

OPTIMISING THE CARBONATATION PROCESS

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Abstract

Refinery carbonatation is widely practised in South Africa and about 80% of the refined sugar produced in South Africa is clarified/decolourised using this method. Attempts have therefore been made to optimise the carbonatation process with regard to impurity removal. Some of the main factors that have been investigated to improve the decolourisation and filterability of the carbonated liquor are:

- Lime quality.
- Method of lime addition.
- Effect of saturator configuration.
- Addition of cationic polymers.
- Addition of hydrogen peroxide.
- Addition of ozone.

The results from both pilot plant and full-scale tests are discussed.

Key words: carbonatation, colour, lime, impurity removal, decolourisation

Introduction

Refinery carbonatation has been used for over 100 years for the refining of raw sugar. It is a cheap and robust process. The process at Hulett's Refinery (HR) consists of adding a slurry of calcium hydroxide in water to the raw melt solution. Then carbon dioxide gas is bubbled into the sugar solution in saturators, under controlled conditions of pH and temperature. Generally the carbon dioxide is added to the saturators in three stages, with the major part of the gassing carried out in the first saturator. The impurities are both absorbed by, and enmeshed in, the conglomerated particles of the calcium carbonate precipitated by the reaction of the carbon dioxide and calcium hydroxide. Separation of the clear liquor and the calcium carbonate is done by pressure filtration. This filtration requires expensive two-stage filtration plant for the separation and desweetening of the calcium carbonate precipitate. A significant portion of the calcium carbonate cake is required to act as a filter aid and growth of a suitable filtering carbonate cake is as important as colour removal. An alternative to traditional filtration was reported by Rein (1988). This summarised preliminary laboratory work where flotation was used to separate the precipitate formed during carbonatation. Jun (1989, 1990) has reported on full scale carbflotation systems. Therefore when the need arose to improve the decolourisation at the Triangle refinery a carbflotation system was considered. The full scale plant has been described by Smith *et al.*, (2000).

One of the main objectives of carbonatation is the removal of the impurities present in the raw sugar entering the refinery. These impurities will have negative effects on some of the unit operations in the refinery. Firstly certain impurities will have a profound effect upon the nucleation and growth or flocculation process (Alexander 1957; Murray *et al.*, 1974) involved in the formation of the calcium carbonate conglomerate. As a consequence such impurities will impact upon the filtration processes (Lee and Donovan, 1995) in the refinery. Secondly the presence of certain impurities will adversely affect the sugar crystallisation process (Morel du Boil, 1995) and lastly refined sugar quality (Clark and Legendre, 1996) will be influenced by some impurities.

Generally about 40 to 45% decolourisation is achieved at the carbonatation station at HR. After carbonatation the liquor is decolourised with resin.

Attempts have been made in the laboratory to investigate the effect of carbonatation on the removal of a variety of impurities. Also work has been done both on a pilot plant and full scale at the Hulett's Refinery (HR) to optimise the carbonatation process. In sugar refining, colour is conveniently used as a measure of the level of non-sugars of a sugar solution due to the fact that most non-sugars are coloured (Hubbard, 1993). Colour therefore was the main impurity that was measured during the optimisation tests.

Experimental procedure

Carbonatation

The procedure to carry out laboratory carbonatation tests has been described in detail by Moodley (2001). The basic procedure was as follows:

- The required amount of lime was added, as a 10% milk of lime solution (mass/mass), to melt with stirring at 80°C.
- After the sample was mixed for 5 minutes, the carbonatation reaction was initiated by introducing carbon dioxide into the reaction vessel.
- As soon as the pH of the liquor reached the required value, the gas supply was stopped.
- The carbonated melt was stirred for a period of one minute.
- The carbonated liquor was then filtered, cooled and stored in a freezer for analysis.

Filterability tests

The filterability tests were according to the procedure described by Bennett (1967). The index of carbonatation filterability (\sqrt{F}) was then calculated. We note that the higher the \sqrt{F} the better the filtration performance.

Analytical methods

All liquors were analysed according to methods in the SASTA Laboratory Manual (Anon, 1985).

