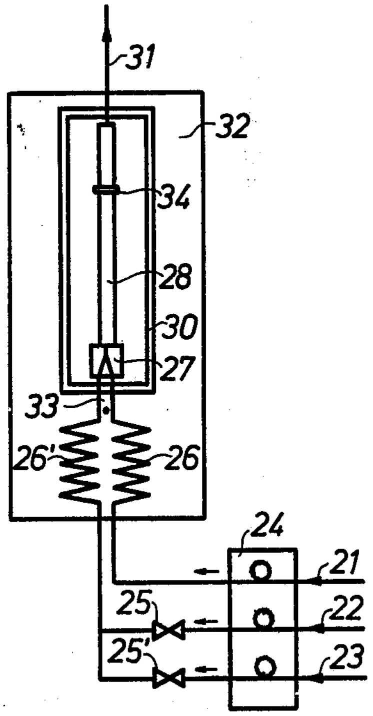


Fig. 3

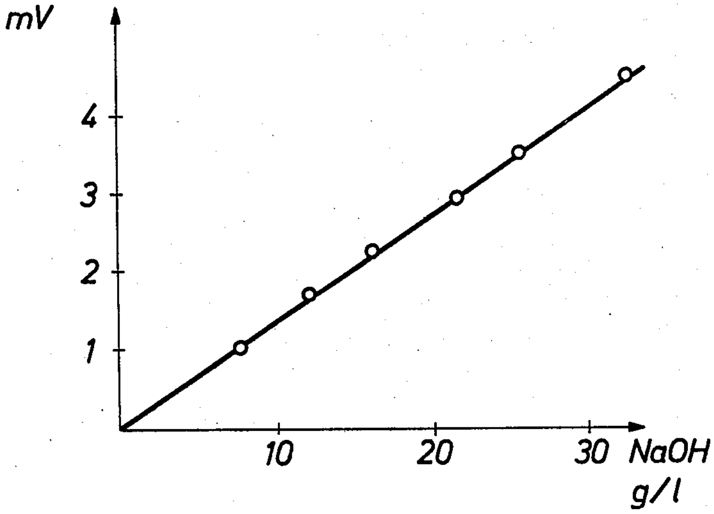
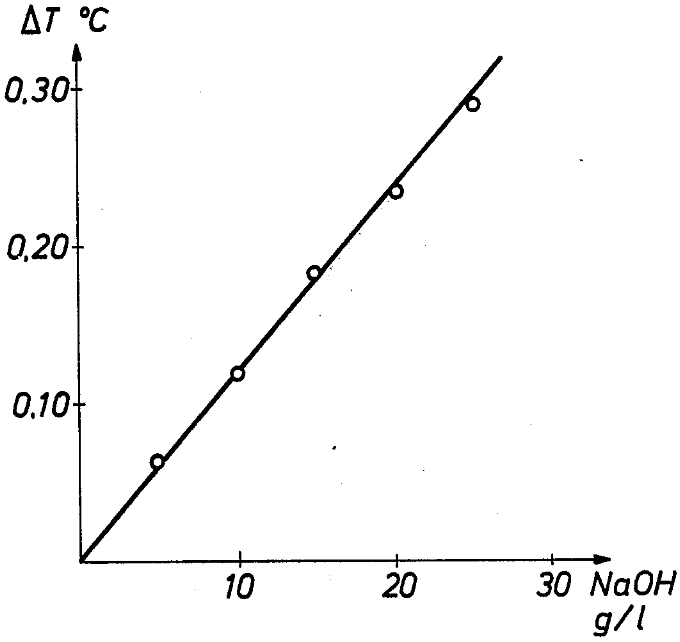


Fig. 4



PROCESS FOR DETERMINING ALKALI CONTENT IN ALKALINE PULPING LIQUOR BY A CALORIMETRIC MEASUREMENT OF THE HEAT OF PARTIAL NEUTRALIZATION OF THE PULPING LIQUOR

At the present time chemical processes involving reaction with or upon a cellulosic material are generally controlled by control of the process conditions, such as pressure, flow rate, temperature, pH, refractive index, density and electrical conductivity. In part, this is due to the complexity of the cellulosic material, and the variations in the reactivity of the cellulosic material according to the natural product in which it is found, and the complexity of the chemical reactions that may take place, simultaneously or concurrently, in the reaction mixture. This complexity is increased if, for example, the cellulosic material is being degraded by alkali attack as in the chemical pulping of cellulose. since the alkali can react not only with the cellulosic material but also with the degradation products produced in consequence of this attack on the cellulosic material.

For these reasons the reaction conditions for chemical reactions with cellulose are largely determined by an empirical approach. Attempts to reduce the control of the reactions to an exact science based on analytical methods for following the course of the reactions have been frustrated by the difficulty of determining what reactions are actually taking place at any given time, and what expedients are needed to control them. Thus, of the process parameters that have been controlled in chemical pulping processes, only pH measurements are in fact specific for a certain component, in the case of a sulphate pulping process, the alkali content.

Attempts have been made to devise methods and techniques by which more exact measurements of the cellulose pulping conditions and the contents of the cellulose pulping reaction mixture can be taken, so as to make it possible to control the pulping process better. Thus, a method has been proposed to control a sulphate pulping process by analysing the alkali content of the pulping liquor, and correlating this with the reaction temperatures applied during the pulping. However, the method for determining alkali content itself poses a challenge. Because of the complex mixture of chemicals present, many of which can react with titrating acid, the course of the titration follows no predictable pattern common to other titrations. There may be not one but several end points, and it is difficult to know which end point to accept. One may arbitrarily select a given end point, and reproducibly apply such a titration to determination of the pulping conditions; this will certainly give pulping results and a control of the pulping which is far better than previously available procedures. With a better alkali determination, it might be possible to determine pulping conditions even more precisely, and reproducibly.

