

Valmet

Technical Paper Series

Production of Sulfuric Acid from Incineration of Pulp Mill Non-Condensable Gases – a Biorefinery Concept

Executive Summary

Sulfur is an essential chemical element in Kraft pulp mills and it actively participates in reactions with wood chips to produce pulp. Sulfur is present in black/white liquors and discharge waters and escapes pulp mill processes as non-condensable gases (NCG). Traditionally, NCG are carefully collected and incinerated either in the recovery boiler / power boiler / lime kiln or separate NCG boiler. In many cases oxidized sulfur in flue gas is not recovered and thus increases the emission levels of the mill. To benefit all pulp mills, Valmet has developed sulfuric acid production technology from the incineration of NCG.

The sulfur dioxide produced from NCG incineration is oxidized to sulfur trioxide in a catalytic converter and condensed along with water vapor to yield sulfuric acid. The first sulfuric acid plant of this type started up in 2017 at Äänekoski, Finland and has continuously operated. The internally produced sulfuric acid can replace purchased acid at several locations within the mill. The present work describes production of sulfuric acid from NCG incineration, environmental advantages and closing the mill chemical balances with sulfuric acid plant. This plant is one step closer to achieving the realization of future biorefinery concepts.

Introduction

Active chemicals containing sulfur (S) and sodium (Na) as main elements play a vital role in chemical pulp mills. In any given mill process, Na/S exists as combination of different chemical forms, i.e. in cooking as Na_2S , in black liquor as Na_2S , Na_2SO_4 , Na_2SO_3 , in the dissolving tank mainly as Na_2SO_4 , Na_2SO_3 and many other forms. Efficiency of a pulp mill is defined by the amount of pulp it produces by maintaining an active chemical recycling process. However, chemical recycling is disrupted due to the complexity of chemicals coming in and going out of the mill processes. Many mills around the world are facing Na/S chemical balance problems whether they are old or new, softwood or hardwood mills.

