

## A New Approach to the Non-Wood Black Liquor Problem

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### Abstract

Silicate ions in black liquor from soda cook of non-wood fiber materials cause problems in the recovery of sodium and energy from the liquor. When adding carbon dioxide to the liquor, the pH of the liquor decreases and the silicate solidifies as silica that can be separated from the liquor by filtration. The new approach differs from previous attempts in three ways: The black liquor is saturated with carbon dioxide, technically pure carbon dioxide is used, and the precipitate is separated from the liquor in efficient variable-chamber filter presses. Black liquor burnt in an oxidizer with oxygen instead of air generates the required carbon dioxide. The oxidizer can be used to burn all the black liquor generated at the mill, or only about 10% of the liquor, which is sufficient to generate the carbon dioxide required for desilication of the total amount of black liquor.

### Introduction

The production of chemical pulp for paper manufacture chiefly uses wood as raw material. However, about 10% of the chemical pulp produced worldwide is using non-wood materials, such as bagasse, straw, reed and grass, as fiber source. For the cooking of non-wood raw materials, sodium hydroxide alone is required as an active chemical, so the major part of chemical pulp production from these raw materials is utilizing the soda process.

In contrast to wood, the non-wood raw materials contain a significant portion of silica. In the soda process, the raw material together with the cooking liquor is heated to a temperature in the range 140 to 170 °C under pressure and at high alkalinity. Under these conditions, the main portion of non-fibrous matter in the raw material is dissolved into the spent cooking liquor, the black liquor. However, also the main portion of the silica reacts with the hydroxide, forming water-soluble silicate ions. The content of silicate in the dissolved solids (ds) of the non-wood black liquor varies between 10 and 150 kg SiO<sub>3</sub> per ton of ds; values in the low end of the range are valid for bagasse, and in the high end for rice straw.

The presence of silicate ions causes serious problems when recovering sodium and energy from the black liquor. The main problems are:

- Scaling on the heat transfer surfaces in the evaporator in which the black liquor is concentrated.
- High viscosity of the concentrated liquor, which impedes both with evaporation and combustion of the liquor.
- Problems in causticizing, i.e., in converting sodium carbonate to sodium hydroxide.

Due to these problems, pulp mills using straw as raw material have difficulties to recover the cooking chemical and utilize the black liquor as fuel, but discharge the liquor. This is evidently a heavy economic burden for the mills and very detrimental to the environment around the mills.

### Black Liquor Desilication

It is a well-known fact that when the alkalinity, i.e., the pH, of the black liquor is reduced, the silicate ions and a part of the organic substance will agglomerate to colloidal form and, when the pH is sufficiently low, solidify as amorphous silica and organic matter. The solidified matter can be separated by filtration or centrifugation from the liquor.

In previous desilication attempts, reviewed, e.g., in [1], carbon dioxide in flue gas has been used to reduce the pH of the black liquor. Because of fear of decreased heating value of the desilicated black liquor due to coprecipitation of organic matter, the pH drop was limited to a pH window, where silica was supposed to precipitate without significant precipitation of organic substance. In laboratory and pilot-scale trials, such a pH window could be found and maintained, but no desilication unit on commercial scale has been successful.

Another problem when using flue gas is excessive foaming because of the large amount of inert gas passing the acidification reactor. Furthermore, the devices used to separate the precipitate were not working satisfactorily.

The proposed new technology [2] differs from the previously studied in three significant ways:

- Black liquor is saturated with a surplus of carbon dioxide.
- Strong carbon dioxide, generated by burning black liquor with technically pure oxygen, is used in the process.
- Efficient variable-chamber filter press is used for solid-liquid separation.

When the black liquor containing silicate ions is neutralized with a surplus of gas containing mainly carbon dioxide, a difficult pH control problem is avoided. The pH is allowed to drop as low as possible with carbon dioxide addition, i.e., about 8.0–8.5 at 90 °C temperature. At this pH the colloidal intermediate state in precipitation is largely eliminated, making the separation of precipitate easier. In trials, up to 95% of the dissolved silica in rice straw black liquor has been removed as filter cake.

When a gas with a high carbon dioxide content, typically about 90% CO<sub>2</sub>, is used, no foaming occurs. Furthermore, when the gas is distributed as bubbles in the black liquor, the CO<sub>2</sub> partial pressure in the bubbles is about five times higher than when flue gas from combustion with air is used as carbon dioxide source. An enhanced mass transfer is obtained and a smaller desilication reactor needed.

Although only little colloidal matter is present in the liquor after acidification, efficient equipment for separating the precipitate from the liquor must be used, because the particles are very small. Included in this new approach is the use of variable-chamber filter presses for solid-liquid separation. In the chamber filter press, a high-pressure drop across the filter cake can be applied. Although the flow resistance in the filter cake increases rapidly with the thickness of the cake, a sufficient filter capacity can be attained. In the variable-chamber type of filter press it is possible to reduce the liquor content of the filter cake by pressing. In desilication trials with straw black liquor, typically 50% dry solids content of the filter cake has been obtained.

### **Carbon Dioxide Generation**

The desilication process is based on the use of strong carbon dioxide gas. When black liquor is burnt with technically pure oxygen instead of combustion air, such gas is generated. A thermal oxidizer [3] capable of burning liquors with low calorific value and low slag melting point has been developed. In this pressurized oxidizer there is no nitrogen in the combustion gas, so the carbon dioxide content of the outgoing gas is very high, typically about 90%. This gas leaves the device at about 9-bars pressure and is very suitable for carbonation of the black liquor.

