

**Preparation and Evaluation of Performance of Lime Saccharate for
Improving Juice Clarification: The Case of Wonji Sugar Factory**



By

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A Thesis Submitted to Department of Applied Chemistry

School of Applied Natural Science

Office of Graduate Studies

Adama Science and Technology University

July, 2020

Adama, Ethiopia

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Approval Page

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I hereby declare that this MSc Thesis entitled '*Preparation and Evaluation of Performance of Lime Saccharate for Improving Juice Clarification: the Case of Wonji Shoa Sugar Factory*' is my original work and has not been presented for a degree in any other university, and all sources of material used for this thesis have been appropriately acknowledged.

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ABBREVIATIONS

Abs	Absorbance
Bx	Brix
CJ	Clear Juice
CJ Bx	Clear Juice Brix
CJ pol	Clear Juice Polarization
CJ pty	Clear Juice Purity
EDTA	..Ethylene Diamine Tetra Acetic acid
FHLJ	..First Heated Limed Juice
ICUMSA.....	International Commission for Uniform Methods Of Sugar Analysis
IU	ICUMSA Color Unit
LSD	List Significance Difference
MJ Bx	Mixed Juice Brix
MJ pol	Mixed Juice polarization
MJ pty	Mixed Juice Purity
MOL	Milk of Lime
Pol	..Plane Polarized Light.
ppm	..Parts Per Million
RCBD	Randomized Complete Block Design
SACCH	..Lime Saccharate
SD	Standard Deviation
SRI	Sugar Research Institute
SRT	Short Retention Time
TCD	Tones of Cane per Day
TU	Turbidity Unit

ABSTRACT

In this study, lime saccharate, has been prepared, the efficiency of lime sacharate was also evaluated, further its performance has been compared with milk of lime (MOL). For the preparation of lime saccharate, milk of lime, $\text{Ca}(\text{OH})_2$ of 15 degree Baume was used with evaporator syrup collected from Wonji Shoa Sugar factory. Nine mixed juice samples were taken from weighed mixed juice tank and pretreated so as to be used for settling and mud volume tests. The required response variables color, turbidity and CaO content were determined for the clarified juice obtained for each treatment replicated twice. The experiment was arranged using RCBD (Randomized complete block Design). Then, the data obtained from the comparative experiments were subjected to statistical analysis using SAS statistical software. The result of the experiment has shown that the settling rate and CJ purity have shown little variation in quality parameters at 5% level of significance. As observed in the data in the defecation process, lime saccharate treated clear juice gave better results for mud volume, ICUMSA color, CaO content, and CJ turbidity compared to the milk of lime treated clear juice. The work here presented a solution to the existing juice clarification problems by proving that the use of lime saccharate (SACCH) instead of the conventional milk of lime (MOL), during clarification of sugarcane juice, which can improve turbid particle removal, improve clear juice clarity, reduce calcium oxide content in clear juice and be used as a tool by sugar processors to reduce expensive sucrose losses and scaling in evaporators.

Key Words: Lime saccharate, Juice Clarification, Flocculation, Clear juice.

CHAPTER ONE

1. Introduction

1.1. Production and Processing of Sugar Cane in Ethiopia

Sugar production in Ethiopia started in 1954/55 G.C when the Wonji Sugar Factory was commissioned and produced 15,843 tonnes of white sugar in the first campaign [1]. When sugarcane development began in 1951, the company was owned by Dutch Company. The development of the sugarcane plantation was started on 5000 hectares in the upper reaches of the Awash basin, 100km. Southeast of Addis Ababa.

Currently, there are eleven large-scale sugar factory establishments in the country; four of them are in the Awash Basin (Wonji Shoa, Metehara, Kesem and Tendaho); two of them (Finchaa and Arjo Dedesa) in the Blue Nile Basin; the other three (Omo 1, Omo 2 and Omo 3) are in the southern region of Ethiopia and two sugar factories (Tana Beles 1 and Wolkayit) in the northern part of the country are under erection. These sugar companies except Omo 1, Tana Beles and Wolkayit are presently producing plantation white sugar for the local market with lower capacities due to different reasons for each factory.



