COMPARING THE EFFECTS OF SULPHUR DIOXIDE ON MODEL SUCROSE AND CANE JUICE SYSTEMS

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ABSTRACT

Sulphur dioxide (SO_2) has been used for centuries to minimize color in food processing and fruit and vegetable storage. In the sugar industry, it is used routinely by sugar beet processors to reduce and prevent color formation in white refined sugar. Sugarcane processors throughout the world use SO_2 to produce plantation white sugars**.** This study was undertaken to determine the effect of SO_2 on pure sucrose solutions in comparison to real factory sugarcane juice streams. Sugar systems included 15 brix pure sucrose, clarified juice and mixed juice from a Louisiana sugarcane mill. A pH of 8.0 was obtained by adding milk of lime then lowered to approximately pH 5.0 with either SO_2 or HCl (control). Several samples ranging from pH 5 to 8 were processed at 0-120 min at 85^0 C**.** Analyses included pH, SO_2, color, calcium, and invert (as a measure of sucrose loss). Results indicated that the model system was much more sensitive to low levels of SO_2 than real juice samples which demonstrated a greater buffering capacity. The pH levels of the model sucrose solution dropped rapidly, and invert levels increased with time. There was 1.6 % loss of sucrose in the SO_2 trial as compared with no sucrose loss with HCl. Clarified juice resisted changes in pH with both SO_2 and HCl. Sucrose loss at 120 min of processing and a pH of 5.0 was only 0.88 %. There was a maximum color reduction of 10-15 % in the SO_2 trial, whereas no color reduction or sucrose loss was observed in the HCl trial. The mixed juice was very resistant to pH changes, and a minimum pH of 6.0 was achieved with 4800 ppm $SO_{2.}$ No sucrose loss was observed in either trial with mixed juice, and color reduction was the same in both the SO_2 and HCl trials. In real juice streams, SO_2 reduced color by 10-15 % more than clarification alone but also induced some sucrose loss (0.88%) after a lengthy time.

INTRODUCTION

Sulphur dioxide has traditionally been used in food processing and produce storage to minimize color formation due to browning reactions associated with amino acids interacting with invert sugars in the Maillard reaction. Sugar beet processors routinely use sulphur dioxide in process streams for the same purpose. Among sugar cane processors worldwide there is mixed interest in usage of sulfitation. In the United States, sulfitation has rarely been used in cane raw sugar factories since the 1950's. Today, there is renewed interest in the effectiveness of sulfur dioxide as a color retardant as many US factories are considering the production of high quality low color raw sugar to be sold as a food grade sugar.

Under normal ambient temperature and pressure, sulphur dioxide is a colorless, pungent smelling, nonflammable gas. In very low concentrations this gas can cause extreme eye and respiratory irritation, thus must be used in a controlled environment (Anonymous, 1996). The Egyptians and Romans burned sulfur to form sulfur dioxide (SO_2) as a means of sanitizing wine-making equipment and today SO_2 is used to treat most light colored dehydrated fruit and vegetables to prevent undesirable enzymatic and nonenzymatic "browning" reactions. Sulfur dioxide provides the added benefit of acting as a food preservative and functions as an antioxidant (McWeeny, 1981). Sulfite additive has been used extensively in the food industry to retard Maillard reactions. McWeeny (1981) discussed the two main groups of reactions between sugars, ascorbic acid and their dehydration products and bisulfite, primarily the hydroxy sulfonate and organo sulfur compounds.

Browning reactions, of whatever type, are caused by the formation of unsaturated, colored polymers of varying composition. Compounds that engender browning usually contain a carbonyl or potential carbonyl grouping (Hodge, 1953). Browning can be inhibited by compounds that block or eliminate or combine with carbonyl groups. The multiplicity of studies regarding browning reaction theories is reviewed thoroughly in Hodge's (1953) review article.

