REFEREED PAPER

COLOURANT BEHAVIOUR DURING SUGARCANE PROCESSING

BOOYSEN KC AND DAVIS SB

Sugar Milling Research Institute NPC, c/o University of KwaZulu-Natal,
Howard College Campus, Durban, 4041, South Africa
kbooysen@smri.org, sdavis@smri.org

Introduction

The quality of raw sugar is considered to be suitable if it is aligned with defined quality specifications. One of the quality parameters is raw sugar colour. If the colour of raw sugar delivered to the South African Sugar Terminal exceeds the set colour specification, colour penalties will be imposed. Although the mass quantity of colourants in raw sugar is small compared to sucrose, the impact of colourants on raw sugar quality is significant (Bourzutschky, 2005a). The formation of factory produced colourants can be exacerbated by shortcomings in the control and management of sugar production processes. Although it is widely accepted that the extent of colour formation in the factory can be controlled by implementing appropriate factory operating conditions, the most important cause of high raw sugar colour is considered to be the quality and physical condition of the cane received by the miller (Rein, 2007).

Factors affecting colourant formation

The colour of sugarcane processing streams is typically measured using the ICUMSA[1] method by measuring the absorbance of light by a filtered sample of dissolved sugar at a wavelength of 420 nm and a pH of 7 for which the total solid concentration has been determined (Anon, 2009a; Anon, 2009b; Anon, 2009c). ICUMSA 420 colour is reported in ICUMSA units (IU) and is a quality measure that is influenced by the amount and type of coloured compounds in the sugar stream. Besides determining the ICUMSA 420 colour, the colourants present in sugarcane processing streams across the factory can be analysed. The different types of coloured compounds may have different origins and may respond differently to changes in processing conditions. The types of sugarcane colourants found in processing streams can be classed as either sugarcane plant-derived colourants and precursors or as factory colourants (Davis, 2001). An overview of the origin, nature and fate of different types of colourants found in sugarcane processing streams can be found in Booysen (2019). The origin of each colourant type is described below.

Sugarcane plant-derived colourants and colour precursors

The sugarcane-derived colour contributing components can be classed as insoluble colourants, colour precursors and flavonoids. The insoluble colourants, chlorophyll, xanthophylls and carotenes, are easily separated during the clarification of cane juice (Bento, 2009). Colourless phenolics are constituents of the cane plant and although they do not contribute to colour when entering the factory, they can be converted to colourants by reacting with impurities, such as iron, amines and amino acids, when exposed to various conditions during sugarcane processing (Bento, 2009). Flavonoids are a group of sugarcane plant pigments that are soluble and can pass through the sugar production process without being removed during clarification. Some of these compounds have a glycoside functional group in

[1] International Commission for Uniform Methods of Sugar Analysis.

their structure and therefore have an affinity[2] to sucrose (Bento, 2003), making them susceptible to incorporation in the sugar crystal.

The main factors which determine the type and quantity of sugarcane plant-derived colourants are the quality and variety of the cane being processed. Poor quality cane generally results in higher colour levels in raw sugar (Smith, 1990). As a result, raw sugar colour tends to be lowest in the middle of a season when the quality of sugarcane being processed is superior. Processing fresh, mature and well-topped cane with no brown leaf (referred to as trash in the classical literature) produces the best quality raw sugar.

Melanoidins

Melanoidins are high molecular mass compounds with an intense colour (Bento, 2009). These colourants are produced by the Maillard reaction through many complex reaction pathways involving reducing sugars (glucose and fructose) and amino nitrogen compounds (Rein, 2007). The factors affecting these reactions include the type of reactant species, pH, water content and temperature (Paton and McCowage, 1987). The Maillard reaction can occur throughout the factory since the reactant species (reducing sugars and nitrogen-containing compounds such as amines and amino acids) are usually present throughout the process (Rein, 2007). Melanoidins can form at ambient temperatures but their formation is promoted when the mixture of reactant species is subjected to higher temperatures (Clarke *et al*., 1986), with the rate of reaction accelerating with increasing temperature and alkalinity (Davis, 2007). A temperature increase of 5°C can result in the doubling of the Maillard reaction rate (Rein, 2007; Newell, 1979). The rate of melanoidin formation peaks during juice evaporation when the temperatures are high (Mersad *et al*., 2003) and the polymerisation reactions continue during crystallisation. Melanoidins also form at lower temperatures over long periods such as during the storage of raw sugar, mainly in the molasses film surrounding the crystal (Clarke *et al*., 1986; Paton, 1992).