Figure 1: Location of Sugar Factories in Ethiopia [3]

1.2 General Overview of Wonji Sugar Factory

The factory is found in Oromiya regional state near Adama city at 110 kilometers from Addis Ababa. Commencing production in 1954; it is the oldest and the pioneer in the history of Ethiopia's sugar industry. Shoa Sugar Factory constructed in 1962 is the second oldest and both being obsolete have stopped production since July, 2012 and July, 2013 respectively. The sugarcane plantation land of these two factories was 7,000 hectares out of which 1,000 had been planted by out growers [1].

In a bid to replace these two oldest factories with a new and modern one, an expansion project had been carried out both in the cane cultivation field and the factory since 2010. And the factory plant expansion project was come into its completion in July, 2013. Accordingly, the newly built and modern Wonji Shoa Sugar Factory has currently a design capacity of crushing 6,250 tons of cane a day (TCD) and producing over 174,000 tons of sugar per annum which with further expansion will reach up to 12,500 TCD maximizing its production to 220,700 tons of sugar a year. The factory with the help of this agricultural expansion project will have 16,000 hectares of sugarcane plantation field in total [2].



Figure 2: New Wonji Sugar Factory

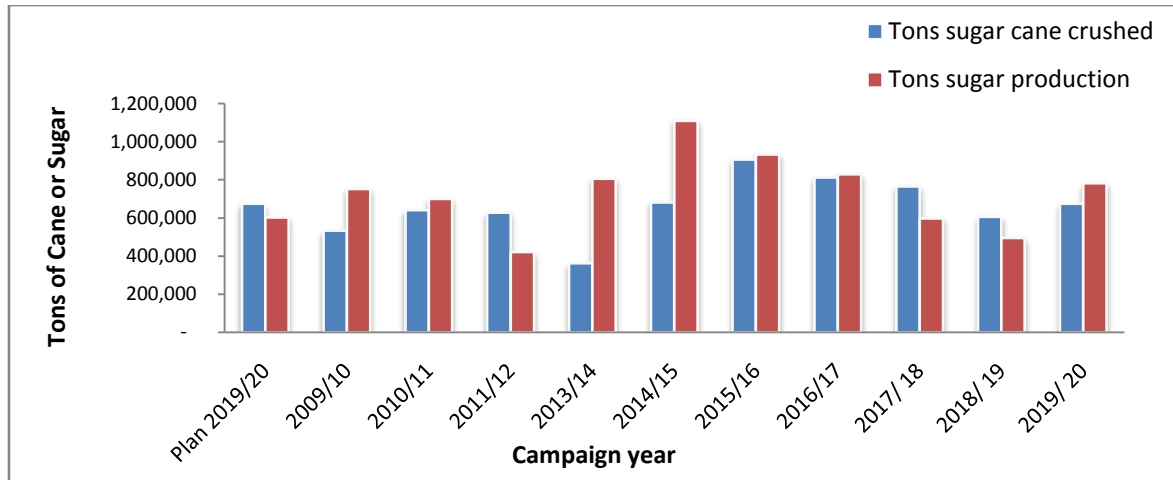


Figure 3: Production Trend of Wonji Sugar Factory [3]

1.3 Background of the Study

The production of sugar from sugarcane consists of a series of units of operation, which begins with the extraction of the cane juice from the cane stalks and subsequent removal of the non-sugars. Sucrose is first extracted from the cane by the addition of water through counter current milling or diffusion. Extracted juice then undergoes an extensive process of cleaning, which involves screening, heating, and addition of milk of lime (calcium hydroxide) to adjust pH and enhance flocculation [4].

The limed juice is then allowed to settle out suspended particles in a clarifier. Following the juice evaporation process the clear or clarified juice is then evaporated to approximately 65 % dry solids in a stepwise evaporation process [5]. The juice, which is now concentrated clear juice the so called, syrup is then put through a final crystallization of sugars from non-sugars by crystallization in vacuum pans via evaporation and concentration and in crystallizers by cooling. In centrifuging effects, the final separation of the sugar from the mother liquor, and the sugar is then stored for transportation and distribution to the customers [6].

Clarification as used in the sugar industry refers to the precipitation and removal of all possible non-sugars, organic and inorganic, and the preservation of the maximum possible sucrose in clarified juice. In a well conducted clarification, the pol (sucrose and reducing sugars) expected to be remained intact. But the Brix of the juice is expected to be decreased since a portion of the dissolved impurities are removed by settling. Therefore, in an efficient clarification procedure, the purity (the ratio of pol to Brix) of the clear juice will rise by 1 to 2 units to that of the mixed juice which is known as rise in purity between the mixed juice and the clear juice [5, 7].

