EXPERIENCES WITH OXIDATIVE DECOLOURISING PROCESSES IN THE SOUTHERN AFRICAN SUGAR CANE INDUSTRY

By

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Abstract

Hydrogen peroxide and ozone are two strong oxidants that may be used as decolourising agents in cane sugar refining, although thus far they have generally been little used. A review is presented of research done by the Sugar Milling Research Institute over the past 10 years into the application of these chemicals in the context of the Southern African sugar industry. Both hydrogen peroxide and ozone have proved to be effective in removing both colour and colour precursors when added to raw melt ahead of carbonatation. Factory trials have demonstrated significant improvements in refined sugar colours with dosages of 100–200 ppm on brix. Further trials are being undertaken in the 2001 season.

Introduction

Approximately 50% of the raw sugar produced in Southern Africa is refined to produce white sugar for industrial or domestic consumption, with a small proportion being exported. Raw sugar colours vary between 1000 and 2000 ICUMSA units, while typical refined sugar colours are between 30 and 40 ICUMSA units. However, occasional periods of poor cane quality lead to high raw sugar colours and, consequently, the refineries struggle to meet the refined sugar colour specifications.

Hence, a need was identified for additional colour removal processes that could be used to enhance the performance of the conventional processes during these times. This was investigated as part of the research program of the Sugar Milling Research Institute (SMRI). Oxidative processes were considered for this investigation as relatively little work had been done in this area, particularly in the South African industry. This work showed potential in other countries, for example Jadhav et al. (1988) and Mane et al. (1992) in India, and Gomez et al. (1980) in Cuba. These processes are also well-suited to an 'add-on' application, and have the advantage of being 'clean' processes that do not produce liquid effluents or extra solid waste that require disposal. The two oxidants investigated were ozone and hydrogen peroxide; hypochlorites were not considered because of the chloride residues. This paper describes the work performed in South Africa in this area.

Chemistry of oxidative decolourants

Ozone is a molecule that consists of three oxygen atoms bound together to form an unstable gas which is a very reactive oxidant. It is produced commercially by passing a high voltage electrical discharge through a stream of dry air or oxygen. It is so unstable that it cannot be stored in cylinders, and must be generated on site as required. Although it is toxic, its characteristic odour is detectable at concentrations well below dangerous levels, as is the case with sulfur dioxide. It reacts readily with organic substances via an oxygen free radical mechanism at neutral or acidic pH and via a hydroxyl radical mechanism at basic pH.

Hydrogen peroxide is better known as a decolourant, being used in many industries for bleaching purposes. It consists of two hydrogen and two oxygen atoms, with the unstable oxygen-oxygen bond being the key to its oxidising power. It is supplied as aqueous solutions of varying strengths, is relatively stable when stored in cool conditions, and decomposes to oxygen and water. Its reaction mechanisms are similar to those of ozone, although its oxidising power is slightly less.

Both chemicals decolourise sugar liquors by a number of routes, as listed below (Davis, 2001).

- Oxidation of double bond systems and cleavage to carboxylic acids and alcohols.
- Opening of the aromatic rings of phenols, which may be further oxidised as above.
- Oxidation of other aromatic groups to form quinones and polymeric ozonides.
- Oxidation of primary amines to nitro compounds.
- Oxidation of secondary amines via intermediate radicals to separate substituents.
- Oxidation of tertiary amines to amine oxides.

These pathways have the dual effects of destroying colour directly and destroying colour precursors that take part in colour formation reactions during pan boiling. It must be realised, though, that some of these reaction products can themselves undergo further reactions and form colour later in the process. Hence, it is necessary to follow the oxidation step by a precipitation and filtration stage, such as carbonatation, in order to remove these reaction products.

With such powerful oxidants and the range of reactions that they can give rise to, there has naturally been some concern that they might also attack sucrose and the reducing sugars. However, this only happens via the hydroxyl radical pathway, and so, by keeping the liquor pH below 8 during oxidation, no sugar destruction occurs.