It is generally understood that glucose is consumed more readily than fructose in the Maillard reaction during sugarcane processing (Rein, 2007; Newell, 1979). However, the water content of sugarcane processing streams can have an effect on the reactivity of the reducing sugars for melanoidin formation. Bourzutschky (2005a) states that fructose reacts more readily than glucose in aqueous solutions, forming stable acidic products. When the water content is low, such as with high brix solutions in evaporators, glucose and fructose react in equimolar amounts with amino acids (Bourzutschky, 2005a). Generally, melanoidins develop slowly in an acidic medium and more rapidly in a basic medium (Mersad *et al*., 2003). Reaction rate increases with increasing pH value but the extent of increase is greater for glucose than for fructose (Bourzutschky, 2005a). A study by Morel du Boil and Schäffler (1978) showed that almost one-third of the amino nitrogen in syrup was not present in molasses implying that the concentration of amino nitrogen is important, since the Maillard reaction can occur to a greater extent in the presence of higher concentrations of amino nitrogen (Paton, 1992).

Strecker degradation occurs through the degradation of amino acids by monosaccharide breakdown (Bourzutschky, 2005a). During this process, carbon dioxide and ammonia are released in the form of gas bubbles. Due to their small size, the bubbles are retained in massecuite. Aeration of massecuite in this way significantly increases viscosity. Strecker degradation is exothermic and can cause foaming in crystallisers and molasses swelling as well as explosions in molasses tanks (Rein, 2007).

Melanins

[2] Affinity is the tendency of different chemical species to have strong chemical interactions with each other.

Melanins are high molecular mass compounds formed by the enzymatic reaction of phenols with nitrogen-containing compounds. These colourants are particularly difficult to remove in processing (Clarke *et al*., 1986). Melanin formation occurs at temperatures between 18 and 55°C and in mildly acidic conditions when the pH value is between 4.5 and 8.0. Their formation is prominent during extraction where the enzymes, which originate from cane, are active but they do not form to a great extent in subsequent processing stages since the higher operational temperatures in those processing units denature enzymes (Mersad *et al*., 2003). In some cases, they can be removed to a small extent by factory clarification (Rein, 2007). Melanins are preferentially occluded inside the sugar crystal during crystallisation (Clarke *et al*., 1986).

Caramels

Caramels are produced by the degradation of sugars when exposed to high temperatures. The composition of the caramels produced depends on the reaction time, temperature and pH value (Bourzutschky, 2005a). Caramelisation reactions occur more intensely when conditions are alkaline. The effect of increased pH values on caramel formation is more significant than that of increased temperatures. The high temperatures required for caramelisation are only available during evaporation and crystallisation (Bourzutschky, 2005a) where intense heating supplies the high temperatures that are necessary for the dehydration and condensation reactions that occur during caramelisation (Bourzutschky, 2005a; Mersad *et al*., 2003).

Hexose alkaline degradation products (HADPs)

The formation of hexose alkaline degradation products (HADPs) occurs during sugarcane processing where monosaccharides are present and conditions are alkaline (Bourzutschky, 2005a). The optimum pH for their formation is 11. The alkaline degradation reactions occur at ambient temperatures but intensify as the temperature rises to form dark coloured compounds (Mersad *et al*., 2003). The low concentration and alkaline conditions of liming during clarification promote the formation of HADPs (Bento, 2003; Bourzutschky, 2005a).

Colourant behaviour during sugarcane processing

The sugarcane factory can be divided into four major processing sections: extraction, clarification, evaporation and crystallisation. These operations are controlled to optimise sugar extraction and recovery and to produce high quality raw sugar.

The increase in colour in the front-end is small when compared to that in the back-end of the factory (Lionnet, 1998; Smith, 1990; Rein, 2007). The boiling house experiences the greatest increase in ICUMSA colour, with increases of up to 70%[3] due to the high temperatures, long residence times and high brix to which streams are subjected promoting the formation of factory colourants (Smith, 1990). There are many process control factors that need to be considered for the optimal performance of a sugarcane factory. This paper only considers those controls that are most important for the prevention and limitation of colour formation during sugarcane production and in the raw sugar factory.

Sugarcane plant

The condition of the cane received by a sugarcane factory has a large effect on raw sugar colour (Rein, 2007). Smith (1990) found that when the levels of sugarcane plant-derived

[3] This was determined by Smith (1990) from the weekly colours of raw syrup, final molasses and raw sugar from the 1988/89 season.

colourants entering the factory were high (usually early and late in the season), it was often impossible to meet raw sugar colour specifications through optimisation of existing factory operations. The main factors contributing to the formation of colourants in the sugarcane plant relate to the production of cane in the field and the harvesting of cane.