The pH of factory liquors is of considerable importance. Below pH 7.0, sucrose is hydrolyzed to the reducing sugars glucose and fructose, while above pH 9, destruction of reducing sugars occurs and colored components are formed [4,7]. Currently, sulphitation method is very popularly used in all sugar factories in Ethiopia. The juice pH was shown to have implications on the inversion losses, color formation, loss of sugar, sugar quality, and scaling in subsequent processes. Studies conducted by Rein[3] also indicated that sucrose loss as a percentage of total sucrose per hour in clarifiers increase as the pH decreases, and range from 0.1% at a pH of 6.5 to 3% at a pH of 5. Reducing sugars are naturally occurring in cane juice as glucose, fructose and mannose [7].

The cane juice comes from the mills contains many soluble and insoluble impurities. It is turbid and viscous in nature, and is not fit to be worked for white sugar manufacturing without suitable chemical treatment of it, it is necessary to remove the maximum quantity of impurities from the expressed juice at the earlier stages to obtain pure crystalline sugar. The clarification of juice is done for two purposes that are: removal of impurities and bleaching effects [9].

The composition of the lime mixtures and the liming conditions used in the cane sugar industries varies throughout the world. Saccharate liming gave Clear juice with the lowest turbidity and led to the wide adoption in Australian sugar mills [8]. Lime (calcium oxide) is added in sugarcane juice clarification for three reasons: (1) neutralize acids; (2) control the pH to minimize the acid inversion of sucrose; and (3) provide calcium ions for the formation of calcium phosphate flocs. Depending on the country and factory, lime is added as milk of lime (MOL) where the lime is not dissolved but instead is suspended in cold water, or as lime saccharate (SACCH), a solution of lime in hot juice or syrup [9].

The use of improved technologies developed through research in different sugar producing countries had increased their production and productivity. In Ethiopia the cane productivity was not maintained from year to year and the potentials are not yet exploited mainly due to the inability to optimize cane production and sugar manufacturing process through the application of improved technologies. Commercial sugar production in Ethiopia was started in 1954 with the establishment of Wonji Sugar Factory. In recent years, the increasing local demand of sugar cannot be met through the existing production system. As a result the government was forced to import annually 150,000 ton which is valued at 50 to 60 million USD. To solve this problem the government was undertaking expansion programs and established ten huge sugar factories [2].

In this research work, the efficiency of lime saccharate juice clarification compared to milk of lime was studied at Wonji Sugar Factory so that result could further be adopted to other sugar factories in Ethiopia.

1.4 Statement of the Problem

Wonji sugar factory is facing problems in juice clarification, like other sugar factories in Ethiopia. High clear juice colours, high turbidity of the clear juice, sucrose loss due to acid inversion and off coloured final product are the main problems mentioned.

Currently, at Wonji sugar factory, the pH of treated juice in most cases fluctuates due to lack of proper maintaining of the required pH during the process and leads to destruction of reducing sugar and inversion of sucrose that causes high color development in final product and enhance loss of sucrose with molasses. This is the reason why in most cases the ICUMSA color value rising above 700 IU against 150 IU for the plantation white sugar production. If the neutralized pH value is too low, this will speed up the sucrose inversion, which results in loss of sucrose. In line with this, one of the most outstanding problems that Wonji sugar factory is currently facing is frequent fouling of evaporator tubes mainly due to CaO content in clear juice. This condition is a major setback which calls for improvement in the existing clarification system, particularly on the liming system. The present study was therefore meant to evaluate the adoption of saccharate liming as an option to minimize the existing processing problems and thereby to secure benefits process efficiency.

The pH control during liming and sulphitation in the juice clarification process was a problem in most sugar factories due to heavy fluctuation of pH for limed juice by the use of MOL, slower settling of flocs and high turbidity of clarified juice, which creates an alarming challenge to the sugar manufacturing process. This problem invites to work on the juice clarification efficiency of lime saccharate compared to MOL in maintaining pH of pre-liming during the clarification process based on the following objectives:

1.5 Objectives

1.5.1 General Objective

The general objective of this study is to prepare and evaluate the performance of lime-saccharate for juice clarification and compare it with milk of lime (MOL) already in use.