Conductometric techniques can be used for determination of alkali concentration. If a direct conductometric measurement is made in the pulping liquid the correlation between alkali concentration and the conductivity of the sample is poor. On the other hand if a conductometric titration is made, a very complex apparatus is needed in order to obtain accurate results. Potentiometers using ion selective electrodes are liable to drift, and provide unreliable results. Moreover, the signal given by such an electrode is dependent upon the alkali content in a logarithmic relation, which requires a high degree of accuracy in the measurement of electrode potential, if the process is to be useful commercially.

A basic difficulty in determining alkali content by conductivity of the reaction mixture is that ions other than those contributing to alkali content also carry an electric current. In order for the conductivity measuring process to give any useful results, as a measurement of alkali concentration, it is necessary to plot a titration of conductivity against the volume of the titration acid. An apparatus constructed for this analysis is relatively complicated, since it is necessary to record and evaluate a complete course of titration sequences. It is also difficult to make continuous measurements of alkali content using such techniques, which is a disadvantage in determining alkali concentration using a continuous pulping process. If the analysis is to be fully automatic, some provision must be made to somehow select the end point of a given titration. If a computer is used for this purpose, the cost of the analytical equipment is correspondingly increased. It is obvious that this technique is complicated, but it can be used to obtain accurate measurements of the alkali concentration in pulping liquors, for instance, black liquor.

In determining alkali concentration potentiometrically, alkali content is found to be in a logarithmic relationship to electrode potential which makes it difficult to measure the alkali concentration directly with sufficient accuracy. Moreover, it is difficult to maintain pH electrodes in good condition when immersed in the corrosive highly alkaline pulping liquor.

It is rather important to be able to determine the amount of alkali present in the pulping liquor at different times and stages of the pulping process. If the pulping liquor contains too little alkali, the pulping process will be incomplete, which may result in an unsatisfactory cook. On the other hand, if the pulping liquor contains too much alkali, the cellulose will be degraded excessively, which results in a loss in yield, and a weaker pulp. There is therefore a great need for a process which would make it possible to measure automatically and continuously and with great accuracy the effective alkali content of a pulping liquor from the beginning to the end of either a batch or a continuous pulping process. By "effective alkali" is meant the alkali evidencing its presence by reaction with a suitably chosen alkaline buffer, which acts as an acid towards the more alkaline pulping liquor.

The method of the present invention makes it possible to determine effective alkali content of pulping liquor accurately and continuously, without the need for expensive instrumentation, thereby making it possible to continuously control a pulping sequence according to its alkali content at any given stage. It has been found that the effective alkali determined by reaction with a buffer and calorimetric analysis is a good measurement of effective alkali according to the first mentioned definition, if the buffer has a pH in the range of 9.5–12.5. Consequently, the calorimetrically determined concentration of effective alkali can be used to control pulping processes.

In the method in accordance with the invention, the heat liberated by a pulping liquor in the partial neutralization of the alkali by an acidic substance is determined calorimetrically after mixing a sample of the pulping liquor with a buffer in an amount to provide a pH within the range from about 9.5 to about 12.5, and preferably within the range from about 10.5 to about 11.5, in the resulting mixture. It has been determined in accordance with the invention that the heat liberated by partial neutralization of the alkaline pulping liquor only to this extent is an accurate measure of the effective alkali content of the pulping liquor at the time of the measurement. Thus, by sampling the pulping liquor at any stage of the pulping process, continuously or intermittently, one can obtain information on the effective alkali content which is sufficient to enable one to modify the pulping conditions so as to control the pulping as desired.

In the process in accordance with the invention, the particular final pH selected for the measurement is not critical, but for reproducible measurements in any given cook, it is desirable to select and utilize for the measurements throughout the cook a fixed final pH for the buffer-pulping liquor mixture. This is important in order to obtain reproducible results, that are meaningful in comparison to previous and subsequent alkali determinations in a given cook. This can be done by using the same buffer solutions throughout, and the same proportions between the sample volume of pulping liquor and the volume of buffer solution.

In the first step of the process, a sample of the alkaline pulping liquor is diluted to a suitable concentration at which the reaction with the buffer can take place. This concentration is in no way critical, and any desired concentration can be used, without exception. The concentration range of alkali as NaOH in normal undiluted pulping liquor is from about 1 to about 10 g NaOH per liter at the end of the cook, at the beginning of a cook from about 50 to about 90 g NaOH per liter. It is possible to use a sample of the pulping liquor undiluted, but because of the high alkali content, a relatively large amount of buffer solution will then be required and corrections for the heat of dilution when mixing concentrated sample with buffer may also be necessary, if a high degree of accuracy is needed, and this is quite unnecessary, since a smaller amount of alkali although liberating a smaller amount of heat will nonetheless liberate a proportionate quantity of heat, which can be accurately measured. The lower limit of the dilution is of course that at which the amount of heat liberated by the amount of partially neutralized alkali is too small to be measured. This dilution is not reached until the alkali concentration has been reduced to approximately 0.05 gram per liter of sodium hydroxide in the diluted sample. Normally, the pulping liquor is diluted with from 3 to 20 times its volume of water, and preferably with from 8 to 12 times its volume of water.