The colourants formed during the production of cane are dependent on the climatic conditions, cane variety being grown, the presence of pests and diseases, and soil health and nutrition (Murray, 2007). It is critical to apply good harvesting practices so that the benefits of the good quality cane produced in the field are realised during sugarcane processing. Minimum colour is present in raw juice when clean and fresh cane stalks are processed. Clean cane is obtained by employing harvesting techniques that limit the amount of tops and trash (brown leaf) remaining on the cane stalk. The colour of juice extracted from cane increases with the greenness of cane and the amount of tops and brown leaf entering the extraction plant (Payne, 1982). Tops and brown leaf contain many impurities, with the coloured impurities being some of the most critical in sugarcane processing (Lionnet, 1998). Fresh cane is obtained by maintaining as short as possible burn-harvest-to-crush-delays which minimises cane deterioration (Russell, 2007).

Lionnet (1991) performed a comprehensive study on the effect of different controllable factors such as time of harvest, cane variety, cane constituents and cane age on the colour and impurity content of cane. It was found that the time of harvest, variety and the constituents of cane had marked effects on colour while the age of cane had the least significant effect. In a study by Naidoo and Lionnet (2000), the impacts of cane variety, geographical location, cane age, ratoon number, month of harvest, whether cane was irrigated or rainfed and burnt or trashed at harvest, on various sugar processing parameters including ICUMSA colour were investigated. It was found that colour is predominantly a varietal effect. Besides month of harvest and geographical location, the effect of all the other factors on colour was not statistically significant. A similar study by Barker and Davis (2005) produced comparable results. Both these studies (Naidoo and Lionnet, 2000; Barker and Davis, 2005) mentioned that the effects reported and their significance should be regarded with caution since interacting effects of the various factors could have influenced the results.

Strategies for minimising colour formation during cane production and harvesting

Cane production can be managed appropriately through careful management of the season length, selection of appropriate varieties, time of harvest and by keeping pests and diseases under control (Murray, 2007; Meadows, 2007; Payne, 1982; Rein, 2007). Harvesting strategies include avoiding overburning cane, careful topping of cane and removal of as much brown leaf as possible. It is important to carefully manage cane harvesting when temperature and humidity are high. Short burn-to-harvest-delays ensure that the best possible quality of cane arrives at the factory. This can be achieved through managing allocations and overtime. Furthermore, it is important to avoid infield loading in wet weather and stockpiling. Once harvested cane reaches the factory, limiting the amount of extraneous matter entering the extraction plant is essential (Meadows, 2007).

Extraction

Extraction of juice from prepared sugarcane is achieved with either a milling tandem or a diffuser. The South African sugarcane industry mainly uses diffusers, with 76% of all cane being handled by diffusion. The colours of juice, syrup and raw sugar are generally higher for diffusers than for milling tandems due to the higher temperatures at which diffusers are operated. Milling tandems have temperatures which range from ambient to over 60°C at the last mill if hot imbibition is used. To avoid high sugar losses in diffusers through microbial action and enzymatic inversion, diffusers are usually operated at an average temperature of about 85°C to ensure that the temperature in all stages is above 75°C (Rein, 1995). A study found that when hand-cleaned cane is processed in a diffuser, a 10˚C drop in temperature can result in a mixed juice colour reduction of up to 25%. However, operating a diffuser at lower temperatures is not ideal since sucrose losses under these conditions are severe (Rein, 1995).

ICUMSA colour changes during extraction: comparison of diffusion and milling

When comparing the colours of juices from a diffuser with those of a milling tandem, the average colour of diffuser juice was found to be up to 25% higher than the colour of juice from a milling tandem, but this was affected by a number of factors such as cane variety, the cleanliness (low tops and brown leaf) of the cane, climatic conditions and time of season (Rein, 1999). The presence of tops and brown leaf during extraction was found to have a more significant effect on diffuser juice colour than on the colour of juice from a milling tandem (Rein, 1995). It was also noted that when long stops of more than six hours occurred due to a mechanical breakdown in a sugar factory, the extent of deterioration of sucrose was much more significant in a diffuser than in a milling tandem (Rein, 1995). The sucrose degradation products can contribute to the formation of colour during processing.

