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Determination of Sodium Sulfate Requirement for Obtaining Sodium Sulfide Content in Green Liquor at the Recovery Boiler Unit in PT XYZ North Sumatra

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A B S T R A C T

Black liquor is a residual cooking liquid containing organic chemicals utilized as fuel in the recovery boiler and inorganic chemicals that can be recovered into cooking liquid through the recovery boiler process. The recovery boiler is a specialized boiler unit used to restore black liquor by reducing sodium sulfate into sodium sulfide. The research method involved field observations, liquor content analysis, and stoichiometric calculations to determine the sodium sulfate requirement. The calculations revealed that the sodium sulfide content obtained from the recovery boiler process in green liquor was 24.428 g/l Na_2O, requiring a reactive amount of 46,5225.0328 kg/day of sodium sulfate. The target sodium sulfide content in the green liquor aimed for was 18-30 g/l. The results indicated that the sodium sulfide content has met the predetermined target and can be utilized for subsequent processes.

INTRODUCTION

The Recovery Boiler is a unit designed to recover inorganic chemical compounds present in black liquor that the residual cooking solution derived from the pulp making process in a digester. Black liquor is the leftover solution produced during the pulp-making process (pulping process). It contains 20-30% inorganic compounds, mainly sodium carbonate and sodium sulfate originating from residual cooking chemicals and reaction byproducts during the cooking process, 40-50% organic compounds derived from wood chips in the form of wood fibers and lignin, with the remainder being water. The inorganic compounds in black liquor can be reverted back into white liquor through a chemical recovery process (Hupa, 2007; Shalihin, 2021).

White liquor is a cooking solution primarily composed of 58.6% (w/w) sodium hydroxide, 27.1% (w/w) sodium sulfide, and 14.2% (w/w) sodium carbonate. Sodium hydroxide (NaOH) in the cooking solution (white liquor) functions to degrade and dissolve lignin, making it easier to separate from cellulose and hemicellulose (Betova et al., 2011; Sevimli et al., 2014). In the process of recovering black liquor into white liquor, black liquor derived from pulp washing initially undergoes concentrated from 15-17% to 70-75% dry solid concentration. This concentrated aims to evaporate the water content in the black liquor to facilitate the combustion process. Following the concentration, salt cake (Na_2SO_4) is added to replace oxidized sodium sulfide after the concentration process (Cardoso et al., 2006; Shalihin, 2021). The concentrated black liquor is then sprayed into the recovery boiler furnace, where organic compounds are burned, and Na_2SO_4 is reduced to Na_2S. The burnt black liquor in the recovery boiler furnace contains high-energy content (5,800-6,600 Btu/lb dry solids) used to produce steam (PT XYZ Sumatera Utara, 2002).

From the combustion process of concentrated black liquor, apart from generating heat, this combustion process also yields the melting of inorganic salts commonly referred to as 'smelt,' which accumulates in the char bed. The char bed constitutes the heart of the recovery boiler. Char bed is a stack of material comprising carbon, some solidified black liquor solids, and smelt. The reduction of sodium sulfate to sodium sulfide in the char bed is the primary chemical process in the recovery cycle. The release of sodium, potassium, and chloride also occurs in the char bed (Maggs, 2021).

Smelt is an inorganic reaction product in the recovery furnace. Smelt contains sodium carbonate (Na_2CO_3) at 60-65%, sodium sulfide (Na_2S) at 25-30%, and sodium hydroxide (NaOH) at 2-3%. Smelt exits the furnace through a smelt spout and is dissolved with weak wash liquor in the smelt dissolving tank, resulting in a carbonate salt solution called green liquor. Green liquor is obtained by diluting smelt (the molten product from burning black liquor) discharged from the recovery boiler's combustion chamber, diluted with weak wash liquor. Green liquor consists mainly of sodium hydroxide (NaOH) at 14.2%, sodium sulfide (Na_2S) at 27.1%, and sodium carbonate (Na_2CO_3) at 58.6%, with a density of 1.185 kg/l (Balint et al., 2023; Juliani, 2014). Subsequently, green liquor undergoes a reaction with calcium hydroxide ($Ca(OH)_2$) to recover NaOH in the recausticizing unit. The causticization product is then directed to the white liquor clarifier to remove $CaCO_3$ deposits, producing white liquor suitable for reuse in the digester cooking process (Damasceno et al., 2020).