The diluted sample is then mixed with an amount of an acidreacting buffer sufficient to bring the pH of the resulting mixture within the range from about 9.5 to about 12.5, and preferably from about 10.5 to 11.5. Neither the amount of buffer used nor its pH are critical, provided both are at least sufficient to bring the pH of the mixture to within this range. It is not even necessary to control the amount of buffer added, provided an excess of buffer is added, and the relative proportions of buffer and sample are always the same, since an excess of buffer itself having a pH within this range prior to mixing with the pulping liquor merely ensures that the resulting mixture will also have this certain pH within this range. However, although the buffer solution does not change appreciably in pH as a result of the mixing, the pulping liquor changes from a pH in excess of 12 to a considerably lower pH, according to the buffer used and its pH.

The pH of the pulping liquor is reduced because hydroxyl ions of the effective alkali are reacting with hydrogen ions supplied from the acid component of the buffer, resulting in the formation of water in an equivalent amount. Accordingly, the consumption of the acid component of the buffer, converted to sodium hydroxide concentration by calculation, provides a good measurement of the effective alkali content of the sample of pulping liquor, and therefore presents a characteristic feature of the pulping liquor at the selected stage of the pulping at which the sample is taken. In effect, the pulping liquor is titrated by acid to an arbitrarily selected partial neutralization end point represented by any desired pH within the range from about 9.5 to about 12.5 in a single step, by mixing the pulping liquor with the buffer, the end point of the titration being determined by the pH of the buffer and being the pH of the buffer when an excess of buffer is used. The heat liberated in so doing is then measured calorimetrically.

In contrast, if a buffer of pH approximately 11 is mixed with liquor and an attempt is then made to measure changes in conductivity, any changes in the content of hydroxyl ions based on the pulping liquor sample will be difficult to establish, because of the presence of other ions in the liquor which also contribute to conductivity. However, by measurement of the heat liberated by the mixture upon mixing with an acid-reacting buffer in accordance with the instant invention, the change in hydroxyl ion content is measured directly, and this change can be measured accurately, because there is a linear relationship between the heat of partial neutralization of the pulping liquor and the alkali content thereof.

That the effective alkali content is in fact being measured by this technique has been demonstrated by comparison measurements with pure sodium hydroxide solutions of known hydroxyl ion concentrations. Tests carried out on a large number of pulping liquor samples taken at different stages of the pulping process show that the calorimetric method of measuring the heat of partial neutralization and a conventional conductometric titration technique to the same pH end point give the same effective alkali content.

It should be noted that the reaction carried out in the process of the invention resulting in the formation of water from hydrogen ions of the buffer and hydroxyl ions in the pulping liquor is not a full neutralization between a large excess of strong acid and a small quantity of alkali, in which case the excess acid determines that the final pH be on the acid side, but partial neutralization of the effective alkali with an acid-reacting buffer (in its behavior towards the alkaline sample), where an alkaline terminal pH within the range from about 9.5 to about 12.5 is selected as the end point. If the titration is effected with an excess of acid, lignin would precipitate out, upsetting the measurement results, and clogging the apparatus.

In determining the alkali content of pulping liquor, the absolute alkali defined by neutralization to pH 7 is not required. It is only the effective alkali content that needs to be determined, and this is what is measured in accordance with the process of the invention, by titration to a pH within the range from about 9.5 to about 12.5, using an acid-reacting buffer.

Buffers which can be used in the process of the invention are known, and form no part of the instant invention. Pure acids are not included, but acid mixtures with their corresponding bases are, which in aqueous solution impart a pH within the range from about 9.5 to about 12.5, preferably from 10.5 to 11.5. As exemplary of such buffers are mixtures of alkali metal phosphates with monohydrogen phosphates, and/or dihydrogen phosphates; mixtures of alkali metal carbonates with bicarbonates; mixtures of alkali metal borates and hydrogen borates; mixtures of ammonium phosphates, carbonates or borates and ammonia; quaternary ammonium compounds; organic amines; and mixtures of two or more of these systems. The relative proportions of these salts in the mixtures are selected so that the aqueous buffer solution has a pH within the range from about 9.5 to about 12.5, as stated.

The pH of the phosphate-hydrogen phosphate buffer is given by the expression:

$$pH = 11.0 + \log [PO_4^{\equiv}]/[HPO_4^{=}]$$

This buffer has its maximum buffer capacity at the pH $= pK_s$ for the equilibrium $HPO_4^{=} \rightleftharpoons H^+ + PO_4^{\equiv}$, that is at pH ≈ 11. The buffer used in accordance with the invention has the same molar concentration of $PO_4^{\equiv}$, which is a base, and of $HPO_4^{=}$, which is an acid. Consequently this buffer is acid-reacting when it is mixed with the sample of pulping liquor.

The term "acid reacting buffer" as used herein refers to a buffer which acts as an acid towards the sample of alkaline pulping liquor.

The determination of effective alklali content in accordance with this process is then used to select appropriate pulping conditions to obtain the desired cellulose pulp. Thus, if the quantity of effective alkali in the pulping liquor sample at a suitable point of time or stage in the pulping reaction is determined, it is possible to establish a suitable time-temperature sequence for the cook, so that a pulp having the desired degree of delignification is obtained, by applying the socalled "H" factor, as defined by Vroom, *Pulp and Paper Magazine of Canada* **1957** pages **228** to **231**, the disclosure of which is hereby incorporated by reference.

Thus, for example, wood can be pulped to a desired Kappa value under pulping conditions established on the basis of H factor determined from a graph of H factor against Kappa value over a range of alkalinities (in terms of g/l. NaOH) corresponding to the alkalinites required for the pulping of the type of wood selected. A family of such curves, one for each of a series of alkalinities within such range, serves as the reference graph. The alkalinity of one or more samples taken at an early stage from a pulping liquor used to digest the same type of wood is determined by the calorimetric method according to the invention. Thus, the alkalinity of the sample obtained by this measurement establishes the curve of the reference graph applicable to this sample of wood, and from this curve that is thus selected, the H factor applicable to obtain a sulfate cellulose pulp having a predetermined Kappa value is read off. The H factor in turn establishes cooking time and/or cooking temperature for the selected degree of delignification.