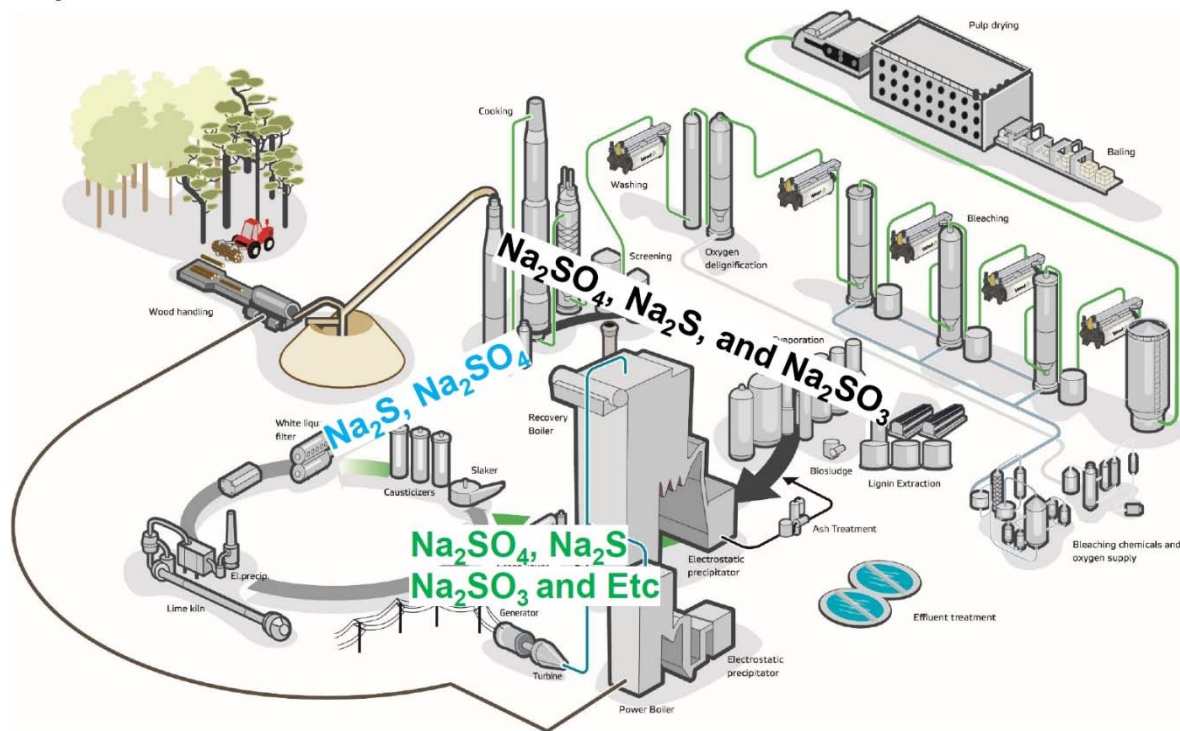


Figure 1: Sulfur in the Kraft pulp mill

Pulp mills running at stable conditions get their excess sulfur supply through by-products of side processes such as tall oil production in softwood mills, the hot sulfuric acid stage mainly in hardwood mills and chlorine dioxide generation in almost all mills. In the case of new LignoBoost® plant installations, the sulfur intake to recovery is much greater and the mill sulfur balance may face problems.

As a common practice, pulp mills purge a sulfur rich stream e.g. recovery boiler ash and neutralized spent acid from the chlorine dioxide plant. Several pulp mills reduce their sodium intake by using oxidized white liquor at oxygen delignification to maintain pH. Recovery boiler ash mainly contains Na_2SO_4 which leads to a lot of sodium being lost when the S-level is controlled. Due to the loss of sodium with the ESP ash, sulfur-free sodium must be added to the system. Therefore, sodium carbonate or sodium hydroxide (normally sodium hydroxide) is added since it is easier to handle and is an active chemical directly. However, sodium hydroxide is expensive due to the high-power consumption in production. Intake of sodium increases operation costs.

Environmental and economic forces have reduced the ash purging and the consumption of fresh water. Additionally, improved pulp washing has reduced the loss of chemicals when the pulp leaves the washers. Reduction of sodium loss from the washing process is more difficult to achieve since sodium is adsorbed

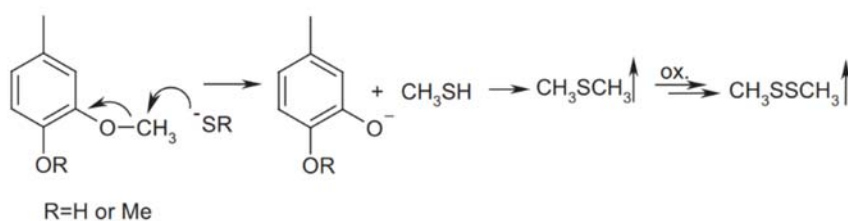
on the fiber that leaves the closed liquor cycle. Although these methods are applied in some modern mills, they still face difficulties in controlling sulfur.

One of the development trends in kraft pulping is to create valuable side streams from the process. Such streams are in many cases created by a primary acidification with sulfuric acid. Examples are tall oil production and lignin extraction. Sulfur from these processes increases the sulfur load on the mill recovery cycle. Therefore, internally produced sulfuric acid will close the mill chemical balance and the acid can be used in ash leaching, tall oil production and chlorine dioxide production. In the pulp mill, sulfuric acid can be produced from non-condensable gases (NCG).

The presence of sulfur is not only found in black/white liquors but also leaves the pulp mill processes as NCG [1]. These undesirable sulfur-containing gases are found in the cooking process, black liquor evaporation, foul condensate, foul condensate stripper of gases, dissolving tank vent gases, sludge de-watering operations, tall oil acidification, brown stock washer hoods, digester blow vents, turpentine production and waste treatment areas. The level and composition of reduced sulfur in NCG vary considerably at each point in a Kraft pulp mill and from one mill to another mill. Great efforts must be made to collect these NCG to convert them to less harmful compounds by oxidation. Sulfur emissions negatively impact the environment. The reduced sulfur compounds create a pungent smell in the mill's surroundings and oxidized sulfur contributes to the large-scale acidification of soil, which negatively affects vegetation and biodiversity.