Results and Discussion

Impurity removal by carbonatation

The results of laboratory tests done by Moodley *et al.* (2002) have shown that carbonatation is very effective in the removal of the following impurities:

- About 40 to 50 % of the colour was removed.
- Most of the turbidity (95%), starch (93%), sulphates (86%) and phosphates (100%) were removed.
- A small amount (29%) of the gums was removed.
- A high proportion (67%) of magnesium was removed.

In addition, it was shown that during carbonatation most of the glucose, fructose and acetic acid were destroyed and there was an increase in lactic acid. The reasons for this have been described by Cox *et al.* (1990). The results have also shown that carbonatation has no significant effect on the levels of theandrose and 1-kestose present in the melt. A calcium mass balance over carbonatation showed that most of the lime added during carbonatation was removed in the form of calcium carbonate. The results have shown that with the adequate addition of lime the carbonatation process is very effective in the removal of most impurities. It has also been shown by Dunsmore *et al.* (1978) that carbonatation removed floc-forming impurities and it has generally been accepted that carbonatation refineries produce floc-free refined sugar. In South Africa, Morel du Boil (1996) and Lionnet (2002) carried out a literature review on acid beverage floc. It was concluded by these workers that two main components responsible for the formation of floc are proteins and polysaccharides.

Tests were therefore done in the laboratory where the effect of carbonation on floc was investigated. The results showed that about 30% of the polysaccharide present in melt was removed during carbonation. In all cases, the melt samples were floc positive in terms of both the alcian blue and 10-day tests. This indicates that the floc precursors are generally present in the melt samples. All the carbonated liquor samples irrespective of the original melt were floc negative. This confirms the findings of previous work (Dunsmore *et al.*, 1978) done that carbonation removed the floc precursors.

It has also been shown by Moodley *et al.* (2002) that colour removal during carbonation is a function of the melt colour, amount of lime added and the final pH.

It would be worthwhile to evaluate ways of improving the performance of carbonation, as any improvement would have major benefits for a refinery.

Optimisation of carbonation process at HR

Effect of lime

Quality of lime

Traditionally the Hulett's Refinery used rock lime, at the slaking plant, to prepare milk of lime. A number of problems were experienced with the handling of rock lime. In view of these problems and based on the successful operation of a powdered lime system at one of the Hulett's raw sugar factories (MacNaughton, 1995) for a number of years, it was decided to replace rock lime with powdered lime at the refinery.

Although suppliers indicated that the two types of lime were identical, this needed to be confirmed by analysis of the materials received. Samples were analysed by x-ray fluorescence (XRF, inorganic chemical composition) and x-ray diffraction (XRD, crystalline mineral identification). A comparison between the qualities of rock lime and powdered lime are given in Table 1.

The results show that the powdered lime contains significantly more silica than the rock lime. The XRD results indicate that this is almost all present as quartz. Since quartz is practically inert this should not dissolve in the slaking process.

Table 1. Comparison between powdered and rock lime.

	Powdered lime	Rock lime
SiO ₂	2.1%	0.3%
Al ₂ O ₃	0.7%	0.3%
Fe ₂ O ₃	0.3%	0.2%
MnO	0.9%	0.9%
MgO	1.7%	1.5%
CaO	94.1%	96.3%
Other	0.2%	0.5%
Total	100.0%	100.0%
LOI [#]	4.75	1.39

[#] - Loss on ignition

Carbonation tests were also done in the laboratory where the performances of rock and powdered lime were compared. The results (Table 2) showed that with powdered lime there was a slight improvement in the filterability of the carbonated while colour removal was very similar. However, there was a significant improvement in the lime handling system.

Table 2. Comparison of the performances of rock and powdered lime.

Amount of lime (% CaO on brix)	Rock lime		Powdered lime	
	\sqrt{F} (m)	Colour	\sqrt{F} (m)	Colour
0,5	28×10^{-8}	919	36×10^{-8}	837
0,8	21×10^{-8}	895	41×10^{-8}	856
1,1	17×10^{-8}	707	31×10^{-8}	736

Ageing of lime

The effect of lime ageing on carbonatation was evaluated. The results on powdered lime (0,8% CaO on brix) are given in Table 3.

Table 3. Effect of lime ageing on the filterability and colour removal on melt of 1830 colour.