To obtain a sample of alkaline liquor for the determination, the sulfate cooking is begun in the conventional manner, by charging and thoroughly mixing wood chips and alkaline cooking liquor in the digester. A sulfate cooking liquor, as is well known, is an aqueous solution of alkali, usually NaOH, and Na_2S. The digestion is then begun, and allowed to continue for an initial cooking period during which at least 20% of the alkali added initially up to about 85% of the alkali added initially, preferably from 40% to 75%, has been consumed, after which a sample of the cooking liquor is taken, and titrated with an acid-reacting buffer to an end pH within the range from about 9.5 to about 12.5. Either a gradually or rapidly increasing temperature during the initial cook can be used as desired, but approximately the same rate of increase would be used afterwards as before. The determination is usually valid only for initial heating rates and temperatures approximating those used in obtaining the sample.

In preparing the pulping sample for calorimetric analysis, the rate of temperature increase during the initial digestion stages can be within the range from about 0.1° C/minute to about 25° C/minute, preferably from about 0.5° to about 10° C/minute.

The calorimetric determination of alkali concentration makes it possible to select the correct curve to determine H factor for a given (desired) Kappa value on the reference graph. The reference graph is composed of a family of curves, one for each alkali concentration (NaOH in g/l) at which a cooking can be carried out over the entire range of useful alkali concentrations. One reference graph is set up for each type of wood to be digested, for instance, spruce, fir, pine, birch, eucalyptus, beech, oak, maple, aspen, cedar, hemlock, cherry, chestnut, locust, elm, and the curves are based on the Kappa values obtained for pulps processed at given H factors in the digestor to be used. Thus, each plant would establish its own reference graph empirically, based on actual digestion experience for the type of wood to be pulped.

After the correct curve for the determined alkali concentration has been ascertained, the H factor for the Kappa value of pulp desired can be read off, and from the H factor the cooking temperature and cooking time can be ascertained.

The H factor corresponds to a unit of digestion, and represents the number of hours of digestion at 100°C. At a higher temperature, more units of digestion can be completed within a given time, and at a lower temperature, less. Thus, H factor is a measure of how much digestion is needed — at 100°C., or at temperatures above and below 100°C.

In fact, any digestion temperature can be used in the process of the invention, within the range from about 110° to about 180°C., and the cooking times also can be widely varied, from about 1 minute to about 10 hours, preferably from about 160° to about 180°C. for from about 15 minutes to about 3 hours. The H factor determines how long the cook must be at a selected temperature, and vice versa, for a given Kappa value, at the alkali concentration determined in the calorimetric analysis.

The first step in the development of the H factor by Vroom was the establishment of relative reaction rate values corresponding to a range of temperature levels. Vroom quite arbitrarily chose the reaction rate at 100°C. as unity, and rates at all other temperatures were releted to this standard. The Arrhenius equation was used in the form

$$\ln k = B - A/T$$

where

k = reaction rate,

T = temperature in degrees absolute, and

B and A are constants.

The value for A was based on the work by Larocque and Maass, *Canadian Journal of Research*, **B19:1–16 (1941)**. Then, at the arbitrarily chosen rate of unity at 100°C, the equation becomes

$$0 = B - 16{,}113/373$$

and the relative rate at any other temperature is given by

$$\ln^{-1}(43.20 - 16{,}113/T).$$

Tables of these reaction rate values can then be prepared for any desired temperature range:

TABLE I

RELATIVE RATE VALUES FOR THE "H" FACTOR IN SULFATE PULPING

Relative Rate	Temp. °C	Relative Rate	Temp. °C	Relative Rate	Temp. °C
1	100	25	130	401	160
1	101	28	131	435	161
1	102	31	132	471	162
1	103	34	133	511	163
2	104	37	134	563	164
2	105	41	135	610	165
2	106	45	136	661	166
2	107	49	137	716	167
2	108	54	138	777	168
3	109	60	139	855	169
3	110	66	140	927	170
3	111	73	141	1005	171
4	112	79	142	1089	172
4	113	87	143	1180	173
5	114	96	144	1279	174
5	115	105	145	1387	175
6	116	114	146	1503	176
7	117	126	147	1629	177
7	118	138	148	1766	178
8	119	150	149	1914	179
9	120	165	150	2042	180
10	121	182	151	2213	181
11	122	197	152	2398	182
12	123	217	153	2600	183
14	124	236	154	2818	184
15	125	260	155	3054	185
17	126	281	156	3258	186
18	127	305	157	3531	187
20	128	336	158	3827	188
22	129	364	159	4082	189

Employing these relative rate values, a curve of rate against time in hours can be plotted for any cooking cycle, and the area under such a curve is designated as the H factor.

The H factor represents the number of units of digestion per hour at 100°C. The total number of digestion units needed, the H factor value from the reference graph curve, can be obtained using the above table as a multiple of the lower number of units per hour at lower temperatures, or as a fraction of the higher number of units per hour at higher temperatures.

As a simplified example, let it be assumed that the H factor indicated by the reference graph curve is 401. Then, the desired Kappa value will be obtained after the equivalent of a 1 hour cook at 160°C, or a two hour cook at 152°C, or a 3 hour cook at 147°C; or a one-half hour cook at 168°C. This is an oversimplification because as a practical matter, however, the cook is not carried out solely at the temperature of the table, but over a gradual heating to the cooking temperature, and the H factor represents the units of digestion over the entire cooking cycle. Thus, the computation is slightly more complicated, and in fact the H factor for any cooking cycle represents the area under a relative reaction rate versus time curve. Thus, the H factor determines the shape of any of an infinite number of curves that can be used for a given cook.