Non-condensable gases mainly contain hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), dimethyl sulfide (CH_3SCH_3), dimethyl disulfide ($CH_3S_2CH_3$) and other reduced sulfur compounds. These harmful gases [2] are formed during the kraft pulping process. During pulp cooking, strong nucleophile HS^- causes a partial demethylation reaction at the methoxyl groups of lignin and the reaction yields methyl mercaptans [3]. The formed methyl mercaptan is itself a strong nucleophile, and reacts further with another methoxyl group to yield dimethyl mercaptan (**Scheme 1**).

The mixture of hydrogen sulfide (H_2S) and mercaptan are responsible for the characteristic odor of the Kraft process. Hydrogen sulfide is formed in stock washing and black liquor storage at the time when the pH of the black liquor decreases. However, H_2S is not formed during cooking as it operates at high pH. A high amount of hydrogen sulfide is generated during black liquor evaporation because of the decreasing pH.



Scheme 1: Formation of mercaptans from nucleophilic demethylation of dissolved lignin moieties

NCG compounds have very low olfactive detection levels and thus are easily detected by humans even in small quantities and at far distances from emission sources. At these detection levels, the toxicity of reduced sulfur compounds is negligible. However, being a nuisance, they are to be taken seriously for the wellness of people living near or working at the mill site.

Regulatory pressure increased during the early 1990s and resulted in lower emission levels for NCG. The collection, combustion and scrubbing of the remaining NCG has become a standard procedure. It is now accepted that through sound design, the safe and efficient collection of NCG can be accomplished.

