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A Review: Cane Sugar Colour and Colourants

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Abstract

The problem of evaluating the colour of a commercial sugar product must first be defined in recognized colorimetric terms. According to the committee on colourimetry of the 'Optical Society of America', the "colour" has been defined as "colour" consists of the characteristic of light other than spatial and temporal in-homogeneities; light being that aspect of radiant energy of which human observers are aware through the visual sensation which arises from the stimulation of the retina of the eye. The colourants are among the most troublesome impurities in the production of white cane sugar. Despite the diversity of colourants in sugar solutions, presently, colouration is assessed by measuring absorbance at 420 nm as per ICUMSA protocol.

1.1. Cane Sugar Colour

The visual appearance of sugar has been used as an index of the impurities present in sugar crystal. Despite a general advancement in instrumentation, determination of the perceptual colour is still frequently the primary control in the manufacture of white or nearly colourless sugar. Hence an understanding of the chemistry of the colour reaction is necessary for efficient and refining. In an optical study of sugar in solution generally three aspects are of interest. First, the colour and it should be reserved solely as an expression of visual appearance to a normal observer and it may be a primary concern and in this sense, the evaluation may be accurately termed as "colour measurement". Second, the "absorbency" of sugar solution which may be considered as a result of the interaction between the electromagnetic radiation (EMR) and the solution, and third, the amount and nature of the absorbing material (colourants), responsible for the observed optical effects.

The problem of evaluating the colour of a commercial sugar product must first be defined in recognized colourimetry terms. According to the committee on colourimetry of the 'Optical Society of America', the "colour" has been defined as "colour" consists of the characteristic of light other than spatial and temporal inhomogeneity; light being that aspect of radiant energy of which human observers are aware through the visual sensation which arises from the stimulation of the retina of the eye.

The traditional indicators of sugar quality are polarization, colour, invert, moisture, ash and grain size have been used as quality indicators in the market for the last 50 years or more. The visible appearance of sugar is known as the sugar colour. Colour is the one of the most important quality criteria for sugar; the lower the colour value the higher the quality of sugar.

Colour determines the grade of sugar - raw or white - and is the main concern of buyer and consumers (Ellis, 2004). Therefore, significant effort has gone into the research of the nature of colour, prevention of its formation and methods of its removal. Higher colour raw sugar requires more effort to produce a white product.

1.2. Cane Sugar Colourants

It has been found impossible to avoid the semantic confusion when the term "colour" is used without qualification in the sugar industry Furthermore, with the advent in recent years of a variety of photoelectric instrument, an deerstalking of the fundamental factors involved in the use of each type of optical measurement has become increasingly important. Experience has shown that the two terms "colour bodies" and "colouring material" tend to be abbreviated to 'colour' and thus lose their distinctive meaning. This general term 'colourant' has been coined by Judd (1952) in order to indicate material which is either a dye (a compound which absorbs light with neglible scattering and a pigment (a compound which absorbs light with scattering). Then term colourants is useful for two reason; (1) it focuses on the difference between the concepts of visual colour" and "material colour," (2) it provides a general term covering all the materials that otherwise would have to be visually as coloured turbid, colour precursor, etc. The colourants are among the most troublesome impurities in the production of white cane sugar. Despite the diversity of colourants in sugar solutions, presently, colouration is assessed by measuring absorbance at 420 nm as per ICUMSA protocol (Barton, 2009).

1.3. Composition of Cane Sugar Juice

The typical composition of mixed juice extracted from cane is described (Walford, 1996) with emphasis as below:

Table 1. Cane Juice Composition

Constituents		% Bx
Sugars	Sucrose	81-87
	Reducing sugars	3-6
	Oligosaccharides	0.06-0.6
	Polysaccharides (including gums and dextrans)	> 0.2-0.8
Salts	Inorganic salts	1.5-3.7
Organic non-sugars	Organic acids	0.7-1.3
	Amino acids	0.5-2.5
	Dextrans	0.1-0.6
	Starch	0.11-0.5
	Gums	0.02-0.05
	Waxes, fats, phospholipids	0.05-0.15
	Colourants	0.1
Insolubles	Sand, bagasse, etc.	0.15-1

1.4. Types of Colourant:

Sugar colourants are not one single molecular species but it consists of a wide range of materials each with its own molecular weight (MW), pH sensitivity, charge, and chemical structure (Godshall & Baunsgaard, 2000). Research into the complex organic nature of cane sugar colourants has been a major area of interest in the sugar industry since its beginning. Better understanding about the character of colourants allows designing new and better techniques for its removal.