As a further example, let it be assumed that the H factor is 1594. To obtain such an H factor value, one can use a cooking cycle of 1½ hours in the rising temperature stage from 80°C to 170°C, and 1½ hours at 170°C in the final cooking stage. This is shown by the following computation:

TABLE II

Time from start (hours)	Temp. °C	Relative rate of reaction	Average rate	x	Time Interval (hours)	=	"H" factor[1]
0.00	80	0					
			0	x	1/4	=	0
0.25	95	0					
			2	x	1/4	=	1
0.50	110	3					
			9	x	1/4	=	2
0.75	125	15					
			41	x	1/4	=	10
1.00	140	66					
			163	x	1/4	=	41
1.25	155	260					
			594	x	1/4	=	149
1.50	170	927					
			927	x	1 1/2	=	1391
3.00	170	927					
			Total				1594

[1] Calculated to the nearest whole number.

In the above calculation, in the rising temperature stage of the cycle, the relative rate values have been averaged over one-quarter hour periods. While of course this is an approximation, it is satisfactory for most purposes. More accurate approximations can be obtained by taking smaller time intervals, or other methods such as Simpson's rule or the trapezoidal rule may be employed.

Thus, any conditions of cooking temperature and time which give the H factor that has been determined can be used.

A computer can be used for calculating the H-factor and the cooking conditions from the H factor, and the computer can also be adapted to control the cooking automatically by sending direct signals to the control board establishing the cooking conditions.

In a continuous or in a batch process, it is possible to adapt the sampling operation to the particular digester being used, for example, using continuous sulfate digesters of the type having two cooking zones, with the cooking sequence regulated in said zones. Even in the case of batch cookings, more than one sample can be taken, if suitable, in order to have a greater control over the cooking sequence. However, it has been found that the cooking sequence can be established fully from the results provided by a single sample measured in accordance with the invention.

In a conventional pulp digestion, the same temperature and time schedule is used for all cooks, in a batch operation, or continuously, from day to day, in the continuous operation. In the process of the invention, in contrast, the cooking conditions for each batch, in a batch operation, or continuously, in a continuous operation, are varied according to the H factor determined for the particular lot of work being pulped, as shown by the sample.

Such variation can be effected in cooking temperature or in cooking time, or both, and this type of variation is the usual one, but it is also possible to adjust the alkali concentration by adding either water, black liquor or alkali to move to a different alkali concentration curve in the reference graph, and so obtain a more favorable or more convenient H factor. It may be desirable, but it is not essential, to take another sample, if more alkali is added, since the presence of a higher alkali concentration may affect the wood in a different way. If the additional alkali is added at a later stage of the digestion, however, the effect is minimal, and another sample is unnecessary.

In apparatus designed for a continuous digestion process, the chips are fed through a preheater where they are heated by steam and hot gases led from a digester and gas evaporator and are then passed continuously via a high-pressure feeder into the digester by means of circulating cooking liquor. The excess of chips and cooking liquor, if any, is recirculated. The digester is a long reactor through which the chips and liquor progress at a steady rate. The temperature is adjusted at the heaters of the fluid taken from the cooking zones and circulated to achieve the desired rate of temperature increase and cooking temperature. Liquor sample lines go to a calorimetric analyzer of the type shown in FIG. **1** or FIG. **2** which determines effective alkali content. The calorimeter can be made to signal a computer which is programmed to adjust the temperature at the heaters and in this way control the cook by prescribed variations in cooking temperature.

Provision can be made to adjust alkali by adding white and black liquor, if this appears desirable.

The pulp is removed at the bottom of the digester and is fed to a blow tank. Spent black liquor is led to the recovery plant and the evaporators, while the hot gases from the evaporators are led to the condensers and preheater.

The pulp has a substantially constant Kappa number, due to the control of the cooking conditions in accordance with the invention.

Techniques and apparatus for measurement of the heat liberated in the course of a chemical reaction are of course well known. A calorimeter is normally used for the purpose. However, prior to the instant invention this technique has not been applied to determination of the effective alkali content of a cellulose pulping liquor. When applied to the determination of effective alkali in cellulose pulping liquor, the calorimetric process of the invention affords a number of advantages over previously-used alkali determination techniques.

The calorimetric method makes it possible to carry out the analysis of effective alkali content of the pulping liquor continuously, which is of particular importance with continuous pulping processes. This means that one can continuously meter the effective alkali

content of the pulping liquor from the start to the end of the pulping process with a very short time lag, due only to the transport time for pumping the sample to the calorimetric analyzer. The calorimeter is of simple construction, and gives strong signals using, for example, thermal emf measurements from thermopiles, or resistance changes from thermistors. There is moreover a linear relationship between the signal and the effective alkali content, which makes it possible to determine the effective alkali content, which makes it possible to determine the effective content with a considerable degree of accuracy.

Purity requirements imposed on the buffer are moderate, which means that available chemicals can be used, without the necessity of special purification techniques. The buffer reagent is added in excess, and hence the terminal point of the chemical reaction on which the analysis is based is automatically reached, and the endpoint does not have to be determined by any complicated procedure. Even if excess buffer is present, there can be no neutralization reaction beyond the pH determined by the buffer. The accuracy of the analysis is in fact very high, and the standard deviation is 0.2 gram per liter NaOH, or better.