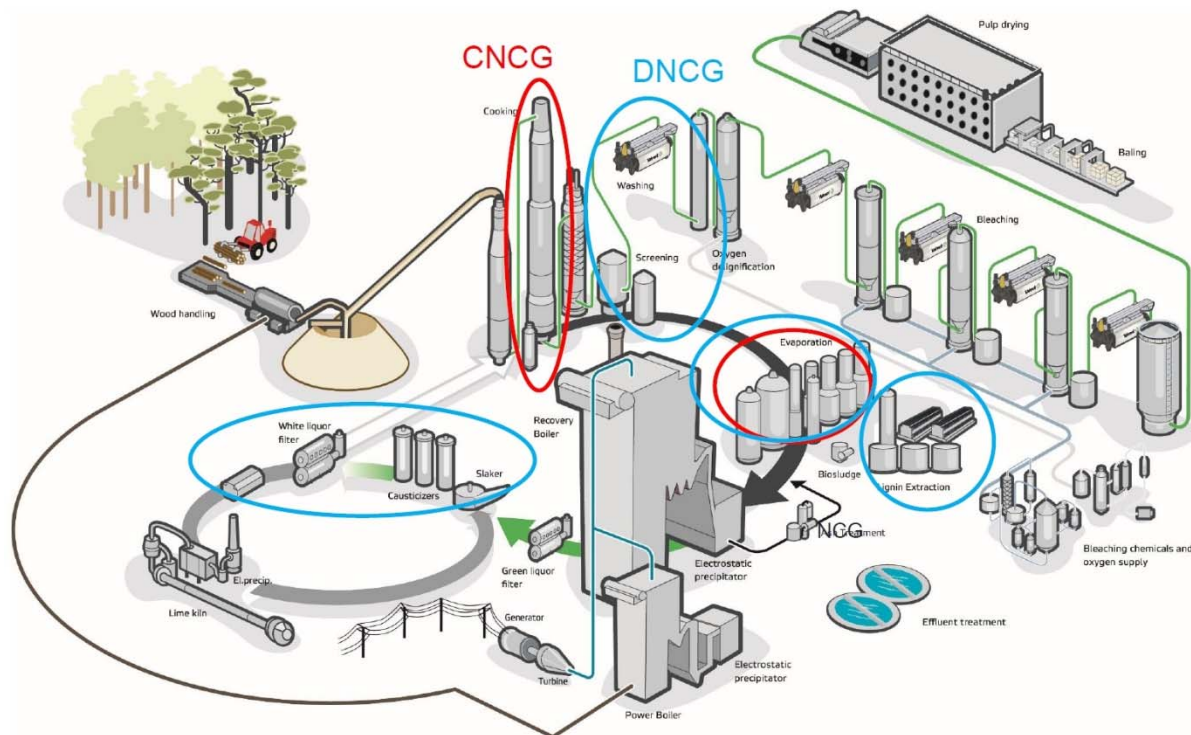


Figure 2: NCG sources in the Kraft pulp mill

Environmental authorities have enforced stringent laws to curb NCG release to the environment and most modern mills have practically eliminated/reduced NCG emissions to the atmosphere. The present paper describes a success story built on adopting the principles of biorefinery concepts. It illustrated how toxic NCG are converted to very good quality sulfuric acid that can be used in several pulp mill processes.

The sulfuric acid plant

To minimize odorous emissions, non-condensable odorous gases are usually collected and incinerated. In some mills, a bisulfite scrubber is used to recover sulfur after incineration, and sodium bisulfite is produced. Sodium can be used for pH control or in the bleaching plant where it is used to wash remaining chlorine components from bleach plant gases. A downside of sodium bisulfite is the fairly high pH (above 5), which prevents it from being used more in controlling pH. Limited usage of bisulfite hinders the potential of active sulfur which could be converted to different active chemicals to be used in mill processes. Therefore, a new system for sulfur recovery has been designed, built and is being operated at the Metsä Fibre Äänekoski bioproduct mill in Finland. This is a sulfuric acid plant, where sulfur from NCG is used to produce H_2SO_4 .