1.5.2 Specific Objectives

- ✓ To prepare lime saccharate
- ✓ To test the settling rate, mud volume, turbidity, color level and calcium content in clarified juice at different pH for both MOL and Lime saccharate
- ✓ To evaluate the juice clarification efficiency of the lime saccharate as compared to MOL.

1.6 Scope of the Study

For any sugar factory, juice clarification system is among the critical unit operations which can lead to either success or failure of the sugar manufacturing process. Good work performed at the clarification stage pays a considerable benefit in terms of production. The existing method of clarification using milk of lime has certain drawbacks. In this work, lime saccharate preparation and its efficiency on juice clarification particularly at Wonji Shoa sugar factory has been studied. The prepared lime saccharate and milk of lime were used for mixed juice clarification within the same operating conditions and their juice clarification efficiency parameters have been compared. More importantly, the effect of increasing pH for both milk of lime and lime saccharate for the mixed juice clarification in the defecation process has been considered.

1.7 Significance of the Study

This study may increase awareness on the preparation of lime saccharate for juice clarification as alternative to MOL. The results obtained would be used as bench mark for other future researches in the area. In addition, sugar industries may benefit from the result to improve their product and productivity. It may also improve overall final commercial sugar quality and reduce sucrose losses from acid inversion. By implementation of the result, the sugar factory can minimize downtimes for cleaning pipes, pumps, tanks and valves for blockages since lime saccharate is a solution and requires less cleaning, in addition to its economic benefits in case of lime consumption.

CHAPTER TWO

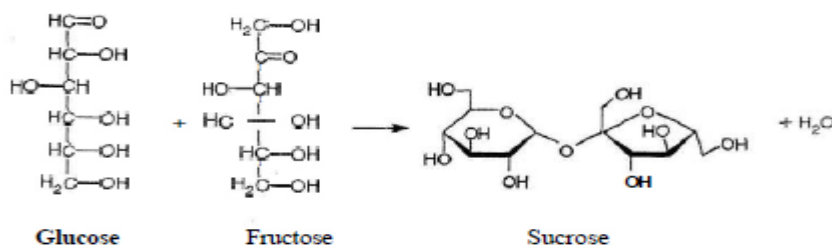
2. Literature review

2.1 Sugar Cane

Sugarcane is a grass grown in tropical and subtropical countries. It is a complex hybrid of various species, derived largely from *Saccharum Officinarum* and other *Saccharum* species [3, 8]. It is propagated by planting pieces of cane stalk. New growth emanates from buds on the cane nodes, ensuring uniform progeny. In the process of cane breeding, new varieties are produced and tested in a constant search for new and better varieties. This has been a major factor in improving productivity in the sugarcane industry [6].

Yields of cane vary tremendously from one area to another, depending on cane variety, climatic factors, and availability of water, cane growing practices and the length of the growing season [1]. Cane yields may vary from 50 t/ha in poor conditions to values approaching 200 t/ha under exceptional conditions with long growing periods. Yield of sugar may vary from 5 t/ha to 25 t/ha. Cane is generally not replanted every time it is harvested, but is allowed to re-grow and produce another crop, called a ratoon or stubble crop. The yield declines after a number of ratoons and at some point the cane has to be ploughed out and replanted. Cane is generally harvested in the winter and the length of the crushing season is dictated by weather conditions, principally rain. In some countries such as Colombia, Peru and Hawaii, cane may be processed virtually all year round [7, 11].

The major reason for processing cane is to recover sugar, which in its pure state is referred to by its chemical name sucrose and has the formula $C_{12}H_{22}O_{11}$ and is termed a disaccharide. It is formed in plant by a complex process but essentially consists of a combination of the two monosaccharide sugars, fructose and glucose [11].



Scheme 1: Sucrose formation from glucose and fructose

The reverse of this reaction is termed inversion when under the right conditions; sucrose will be hydrolyzed, and together with a molecule of water, to the formation of the two component

sugars. The sugars are in solution in water together with other soluble components: this liquid phase is referred to as juice. Other than juice, the cane stalk contains about 13 g vegetable fiber as a solid phase/100 g cane, giving the stalk its rigidity [6, 11].

Table 1 : Composition of mixed juice [12]

Parameters	Values
Brix	15°-18°.
Purity	80-87.
Reducing sugars	0.4—1.0%.
Ash	0.4—0.7%.
P ₂ O ₅ mg/L	60-300.
N ₂	0.03-0.04%.
pH	5.2-5.4.