The purpose of sulfiting purified and clarified thin beet juices are 1) to control juice color formation; 2) to improve the boiling properties of the juices; and 3) reduce the excess alkalinity (McGinnis, 1982). Two methods of sulfuring are 1) by sulfur stove, burning elemental sulfur for production of sulfite and 2)bubbling sulfur dioxide through process streams. Also produced during these processes is the undesired sulfate ion that can interfere with crystallization causing an increase in molasses purity and production. The oxidation of sulfite to sulfate is greatly retarded as the sugar concentration is increased. Sulfitation can control juice color by interfering with chromophoric molecular groups include carbonyl (ketones), carbonyl (aldehydes), carboxyl, and amido. "These compounds are characterized by an electron imbalance, an electronically excited state, a molecular resonance, an absorption of specific bands of transmitted light, and to the beholder, color" (McGinnis, 1982). Color compounds in cane and beet sugar products include naturally occurring pigments along with a large heterogeneous variation of color compounds produced during processing. It has been estimated that for a 98.5º pol raw sugar, colorants account for approximately 15-20 % of the weight of non sugars. In granulated refined sugar the estimate is approximately 30 ppm (Clarke and Godshall, 1988).

In the cane sugar factory, the major role of sulfur dioxide has been to make white sugar rather than raw sugar through inhibition of color forming reactions. This is achieved by addition of SO_2 to the alkenic double bond in an α,β- unsaturated carbonyl intermediate as well as to the carbonyl group, which yields β-sulfonated aldehydes that are of comparatively low reactivity in reactions leading to the production of browning compounds by the Maillard reaction and degradation of invert sugars (Shore, et al., 1984). Sulfur dioxide also has the ability to inhibit or retard enzymatic browning reactions. Sulfur dioxide added as 300-500 ppm to raw beet juice resulted in minimal (5%) color reduction (Shore, et al., 1984). Onna and Sloane (1978) reported that 300 ppm decreased color in syrup and whole raw sugars by about 25% with crystal color reduced by 46%. Final refined granulated sugar from this process had 35% less color.

During processing and storage at elevated temperatures, sugar products will darken. All industries that use sugar products are in turn susceptible to color changes in their products which may or may not be desirable (Zerban, 1947). When cane and beet juices are heated and limed during clarification, invert sugar disappears and the color of juices increases with the amount of lime added. Much of this color is bound to calcium precipitate in the defecation process. Color changes additionally occur during heating and evaporation processes, since the juices are exposed to continual heating (70-75^{o} C) over several hours at slightly alkaline pH in the beet industry and slightly acid pH in the cane industry. The higher the alkalinity of clarified beet juice, the greater the color increase. The color of clarified cane juice also increases during evaporation and crystallization even though it is kept on the slightly acid side.

In cane and beet processing, there are many variations in procedure for adding sulfur dioxide. There is cold sulfitation with SO_2 added to cold raw juice then limed; alkaline sulfitation where juice is limed then sulfited and again sulfite added to syrup prior to pan boiling. Hot sulfitation where juice is heated first then sulfited and limed, this method is used to reduce the solubility of calcium sulfite. Other modification of these procedures are used according to plant capabilities etc. In Northern Europe, a method of combining sulfitation with preliming of diffusion juice was developed. Small additions of SO_2 to an acidic(pH 5.5-6.0) diffusion juice improved filtration and sedimentation, as well as reduced juice color development (Dandar, et al., 1973) Effect on sucrose recovery was not discussed. Indonesian cane processors have developed a similar process using sulfitation with lime with the production of a high standard quality white consumption sugar for export (Marches, 1953). This plantation white sugar is the result of two sulfitation procedures, first at original clarifier when added with lime and second as syrup sulfitation prior to vacuum pan.

Sulfitation in Louisiana is a very old process, possibly originating with French or English settlers (Spencer, et al.,1945). Cold raw juice was pumped through a sulfur tower with a countercurrent of sulfur dioxide to produce a fairly good, irregular, near or off-white sugar. By the late 1930's use of sulfur dioxide was on the decline and was then mainly used for production of direct consumption molasses.

This study was undertaken to determine the effect of sulphur dioxide on model and real cane process streams. This work is part of SPRI’s continuing research on determining the effect of invert and pH on sucrose recovery and color formation.

MATERIALS AND METHODS

Sugar Solutions: 15 brix pure sucrose, clarified cane juice and mixed raw cane juice.

Sulfitation: Sugar systems were brought to a pH of 8.00 with milk of lime (cold lime). The pH was then adjusted with either sulphur dioxide (SO_2) or hydrochloric acid(HCl), as a control, to approximate cane juice pH of 5-6. Sulphur dioxide was bubbled through the sugar system using a micro valve controller. Samples were taken as pH dropped from 8 to 5.