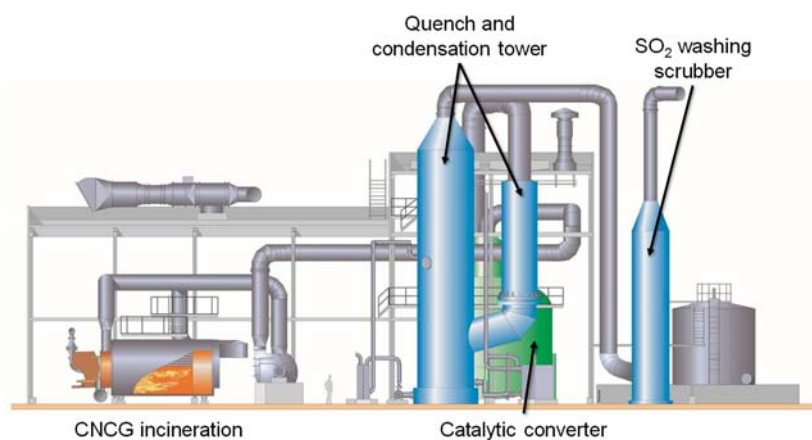


Figure 3. NCG to sulfuric acid

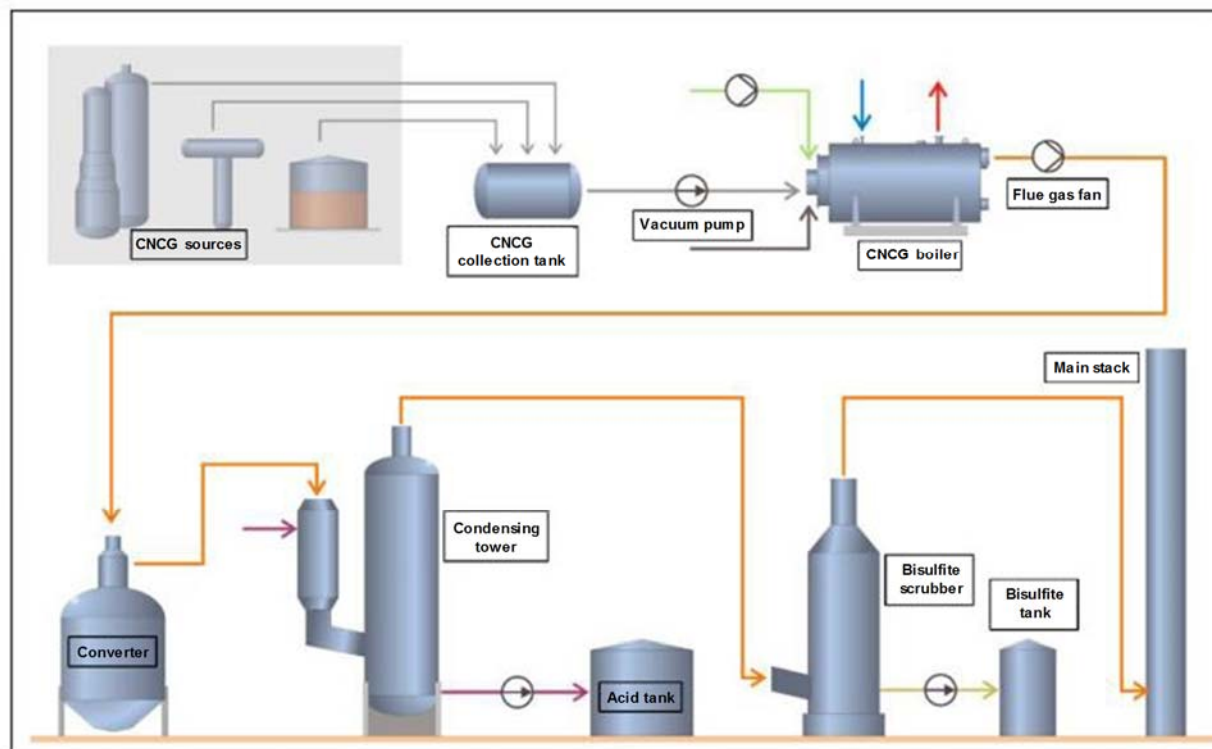


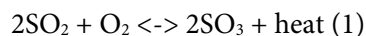
Figure 4. Process overview of sulfuric acid plant

CNCG incineration

Concentrated non-condensable gases (CNCG) are collected and lead to a collection tank, from which they are taken to a separate incinerator (Figures 3 & 4). Depending on the sulfidity and heat treatment during evaporation and cooking, the sulfur release to NCG is 3 to 7 kg/ADT as elemental sulfur. In the separate incinerator, total reduced sulfur compounds in the CNCG are oxidized into SO₂. The burner and boiler are otherwise designed as for traditional CNCG incineration, but residual oxygen and flue gas exit temperature are adjusted to an optimum level. One limit is set by the catalyst process and another by the boiler heat surfaces that, to avoid corrosion, require a sufficiently high temperature.

Catalytic converter

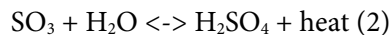
The flue gas from the boiler is led to a catalytic reaction vessel (Figures 3 & 4). The reaction vessel is a cylindrical tank filled with solid catalyst. The catalyst oxidizes SO₂ by using excess oxygen supplied through combustion air into SO₃ by means of an exothermic reaction (1). The temperature of flue gases are higher after the catalytic oxidation and very corrosive due to the presence of SO₃ and water vapor which may form sulfuric acid if the temperature is reduced at any point.



Condensation processes

Flue gases from the catalytic converter are passed into a condensing tower (Figures 3 & 4) called a quench tower. Flue gases are cooled down in the quench tower and then passed further into the condensing tower. To protect the system from overheating, the gas temperature must be adjusted to the proper level before the gases enter the tower. In the concentration tower, liquid is recirculated through a plate heat exchanger. The heat exchanger cools the liquid, and the cooled liquid is pumped back to the tower. The

temperature of the flue gases is reduced with the cooling liquid and the SO₃ in the flue gases reacts with H₂O to produce sulfuric acid (2).



