

EVALUATION OF HYDROGEN PEROXIDE AT HULETTS REFINERY: PRELIMINARY RESULTS

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Abstract

Hydrogen peroxide (H₂O₂) has been tested in the past as a colour removal agent in the sugar refining process. The high costs and the very high reactivity of this chemical are negative factors that have prevented its full-scale application in sugar factories. Work was done in the USA to reduce the quantity of H₂O₂ required by dosing as wash water in raw sugar centrifugals. Based on the promising results, trials were done in the Technology and Engineering Group of Tongaat Hulett laboratory on raw sugar and WSM sugar. Full-scale tests were carried out at the Hulett's refinery (Hulref) centrifugals on the fourth white boiling at varying concentrations of between 30-1000 ppm on refined sugar in 2009 and 2010. The effect of H₂O₂ on colour removal and on pH of both sugar and jet were investigated.

Regardless of the H₂O₂ concentration, 11-15% colour removal in sugar was achieved, with insignificant reduction in pH. Contrary to sugar, jets showed an increasing trend in colour removal with an increase in H₂O₂ concentration. The optimum H₂O₂ application appears to be at a concentration of 300 ppm. The amount of H₂O₂ consumed per ton of refined sugar produced shows that the use of this chemical may be an alternative for colour removal.

Keywords: hydrogen peroxide, centrifugals, colour, concentration, shelf life, pH

Introduction

Raw sugar quality changes with cane quality throughout the season and with the problems experienced in a particular mill. Irrespective of this, the quality of refined sugar is not negotiable and needs to be processed according to customer specifications. Raw sugar colours above 1350 ICUMSA Units (IU) put pressure on the refinery and some measures have to be put in place to maintain throughputs while still achieving refined sugar quality. This is currently achieved by dosing with decolourising agents to reduce the fine liquor colours before crystallisation and using sodium hydrosulphite during pan boiling to assist during curing.

The use of hydrogen peroxide (H₂O₂) for colour removal in the sugar industry has been documented by a number of authors (Davis *et al.*, 2000; Moodley, 1992). Laboratory tests when dosing H₂O₂ on melt (Moodley, 1992) showed that it is not feasible to use hydrogen peroxide alone due to costs and processing problems. Further tests in Gledhow refinery (Davis *et al.*, 2000) produced a significant drop in third and fourth sugar colours, with little change in first and second sugar colours. Colour reversal was experienced with some trials (Cordovez *et al.*, 1991).

In his work, Riffer (1980) describes the mechanism of H_2O_2 on sugar refining to be mainly the cleavage of unsaturated sites and diketones in colourants forming carboxylic acids, thus permanently destroying the colour forming bodies. For this reason, the authors do not anticipate any sugar colour return with storage. This also involves oxidation of certain colourants to forms that are more readily removed by adsorbents.

The high cost of using H_2O_2 in factories has been one of the constraints in large-scale application. In an attempt to optimise costs and quantity, Saska (2007) applied the H_2O_2 through the wash water at 100-500 mg/kg sugar in raw sugar centrifugals. The results yielded 20-30% colour reduction with no colour reversal after six months.

Laboratory tests as described by Saska (2007) were carried out in the Technology and Engineering Group of Tongaat Hulett Sugar (TEG) laboratory on raw sugar and plantation white sugar (produced directly from raw sugar syrup, called WSM) samples using 250-500 ppm of H_2O_2 . Decolourisation of 10-30 % and 30-60 % was achieved for raw sugar and WSM sugar, respectively. The original colours were 2679 and 118 IU, respectively.

The pressure for producing export quality refined sugar at a reasonable cost prompted Huletts refinery (Hulref) to explore the idea of hydrogen peroxide. Several benefits might be derived if it is successfully implemented on a full scale. These include improved yield, less wash water in the centrifugals and less sugar recycling.