KEYWORDS: Decolourisation, Hydrogen Peroxide, Ozone, Refining.
Laboratory investigations

Patel and Moodley (1991) investigated the use of hydrogen peroxide and ozone for colour removal from several raw house and refinery liquors. They found that peroxide improved the colour removal across sulphitation and phosphatation, but colour removed from brown liquors returned on standing. Small colour transfers to crystal resulted from peroxide dosing, but purity drops were encountered due to the pH drop caused by the formation of organic acids. However, they used high dosages (up to 1500 ppm on liquor), which is certain to lower the pH. Similar results were obtained with ozone addition, although the ozone dosages were not given. Ozone was concluded not to be worth pursuing as the capital cost of ozone generation equipment was then so high as to make the process unattractive.

In further work using hydrogen peroxide with conventional refining processes, Moodley (1992) found that dosages of 200–400 ppm of peroxide in place of a certain portion of sulfur dioxide, carbon dioxide or phosphoric acid resulted in some cost savings for the same colour removal.

In 1995, the author continued the laboratory investigations into colour removal from refinery liquors using ozone (Davis, 1996), and found that the optimum pH for colour removal was between 6 and 7, and that virtually no sucrose destruction occurred under these conditions. It was also found that treatment of raw melt with 900 ppm of ozone on melt followed by carbonatation, sulphitation or phosphatation yielded liquors comparable in colour with conventional fine liquors that had been subjected to a secondary colour removal process. Sugars boiled from these liquors were of low colour, and did not demonstrate the colour return that had been experienced in Moodley’s work with peroxide. Most notably, colour measured at pH 9, indicative of plant pigments that are readily transferred to crystal, was strongly reduced by ozonolysis. The work also demonstrated the necessity to follow ozonolysis with a precipitation and a filtration step, for the reasons described in the section on the chemistry of oxidative decolourants.

Later work (Davis, 1999) continued this investigation to test whether ozone addition prior to carbonatation could significantly reduce the load on ion exchange decolourisation. This was the result of tightening legislation and increasing costs that made disposal of the brine effluent from ion exchange more expensive. In a laboratory project, raw melt was treated with various combinations of ozone, carbonatation and ion exchange, and the resulting liquors were boiled in a pilot pan. Difficulties were encountered with the semi-continuous laboratory carbonatation, and some colour increase across carbonatation was noted. In addition, the laboratory ion exchange process worked more efficiently than in a refinery, and this tended to bias the results.

However, the work showed that ozonolysis with carbonatation complemented ion exchange, in that different types of colour were removed by the two processes. Smaller colour increases during pan boiling and reduced colour transfer rates to the crystal with ozone treated liquors were clearly demonstrated. It was concluded that, if ozone was added to melt at 200 ppm on brix, only half of the brown liquor needed to be treated by ion exchange. The remaining brown liquor could bypass ion exchange and be combined with the treated liquor for pan boiling and still achieve the target refined sugar colour.

More recently, a similar investigation was started to consider the benefits of ozone addition before phosphatation and ion exchange. This work is still in progress and no results have yet been published. However, the preliminary findings do not indicate such clear effects as were found in the carbonatation work. It is thought (Davis, 2001) that the strong oxidation effects of ozone may be detrimental to the colour precipitants and flocculants used in phosphatation clarifiers, although the oxidised colour bodies and colour precursors should be as well removed by calcium phosphate as by calcium carbonate. This work is continuing, but initial results are not promising.

Factory trials

Hydrogen peroxide

Following Moodley's work, two short full-scale trials with peroxide dosing were performed in 1994 at a local refinery. In the first, peroxide was dosed into the C-saturator at 200 or 300 ppm on brix. Brown liquor colours improved slightly, and a small improvement in fourth sugar colours was noted. In a later two hour trial, peroxide was dosed at 250 ppm on brix into the melter, resulting in reduced melt colours going to the carbonatation station. However, the results of both trials were disappointing and were never published.