At the Gledhow Sugar Company in South Africa, extraction of prepared cane proceeds either through a milling tandem or a diffuser. Koster (1995) reported on tests that were performed at this sugar factory to compare the effect of the extraction process on the colour of mixed juice. He stated that the results obtained from determining the ICUMSA colour levels of DAC (direct analysis of cane) extract and mixed juice showed that the colour increase across the diffuser was 90% while that across milling was 8%. However, no experimental details confirming this statement made by Koster (1995) could be found in the literature. Furthermore, it is important to note that the colour of DAC extract is not characteristic of cane juice colour since the DAC preparation method may result in the formation of colourants. Values reported by Sahadeo *et al*. (2002) indicated that the mixed juice obtained from Gledhow's diffuser was approximately 20% higher in ICUMSA colour than the mixed juice from the milling tandem. At the Umzimkulu sugar mill in South Africa, it was found that when changing from a milling tandem to a diffuser in 1991, a 30% increase in clear juice and syrup ICUMSA colour was observed (Koster, 1995), while the colour of affinated sugar showed a step change from about 650 to 900 IU (Lionnet, 1998). At Maidstone, the replacement of a milling tandem by a second diffuser in 1995 resulted in an increase in affinated sugar colour (Lionnet, 1998). However, this change in sugar colour closely followed the change observed in the industry average colour. Therefore, it is thought that the changes in colour at Maidstone as a result of the conversion from milling to diffusion may not all have been contributed by the change in extraction method (Rein, 1999).

Behaviour of colourants during extraction (Table 1)

In a milling tandem, the ICUMSA colour and the concentration of sugarcane plant-derived flavonoids in raw juice increase as extraction increases from the first mill to the last one (Bento, 2009; Rein, 2007). Increasing extraction in milling results in a greater release of monomeric colourants (Smith *et al*., 1981). Paton (1992) reports that the colour of first expressed juice contains a large contribution from high molecular weight colourants with about 70% of the colour of juice being from compounds with molecular sizes greater than monomeric flavonoids. Although the conditions of extraction (low brix and neutral to slightly acidic conditions) are not favourable for the formation of melanoidins, they can form to a very small extent in diffusers since diffuser temperatures, and in some cases pH, are higher than in milling (Bourzutschky, 2005a). The formation of melanins is prominent during extraction (Mersad *et al*., 2003).

Table 1. Summary of colourant behaviour during extraction*.

DAC EXTRACT[4]	EXTRACTION		MIXED JUICE
Obtained by blending a cane sample with water in a cold digester, digesting for 20 minutes, and then decanting, filtering and analysing the resultant mixture	**Typical operating conditions**		**Stream characteristics**
	Milling tandem 25 – 60°C pH 4.5 – 5.5	**Diffuser** 75 – 85°C pH 6.0 – 6.5	65°C pH 5.5 12°Bx
Colourant composition	**Colourant behaviour during extraction**		**Colourant composition**
9 000 – 20 000 IU • Sugarcane plant-derived colourants • Colour precursors	**Formed:** Melanins **Removed:** None **ICUMSA colour changes:** 90% increase (diffuser) 8% increase (milling tandem)		15 000 – 30 000 IU • Sugarcane plant-derived colourants • Colour precursors • Melanins

*The ranges presented in this table were collated from various literature sources and for different mills and therefore are not the same as the normal ranges of variation within a particular mill.

Process control strategies for minimising colour formation during extraction

An important consideration for limiting colourant formation during extraction is the temperature of imbibition water. Imbibition water temperatures that are too high can result in the acceleration of colour formation reactions (Bourzutschky, 2005b). Sanitation and regular cleaning of milling and diffusion equipment is required to limit bacterial activity. Bacterial activity can result in the formation of colourant precursors through the degradation of sucrose to monosaccharides and the further degradation thereof (Bourzutschky, 2005b; Rein, 2007).

For sugar milling companies considering the production of a new product using a sucrose stream, the possibility of diverting a highly coloured stream from the extraction unit for the production of a new product could be investigated. One way that Brazilian sugarcane factories are able to decrease mixed juice colour and the subsequent colour of raw sugar, is by separating the juices from the later mills in a milling tandem from first expressed juice and diverting this stream for ethanol production (Bento, 2009).

Clarification

The purpose of clarification in a sugarcane factory is to remove non-sugar soluble impurities, suspended matter and colloidal particles. Clarification also serves to increase the pH of the sugar stream in order to minimise inversion of sucrose during subsequent processing steps (Doherty and Edye, 1999). Phenol and amino compounds are present as soluble species in mixed juice and since they are not removed during clarification, these compounds have the potential of forming factory colourants during sugarcane processing, especially in the heat intensive (evaporation and crystallisation) processes following clarification.