Calorimetric measuring apparatus which can be used are illustrated in the drawings, in which:

FIG. **1** illustrates diagramatically one embodiment of an isothermal calorimeter suitable for the calorimetric effective alkali analysis of alkaline pulping liquor;

FIG. **2** illustrates diagrammatically one embodiment of adiabatic calorimeter, suitable for the calorimetric effective alkali analysis of alkaline pulping liquor;

FIG. **3** is a typical titration curve showing analytical results obtainable with the instrument of FIG. **1**; and

FIG. **4** is a titration curve showing analytical results obtainable with the instrument of FIG. **2**.

The calorimeter of FIG. **1** utilizes the principles of isothermal calorimetry, and includes a three-line peristaltic pump **4**, and thermostat coils **6**, **6'** arranged in a thermostat bath **12** together with a mixing vessel **7** and a reaction vessel **8**. A thermopile **9** is in heat-receiving relation to the reaction vessel **8**, and the thermopile **9** in turn is in heat-conducting contact with a metal vessel **10**, immersed in the thermostat bath **12** and surrounding the mixing vessel **7** and reaction vessel **8**. Reaction heat liberated in the reaction vessel **8** thus can be conducted through the thermopile to the thermostat bath, and the signal voltage developed as a result of this heat exchange can be taken out through the line **13** from the thermopile, as a measurement of the heat of partial neutralization conducted from the reaction vessel **8** to the thermostat bath **12**.

Line **1** conducts buffer solution to the peristaltic pump **4**. Line **2** conducts pulping liquor to the peristaltic pump **4**. Line **3** conducts a reference solution to the peristaltic pump **4**. The valves **5**,**5'** in lines **2**, **3** on the other side of the peristaltic pump make it possible to pass either a pulping liquor solution or a reference solution through the thermostat coil **6'** to the mixing vessel **7**, while the line **1** passes an acid-reacting buffer solution through the thermostat coil **6** to the mixing vessel **7**.

In operation at the start, valve **5'** is open and valve **5** is closed, the acid-reacting buffer solution and the reference solution are pumped (in the same proportions as those later used for mixing the cooking liquor sample and acid-reacting buffer) through lines **1** and **3**, respectively, by the peristaltic pump **4** through the thermostat coils **6, 6′** to the mixing vessel **7**, from which the mixture enters the reaction vessel **8.** The heat liberated upon this mixing is conducted to the thermopile **9.** The mixture is then removed through the outlet line **11.**

The signal obtained at **13** when the acid-reacting buffer solution and reference solution are mixed can be taken as a base or zero line.

After this line has been determined, the supply of reference solution through line **3** is cut off by closing valve **5′**, and the pulping liquor is then substituted via line **2,** by opening valve **5.** A stream of pulping liquor is passed to the reaction vessel **7.** The heat of partial neutralization now developed is considerably greater than the heat liberated from mixing the buffer and reference solutions, and give a different signal by way of the thermopile. The difference between the two signals is a measurement of the effective alkali content of the sample. By carrying out analyses using this calorimeter on solutions of known alkali contents, it is possible to calibrate the instrument. An instrument of this type gives a linear relationship between the signal in millivolts (above the signal obtained with the reference solution), and the content of sodium hydroxide in grams per liter. This is shown in FIG. **3**, which illustrates a calibrating curve for an instrument of this type. In this instance, a solution of sodium sulfate was used as the reference solution.

The calorimeter illustrated in FIG. **2** is adapted for adiabatic calorimetric measurements. The apparatus includes a peristaltic pump **24**, thermostat coils **26,26′**, a mixing vessel **27**, a reaction vessel **28**, thermistors **33**, 34 in the thermostat bath at the outlet ends of the thermostat coils **26,26′** and at the reaction vessel **28**, and a thermostat bath **32**. The inlet line **21** leads buffer solution to the peristaltic pump **24**, and then through the thermostat coil **26** to the mixing vessel **27**. The inlet line **22** leads a cooking liquor sample solution to the peristaltic pump **24**, whence (according to the position of the valve **25**) the solution passes through the thermostat coil **26′** to the mixing vessel **27**, while the inlet line **23** leads a reference solution (according to the position of valve **25′**) through the thermostat coil **26′** to the mixing vessel **27.**

When the buffer and reference solutions are pumped via lines **21,23** through the mixing vessel **27** into the reaction vessel **28**, the thermistors **33, 34** will register a small rise in temperature owing among other things to friction in the mixing vessel, and to the fact that the buffer and reference solutions can liberate a small heat of dilution. When mixing the buffer and pulping liquor solutions, however, a very large amount of heat is liberated, in proportion. By making corrections for the temperature increase registered when the buffer and cooking liquor samples are mixed, and plotting the results as a function of the sodium hydroxide content of the calibrating solution, the results shown in FIG. **4** are obtained.

The following Examples represent preferred embodiments of the calorimetric analytical technique of the invention, and compare the results obtained with the results obtained using a conductometric titration according to Ser. No. 142,226, filed May 11, 1971, now abandoned, and its continuation-in-part, Ser. No. 402,697, filed Oct. 2, 1973 which is accurate but time-consuming.

EXAMPLE 1

This Example illustrates the analysis of the effective alkali content in black sulphate liquor.

Pine wood chips were charged to a 30 liter circulating digester, and cooked with a sulphate pulping liquor under the following conditions:

Effective alkali	22%
Sulphidity	29.4%
Wood/liquor ratio	1:3.7
Maximum temperature	170°C
Temperature rise	80 to 170°C/150 minutes
Time at maximum temperature	60 minutes

Samples of the pulping liquor were taken at 110°, 130°, 150°, 160° and 170°C during the cook. Samples were also taken after 1 hour at the maximum cooking temperature of 170°C. The pulping liquor samples were then analyzed by an accurate conductometric titration, adiabatic calorimetric analysis using the apparatus of FIG. **2**, and isothermal calorimetric analysis using the apparatus of FIG. **1**.