Ageing time (minutes)	\sqrt{F} (m)	Liquor colour	% decolourisation
20	31×10^{-8}	958	48
60	27×10^{-8}	976	47
240	24×10^{-8}	958	48

In terms of colour removal the results in Table 3 indicate that 20 minutes is the optimum time for the ageing of lime. The results also indicate that when the lime was aged for more than 20 minutes, the filterability was adversely affected. This is different to the results obtained by Bennett (1998) where an ageing time of 24 hours was recommended and Murray and Runggas (1975) who found that milk of lime that was aged for 2 hours gave the best filterability results. These findings indicate that the quality of the lime may be important with regard to the ageing of lime.

Saccharate liming

The results of the tests done in the laboratory have shown that the addition of lime as lime saccharate when compared to milk of lime improved both the decolourisation and filterability of the carbonated liquor by about 20 %. A full scale trial is currently being planned at the refinery.

Saturator configuration

In an attempt to improve the performance of carbonatation, the configuration of the saturator station at the refinery has been recently modified (unpublished data). In the previous system there were two parallel A-saturators followed by two parallel B-saturators and finally one C-saturator. In this arrangement it was observed that the gas flow to the A-saturator was often restricted to its maximum limit. Based on the recommendations (Anon, 1974) that better carbonatation would be achieved if a larger proportion of the retention time is in the A-Saturators it was decided to modify the configuration to a two saturator system. In the new arrangement one of the B-saturators has been converted to an A-saturator and the C-saturator is used as a heating vessel only. This means that the gassing takes place in the three A-saturators and the B-saturator. The modified system has been in operation for about six months. The preliminary results indicate a significant improvement in the pH control and gas utilisation at the carbonatation station.

Effect of chemical additives on the carbonatation process*Cationic flocculants*

The results of tests done on unfiltered carbonated liquor from the refinery have shown that the addition of 200 mg/kg on brix of these chemicals improves both the liquor and sugar colour by 30-40%. The results of full scale tests done at the refinery are given in Table 4.

Table 4. Full scale tests at the refinery with a cationic flocculant (Moodley, 1993).

	No chemical	Chemical added	No chemical
Melt colour	1717	1630	1726
Carbonated liquor colour	997	766	895
Number of colour units removed	720	864	831
% decolourisation	42	53	48
Fine liquor colour	414	338	370
Number of colour units removed	583	428	525
% decolourisation	58	56	59
First sugar colour (affinated)	17	12	18

The results show that the addition of the flocculant improved the colour units removed during carbonatation by about 20%. The first sugar colour improved by about 29%.

Hydrogen peroxide

Laboratory tests done on melt by the Sugar Milling Research Institute (Moodley, 1992) have shown that about 25 to 30% decolourisation can be achieved with the addition of about 200 mg/kg brix of hydrogen peroxide. Full scale tests done at the refinery where 200 mg/kg brix of hydrogen peroxide was added to the melter showed that the melt colour improved by about 15%. With regard to sugar colours similar observations were made to those of Davis *et al* (2000) in that the major improvement was in the third and fourth refined sugar colours. The most significant improvement was in the fourth refined sugar where a 30% improvement was measured. A similar improvement was measured in the refinery exhaust jet colour.

Combination of hydrogen peroxide and cationic flocculant

Laboratory tests were done on unfiltered carbonated liquor where the effect of a combination of hydrogen peroxide and the cationic flocculant on the colour removal was evaluated. The results are shown in Figure 1.