Behaviour of colourants during clarification (Table 2)

The result of clarification is that the colour of evaporator supply juice (clear juice) is always lower than that of the corresponding mixed juice (Paton, 1992). The insoluble sugarcane plant-

[4] It is important to note that the colour of DAC extract may differ slightly to that of cane juice colour since the DAC preparation method may result in the formation of colourants.

derived pigments (chlorophyll, xanthophylls and carotenes) are removed during clarification. Some sugarcane flavones, especially those containing glycosidic linkages in their structure (Clarke *et al*., 1986), are soluble and stable at high pH values and as a result are not destroyed during clarification (Bento, 2009).

Table 2. Summary of colourant behaviour during clarification*.

MIXED JUICE	CLARIFICATION	CLEAR JUICE
Stream characteristics	**Typical operating conditions**	**Stream characteristics**
65°C pH 5.5 12°Bx	85 – 112°C pH 7.8 – 8.0	95°C pH 7.2 12°Bx
Colourant composition	**Colourant behaviour during clarification**	**Colourant composition**
15 000 – 30 000 IU • Sugarcane plant-derived colourants • Colour precursors • Melanins	**Formed:** HADPs **Removed:** Insoluble sugarcane plant-derived pigments **ICUMSA colour changes:** 20 – 25% decrease	14 000 – 28 000 IU • Flavonoids • Colour precursors • Melanins • HADPs

*The ranges presented in this table were collated from various literature sources and for different mills and therefore are not the same as the normal ranges of variation within a particular mill.

It has been reported that an ICUMSA colour reduction of 20-25% can be achieved over clarification (Rein, 2007). Clear juice usually has a higher indicator value[5] than mixed juice which demonstrates that some high molecular weight colourants are removed during the process (Paton, 1992). Bento (2009) reported that more than 50% of the high molecular weight colourants can be removed during clarification. The contribution of high molecular weight colourants to the colour of typical evaporator supply juice is over 60% (Paton, 1992).

Although some colourants are removed during clarification, the low concentration and alkaline conditions of this unit operation can cause hexoses to degrade and the formation of HADPs is prominent (Bento, 2003). It has been observed that excessive liming of juice to a pH greater than 8.0 results in considerable colour formation when the juice is stored for 16-45 hours (Paton and McCowage, 1987). Due to the low brix conditions during clarification, Maillard reactions rarely occur even in the presence of amino compounds (Bento, 2003; Bourzutschky, 2005a).

Process control strategies for minimising colour formation during clarification

Maintaining a constant temperature and pH value, utilising the shortest residence time possible in reactors and clarifiers, and the correct addition of chemicals are important for minimising colour formation. Additional factors to consider are the correct preparation of flocculants and proper functioning of instruments and controls (Bourzutschky, 2005a).

For those sugar mills using lime saccharate as the liming agent, it is important that a temperature below 58°C is maintained during its preparation. Since the lime saccharate solution is alkaline, temperatures exceeding 58°C could result in colour formation[6]. Over-liming can result in highly alkaline conditions. Although an alkaline environment can reduce sucrose losses due to inversion, it would exacerbate scaling in the evaporators and promote

[5] The indicator value (IV) is defined as the ICUMSA colour at pH 9 divided by the ICUMSA colour at pH 4. A high IV gives an indication of the presence of sugarcane plant-derived colourants.
[6] Lime saccharate is produced through the reaction of milk of lime and a sucrose solution. Lime saccharate produces clarified juices of lower turbidity than those from milk of lime (Rein, 2007).

the formation of colourants from the alkaline degradation of glucose and fructose (Eggleston *et al*., 2004). It is therefore important to ensure reasonable accuracy of the probes monitoring the pH of limed juice for the accurate application of the correct dose of lime.

Evaporation

The evaporator station is the location in a sugarcane factory where juice is exposed to the highest temperatures, and therefore it is expected that colour formation would be prominent in this unit operation. However, laboratory and factory trials conducted in Australia have shown that the colour increase during evaporation is relatively small when compared to the colour increases occurring in later processes of the factory (King, 2005). Evaporator stations and heating steam systems in the sugarcane factory were designed to limit the maximum juice temperature to 120°C in the first effect and thereafter the temperature gradually decreases across the remaining effects to a final temperature of 60°C. Long residence times and high temperatures during evaporation can create a potential loss of between 1% and 2% of incoming sugar by inversion (Smith *et al*., 2000), and the resulting reducing sugars can undergo degradation reactions to form colourants. Edye and Clarke (1996) present a summary of the sucrose loss and colour formation processes which occur in evaporators of a sugarcane factory.

