Managing TRS emissions during black liquor processing: New discoveries

By M. Ellis and A. Urry

Abstract: Total reduced sulphur (TRS) compliance projects from recovery boiler mix tanks, black liquor oxidation (BLOX) and crude tall oil (CTO) cooking are described. Elevated black liquor temperature was shown to increase organic sulphur emissions from recovery boiler black liquor mix tanks and BLOX tank vents with low liquor sulphide levels. High turpentine levels in soap were shown to be the primary cause of high organic sulphur emissions from a CTO vent scrubber.

MODERNIZATION OF Carter Holt Harvey’s Kinleith integrated pulp and paper mill commenced in late 1998. The project scope included the introduction of modified continuous cooking, upgraded batch digesters and a paper machine rebuild. The modernized mill reached design production rate on a sustained basis at the end of 2000, placing greater pressure on recovery operations environmental compliance.

With the trend to increased process closure the interdependence of pulping and recovery operations is intensified. More often pulping process changes will directly effect recovery unit operations. Recent mill experience has shown that pulping process changes can influence recovery operations environmental compliance on sulphur gases.

Total reduced sulphur (TRS) gases from pulp mill operations are composed of four components; hydrogen sulphide (H2S), methyl mercaptan (MeSH), dimethyl sulphide (DMS) and dimethyl disulphide (DMDS). Regular compliance monitoring for TRS compounds is a site requirement under New Zealand legislation.

MILL DESCRIPTION

Kinleith is similar in design to most modern integrated Kraft pulp mills. Three fibres lines produce pulp furnish for use in production of linerboard and bleached market pulp. A common chemical recovery loop processes the combined liquor from all three fibres lines.

Dual evaporators and recovery boilers process the black liquor. The older equipment line contains an LTV evaporator, black liquor oxidation (BLOX) and Combustion Engineering recovery boiler (No. 4) with cascade evaporator. The newer line consists of a falling film evaporator set and dual evaporators, with black liquor oxidation (BLOX) and crude tall oil (CTO) cooking.

Crude sulphate turpentine (CST) and crude tall oil (CTO) are recovered as valuable pulping by-products, due to the *Pinus radiata* wood supply. CST and CTO are exported to Eka Chemicals where further processing is completed.

EXPERIMENTAL

All gas sampling and testing was completed in accordance with Environment Canada reference method EPSI/RM/6 (1992). Gas samples withdrawn from a stack or vent were pretreated with citrate buffer and phosphoric acid prior to analysis by gas chromatography (GC), typically within 30 minutes of sampling. Pulsed Flame Photometric Detection was used for quantification of sulphur species.

CTO analyses were completed according to Pulp Chemicals Association test methods 6, 11 and 24 [1]. CST in wood chips was measured with an extraction apparatus recommended in the Pulp Chemicals Association textbook [1]. CST levels in black liquor or soap were measured according to Eka Chemicals method TM:2067.

RESULTS, DISCUSSION

Black Liquor Mix Tanks: The dissolving tank vent (DTV) from the No. 5 recovery boiler is regulated for mass discharge of TRS gases (1.2 kg/hr maximum). The DTV is equipped with a Ducon™ scrubber designed to remove hydrogen sulphide using weak wash as the alkali source. Exhaust fans from two black liquor mix tanks prior to the boiler-firing rail are also vented to the same DTV stack, prior to the scrubber. DTV compliance became difficult at the end of 2000, partially in response to a 4% increase in average boiler solids firing rate.

Stack test data revealed substantial amounts of organic sulphur gases in the scrubber vent, predominantly originating from both black liquor mix tanks, Table I.

Initial investigations suggested that high liquor temperatures in the black liquor mix tanks were responsible for generating the organic sulphur vapours, Table II. The laboratory data suggested controlling liquor temperature below 110°C would minimize organic sulphur vapours. Similar results had also been reported at another International Paper mill in the United States.