The oxidizer can burn all black liquor, thus replacing the conventional recovery boiler, or only a portion of the liquor. To cover the carbon dioxide demand for desilication, about 10% of the black liquor to be desilicated must be burnt with oxygen instead of air.

### **Black Liquor Evaporation**

Before the black liquor can be burnt, it must be concentrated to higher ds content. If a conventional recovery boiler is applied, the ds content should be more than 60% to ensure stable and complete combustion. If the silicate is not extracted from the liquor, this ds content is very difficult to reach.

In a Chinese wheat straw pulp mill recovering and burning the black liquor, sharply increasing viscosity of the liquor with increasing ds content prevents evaporation in a multiple-effect evaporation plant to higher ds content than 40%. A further increase of the ds content to about 47% is obtained in a direct-contact evaporator installed in the flue gas duct. Severe fouling occurs in the evaporation plant, so every month it has to be shut down during several days for cleaning.

Pilot-scale desilication trials at this mill showed that when the black liquor was saturated with carbon dioxide and the precipitate separated with a variable-chamber filter press, a substantial part of the silicate was removed. When comparing the viscosity of the original black liquor and the desilicated liquor, a marked decrease of the viscosity when the silicate was removed was found.

If all the black liquor will be burnt in the oxidizer instead of in a conventional recovery boiler, it is not necessary to evaporate the black liquor to higher ds content than about 30–35% by multiple-effect evaporation because the oxidizer has an in-built direct-contact evaporator, the outgoing black liquor ds content from which is about 65%.

### **Combustion in the Oxidizer**

Combustion of black liquor in the oxidizer takes place in a reactor chamber pressurized to 10-bars. The preheated black liquor at final ds content is atomized into small droplets by hot oxygen and burnt in suspension. Oxygen is added around the burner to ensure complete combustion. The reactor is submerged in a pressure vessel filled with boiling water. The water pressure and the gas pressure in the reactor are kept equal, so there is no significant pressure difference across the reactor wall. The reactor wall is efficiently cooled by the water, and 10-bar steam is generated. The steam is separated from the water in a steam drum, and the water is recirculated into the bottom of the pressure vessel.

Inorganic combustion residue, mainly sodium carbonate in a molten state, adheres to the reactor wall and forms a solidified protecting slag layer on the wall. No refractory brickwork is used in the reactor. The solidified slag layer grows to about 5 mm, whereupon the inner slag surface temperature reaches the slag melting point. Molten slag runs by gravity into an also-pressurized dissolver, into which weak white liquor is pumped. The sodium carbonate is dissolved, and the resulting green liquor is extracted through an expansion vessel and pumped to the mill's causticizing department for production of white liquor in the conventional way with burnt lime.

The gas generated in the reactor is led at high temperature to the direct-contact evaporator, also operated at 10-bar pressure. The incoming black liquor is pumped into this pressure vessel, atomized by spray nozzles into the hot gas, heated to the boiling point and partly evaporated. From the direct-contact evaporator, the black liquor is pumped to the reactor burner. The gas passing the direct-contact evaporator is quenched to about 220 °C and saturated with water vapor. The outlet gas is led through the shell-side of two heat exchangers in series, generating 3-bars and atmospheric steam by condensing the water vapor in the gas. These heat exchangers act as efficient wet scrubbers of the gas. At the outlet of the second heat exchanger, the gas pressure is released and the gas discharged at a temperature of about 110 °C. The gas contains about 90% carbon dioxide and can be used for black liquor desilication.

Because there is no nitrogen and very little water vapor in the exhaust gas, and its temperature is low, the heat loss corresponding to the flue gas loss of the recovery boiler is very low. Neither is there any flash steam loss from the dissolver. Therefore the thermal efficiency of the oxidizer is much higher than of a recovery boiler. On the other hand, no high-pressure steam suitable for a back-pressure turbine is produced.

The gas flowing through the oxidizer is pressurized to 10-bars, and there is no nitrogen in the gas. Therefore the gas volume is small, which gives a very compact design of the oxidizer. An oxidizer capable of burning all black liquor generated at a straw pulp mill producing 30,000 tons per year can be built in two skids, complete with piping, instrumentation and electrification, and brought to the site in two standard 40-foot containers. No external gas cleaning devices are required, and the oxidizer can be erected outdoors on a concrete slab.

### **Conclusions**

The discharge of black liquor from non-wood mills into watercourses is considered the last big environmental problem of the paper industry on a global scale. Problems in treating the black liquor containing silicate has also prevented investments in non-wood pulping projects, although the non-wood fiber could replace a portion of hardwood kraft fiber in printing and writing papers and even improve the paper quality. This new approach has shown in practical trials that these problems can be solved.

### **References**

- [1] Myrén, B. A Novel Recovery Process for Small-Scale Non-Wood Pulp Mills. Proceedings from the 1998 TAPPI International Chemical Recovery Conference, Tampa, Florida, 1998.
- [2] U.S. Patent 6,183,598, issued Feb. 6, 2001.
- [3] [www.conox.com/Thermal Oxidiser](http://www.conox.com/Thermal%20Oxidiser).

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