Behaviour of colourants during evaporation (Table 3)

The increase in colour during evaporation is usually between 5-10% (Davis, 2007), with the Maillard reaction and caramelisation being the main contributors to colour formation. Evaporation is the main process unit in a sugarcane factory where caramelisation occurs due to the temperature being sufficiently high (Mersad *et al*., 2003; Bourzutschky, 2005b). Overheating reactions can occur during evaporation due to insufficient circulation in boiling tubes and on heater plates which results in caramel formation (Bourzutschky, 2005a). The high temperatures and the increase in brix during evaporation are favourable for the Maillard reaction (Bento, 2009; Bourzutschky, 2005a; Paton, 1992). Melanoidin formation peaks during evaporation when the tube surface temperature reaches 120°C and the polymerisation reactions continue throughout crystallisation (Mersad *et al*., 2003).

Table 3. Summary of colourant behaviour during evaporation*.

CLEAR JUICE	EVAPORATION	SYRUP
Stream characteristics	**Typical operating conditions**	**Stream characteristics**
95°C pH 7.2 12°Bx	120 – 60°C pH 7.1 – 6.7	56°C pH 6.5 65°Bx
Colourant composition	**Colourant behaviour during evaporation**	**Colourant composition**
14 000 – 28 000 IU • Flavonoids • Colour precursors • Melanins • HADPs	**Formed:** Melanoidins and caramels **Removed:** None **ICUMSA colour changes:** 5 – 10% increase	15 000 – 29 000 IU • Flavonoids • Colour precursors • Melanins • HADPs • Melanoidins • Caramels

*The ranges presented in this table were collated from various literature sources and for different mills and therefore are not the same as the normal ranges of variation within a particular mill.

Process control strategies for minimising colour formation during evaporation

During evaporation, temperature, juice circulation, residence time and concentration levels are important factors for minimising colour formation. The main factors to control are the exhaust steam temperature and the first effect circulation rate. Poor circulation can cause drying out of the tubes (Shah, 2013) which reduces the heat transfer rates and can lead to localised overheating of the juice. Long exposure times of the juice in the evaporators can lead to inversion of sucrose and subsequent colour formation (Smith *et al*., 2000). The residence time can be managed through level control and by reducing scaling on heating surfaces (Bourzutschky, 2005b). Bosnjak (1969) reported that there is an optimum liquid level which gives the highest value for the heat transfer rate and that this optimum level also gives the lowest colour increase.

Robert vessels are one of the most commonly used evaporator designs in the southern African sugar industry (Peacock, 1999). A challenge with the classical Robert evaporators is that when they are poorly controlled, they run the risk of being operated at juice levels that are too high, which increases the exposure time to heat and decreases evaporation performance. With other types of evaporators, the residence times are much lower, which means that colour generation is greatly reduced in these evaporators (Bourzutschky, 2005b; Rein, 2007).

It is expected that conditions which lead to an increase in sucrose degradation will also lead to increased colour formation. As with sucrose degradation, the majority of the colour formation in standard multiple effect evaporator stations occurs in the first vessels, where the brixes are the lowest and juice temperatures are at or above 100°C, with negligible colour increases being experienced in the final two effects (Peacock, 2007).

Crystallisation

Crystallisation is the most critical process for colour control in the sugarcane factory. This step is an efficient means of removing colour by crystallisation of relatively pure sucrose while leaving most of the impurities in the mother liquor (molasses). The crystallisation operations are designed to allow modifications during a season to accommodate variations in the quality of the input syrup being processed in order to produce raw sugar having the targeted quality. In South African sugar factories, a three-boiling partial remelt scheme is generally used during crystallisation to produce high grade raw sugar. Sugar produced in this way usually has 3.5% less colour than a conventional three-boiling system (Rein, 2007).

During the crystallisation process, syrup is boiled in pans to grow crystals and to maximise the amount of sucrose recovered in raw sugar. The pans are operated under vacuum which is necessary for maintaining a low temperature for minimal colour formation, sucrose inversion and degradation during the process (Rein, 2007).

Behaviour of colourants during crystallisation (Table 4)

The quality of raw sugar produced in the crystallisation process is dependent on the quality (purity, colour and clarity) of the syrup being processed. The crystallisation conditions and the circulation characteristics of the pan can also have an influence on raw sugar quality but to a lesser extent than the influence of the quality of the incoming syrup (Rein, 2007).

Table 4. Summary of colourant behaviour during crystallisation*.