Processing: The pure sucrose solution was then processed in a gyratory shaker for up to 60 min at 85^{o}C. Clarified juice and mixed juice were treated for up to120 min. Time was extended for juice samples due to lack of significant reactions at 60 min.

<u>Analyses</u>: Samples were analyzed for pH, SO_2 by ICUMSA rosaniline colorimetric method, calcium by HPIC, color by ICUMSA method, invert by HPIC.

HPIC Calcium: DX 500 with IonPac CS12 column with CSRS Suppressor, isometric 1.0 ml/min 20mM H_2SO_4, and conductivity detection.

HPIC Invert: DX 500 with CarboPac PA1 column, gradient 1 ml/min 100-200 mM NaOH and amperometric detection.

RESULTS AND DISCUSSION

In order to achieve a similar pH among the three sugar systems, it was necessary to use different amounts of sulphur dioxide. Figure 1 shows the relative sensitivity of the pure sucrose solution compared to either of the factory process streams. Both juice streams demonstrated a huge buffering capacity that was not present in the pure sucrose solution.

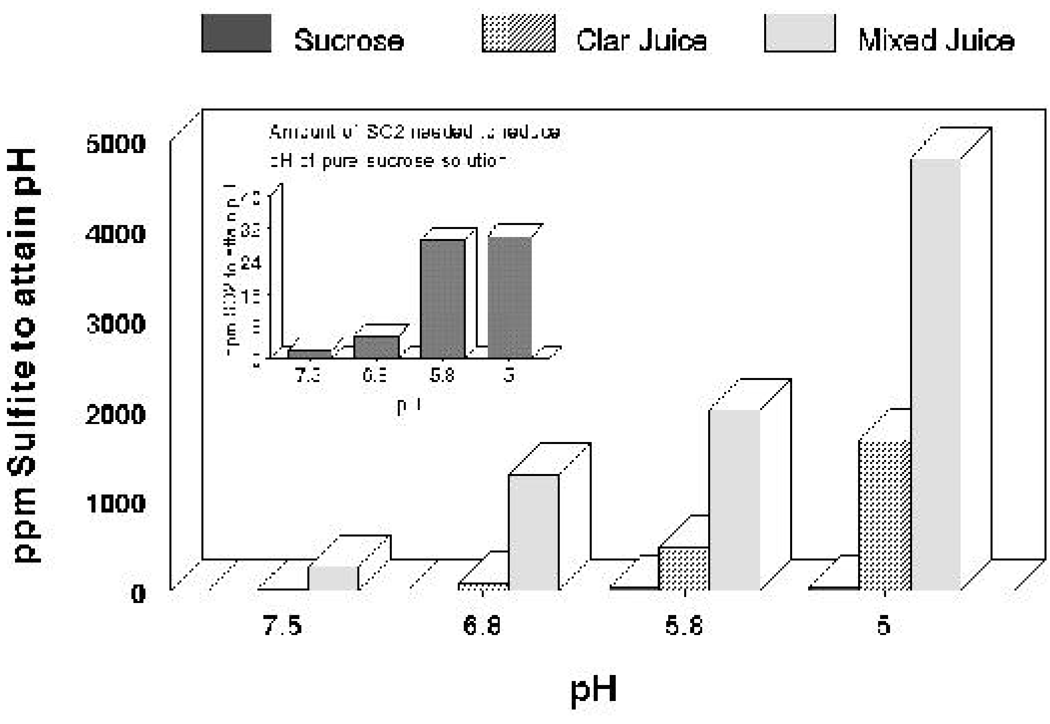

Figure 1. The amount of SO_2 required to adjust the pH of pure sucrose solution, clarified juice and mixed juice from pH 8.0. Insert: Amount of SO_2 required to lower pH of pure sucrose solution.

Tables 1-3 summarize the results of treating the various solutions with sulfur dioxide.