Interest in hydrogen peroxide was renewed in 1999 when further trials were undertaken at the Gledhow refinery, a carbonatation/sulphitation refinery, in order to develop an 'add-on' short-term solution to high colour peaks. Hydrogen peroxide is very suitable in this application as the only equipment required is a small dosing pump to transfer the solution from the bulk container to the process. It was recommended that the hydrogen peroxide should be added into the melter outlet before the carbonatation station, and an initial dosage rate of 120 ppm on brix was set, but was soon increased to 200 ppm on brix. Two trials were run, one of five days and one of eight days, with an eight day break in between.

Problems were encountered during these trials with highly variable melt colours, sampling techniques and operational variations such as fourth sugar rejection and inconsistent forward boiling. The latter two factors were necessary to maintain target refined sugar colours, but meant that the results of the trials could be interpreted only with difficulty. These results (Davis et al., 2000), shown in Table 1, indicated that hydrogen peroxide addition prevented colour increases from the melter to the carbonatation station, and reduced colour formation during pan boilings. The sugar colours were statistically significantly different with and without peroxide for third,
fourth and refined sugar colours, but not for first and second sugars. However, the results of the trials were subject to some uncertainty due to the factors mentioned above, and further trials under better controlled conditions are planned for the 2001 season.

**Table 1**—Results of 1999 hydrogen peroxide trial at Gledhow refinery.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean colour (no H₂O₂)</th>
<th>Mean colour (with H₂O₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampled melt colour</td>
<td>905</td>
<td>774</td>
</tr>
<tr>
<td>Carbonated liquor colour</td>
<td>572</td>
<td>502</td>
</tr>
<tr>
<td>Sulphited liquor colour</td>
<td>433</td>
<td>400</td>
</tr>
<tr>
<td>First sugar colour</td>
<td>26</td>
<td>22</td>
</tr>
<tr>
<td>Second sugar colour</td>
<td>34</td>
<td>32</td>
</tr>
<tr>
<td>Third sugar colour</td>
<td>54</td>
<td>48</td>
</tr>
<tr>
<td>Fourth sugar colour</td>
<td>80</td>
<td>65</td>
</tr>
<tr>
<td>Dryer sugar colour</td>
<td>38</td>
<td>34</td>
</tr>
<tr>
<td>Packing station sugar colour</td>
<td>40</td>
<td>37</td>
</tr>
</tbody>
</table>

**Ozone**

Following the laboratory trials with ozone performed by the author in 1995, an ozone trial was planned at the Malelane refinery of Transvaal Sugar Limited, a carbonatation/sulphitation refinery. The anticipated benefit of smaller colour increases throughout the boiling house could only be proved by a full-scale trial, despite the cost and complexity of such a trial. By this time, advances in the design and the lower cost in real terms of ozone generating equipment meant that it was feasible to do such a full-scale trial.

In 1997, a plant designed to dose 150 ppm of ozone on brix to the raw melt was installed and commissioned. Full details have been reported by Davis et al. (1998), where some of the initial equipment problems have been described. The trial was successful, with dosing continued for much of the season and for the duration of the off-crop refining period at a rate of 90 ppm of ozone on brix.

The improved colour removal achieved with this quantity of ozone was demonstrated by noticeably lower refined sugar colours during the dosing periods in the season. During off-crop refining, the refinery was able to bag five sugars instead of the usual four, and was thus able to increase throughput, despite a lower availability of carbon dioxide for carbonatation. The refined sugar colour was also 5–10 ICUMSA units lower than for previous off-crop refining periods. As a result of the higher throughput, the off-crop refining target was met in a shorter time than predicted, with consequent savings in fuel costs. Analyses and mass balances showed no significant destruction of sugars during the trial periods, and the trial was considered to be a success.

After these trials, the contacting equipment was redesigned and the ozone generator was refurbished before a further five day trial was conducted in October 1999 (Davis, 2000). In this trial, ozone was dosed at 115 ppm on brix, with the results shown in Table 2. An additional 15% colour removal was achieved from melt to fine liquor, and the effect of reduced colour increases during boiling can clearly be seen, in that the fourth sugar colour during the trial was similar to the third sugar colours outside the trial period. This trial thus demonstrated that ozonolysis in combination with carbonatation is highly effective in reducing refined sugar colours.