SYRUP	CRYSTALLISATION	RAW SUGAR	FINAL MOLASSES
Stream characteristics	**Typical operating conditions**		**Stream characteristics**
56°C pH 6.5 65°Bx	65 – 70°C pH 6.5		60°C pH 5.2 – 6.0 78 – 85°Bx
Colourant composition	**Colourant behaviour during crystallisation**	**Colourant composition**	**Colourant composition**
15 000 – 29 000 IU • Flavonoids • Colour precursors • Melanins • HADPs • Melanoidins • Caramels	**Formed:** Melanoidins and caramels **Removed:** None **ICUMSA colour changes:** A-pans: 9% increase; B-pans: 14% increase; C-pans: 19% increase	1 000 – 1 800 IU **In crystal**: Melanins, melanoidins, neutral phenols **In external layer**: Melanoidins, HADPs, caramels, flavonoids, phenolic acids	125 000 – 150 000 IU • Flavonoids • Colour precursors • Melanins • HADPs • Melanoidins • Caramels

*The ranges presented in this table were collated from various literature sources and for different mills and therefore are not the same as the normal ranges of variation within a particular mill.

When operating a three-boiling partial remelt crystallisation system, sugars from the B and C-stations are remelted and returned to the A-station to allow maximum sugar recovery. This has an effect on the crystallisation performance of the A-station since colour and impurities are recycled and the average sucrose retention time is high (Davis, 2007). The colour of remelt is over 50% higher than the colour of raw sugar which causes these returns to account for about 40% of total colour in A-massecuite (Smith, 1990). Therefore, high A-massecuite exhaustion is necessary for the production of good quality raw sugar. For factories having a back-end refinery, there is an additional colour load incorporated at the A-station of the raw factory as a result of the 4th run-off refinery stream entering the crystallisation process at this stage.
The Maillard reaction occurs during pan boilings of the sugar crystallisation process, particularly during low grade purity boilings due to the long retention times and the presence of impurities (Davis, 2007; Rein 2007). This formation of melanoidins continues in the crystallisers and during the storage of molasses (Shore *et al*., 1984).

During the crystal formation and growth stage of the crystallisation process, colourants remain mainly in the mother liquor, but a small quantity will be integrated into the structure of the sugar crystal (Bento, 2009). There are three ways in which colour can be incorporated (Rein, 2007; Bento, 2003):

Co-crystallisation with sucrose. It is crucial that this be avoided, because once colourants are incorporated into the sucrose crystal lattice, they can only be removed by dissolution of the crystal. It is therefore important to try to minimise the amount of colourants that can co-crystallise. High molecular mass polysaccharides have a high tendency to co-crystallise with sucrose and are more likely to be included in the sugar crystal. These high molecular mass polysaccharides can complex with colourants and, as a result, colourants can become incorporated into the crystal by this mechanism.

Coating of the crystal surface. This is presented as a molasses film surrounding the surface of a sugar crystal and can be reduced by washing sugar in the centrifuge. Colourants absorbed on the surface of the crystal can also be removed by affination. It has been reported that the affinated crystal usually has a colour that is in the range of between 0.025 and 0.05 times the colour of the mother liquor.

Trapped in a liquid inclusion in the crystal. Colourants trapped in this way result from uncontrolled rapid crystallisation. This is considered a minor problem since correct boiling practices would eliminate this mechanism of colour incorporation.

Certain colourants are incorporated into the sugar crystal to a greater extent than others. Bento (2009) defined the colour transfer as the ratio between sugar (or crystal) colour and feed liquor (or massecuite) colour and is used to quantify the tendency of colourants to be incorporated into the crystal. Paton (1992) reported that a partition coefficient can be determined as the ratio of massecuite (or mother liquor) colour to sugar colour. Colourants with higher partition coefficients have a lower tendency for incorporation in the sugar crystal. Experimental crystallisation tests have shown that synthetic HADPs and melanoidins have higher partition coefficients than sugarcane plant-derived colourants (Paton, 1992).

It is thought that the colourants having a greater tendency for incorporation into the sugar crystal are those which have a high affinity to sucrose (Bento, 2003). The molecular mass and pH of a particular colourant has an effect on its tendency for incorporation in the sugar crystal with higher molecular weight colourants (Bento, 2009) and neutral polymeric colourants (Paton, 1992) more readily included in the raw sugar crystal than lower molecular weight and acidic polymeric colourants. Table 5 presents the incorporation capacity of different colourant types as reported by Bento (2009).

Table 5. Distribution of colourant types in raw sugar (adapted from Bento, 2009).