The pure sucrose model system responded to minimal amounts of sulphur dioxide (2-29 ppm) with a rapid reduction in pH (Table 1). Processing times up to 60 minutes with pH below 6.1 also indicated rapid deterioration in sucrose as evident by the increase in glucose. When sucrose loss is calculated as 2 X the relative increase in glucose (DeBruin, 1998), in this model system, glucose increased by as much as 8000 ppm on solids after 60 minutes of processing at a beginning pH of 5.9. This calculated to loss of 1.6% sucrose based on solids. In contrast, under the same conditions, the HCl control system had minimal sucrose loss (.03% on solids) which was directly attributable to acid hydrolysis. No changes occurred in color or calcium residuals with either of these process systems. After heat treatment no residual SO_2 remained.

The clarified juice results (Table 2) were very different from those of the model sucrose system. The observation time was increased to 120 min because no significant changes were noted at 60 min. The juices were treated with 0-1700 ppm SO_2. These high levels were needed to bring the pH down to the desired level. The SO_2 treated samples generally showed a decrease in color over time, with more color decrease (up to 15 %) in the highest treatment level. These results were similar to those reported by Kort (1995) who showed a 15% reduction in color with >200ppm SO_2. However, some earlier papers reported a somewhat better color reduction of 25-35% with 250-500 ppm SO_2 (Onna and Sloan,1978; Fort and Walton, 1932). The HCl-treated samples showed some color increase. Glucose formation was insignificant throughout, indicating little or no sucrose hydrolysis with either SO2 or HCl. No residual SO_2 remained when initial treatment was <500 ppm.

The mixed raw juice results (Table 3) were also different from those of the model sucrose system. As with the clarified juice, the process time was increased to 120 min because few significant changes were noted at 60 min. These juices were treated with up to 4700 ppm SO_2 to achieve the same pH range as with the model system. The rate of clearance of SO_2 from the juice systems during processing is noted on the table. Calcium levels (data not shown) dropped an average of 100-400 ppm with the lower pH and greater SO_2 concentrations. This in effect was a sulfo-defecation or clarification process induced by liming, reduction to acid pH, and heat processing. The calcium likely becoming bound up in colorant and/or polysaccharide and was precipitated. There was a small but consistent drop in glucose in both SO_2-treated and HCl-treated samples. There was also a significant color drop in both SO_2-treated and HCl-treated samples. Silva and Zarpelon (1977) reported a similar drop in color using mixed juice systems through the sulfo-defecation process.

CONCLUSIONS

There is renewed interest in the United States to produce a high quality food grade sugar at the raw sugar mill. Several means for achieving high quality, low color sugar exist, one of which is sulfitation. The USFDA currently has a 10 ppm limit on residual sulphur dioxide allowed in food products. If sulphitation is being considered for white sugar production, the manufacturer must take caution to keep residuals below this limit.

It is apparent through these studies that attempting to predict juice stream behaviors by model sucrose solutions is not a valid hypothesis for SO_2 treatment. However, a positive result gained from this study was that with minimal application of sulphur dioxide, color can be reduced by at least 10-20%. Currently in Louisiana during late season, raw sugar quality meets all the criteria for Blanco-Directo (Bennett and Ross, 1988) except for color and turbidity (Table 4). The authors feel that by using a color minimizer, such as sulphur dioxide or other, Louisiana raw sugar could meet the quality standards for food ingredient sugar such as the Blanco-Directo sold to soft drink processors in some Caribbean countries, or other locations where sugar is used to sweeten food ingredients.

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Table 1: Effect of SO_2 on 15.2 Brix model sucrose solutions. Solution initially brought to pH 8.0 with milk of lime.

Minutes at 85^0C	Initial and residual SO_2 , ppm	Final pH with SO_2	Glucose * with SO_2 ppm solids	Final pH with HCl	Glucose * with HCl ppm solids
0	0	7.9	35	7.9	45
15	0	7.5	27	7.3	49
30	0	7.4	33	7.1	50
60	0	7.3	48	7.0	65
0	2	7.6	28	7.3	37
15	0	6.9	37	6.85	43
30	0	6.6	76	6.75	32
60	0	6.5	78	6.5	79
0	5.4	7.0	28	6.8	28
15	0	6.3	65	6.6	64
30	0	6.2	80	6.3	71
60	0	6.1	132	6.15	130
0	12.6	6.5	27	6.5	30
15	0	6.0	565	6.3	44
30	0	5.9	1073	6.1	78
60	0	5.6	1406	5.9	121
0	29	5.9	27	6.0	28
15	0	5.1	2166	5.9	66
30	0	4.9	2983	5.8	87
60	0	4.6	8193	5.7	152

*Fructose showed near identical values to glucose, indicating the acid hydrolysis of sucrose.
No color formation was observed in any of the treated solutions

Table 2: Effect of SO_2 on 13.3 Brix clarified juice. Solution initially brought to pH 8.0 with milk of lime.