The only opportunity for controlling liquor temperature prior to the mix tanks was at the evaporator product flash tank. Improved liquor temperature control was implemented by venting the product liquor flash tank to the evaporator set fourth effect, instead of the third effect. Calculations estimated the extent of liquor flashing at this pressure, would enable controlling the liquor temperature below 106°C. DTV TRS emissions were reduced on average 60% following the plant changes implemented in July 1999, Fig. 1.
Occasionally TRS compliance was not achieved, even with liquor temperature under control. These apparent inconsistencies in measured emissions suggested that intermittently non-compliance might have been related to changes in liquor composition.

Laboratory pulping studies have shown methyl mercaptan formation in black liquor increased with higher sulphidity and decreasing kappa number [2]. Hence kraft pulping process changes may have the ability to generate black liquors with decreased levels of TRS components. For this reason, it was possible pulping process changes contributed to DTV emission non-compliance.

**Black Liquor Oxidation:** Heavy black liquor following evaporation (46% solids) is processed through a two-stage black liquor oxidation (BLOX) plant. Liquor residual sulphides are oxidized prior to the direct contact cascade evaporator integral with the No. 4 recovery boiler. The total mass discharge from both BLOX stage vents is permitted at 4 kg/hr. Compliance failures had never occurred until early 2000. Table III shows some of the test data for each TRS component from the laboratory.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>H2S mg/m³</th>
<th>MeSH mg/m³</th>
<th>DMS mg/m³</th>
<th>DMDS mg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>110°C</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>112°C</td>
<td>0</td>
<td>0</td>
<td>112</td>
<td>24</td>
</tr>
<tr>
<td>114°C</td>
<td>28</td>
<td>464</td>
<td>576</td>
<td>1,068</td>
</tr>
</tbody>
</table>

**TABLE III. BLOX plant TRS emissions data.**

<table>
<thead>
<tr>
<th>Month</th>
<th>H2S</th>
<th>MeSH</th>
<th>DMS</th>
<th>DMDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>July 99</td>
<td>42</td>
<td>0</td>
<td>112</td>
<td>21</td>
</tr>
<tr>
<td>Sept 99</td>
<td>33</td>
<td>6</td>
<td>157</td>
<td>43</td>
</tr>
<tr>
<td>Nov 99</td>
<td>8</td>
<td>3</td>
<td>142</td>
<td>18</td>
</tr>
<tr>
<td>Feb 00</td>
<td>19</td>
<td>1</td>
<td>155</td>
<td>38</td>
</tr>
<tr>
<td>Mar 00</td>
<td>51</td>
<td>5</td>
<td>200</td>
<td>50</td>
</tr>
</tbody>
</table>

This reaction is reported to only occur when liquor sulphide levels are low, i.e., during the second stage of liquor oxidation. The fact that vent DMDS concentrations increased from the first to second stage where there were low sulphide levels, strongly suggested the above reaction was occurring.

Plant operating logs had identified an increased flow of steam to the second-stage inlet airflow. Steam is introduced into the inlet air for temperature control. The introduction of steam could increase local liquor temperatures and also promote DMDS removal from the liquor. DMDS is the most volatile of the organic sulphur compounds with a normal boiling point of 110°C. As DMDS is insoluble in water, steam stripping is an effective way of removing it from black liquor. During March 2000 the second stage temperature set-point was reduced from 93°C to 90°C, in order to reduce the steam added with the blower air. This reduction in temperature reduced the contribution from the second stage vent and the total TRS emissions, Fig. 2.

Addition of the steam to the second oxidation vessel seemed to promote a steam stripping reaction, volatilizing DMDS. Therefore minimizing the steam addition minimized DMDS generation. Reducing the second-stage vessel temperature would also have reduced oxidation reaction effectiveness. However, no measurable change in air required to the second oxidation stage was recorded. Similarly, no detrimental effects on liquor firing or boiler TRS were observed.

**Tall Oil Processing:** Acidulation of black liquor soap is performed on-site to produce CTO for export to Eka Chemicals. Acidulation is performed as a batch process after residual black liquor has been washed from the soap. Vent gases from the reaction vessel pass through a water scrubber then to a packed column using caustic as the scrubbing medium. A persistent TRS emission problem from the CTO plant scrubber had been encountered, regularly exceeding the emission limit of 350 mg/m³.