In taking the calorimetric measurement using these calorimeters, the pulping liquor sample solutions were diluted to 10 times their volume with 0.6 molar sodium sulphate solution. The diluted samples were then pumped at a flow rate of 1.8 ml/min to the calorimeters.

The buffer solution was an aqueous solution of disodium monohydrogen phosphate and trisodium phosphate, having the composition 0.2 molar Na_2HPO_4 plus 0.2 molar $Na_3PO_4 \cdot 12\ H_2O$ to 2 liters of buffer solution. The ionic strength of the buffer was 1.8.

The reference solution was 0.6 molar sodium sulphate whose ionic strength was 1.8. Thus, these three solutions, the buffer, the cooking liquor sample and the reference solution, all had the same ionic strength. Sodium sulphate was used as the reference solution and as a diluent because of the small amount of heat of dilution liberated thereby. The flow of buffer and reference solution was 1.8 ml per min. for each.

To calibrate the calorimeters, pure sodium hydroxide solutions were diluted with sodium sulphate in the same way as the samples of pulping liquor. The following results were obtained:

TABLE III

Concentrated solution NaOH, g/l	Diluted solution NaOH, g/l	Signal from calorimeter in FIG. 1, mV
10	1	1.37
20	2	2.75
30	3	4.10

The results are shown in FIG. **3**, which can be used as a calibration curve when determining the alkali content of pulping liquor.

TABLE IV

Concentrated solution NaOH, g/l	Diluted solution NaOH, g/l	Signal from calorimeter in FIG. 2 Δ T °C
10	1	0.117
20	2	0.235
30	3	0.350

The results are shown in FIG. **4**, which can be used as a calibration curve when determining alkali content of pulping liquor.

The analytical results obtained for the alkali content as g per liter of NaOH is shown in the following Table:

TABLE V

Alkali content (g/l NaOH) Comparison of different methods

	FIG. 1		FIG. 2		
	Isothermal calorimeter		Adiabatic calorimeter		Conductometric Titration
Sample	mV	NaOH g/l	Δ T°C	NaOH g/l	NaOH, g/l
110°C	4.46	32.5	0.382	32.5	30.6
130	3.50	25.5	0.306	26.0	23.7
150	2.92	21.3	0.249	21.2	18.6
160	2.22	16.2	0.191	16.2	14.6
170	1.64	12.0	0.144	12.2	9.2
170	1.02	7.4	0.087	7.4	5.6
	From calibration curve shown in FIG. 3		From calibration curve shown in FIG. 4		

The results show good agreement between the adiabatic and isothermal calorimetric measurements and the conductometric titration measurement.

EXAMPLES 2 to 11

These Examples represent a determination of effective alkali in a black sulphate liquor on a plant scale.

From a sulphate pulping system for birch and pine, having a daily production of 1250 tons, were taken a series of samples for determining the alkali content of the pulping liquor. The samples were diluted with sodium sulphate solution as in the previous Example and the composition and flow of buffer and reference solution was also the same as in the previous Example. In order to cover the widest possible range of alkali contents, the pulping liquor samples were taken at several different cooking temperatures during the cook. Furthermore, in order to cover variations in the composition of the pulping liquor as a result of other factors than the alkali content, such as conditions in the recovery system, the time during which the different samples were taken was relatively long, in fact several weeks. The results obtained are recorded in Table VI below.

TABLE VI

Alkali content (g/l NaOH) registered by Apparatus of FIG. 1

Example	Temp. °C	mV	Calorimeter g/l	Conductometric Titration
2 Birch	120	2.33	16.9	17.0
	130	2.17	15.7	14.8
	140	1.95	14.1	12.7
	150	1.63	11.8	11.2
3 Birch	120	2.75	19.9	19.2
	130	2.51	18.2	17.8
	140	2.31	16.7	16.1
	150	2.03	14.7	14.2
4 Pine	120	2.34	17.0	16.1
	130	2.28	16.5	15.9
	140	2.11	15.3	14.3
	150	1.18	14.3	14.0
	160	1.67	12.1	12.0
5 Birch	120	2.77	20.1	19.3
	130	2.50	18.1	17.4
	140	2.21	16.0	15.1
	150	1.98	14.3	13.8
6 Pine	120	2.55	18.5	18.3
	130	2.48	18.0	17.3
	140	2.25	16.3	16.2
	150	2.07	15.0	14.8
	160	1.85	13.4	13.6
7 Birch	120	2.63	19.1	19.6
	130	2.46	17.9	17.6
	140	2.19	15.9	16.2
	150	1.76	12.8	13.8
8 Pine	120	2.25	16.4	16.9
	130	2.19	15.9	15.6
	140	2.05	14.9	14.4
	150	1.75	12.7	12.8
	160	1.49	10.7	10.3
9 Birch	130	3.03	22.0	21.9
	140	2.83	20.6	20.6
	150	2.64	19.2	19.5
	160	2.53	18.4	18.7
10 Pine	120	3.35	24.3	24.9
	130	2.89	21.0	21.3
	140	2.46	17.9	18.0
	150	2.70	16.0	16.2
	160	1.76	12.8	13.3
11 Pine	120	3.14	22.8	22.4
	130	2.89	21.0	30.9
	140	2.64	19.2	19.3
	150	2.49	18.1	17.9
	160	2.31	16.8	16.5

As the Table shows, good agreement is obtained between the conductometric titration and the calorimetric measurement. Regression analysis on the analysis values gives the relationship $y = 0.98\ x + 0.50$, where y is the calorimetric analysis NaOH g/l,x is the conductivity titration NaOH g/l, the regression coefficient is 0.980 and the correlation coefficient is 0.993.