The recovery boiler at PT XYZ in North Sumatra is one of the boilers used to recover cooking chemicals in the black liquor by burning it in the recovery boiler furnace. Here, Na2SO4 in the black liquor is reduced to Na2S, resulting in the production of green liquor. Subsequently, this sodium sulfide will hydrolyze to form sodium hydroxide and sodium hydrosulfide. The desired sodium sulfide content in the green liquor is within the range of 18-30 gpl (PT XYZ Sumatera Utara, 2002). Therefore, to determine the sodium sulfide content in the green liquor according to the target, research is conducted to ascertain the sodium sulfate requirement in the recovery boiler process.

LITERATURE REVIEW

Sodium sulfate

Sodium sulfate is the sodium salt of sulfuric acid. In its anhydrous form, this compound appears as white crystalline solids with the chemical formula Na_2SO_4, also known as the mineral thenardite; meanwhile, in its decahydrate form, it's represented as $Na_2SO_4.10H_2O$. Sodium sulfate is used in detergent production and in the paper pulp-making process (kraft process). It isn't an active chemical during the kraft pulp-making process but rather a source to produce sodium sulfide (Na_2S). Most of the sodium sulfate in the recovery boiler is reduced to Na_2S. This reduction efficiency is referred to as the reduction efficiency. Sodium sulfide (Na_2S) is produced during the creation of kraft cooking liquor (by reducing Na_2SO_4 into Na_2S); this chemical doesn't directly participate in the delignification reaction. Sodium sulfide reacts with water (i.e., in the white liquor) and produces sodium hydrosulfide (NaSH) and sodium hydroxide (NaOH). The active chemicals during the kraft pulp-making process are sodium hydroxide (NaOH) and sodium hydrosulfide (NaSH), which degrade and dissolve lignin. The addition of NaOH aids in degrading and dissolving lignin, making it easier to separate from cellulose and hemicellulose. Meanwhile, Na_2S not only accelerates delignification but also protects carbohydrates from degradation, resulting in high yields and good physical strength (Balint et al., 2023; Maggs, 2021).

Black liquor

In the kraft pulp-making process, black liquor basically consists of three different parts: lignin, carbohydrate degradation products, resin, and fatty acids (tall oil). Currently, lignin and carbohydrate degradation products are predominantly utilized as fuel to generate energy for the process needs. Black liquor is a highly complex mixture containing a large number of components with different structures and arrangements. The organic components in black liquor produced after the pulp-making process essentially comprise lignin, carbohydrate degradation products, alongside small portions of extractives and their reaction products. Black liquor is a residual solution generated during the pulp-making process (pulping process). The main components of black liquor are water, inorganic compounds from residual chemicals used in wood chip cooking, reaction byproducts during the cooking process, and organic compounds from the wood chips. Black liquor is a significant environmental pollutant if discharged without treatment, hence efforts are made to reduce its discharge impact. Usually, the organic compounds in black liquor are used as fuel, while its inorganic compounds can be recovered. Black liquor serves as fuel in the recovery boiler. Typically, this mixture originates from both hardwood and softwood. The physical and chemical properties of black liquor significantly influence its evaporation process. Before passing through the recovery boiler furnace, concentrated black liquor is mixed with sodium sulfate, commonly known as "salt cake." Salt cake is another term for sodium sulfate (Na_2SO_4). Adding salt cake aims to replace oxidized sodium sulfide after the evaporation process. Salt cake can be added in granular form to the concentrated black liquor. Salt cake and concentrated black liquor are mixed in a stirring-equipped mixing tank to ensure uniform distribution of salt cake within the black liquor. When concentrated black liquor is burned in the combustion furnace (furnace), salt cake settles at the furnace base. This is where the actual reduction reaction occurs, transforming salt cake into molten liquid. Oxygen within the salt cake is released, forming sodium sulfide (Na_2S). The amount of salt cake added to the concentrated black liquor is adjusted according to the desired sulfidity in the pulp-making process. Sulfidity is measured, and salt cake addition is varied to maintain the desired conditions (Maggs, 2021; Mandal et al., 2021; Reyes et al., 2020; Sumarna et al., 2023).

Recovery boiler

The recovery boiler is a boiler unit used to recover or regenerate inorganic chemical substances within the residual cooking liquid of pulp for reuse. The primary fuel used in the recovery boiler is Heavy Black Liquor (HBL) (70% solid). Heavy black liquor contains 20-30% inorganic chemical compounds, primarily sodium carbonate (Na_2CO_3) and sodium sulfate (Na_2SO_4), and 40-50% organic compounds derived from wood during cooking in the digester, such as wood fibers, lignin, with the remainder being water. In other words, the recovery boiler is a part of the chemical recovery process. Through the combustion of heavy black liquor, approximately 3100-3500 kcal/kg dry solid of heat energy is released. Part of this thermal energy is utilized to convert inorganic compounds, while the rest is used to generate steam (PT.TPL, 2002). The primary function of the recovery boiler is to reduce sodium sulfate (Na_2SO_4) in black liquor to sodium sulfide (Na_2S) inside the combustion furnace. Within the combustion furnace, heat is generated from the combustion of organic content in the black liquor, used to produce steam. Meanwhile, the inorganic content in the black liquor is recovered in the form of smelt (melting liquid) (Hupa, 2007; Shalihin, 2021; Simatupang et al., 2021).