2.2 Cane Juice Clarification

Juice received from the mills or diffuses commonly termed as raw-juice or mixed juice is turbid in appearance and contains suspended impurities of cane origin like fine bagacillo, a number of impurities either in dissolved state or in colloidal condition. The impurities in dispersed and suspended state include soil and fine particles of bagasse extracted during milling, and constitute around 0.3 to 0.5% of the juice [11].

Cane juice clarification aims; at forming flocs to trap all suspended matter, providing conditions of temperature, pH and ion concentration which will maximize the precipitation of soluble impurities from the juice. Producing clarified juice of high quality, with a minimum turbidity, color, and low calcium content with properly settled mud is the main target of mixed juice clarification [13].

There are different systems of clarification but the main objective is to eliminate maximum quantity of non-sugar impurities from the juice. The choice of a particular system of clarification is determined by the type of sugar to be produced. The defecation of juice is employed for manufacture of raw sugar while plantation white sugar plants follow either sulphitation or carbonation process of cane juice purification [13]. In every process of clarification, the treatment of juice by heat and clarifying agents' results in formation of precipitate which when separated yields transparent juice. Yet another common feature of all the

purification processes is the use of lime and heat as agents in combination with different other reagents. It must be noted that the results of clarification have a great bearing on the subsequent sugar crystallization process as well as the overall efficiency of the process of sugar manufacture [15, 16].

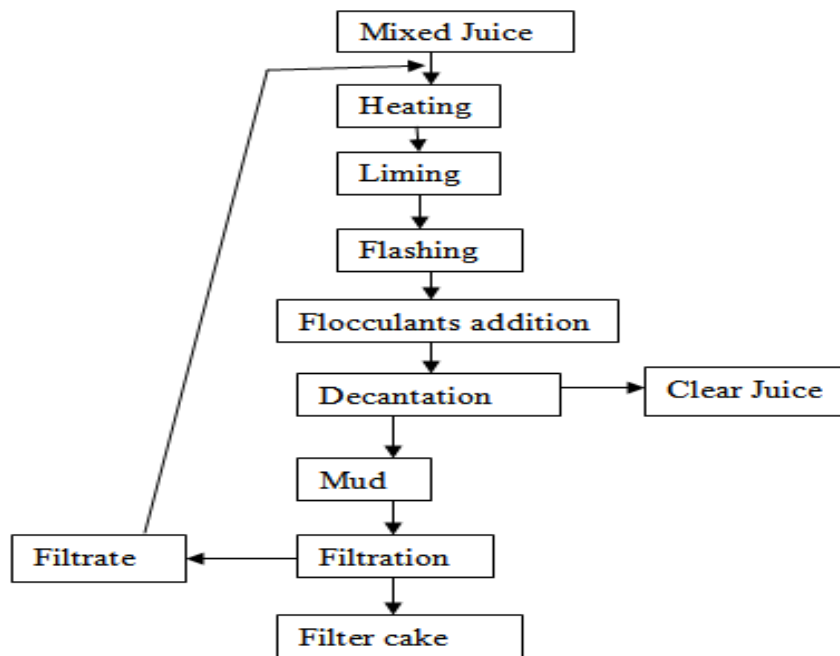
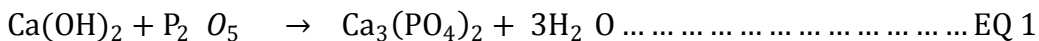


Figure 4: Juice Clarification Steps [9]

2.3 Juice Clarification Chemicals

2.3.1 Lime and its role in Juice Clarification

Lime first neutralizes the free organic acids present in the cane juice forming organic salts of calcium and on continuous addition; lime reacts with phosphoric acid present in juice and forms calcium phosphate [8].



2.3.1.1 Lime and its Quality

In every juice clarification, lime is the main clarification agent ever used. Lime is transported by trucks to sugar factories from manufacturers or lime kiln. Lime can also be purchased in paper bags. The amount of lime transported to the sugar factory should be controlled and be fresh since lime absorbs moisture and carbon dioxide from atmosphere and can be deteriorated. The quality of lime is important, as impurities will pass into the juice, which brings negative effect on clarification and subsequent process. Lime is received from limekiln where lime stone

(calcium carbonate) is burnt at 1200– 1300⁰C and dissociated into quicklime and carbon dioxide [1, 12].