A very good statistical agreement prevails.

Having regard to the foregoing disclosure, the following is claimed as the inventive and patentable embodiments thereof:

1. A process for determining the effective alkali content of an alkaline pulping liquor comprising an alkali metal hydroxide and an alkali metal sulfide, which comprises taking a sample of the alkaline pulping liquor, mixing the sample with an acid reacting buffer having a pH less than the pH of the alkaline pulping liquor, in an amount to bring the pH of the resulting mixture to within the range from about 9.5 to about 12.5, measuring the heat liberated in the resulting partial neutralization of the effective alkali calorimetrically, and from such measurement determining the effective alkali content of the pulping liquor.

2. A process in accordance with claim **1** in which the pulping liquor is diluted with from 3 to 20 times its volume of water prior to mixing with the acid-reacting buffer.

3. A process in accordance with claim **1** in which the buffer is in an aqueous solution having a pH within the range from about 9.5 to about 12.5.

4. A process in accordance with claim **3** in which the acid-reacting buffer is selected from the group consisting of acid-reacting mixtures of alkali metal borates and hydrogen borates; mixtures of alkali metal carbonates with bicarbonates; mixtures of alkali metal phosphates with monohydrogen phosphates or dihydrogen phosphates; mixtures of ammonium phosphates, carbonates or borates and ammonia; quaternary ammonium compounds; organic amines; and mixtures thereof, the relative proportions of the mixtures being selected so that the aqueous solution has a pH within the range from about 9.5 to about 12.5.

5. A process in accordance with claim **1** wherein the calorimetric measurement is effected continuously by continuously mixing a stream of cooking liquor and a stream of acid-reacting buffer, and the heat is liberated in the course thereof.

6. A process in accordance with claim **1** wherein the calorimetric measurement is taken isothermally.

7. A process in accordance with claim **1** wherein the calorimetric measurement is taken adiabatically.

8. A process in accordance with claim **1** in which the alkali metal hydroxide is sodium hydroxide, and the alkali metal sulfide is sodium sulfide.

9. A process for preparing sulfate pulps of relatively uniform quality having a desired Kappa number which comprises pulping wood using an alkaline pulping liquor comprising alkali metal hydroxide and alkali metal sulfide at a cooking temperature and for a cooking time established on the basis of H factor determined by a graph of H factor against Kappa value at an alkali concentration corresponding to the effective alkali concentration determined calorimetrically for the alkaline pulping liquor used for pulping of the type of wood selected by the process of claim **1**.

10. A process according to claim **9** in which the cooking is carried out batchwise.

11. A process according to claim **9** in which the cooking is carried out continuously.

12. A process according to claim **9** in which the metal hydroxide is sodium hydroxide.

13. A process according to claim **9** in which the effective alkali concentration of several samples taken at spaced digestion stages from the alkaline pulping liquor is determined and utilized to adjust the cooking temperature and cooking time for the pulping.

14. A process according to claim **9** in which the graph comprises a family of curves at a series of alkali concentrations and applicable to this type of wood, and the H factor to obtain a sulfate cellulose pulp having a predetermined Kappa value is read off from the curve corresponding to the effective alkali concentration found.

15. A process according to claim **9** in which to obtain a sample of alkaline pulping liquor for the H factor determination, the sulfate cooking is begun by charging and mixing wood chips and alkaline cooking liquor in the digester, the digestion is then begun, and allowed to continue for an initial cooking period during which at least 20% of the alkali added initially up to about 85% of the alkali added initially has been consumed, using an increasing temperature, after which a sample of the cooking liquor is taken and mixed with acid-reacting buffer and the effective alkali content determined and then the pulping is carried out at approximately the same rate of temperature increase during the initial stages until the final cooking temperature is reached.

16. A process according to claim **15** in which the rate of temperature increase during the initial digestion stages is within the range from about 0.1°C/minute to about 25°C/minute.

17. A process for determining the conditions needed in controllably obtaining a predetermined degree of delignification and therefore a predetermined Kappa number in the manufacture of sulfate pulp, using an alkaline pulping liquor comprising an alkali metal hydroxide and an alkali metal sulfide, which comprises taking a sample of alkaline pulping liquor at an early stage in the pulping of wood of the type to be digested, determining the effective alkali content of the sample according to the process of claim **1**, and from this alkali content determining the H factor at the desired Kappa value in the finished sulfate pulp, and from the H factor determining the cooking time and temperature relationship needed to obtain the pulp of this Kappa value.

18. A process according to claim **17** in which the sample is prepared by mixing wood chips and alkaline sulfate cooking liquor, and continuing the digestion for an initial cooking period while consuming alkali until an amount within the range from about 20% to about 85% of the alkali added initially has been consumed.

19. A process according to claim **17** in which the digestion is carried out in the early stage at a rising temperature within the range from about 0.1° to about 25°C per minute.

20. A process according to claim **17** in which the H factor is determined from a graph of H factor against Kappa value at the determined NaOH concentration.

21. A process according to claim **20** in which the graph comprises a family of such curves, one for each of a series of NaOH concentrations required for the pulping of the type of wood selected.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,888,726 Dated June 10, 1975

Inventor(s) Bengt Goran Hultman

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Page 1 [73] : "Mooch" should be --Mo och--

Column 5, line 22 : "$pH = 11.0 + \log [PO_4 \equiv] / [HPO_4 =]$"
should be
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--$PO_4^{\equiv}$ --

Column 5, line 34 : "alklali" should be --alkali--

Signed and Sealed this

twentieth **Day of** *April 1976*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks

UNITED STATES PATENT OFFICE

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