In the crystal	In the external layer
Melanins Melanoidins Neutral phenols	Melanoidins (21.9 Da*) HADPs Caramels Flavonoids Phenolic acids

*The Dalton (Da) is a unit of mass used to express atomic and molecular masses.

Operational strategies for minimising colour formation during crystallisation

It is important that the existing pan boiling scheme of sugar factories is appropriate for crystallising the quality of the syrup to be processed and for producing raw sugar of the desired quality. The factors affecting raw sugar colour formation and colour transfer during the crystallisation process and centrifugation are temperature, residence time and amount of centrifugal wash water used. These and other factors relating to colour during crystallisation are discussed below.

Limited colour formation can be achieved by reducing boiling pan temperatures and keeping the amount of recycle/remelt to a minimum (Rein, 2007). Vacuum pans have relatively small heating surfaces. As a result, the temperature differences are high, which can promote the formation of melanoidins and to a certain extent caramelisation. Caramels can also form due to local overheating and burning which occurs when crusts and massecuite lumps remain attached to the surface of the boiling pans after emptying and cleaning (Bourzutschky, 2005b). Therefore, regular removal of any hardened residue from the boiling pan’s surfaces is important.

The residence times of A-, B- and C- massecuites in crystallisers are approximately 6, 10 and 50 hours, respectively. Low purity massecuites require longer residence times due to the slower crystal growth rate because of higher viscosities. This extended residence time results in high C-massecuite colours (Bourzutschky, 2005b). It has been reported by Paton and McCowage (1987) that storage of C-massecuite over a weekend could result in colour increases of greater than 30%. Although reducing the residence time would result in reduced colour formation, this might mean sacrificing the benefit of improved exhaustion (Bento, 2009). In contrast, Smith (1990) reported that high exhaustions, particularly of A-massecuite, contribute to low sugar colours since the recirculation of impurities is reduced. In addition, high exhaustions also improve recovery and plant capacity (Smith, 1990).

The size of the crystal produced can have an effect on crystal colour and it is therefore important that crystallisation conditions produce sugar crystals with an optimum size. A reduction in 10% of colour is possible when the crystal size is kept within the ideal range (Madho and Davis, 2008). The larger surface area of smaller crystals results in a higher quantity of highly coloured molasses-film surrounding the sugar crystal (Madho and Davis, 2008). As a result, larger crystals are easier to process during centrifugation since the quantity of the molasses-film is smaller due to the smaller surface area per unit mass of larger crystals (Rein, 2007).

A study by Vaccari and coworkers (1989) found that the crystal faces which grew more rapidly were more likely to include coloured mother liquor droplets. Although some authors (Bento, 2009; Lionnet, 1988) indicated that crystal size influences colour transfer, Lionnet and Moodley (1995) emphasised that it is not always possible to directly compare crystal colour, and similarly colour transfer, to crystal size because feed colour also has an influence on crystal colour.

The bulk of the impurities in raw sugar are located within the molasses film surrounding the crystal. It is therefore crucial that the centrifugation process, which separates the sucrose crystal from the mother liquor, is performed efficiently. Strategies for achieving optimal separation efficiency include a well-designed, operated and maintained centrifugal station (Rein, 2007). It is possible to reduce the colour of sugar by washing crystals during centrifugation. This results in the removal of a proportion of the high colour molasses film that surrounds the sugar crystal. However, it is essential to monitor the washing efficiency since extended washing has the risk of sugar loss by dissolution, resulting in reduced exhaustion and increased recirculation (Payne, 1982; Bento, 2009; Madho and Davis, 2008; Rein, 2007).

Conclusion

The different types of colourants that form during sugarcane production in the sugarcane field and during the raw sugar production process in the factory are:

- Pigments, flavonoids and colour precursors (derived from the sugarcane stalk and leaves)
- Melanins (formed during extraction)
- HADPs (formed mainly during clarification)
- Melanoidins (formed mainly during evaporation and crystallisation)
- Caramels (formed mainly during evaporation and crystallisation)

The main factors affecting the formation of colourants during the production of cane are season length, pest and diseases, cane variety and maturity of the cane. Harvesting factors such as over-burning and burn-harvest-to-crush-delays also play a role in the development of colourants in the cane.

The controllable parameters that have an effect on colourant behaviour in the sugar factory are temperature, pH and residence time. Additional factors that could further influence the formation of colourants in a sugarcane factory include sanitation during extraction, correct addition of clarification chemicals, juice circulation and concentration levels in evaporators, and the amount of wash water used during crystallisation. Although factory operations can be managed to minimise colour formation, adjusting these effects could have a negative impact on other factory performance indicators.

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