Minutes at 85ºC	Initial and residual SO_2	Final pH with SO_2	Glucose with SO_2 % solids	Color ICU	Final pH with HCl	Glucose with HCl % solids	Color ICU
0	0	6.7	2.63	11,100	6.6	2.63	10,902
30	0	6.6	2.70	11,346	6.6	2.70	11,686
60	0	6.5	2.66	11,494	6.5	2.55	11,095
120	0	6.3	2.75	10,924	6.2	2.61	11,627
0	83	6.0	2.65	10,581	6.2	2.56	10,744
30	0	6.0	2.66	10,399	6.2	2.55	10,819
60	0	5.9	2.76	10,636	6.1	2.62	11,465
120	0	5.8	2.83	10,769	6.0	2.86	11,781
0	487	5.6	2.74	10,414	5.8	2.54	10,824
30	294	5.5	2.75	9,615	5.7	2.40	11,557
60	194	5.4	2.78	9,527	5.7	2.68	11,435
120	1	5.4	2.91	9,406	5.7	2.81	11,496
0	943	5.2	2.67	10,203	5.4	2.66	10,411
30	825	5.2	2.53	9,677	5.4	2.58	10,830
60	644	5.1	2.82	8,956	5.4	2.48	10,954
120	247	5.1	2.82	9,166	5.3	2.73	11,466
0	1677	5.0	2.68	9,767	5.0	2.53	10,205
30	1554	4.9	2.67	9,121	5.0	2.62	10,584
60	1423	4.9	2.78	8,670	5.0	2.71	10,489
120	1185	4.8	3.12	8,490	5.0	2.89	10,536

Table 3: Effect of SO_2 on 13.3 Brix mixed raw juice. Solution initially brought to pH 8.0 with milk of lime.

Minutes at 85^0C	Initial and residual SO_2	Final pH with SO_2	Glucose with SO_2 % solids	Color ICU	Final pH with HCl	Glucose with HCl % solids	Color ICU
0	0	8.0	4.24	27,167	8.1	4.34	25,333
30	0	7.7	3.38	26,500	7.8	3.83	21,667
60	0	7.6	3.43	26,500	7.6	3.82	18,973
120	0	7.2	3.36	22,825	7.2	3.97	19,116
0	271	7.5	3.58	27,167	7.5	4.18	25,333
30	122	7.4	3.26	25,000	7.5	3.70	21,667
60	5	7.4	3.25	26,333	7.4	3.77	18,260
120	0	6.9	3.31	22,682	6.9	3.86	19,116
0	1291	6.8	3.86	25,833	6.8	4.60	25,833
30	848	6.8	3.19	23,333	6.8	3.63	21,000
60	579	6.7	3.28	24,500	6.5	3.81	17,689
120	0	6.6	3.35	21,398	6.4	3.78	17,974
0	2009	6.2	3.99	26,500	6.3	4.56	25,500
30	1900	6.2	3.25	23,667	6.2	3.81	22,167
60	1549	6.1	3.25	23,833	6.0	3.88	18,117
120	1479	5.9	3.40	20,970	6.0	4.02	18,545
0	4746	5.7	4.43	28,000	5.9	4.62	25,333
30	4653	5.6	3.61	24,333	5.8	4.31	20,167
60	4423	5.6	3.79	24,667	5.6	3.73	17,404
120	3962	5.5	3.87	19,971	5.4	3.79	17,404

Table 4. Quality comparison of Blanco Directo and Louisiana raw sugars**.**

Specification	**Blanco Directo**	**Louisiana Raw**
Pol	99.7	99.8
Color (natural)	150	484
Turbidity	50	100
Ash	0.5	0.06
Invert % solids	0.2	0.05
SO_2 residual	5 ppm	not treated