The acid concentration in the concentration tower depends on the partial pressures of SO₃ and H₂O in the flue gas. As the flue gas cools inside the tower, water is also condensed from the flue gas. The final acid concentration depends on the sulfur amount in the CNCG before incineration. The produced acid is quite aggressive with the contact materials; therefore, the concentration tower must be carefully designed with acid resistant materials.

Acid is taken out of the concentration tower circulation after the heat exchanger and led to an acid storage tank. After the concentration tower, the gases may contain a very low amount of SO₃ aerosols which need to be removed before the gas can be treated further. The biggest challenge in this kind of sulfuric acid production is the end concentration of the acid. Since 50-70 w% is the most aggressive concentration, all materials must be carefully chosen.

After the converter, the gas contains SO₃ which will form sulfuric acid if the gas temperature drops below the sulfuric acid dew point. As long as the gas temperature is higher, normal carbon steel can be used. Acid resistant materials do not tolerate high temperatures well. The system must be designed to operate between these limiting temperatures. This is challenging. In this case, the solution has been found by thorough investigation to find the best materials and by minimizing the area that operates under those conditions. Still it is clear that this area will corrode and need maintenance, so the system is designed to be easily maintained.

Bisulfite scrubber

A bisulfite scrubber (**Figures 3 & 4**) is used for washing the residual SO₂ from flue gases before they are released to the environment. During sulfuric acid production, the residual SO₂ are very low as most of the SO₂ is oxidized and converted to SO₃. Alternatively, flue gases from the boiler can be diverted directly to the bisulfite scrubber and, in this case, the bisulfite amount is highly concentrated and available for mill usage. The scrubber is also used to wash any other contaminants before the flue gas reaches the stack.

Starting up a new sulfuric acid plant in a pulp mill is challenging due to the corrosive and hazardous nature of SO₃ and H₂SO₄. Therefore, the properties of these chemicals and the process conditions must be well understood during the design phase of the plant. In addition, the process must be in coherence with all other mill processes because of its versatile role in the pulp mill. The produced acid can be used in bleaching, the chlorine dioxide production plant, tall oil production, pH control and the waste water treatment plant. Internally produced sulfuric acid avoids the cost of externally purchased acid, increases environmental advantages and closes the mill chemical balances. The sulfuric acid plant is one step closer to achieving the realization of future biorefinery concepts.

Sulfuric acid plant start-up and operation

A sulfuric acid plant based on incineration of NCG has been developed by Valmet and is operated at the bioproduct mill, Äänekoski, Finland (**Figure 5**). The plant consists of a CNCG incinerator, catalytic converter, condensing tower and bisulfite scrubber including



Figure 5. Sulfuric acid plant model at Metsä group Bioproduct mill, Äänekoski, Finland

product storage tanks. The production capacity of the plant is approximately 35 tons of sulfuric acid per day and it can produce higher quantities depending on the incoming NCG sulfur content. This is the world's first larger scale sulfuric acid plant operating at a pulp mill. The plant produces high quality sulfuric acid which can be used in any part of the mill.

Conclusions

The production of sulfuric acid from pulp mill NCG enables the bioproduct mill to become nearly self-sufficient in sulfuric acid usage. A sulfuric acid plant brings significant environmental advantages, one of which is that the amount of sulfate led to the mill's effluent treatment plant is reduced and the sulfate load to nearby waterways is decreased drastically. The CNCG incineration plant can be used as a back-up boiler for producing process steam by incinerating CNCG, tall oil pitch and/or liquid methanol. This innovative plant can produce sulfuric acid and bisulfite simultaneously depending on the requirement. The internal recycling of chemicals also reduces purchasing by 350 truckloads of acid per year.

References

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This white paper combines technical information obtained from Valmet personnel and published Valmet articles and papers.

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Summary

- NCG streams can produce sulfuric acid.
- Great solution to enhance sodium and sulfur balance.
- Produced sulfuric acid is better quality than purchased.
- Sulfuric acid plant can produce 350 truckloads of sulfuric acid/year.