Colourants are often named from their origin and mechanisms of formation (Godshall et al, 1988). Caramelization and alkaline degradation are similar thermal mechanisms except that alkaline degradation occurs at high pH and forms much darker colourant (Godshall, 2000). The Maillard reactions occur throughout the processing and have many complex pathways (Van der Poel et al, 1998). They proceed under almost all conditions, as reducing sugars and amines or amino acids are always present in the sugar. Iron also plays an important role, particularly in plant-derived colourants (Godshall, 1996). Many polyphenolic compounds found in cane juice are able to produce highly coloured iron complexes. The colourants themselves are the compounds that are colour precursors. These, often colourless, compounds can react to form highly coloured species. Colourants can fall into one of three categories: natural, those formed during production and colourants formed during storage.

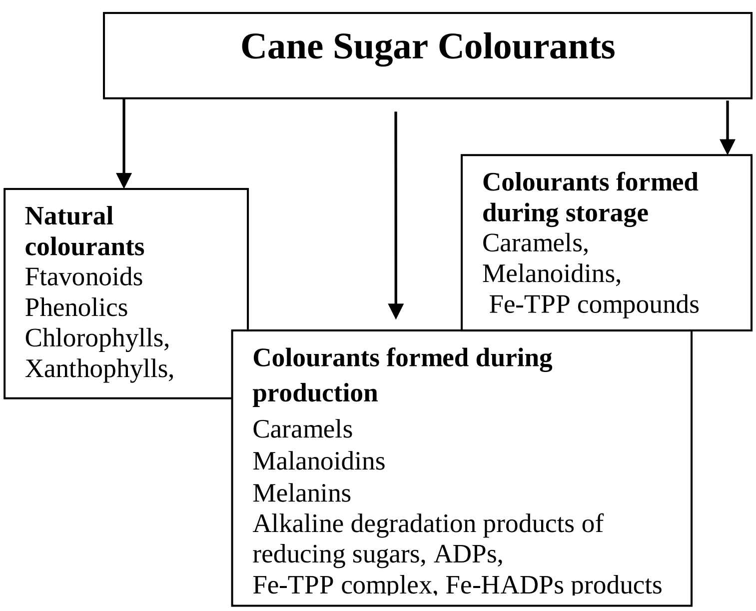


Table 2. Summarizes the General Types of Colourants found in a Cane Sugar:

Colourant Type	General Characteristics
Phenolics and Flavonoids	They have been described as being primarily flavonoids and phenolics (Davis, 2001; Bento, 2003). They can comprise as much as two thirds of colour in raw sugar. Flavonoids can be a considerable problem for sugar production, as they may account for 90% of the colouration of raw sugar at pH 7 (Mersad, 2003). Bento (2003) reported that, due to their solubility, flavonoids can pass through the sugar production process without being removed. The inclusion of a glycoside in their structure causes an affinity for sugar crystals. Phenolics are generally noncoloured until they undergo reactions with compounds such as amines or iron. Both phenolics and flavonoids undergo enzymatic oxidation reactions, which lead to formation of colourants. They are highly ionized, which gives them a high indicator value (IV, ratio of the absorbance at 420 nm of a sample at pH 9 to pH 4). They are readily removed during refining, but are also easily incorporated in the sugar crystal.
Caramel	The result of thermal degradation of sucrose; low net charge; wide colour range from yellow to brown; MW 500 to about 1,000; MW and colour increases as thermal destruction proceeds and over time due to continued polymerization (Davis, 2001). According to Gillett (1953) caramel a complex mixture of anhydrides and classifies into caramelan, caramelen and caramelin. They are slightly charged, and they form at temperature 185°C and in acidic medium.
Melanoidins	They are the products of Maillard reactions (non-enzymatic browning), which are condensation reactions of a carbonyl compound (reducing sugar) with amino acids, proteins or ammonia (Mersad 2003). They form at ambient temperatures, but the reaction is advanced by temperature rise.