Extensive plant trials were completed to minimize TRS emissions by in-process modifications. Process variables including soap liquor content, acid strength, cook time and cook pH were manipulated to reduce the TRS emission. These plant trials were partially successful. However, the scrubber vent remained out of compliance due mainly to the large concentration of DMS present in the scrubber vent, Fig. 3.

Traditional theory suggests that TRS compounds from CTO cooking originate from the black liquor content of the soap [1]. However, efficient soap washing was part of the process, with the soap black liquor content routinely measured at 6-8%. No literature was found relating TRS emissions to any other cause than soap black liquor content.

At a similar time, Eka Chemicals completed mass balances of both CTO and CST around the entire black liquor circuit, with the intention of increasing by-product recovery. This information was of...
interest due to the pulping process changes implemented during the modernization. The introduction of Lo-Solids™ [4] pulping had negatively affected CST recovery for the mill. The CST balances highlighted poor recovery from the modified continuous digester with corresponding higher than normal CST concentrations measured in the black liquor. Of even more interest was that the mass balance showed over half of the unrecovered CST ended up with the soap at the CTO plant, Fig. 4. This new discovery lead us to believe that the high CST content of the soap may have been responsible for the high TRS emissions from CTO cooking. Further analyses were completed to check the CST content of soap samples from CTO cooking when TRS testing was completed. Figure 5 illustrates the DMS concentrations measured during gas testing as a function of the soap CST content.

A clear relationship was observed between the soap CST content and the DMS emissions measured during cooking. The lowest DMS emissions were achieved when the soap CST content was low.

Further laboratory cooks were completed on additional soap samples from Kinleith and another softwood kraft mill without TRS emission problems. Table IV shows the levels of TRS gases measured from the laboratory method. Very similar H₂S, MeSH and DMDS levels were recorded between all soap samples, while DMS levels were an order of magnitude greater from the Kinleith soap samples. This data further confirmed that the high CST levels in our soap were the contributing factor to high DMS and therefore TRS emissions. For our mill situation, the traditional theory linking soap liquor content to TRS emissions was not applicable.

Removal of the CST from the liquor and soap is now the focus of extensive work. Some modifications in digester operations have recently improved CST recovery. However, major capital expenditure is necessary to increase CST recovery to acceptable levels. Achieving acceptable CST recovery from the digester may also have a major energy cost penalty.

**CONCLUSIONS**

Environmental regulations require operation of recovery unit operations within emission standards. Often there may appear to be a conflict between achieving high production efficiencies and maintaining environmental compliance. Often, in reality, changes in pulp mill process conditions can have a more significant effect on maintaining TRS emissions compliance than realized.

Liquor temperature has been shown to influence TRS emissions from black liquor. Elevated temperature increases organic sulphur gaseous emissions. Maintaining temperatures below 110°C can minimize emissions under normal conditions. Yet operating BLOX processes with low liquor sulphide levels requires careful attention to prevent steam stripping of DMDS into atmospheric vents.
Organic sulphur emissions from CTO processing may not originate from soap black liquor content, as traditional theory suggests. High CST levels in soap have been shown to cause high DMS emissions during the CTO cooking process.

**LITERATURE**


**Résumé:** Les projets de conformité en matière de soufre réduit total (SRT) des réservoirs de mélange des chaudières de récupération, de l’oxydation de la liqueur noire et de la cuisson du tall oil sont décrits. La température élevée de la liqueur noire a accru le soufre organique émis par les réservoirs de mélange de la liqueur noire et l’oxydation de la liqueur noire à faible niveau de soufre. Le degré élevé de térébenthine dans le savon a été la cause première des émissions élevées de soufre organique dans les épurateurs-laveurs de tall-oil brut.


**Keywords:** POLLUTION CONTROL, TOTAL REDUCED SULFUR, BLACK LIQUORS, TEMPERATURE, TURPENTINE, RECOVERY FURNACES, TALL OIL.