However, minor improvements to the Malelane refinery and better control of the raw sugar input to the refinery subsequently meant that there was no need for ozone at Malelane, and no further trials were undertaken. Subsequently, the ozone plant has been moved to Ubombo Sugar in Swaziland, also a carbonatation/sulphitation refinery, where trials have recently commenced.

**Conclusions**

Research into oxidative decolourising processes at the SMRI has spanned more than ten years, and much experience and knowledge has been gained in this time. A greater understanding of the mechanisms and interactions will allow these processes to be utilised in the most effective manner in the refining process. There seems little doubt that they have a role to play in the South African industry and, by the end of 2001, definitive answers from well-conducted hydrogen peroxide trials and further data from ozone trials should enable the industry to make sound financial decisions on the value of these technologies.

**Acknowledgments**

The author acknowledges the help and support of the following:

- the Director and staff of the SMRI for support and assistance with this research;
- Messer Fedgas for considerable input to the ozone project;
- Alliance Peroxide for their work with the peroxide project; and
- the Southern African sugar mills that have contributed greatly to the plant trials.

**Table 2**—Results of 1999 ozone trial at Malelane refinery.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Trial average colour</th>
<th>September average colour</th>
<th>October average colour</th>
<th>November average colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw melt</td>
<td>1172</td>
<td>1204</td>
<td>1174</td>
<td>1290</td>
</tr>
<tr>
<td>Clear liquor</td>
<td>510</td>
<td>675</td>
<td>610</td>
<td>681</td>
</tr>
<tr>
<td>Fine liquor</td>
<td>462</td>
<td>593</td>
<td>535</td>
<td>600</td>
</tr>
<tr>
<td>1st Sugar (whole)</td>
<td>18</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>2nd Sugar (whole)</td>
<td>29</td>
<td>34</td>
<td>34</td>
<td>43</td>
</tr>
<tr>
<td>3rd Sugar (whole)</td>
<td>38</td>
<td>48</td>
<td>48</td>
<td>57</td>
</tr>
<tr>
<td>4th Sugar (whole)</td>
<td>46</td>
<td>61</td>
<td>57</td>
<td>57</td>
</tr>
<tr>
<td>5th Sugar (whole)</td>
<td>63</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Refined sugar (whole)</td>
<td>35</td>
<td>46</td>
<td>38</td>
<td>38</td>
</tr>
</tbody>
</table>
REFERENCES


LA DECOLORATION PAR DES PRECEDES OXYDATIFS EN AFRIQUE DU SUD

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Résumé

L’hydroxyde d’hydrogène et l’ozone sont deux oxydants puissants dont on peut se servir en raffinerie. On donne une revue du travail fait par le Sugar Milling Research Institute pendant les 10 dernières années sur l’application de ces produits dans l’industrie locale.


Mots clefs: Décoloration, hydroxyde d’hydrogène, ozone, raffinage.

PROCESOS DE DECOLORACIÓN CON OXIDANTES EN LA INDUSTRIA DE CAÑA DE AZÚCAR EN AFRICA DEL SUR

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Resumen

El peróxido de hidrógeno y ozono son dos oxidantes fuertes que pueden usarse como agentes de decoloración en el refinamiento de azúcar, así y todo estos oxidantes han sido poco usados. En este documento se presenta una revisión de investigación hecha por Sugar Milling Research Institute durante los últimos diez años en la aplicación de estos productos químicos en el contexto de la industria azucarera de africana del sur.

Peróxido de hidrógeno y ozono han demostrado ser eficaces quitando color y precursores del color cuando son agregados a la fusión cruda delante del carbonatador. Los ensayos de fábrica han demostrado significantes mejorías en el color de azúcar refinado con las dosificaciones de 100–200 ppm en Brix. Estos experimentos serán continuados con la zafra de 2001.