A four boiling system is the normal practice at Hulref, i.e. the run-off from the first boiling (called jet 1) is used for a second boiling. This is repeated until four boilings of sugar, progressively increasing in colour, are achieved. These are blended after the driers to produce either local or export quality sugar with colour specifications of 60 and 45 IU, respectively. A possible fifth boiling of sugar of low colour to be blended into the local or export quality sugars can be pursued with the use of H_2O_2 . This will contribute an extra 3% to the total refined sugar tonnage, which is approximately 60 tons of sugar per day.

Hydrogen peroxide is used as a bleaching agent in other industries (e.g. paper and textiles) and is readily available from a local supplier. If successful, the same concept can be applied at the mills to produce raw sugar of low colour, thereby ensuring consistent raw sugar quality to the refinery.

Experimental

Experimental procedure

Hydrogen peroxide is a strong oxidising substance which is corrosive in nature. Also, because of its easy and quick decomposition, it must never be in contact with dust laden or moist air, metals other than stainless steel, and untreated water. These issues were taken into consideration during the design of a test rig. In view of the above, a separate spray nozzle arrangement was introduced in the centrifugal.

Figure 1 shows the equipment used for conducting the trials. The 18 L stainless steel vessel was pressurised and maintained at 600 kPa, which is the same pressure as the centrifugal wash water. Compressed air to the vessel was double filtered and dried to prevent contamination. Distilled water was used for trial purposes. The equipment was mounted on a

trolley, which allowed for movement to different centrifugals or other mills in the Tongaat Hulett division.



Figure 1. Hydrogen peroxide dosing equipment.

Food grade H_2O_2 at 35% concentration, which is supplied locally, was dosed on fourth boiling sugar with a typical colour of 100 IU. The first set of trials was conducted in 2009 at 30-1000 ppm. Due to some missing information and vagueness in shelf life tests, in January 2010 another trial was carried out at lower concentrations of 15-330 ppm. The centrifugal cycle was programmed to wash with H_2O_2 after the normal wash. Although the time was variable, it was fixed at five seconds for the trial.

The above cycle was repeated for different concentrations to determine the optimum point of application. In the first trial, another test was run with an extra five second wash (instead of H_2O_2) to establish whether the colour reduction, if any, was due to increased wash water or H_2O_2 effect. Every set of tests was run using the same batch of massecuite without any changes in the centrifugal cycle setpoints. This was done to form a baseline and make informed comparisons between samples with and without H_2O_2 .

A total of 24 centrifugal cycles were done with the usual centrifugal water wash and diluted H_2O_2 . Every four cycles of the usual water wash were followed by four cycles of H_2O_2 wash. Sugar and jet 4 (run-off) were sampled from each cycle. The process was repeated until 12 pairs of samples were attained. Massecuite samples were also taken while discharging the pan.

About 1 kg of a representative sugar sub-sample from each cycle was placed in a labeled plastic sachet and taken to the laboratory for analysis. The sample was split into two sets and one set was dried atmospherically over night. The jet sample was a composite of the 12 cycles

and only one massecuite was taken per run. There was no drying of sugar samples and the massecuite was not sampled in the 2009 trials, hence the necessity for another trial in 2010.

Sugar, massecuite and jet were analysed for colour, pH and brix where appropriate. The samples were analysed on the following day or within a week from the day of sampling, following methods as described in the SASTA Laboratory Manual (2009 version). The samples were then retained at room temperature for re-analysis six months later to review any colour and pH changes during storage. Random HPLC analysis for both jet and sugar will also be done to determine whether there is any inversion with time. The results will serve as a reference for shelf life analysis.

Results and Discussion

The first trial was conducted using undiluted H₂O₂ (35% m/m), but was aborted before a series of runs could be completed. The jet pipe was blocked, possibly due to the strong oxidising effect of H₂O₂ (gives off oxygen upon heating). The sugar also had some odour, which disappeared with reduced concentration. A significant drop in jet and sugar pH was also apparent; these results are not presented in this paper as they were inconclusive. Saska (2007) also encountered erratic pol results when using raw H₂O₂ and attributed this to invert sugar degradation.