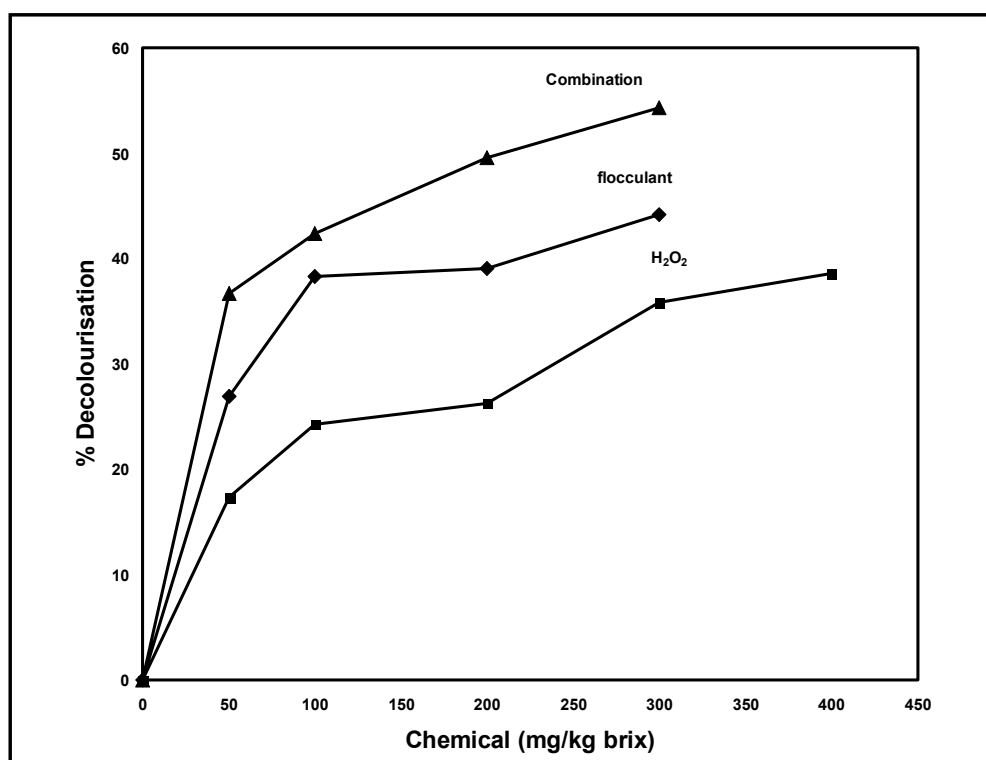


Figure 1. Decolourisation results of unfiltered carbonated liquor.

The results in Figure 1 show that a higher level of decolourisation is achieved with a combination of the chemicals.

Ozone

Due to the promising results obtained with ozone from full scale tests (Davis et al., 1998), the SMRI was asked to undertake some laboratory trials for the refinery. Laboratory carbonatation and ion exchange processes were set up to simulate as closely as possible the performance of the corresponding processes at the refinery. The results (Davis, 1999) showed that ozonation of the raw melt to a level of 200 mg/kg brix would probably permit half of the carbonated liquor stream to bypass ion exchange and still achieve the same refined sugar colour. This has major benefits in term of costs and effluent reduction. At this stage unfortunately the cost of doing a full scale test is too high.

Conclusions

The laboratory tests have shown that carbonatation is very effective in the removal of a number of impurities viz. colour, turbidity, starch, gums, sulphates, phosphates and magnesium. It has also been shown that carbonatation removed most of the floc precursors present in melt. On the negative side, during carbonatation most of the glucose, fructose and aconitic acid are destroyed. There is also a build up of lactic acid during carbonatation. Of the factors evaluated it has now been established that the decolourisation during carbonatation is determined by the feed melt colour, amount and quality of lime added to melt and by the final pH of the carbonatation reaction. It has also been shown that the decolourisation during carbonatation can be improved with the addition of decolourising chemicals such as cationic flocculants, hydrogen peroxide and ozone.

It has been shown that the lime handling system has been significantly improved by the replacement of rock lime with powdered lime. With regard to lime ageing the laboratory results indicated that 20 minutes is the optimum time in terms of colour removal and filterability. The laboratory results showed that the addition of lime as saccharate when compared to milk of lime improved the colour removal and filterability by about 20%. A full scale trial to evaluate the benefits of saccharate liming will be done at the refinery during the season.

The configuration of the saturator station at the refinery has significantly improved the pH control system.

Full scale tests have shown that the addition of these chemicals to unfiltered carbonated liquor improved both the carbonated liquor and sugar colour by 20 to 30%. When the raw sugar entering the refinery is abnormally high then the flocculant is dosed.

Tests done at the refinery have shown that the addition of hydrogen peroxide to melt improved the colour of the melt by 15%. A reduction in the lower grade refined sugars was also observed. Here again hydrogen peroxide is only dosed during periods of poor raw sugar quality.

The SMRI laboratory tests have shown that ozone can be used successfully during carbonatation. Full scale tests need to be done.

The addition of the decolourising chemicals such as cationic flocculants and hydrogen peroxide is the most economical way to improve the decolourisation during carbonatation. The chemical can be pumped directly from the container into the liquor line. Currently at the refinery these chemicals are used when the melt colours entering the refinery are abnormally high.

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