	Their formation is also advanced by high brix and low purity. Melanoidins develop slowly in acidic media and intensify in basic media. They have a slightly negative charge at neutral pH, but are positively charged in acidic conditions. They are insensitive to pH, and have a low IV. They are dark brown in colour.
Melanins	They have been reported by Davis (2001) as a subdivision of melanoidins. Mersad (2003) described that they are formed by enzymatic oxidation of phenolic compounds in quinones by polyphenoloxidases (PPO) to produce indole polymers. They form at temperature between -18 °C and 55 °C and at pH between 4.5 and 8. These conditions are descriptive of cutting and milling, and these activities create contact between the PPO and its substrates.
Alkaline Degradation Products (ADPs)	They are referred to as ADPs of hexose (Mersad 2003) and ADPs of fructose (Davis, 2001). They are also produced by decomposition of monosaccharides in alkaline media. They tend to be brown in colour, acidic, and, therefore, form more degradation colour products. Since they are produced by high temperatures, their production is continuous throughout the sugar process, particularly on heated surfaces. Similar to caramels, but much darker in colour at high pH.
Fe-TPP complex Fe-HADPs	They are high molecular weight and highly hygroscopic in nature and are extremely detrimental for sugar storage. The electrochemical and viscosity measurements (Singh, 2003) have revealed that humic acids in clarified cane juice behave similarly to materials produced from glucose and polyphenols. During crushing of cane, iron from mills combines with TPP/HADP5 to give darker colour.

1.5. Investigations on Colour Formation

1.5.1. Caramelization

Caramelization is the browning of sugar, a process used extensively in cooking for the resulting nutty flavor and brown colour. As the process occurs, volatile chemicals are released, producing the characteristic caramel flavor. It is a type of non-enzymatic browning. However, unlike the Maillard reaction, caramelization is pyrolysis, as opposed to reaction with amino acids. When caramelization involves the disaccharide sucrose, it is broken down into the monosaccharides fructose and glucose. They form at temperature 185^0-190^{0}C and in acidic medium. Their formation from sucrose has been represented by the following reactions:

$$6C_{12}H_{22}O_{11} \longrightarrow 6C_{12}H_{18}O_9 + 12H_2O$$
Caramelan

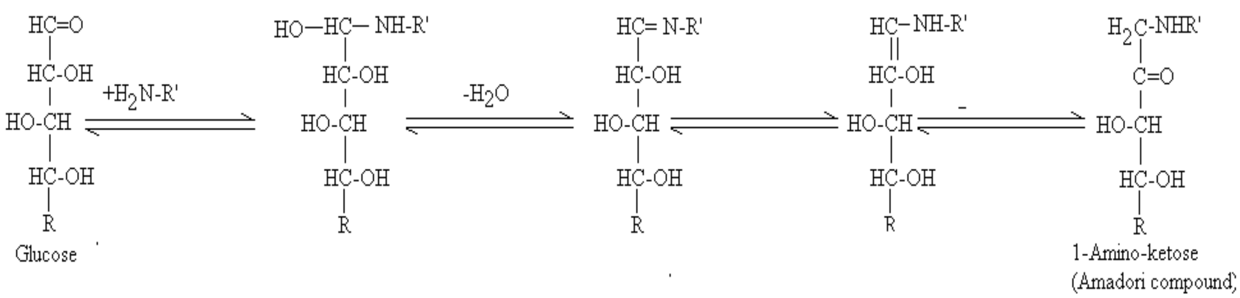
$$6C_{12}H_{22}O_{11} \longrightarrow 2C_{36}H_{48}O_{24} + 8H_2O$$
Caramelen