Green liquor

The smelt is a solid alkali substance resulting from the combustion of concentrated black liquor in the recovery boiler furnace and forms a surface at the bottom of the furnace. Typically, smelt contains sodium carbonate (Na_2CO_3)

at 60-65%, sodium sulfide (Na_2S) at 25-30%, and sodium hydroxide (NaOH) at 2-3%. Smelt resulting from the combustion in the furnace enters the dissolving tank. Inside the dissolving tank, smelt at temperatures of 870-1040 °C is dissolved using weak wash liquor to form green liquor. In the tank, steam is sprayed at a pressure of 3.5 kg/cm^2 to break the smelt flow into smaller droplets, facilitating better reaction with the cold weak wash liquor. This process leads to the formation of green liquor (McKeough, et al., 1995). Green liquor is obtained from diluting smelt, having a density of 1.185 kg/L, a green color, a faint sulfur smell, and containing sodium hydroxide (NaOH) at 14.2% (w/w), sodium carbonate (Na_2CO_3) at 58.6% (w/w), and sodium sulfide (Na_2S) at 27.1% (w/w) (Juliani, 2014).

METHODOLOGY

Tools and materials

Several tools used in this research include a black liquor pump, mixing tank, furnace, smelt spout, dissolving tank, erlenmeyer flask, digital burette, volumetric flask, dropping pipette, volumetric pipette, and pH meter. Some of the materials used include black liquor, sodium sulfate or commonly known as salt cake, 10% barium chloride, 0.5 N hydrochloric acid, 40% formaldehyde, methyl orange indicator, phenolphthalein indicator, and distilled water.

Procedure for direct observation

Dilute black liquor with a concentration of 15-18%, originating from the washing unit, is directed to the evaporator to be concentrated to 70-72%. Subsequently, the concentrated black liquor is pumped into the mixing tank to blend with sodium sulfate, commonly known as salt cake, before being directed to the recovery boiler's combustion furnace. Following this process in the mixing tank, the concentrated black liquor is sprayed or misted into the combustion furnace. The combustion within the furnace produces smelt. This smelt is then pumped into a storage tank or dissolving tank to be diluted with weak wash liquor. The resulting liquid is then sent to the recausticizing unit to be processed into white liquor.

Liquor content analysis

To determine the levels of sodium sulfide and sodium sulfate in black liquor, green liquor, and weak wash liquor, three types of analysis, A, B, and C, were conducted. Analysis A involved pipetting 5 ml of the sample into a 250 ml Erlenmeyer flask. Then, 25 ml of 10% barium chloride was added to the flask containing the sample. Subsequently, 3-4 drops of phenolphthalein indicator were added. The solution was titrated with 0.5 N hydrochloric acid, and the volume of the titration was recorded as volume A. Analysis B followed Analysis A, where after reaching the endpoint of the titration in test A, 5 ml of 40% formaldehyde was added until the solution turned pink. Then, titration continued until the pink color disappeared, and the volume of the titration was recorded as volume B. Analysis C was carried out after reaching the endpoint of the titration in test B. Methyl orange indicator was added in 3-4 drops.

Titrations continued until the solution turned purple-red (at pH 4.0), and the volume was recorded as volume C. The equation for calculating the need for sodium sulfide is formulated as follows.

$$massa\ natrium\ sulfida = \frac{2(B-A)\times N_{HCl}\times BE\ Na_2O}{Volume\ sampel} \ldots\ldots\ldots\ldots(1)$$

RESEARCH RESULT

Table 1. Heavy Black Liquor Composition Analysis

Observation	Conc. Black Liquor (m^3/day)	Volume (mL)	Titration Volume 0,5 N HCl (mL)			Salt Cake (Kg/day)
			A	B	C	
1	1382,2	5	2,42	3,5	9,3	20.000
2	1382,3	5	2,35	3,52	9,5	20.000
3	1382,0	5	2,44	3,49	9,24	20.000