The analytical data obtained were analysed statistically using the f- and t-tests at a 95% level of confidence/reliability. The results were considered statistically significant at p≤0.05.

Colour

The colour of the fourth boiling can range from 60 to 150 IU. This colour is influenced by jet three quality or whether the panboilers have applied the back-boiling technique to improve the overall panhouse yield (using a volume of jet four in the fourth boiling).

Tables 1 and 2 represent the results for sugar and jet colour changes during the 2010 trial, respectively. For ease of comparison, the same data are also presented in Figure 2. Figure 3 shows the data obtained for 2009 trials.

Table 1. Colour (ICUMSA Units) for massecuite, untreated and treated sugar at varying concentrations of hydrogen peroxide (H₂O₂).

H ₂ O ₂ conc. (ppm)	Massecuite	Sugar			% removal
		Untreated	H ₂ O ₂	p-values	
0	–	63	63	0.91	0
15	4428	108	95	< 0.05	12
30	4194	96	84	< 0.05	13
65	4194	96	86	< 0.05	11
165	4586	109	94	< 0.05	14
330	3044	76	64	< 0.05	15

Colour removal was the same throughout the entire trial irrespective of H₂O₂ concentration. This was similar to results obtained in 2009 where the colour removal ranged between 9 and 20% (Figure 3). These results are in agreement with the findings of Saska (2007) that colour removal is proportional to the initial colour of massecuite.

Table 2. Colour (ICUMSA Units) for massecuite, untreated and treated jets at varying concentrations of hydrogen peroxide (H₂O₂).

H ₂ O ₂ conc. (ppm)	Massecuite	Jet		% removal
		Untreated	H ₂ O ₂	
0	–	1259	1293	3
15	4428	5602	5183	7
30	4194	4711	3735	21
65	4194	4711	3357	29
165	4586	4201	2249	46
330	3044	3855	1905	51

The jet, however, denoted a different trend, as there was substantial colour removal with an increase in concentration for both trials. Colour removal ranged from 7-51% and 20-74% in 2010 and 2009, respectively. No statistical analyses were done for jets since only one composite sample was obtained for each trial run.

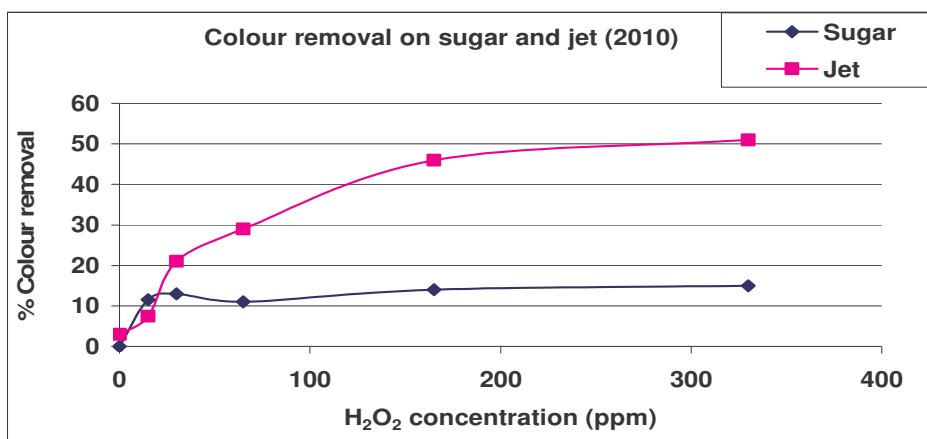


Figure 2. Percentage colour removal for sugar and jet at varying concentrations of hydrogen peroxide for 2010.