$$6C_{12}H_{22}O_{11} \longrightarrow 3C_{24}H_{26}O_{13} + 27H_2O$$
Caramelin

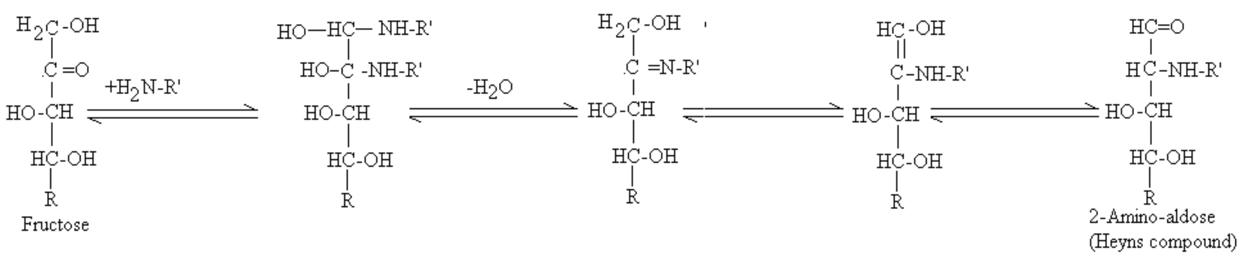
1.5.2. Maillard Reactions

The Maillard reaction is a chemical reaction between an amino acid and a reducing sugar, usually requiring heat. It is important in the preparation or presentation of many types of food, and, like caramelization, is a form of nonenzymatic browning. The reactive carbonyl group of the sugar reacts with the nucleophilic amino group of the amino acid, and forms a complex mixture of poorly-characterized molecules responsible for a range of odors and flavors. This process is accelerated in an alkaline environment, as the amino groups are deprotonated and, hence, have an increased nucleophilicity. In the process, hundreds of different flavor compounds are created. These compounds, in turn, break down to form yet more new flavor compounds, and so on. High temperature and brix but low purity are conditions favoring the Maillard reactions (Newell, 1979). The sequences of the Maillard reaction follow the steps presented in Figure.

Amadori rearrangment



Heyns rearrangement



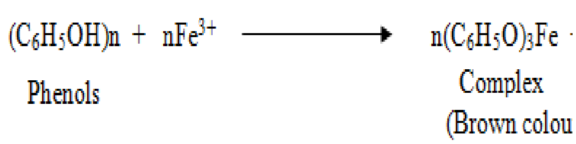
Degradation of the Amadori compounds occurs with increasing pH value at higher rates, they are stable under acidic conditions. All intermediates are unstable and may react with available amino-compounds leading to high molecular mass melanoidins.

1.5.3. Alkaline Degradation Products of Hexose (ADPs)

In alkaline medium, monosaccharides decompose in a series of reactions leading to several carboxylic acids (lactic, saccharinic, formic, acetic, oxalic and other acids) resulting in the formation of a brownish yellowish colour. The chain lengths of the condensation products vary and for this reason ADPs are classified in to ADPs $\leq C_6$, which are usually colourless and ADPs $\geq C_6$. The latter polymers are the source of the brownish colour (Mersad at el, 2003). The monosaccharides glucose and fructose behave differently during these degradation/condensation reactions, which is probably the reason why some authors only refer to the alkaline degradation products of fructose (Clarke et al, 1986 and Chen, 1993), while others regard both rnonosaccharides as degradation sources (Mersad at el, 2003 and Gillett 1953). Gillett (1953) explains that the monosaccharides formed by acid hydrolysis are decomposed during prolonged heating in strong alkaline conditions and that it was found that fructose decomposes more rapidly, followed by glucose and sucrose. In the case of alkaline degradation, the syrup pH was increased with sodium hydroxide to pH 8.8.

1.5.4. Iron – Polyphenols Reaction

Iron also plays an important role, particularly in plant-derived colourants (Godshall, 1996). Many polyphenolic compounds found in cane juice are able to produce highly coloured iron complexes. Godshall (2000) reports that the ferrous iron (Fe^{2+}) can form complexes with phenolics and caramels to form darker products. The control experiment shows only a small change in this range and so the effect seen is the action of iron. This suggests that colour formation in the presence of iron leads to a colourant of a specific molecular weight and that enzymes form relatively small amounts of colourant in ranges. To confirm this conclusion, the enzymes was denatured with mercuric chloride, cane juice produces colourant in the 7,500 to 4,000MW range, this must be due to the formation of colourant by the action of iron.



1.6. Quantifying Colourant

1.6.1. ICUMSA Colour

The industry standard sugar solution colour measurement is the International Commission for Uniform Methods of Sugar Analysis (ICUMSA) colour method (Parton, 2009). The absorbance of the test solutions were recorded using UV-5704SS double beam spectrophotometer. The colours of the samples were determined using the ICUMSA protocol based on IUPAC **(Appendix 1).**

The colour is calculated as follows:

$$\text{I. U.} = \frac{Abs \times 1000}{b \times C}$$

b = cell length (cm)

C = Sugar concentration (gm/ml)

ICUMSA colour is an indication of the overall colour of the sugar solution.

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