Table 2. Green Liquor Composition Analysis

Observation	Green Liquor (m^3/day)	Volume (mL)	Titration Volume 0,5 N HCl (mL)		
			A	B	C
1	1069,1	5	9,6	13,54	39,5
2	1068,9	5	9,8	13,9	39,8
3	1068,8	5	9,67	13,79	39,69

Table 3. Weak Wash Liquor Composition Analysis

Observation	Weak Wash Liquor (m^3/day)	Volume (mL)	Titration Volume 0,5 N HCl (mL)		
			A	B	C
1	1063,3	5	5,4	6,3	7,8
2	1065,8	5	5,6	6,3	7,9
3	1063,1	5	5,3	6,2	7,6

Table 4. Need of Sodium Sulfate and Sodium Sulfide

Observation	Alkali Composition (g/L Na_2O)			Sodium Sulfate (kg/day)	Sodium Sulfide (kg/day)
	Black Liquor	Green Liquor	Weak Wash Liquor		
1	6,696	24,428	5,58	46.225,0328	25.391,2152
2	7,254	25,42	4,34	51.637,3060	28.364,15
3	6,51	25,544	5,58	48.942,6572	26.883,99
Average	6,82	25,131	5,167	48.934,9987	26.879,7880

DISCUSSION

Sodium sulfate is a chemical substance that is inactive until it is converted into sodium sulfide. Its activation process takes place inside the recovery boiler furnace at a combustion temperature of 1130 °C, where sodium sulfate is reduced to sodium sulfide. Sodium sulfide in the pulp-making process functions to expedite the delignification process and protect carbohydrates from degradation, resulting in high yield and good physical strength. Titrimetry or volumetric analysis is one of the widely-used methods for determining the amount of a chemical substance. This method is used extensively for several reasons. Basically, titrimetric methods consist of measuring the volume of a reagent solution required to react stoichiometrically with the substance to be determined (Simatupang et al., 2020; Tarigan & Simatupang, 2019). Based on the titration results from each sample, the data shown in Table 1, 2, and 3 were obtained.

In Table 1, the observation of the heavy black liquor flow rate ranged around 1382 m^3/day conducted three times with a sample volume of 5 mL and salt cake of 20,000 kg/day. The volume of hydrochloric acid titration in analysis test A ranged from 2.35-2.44 mL, 3.49-3.52 mL for analysis test B, and 9.24-9.5 mL for analysis test C. In Table 2, the observation of the green liquor flow rate ranged around 1069 m^3/day with a sample volume of 5 mL and the volume of hydrochloric acid titration increased ranging from 9.6-9.8 mL for analysis test A, 13.54-13.9 mL for analysis test B, and 39.5-39.8 mL for analysis test C. Meanwhile, in Table 3, the observation of the weak wash liquor flow rate around 1063 m^3/day shows that the volume of hydrochloric acid titration decreased ranging from 5.3-5.6 mL for test analysis A, 6.2-6.3 mL for test analysis B, and 7.6-7.9 mL for test analysis C.

In the context of pulp-making processes, determining all components in the cooking liquor on an "Na_2O equivalent" basis, which helps in placing the active constituents on the sodium ion content, is essential. Expressions such as sulfidity, causticizing, effective alkali, and others describe the conditions of the cooking liquor in the kraft process. These expressions provide information about different chemical % or g/l chemical constituents expressed as Na_2O

showing the actual chemical relationship between them (Hocking, 1993). The data from Table 1, 2, and 3 were then processed and analyzed to obtain the requirements for sodium sulfide and sodium sulfate based on equation (1). The amount of sodium sulfide and sodium sulfate requirements are tabulated in Table 4. The analysis of the heavy black liquor content obtained an average concentration of sodium sulfide of 6.82 g/L Na_2O, becoming 25.131 g/L Na_2O in the green liquor. This value indicates that the sodium sulfide content in the green liquor is still within the standard range (18-30 g/L). From this data, it can be concluded that the average required sodium sulfide amounts to 26,879.7880 kg/day with an average requirement for sodium sulfate at 48,934.9987 kg/day.

CONCLUSIONS AND RECOMMENDATIONS

Based on the research findings, it can be concluded that the average sodium sulfate requirement reaches 48,934.9987 kg/day with a sodium sulfide yield of 26,879.7880 kg/day. The sodium sulfide content in the green liquor remains within the standard range of 25.131 g/L Na2O. Recommendations that can be proposed include the need for effective monitoring and control of black liquor concentration, as well as proper maintenance and operation of equipment. Furthermore, to obtain optimal green liquor quality, attention should be given to its density, which should be around 70%, and the continuous supply of black liquor in the combustion process.

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