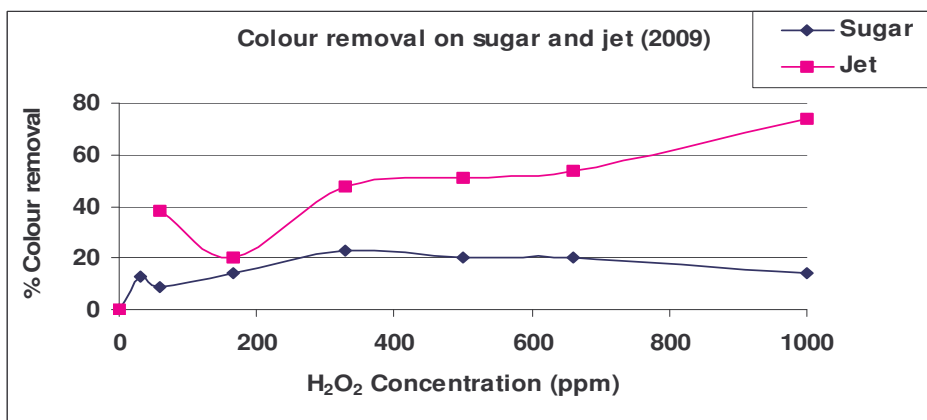


Figure 3. Percentage colour removal for sugar and jet at varying concentrations of hydrogen peroxide for 2009.

Most researchers agree that the colour changes happen within the thin film of molasses surrounding the crystal. However, Payne (1987) insists that colour changes are also happening within the sugar crystal, although at a slower rate than in the molasses film. More H_2O_2 remains in jet solution during spinning. It is assumed that it continues to attack the colour bodies. The use of H_2O_2 in the third boiling could therefore be of advantage as jet three is used for the fourth boiling. The extent of colour removal on the third boiling and behaviour of jet during crystallisation will have to be investigated.

Saska and Kochergirn (2009) reported that sugar colour returned with storage. Contrary to this, Riffer (1980) reported that oxidising agents such as H_2O_2 permanently destroy colour. His argument is based on the mechanism of oxidative cleavage of unsaturated sites to yield carboxylic acids, which is most likely an irreversible reaction, making it difficult to ascertain how colourants could be reformed once destroyed. Conclusions on the effect of H_2O_2 on colour removal for this current study will only be drawn once the shelf life studies had been conducted over a six-month period.

pH

A slight drop in pH from 7.8 to 7.3 in sugar following H_2O_2 treatment has been noted. This has been found to be statistically insignificant, with values ranging between 6.6 and 7.9, regardless of the concentration of H_2O_2 . The data are therefore not presented. This tiny drop in pH is mainly attributed to carboxylic acid formation as a product of cleavage of unsaturated sites of colour bodies by H_2O_2 (Riffer, 1980). The shelf life tests will determine if pH decreases with storage, as reported for VHP (Saska and Kochergin, 2009). This pH decrease has been found to coincide with pol decreases. The HPLC analysis to be carried out for this trial will verify any sugar degradation.

A more pronounced reduction in pH was, however, visible in jets but this was not statistically evaluated due to insufficient data (number of samples). The drop in pH can potentially be offset by addition of dilute NaOH and has been shown by Saska (2007).

Cost of chemicals

The costs of using H_2O_2 per ton of sugar at varying concentrations is presented in Table 3. Considering that H_2O_2 is effective even at 15 ppm, which was the lowest concentration used, its use appears to be economical. The fourth boiling constitutes only 7% of total refined sugar.

Table 3: Comparison of costs of adding hydrogen peroxide (H_2O_2) at varying concentrations.

H_2O_2 Conc. (ppm)	R/ton sugar
15	0.04
30	0.08
65	0.16
100	0.25
150	0.38
165	0.41
330	0.83

Conclusion

The results reported above demonstrate that H₂O₂ can be used to remove colour in fourth boiling sugar even at very low concentrations (15 ppm). However, the tangible effect of this oxidant will be ascertained by shelf life studies that are underway on the set of analyses as reported here, to be conducted over a period of six months from the day of sampling. Positive results will equate to huge benefits, including less recycle and improved sugar yield. It will also enable producing fifth boiling sugar, which will result in about 3% more total refined sugar.

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