A good quality of lime should contain above 95% CaCO₃ and less than 2% insoluble matter. The maximum impurities allowable are: MgO (1.0%), Iron Oxide and Alumina (2.0%), Silica (1.5%), Sulphates (0.5%), Moisture (2.0%) and Carbonic acid (2.0%). The effect of high impurities in lime has many drawbacks. High percentage of iron affects the color of juice, and both iron and alumina salts cause scale on tubes whereas high percentage of magnesia retards filtration and rate of settling. Similarly, more silica in lime retards the settling of juices and results in the formation of heavier scales inside the tubes of heaters and evaporators [12].

2.3.1.2. Solubility of Calcium Oxide, CaO

The solubility of a solute such as CaO is the maximum quantity of the solute that dissolves in a certain quantity of solvent at a specified temperature. Solubility is usually expressed in grams per 100 g solvent (% by mass). The solubility of CaO and Ca(OH)₂ in the juice depends on sucrose concentration, purity of the juice, pH, temperature and stirring.

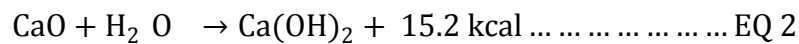
The solubility of lime increases with increasing sucrose concentration. Note that the greater lime solubility in solutions with higher sucrose concentration is due to the formation of mono calcium saccharate, Ca(C₁₂H₂₂O₁₁) [7]. As the pH condition during the liming process increases the solubility of CaO increases [13]. And also, increasing juice temperature decreases the solubility of lime. The reason for the difference in solubility is the higher saccharate hydrolysis at a higher temperature [11, 17].

Table 2: Density and Concentration of Milk of Lime [12]

Degree Baume	Density	Grams CaO per Litre	CaO % By Weight	Degree Baume	Density	Grams CaO per Litre
1	1.007g	7.5	0.75	16	1.125g	159
2	1.014	16.5	1.65	17	1.134g	170
3	1.022g	26	2.55	18	1.142g	183
4	1.029	36	3.5	19	1.152	193
5	1.037g	46	4.43	20	1.162	206
6	1.045	56	5.36	21	1.171g	218
7	1.052	65	6.18	22	1.180g	229
8	1.060g	75	7.08	23	1.190g	242
9	1.067g	84	7.87	24	1.200g	255
10	1.075g	94	8.74	25	1.210g	268
11	1.083g	104	9.60	26	1.220g	281
12	1.091g	115	10.54	27	1.231g	295
13	1.100g	126	11.45	28	1.241g	309
14	1.0106g	137	12.35	29	1.252g	324
15	1.116g	148	13.26	30	1.263g	339

2.3.1.3 Preparation of Milk of Lime

In sulphitation process of juice clarification, milk of lime is prepared as a concentration of 6 to 10 degree Baume. The lime preparation process is an exothermic reaction from which a considerable amount of heat is evolved out.



The solubility of Ca(OH)_2 in water is very small. That is 1 part in 790 parts of water. In the lime preparation process 3 parts of hot water are used to one part of lime. Hence, the milk of lime is a finely divided Ca(OH)_2 particle in water. More than 95% of these particles vary in size from 1 to 5 microns for soft burnt lime and 3 to 25 microns for lime of lower reactivity.

In Sugar Industry, milk of lime is prepared in a revolving drum with interior baffles plates, serves to mix quicklime and water. The drum is revolved by means of an encircling sprocket

and chain. Fresh lime is charged in the rotary slacker through the inlet and sufficient quantity of water is added.

The milk of lime is discharged at the other end. The unslaked pieces of limestone or grits are lifted by mechanism and discharged outside. The milk of lime emerging from the slacker contains fine impurities. It is strained through a screen of 8 meshes. This lime still contains fine grits, which is separated through a hydro cyclone mechanism. The milk of lime is collected in two tanks having each the capacity for about 2 h operations.



Figure 5: Milk of Lime storage and pumping station (Wonji Shoa Sugar Factory)

The tanks have stirrers running at 8 to 10 rpm. The outlet of the tank is supplied with a sieve of 1.3 mm opening to separate foreign matter. The milk of lime is a suspension not a solution and because of that, it has to be kept in a constant motion to prevent deposition of lime. In general, milk of lime is pumped to different consumption points with the excess recycling back to the tank. The velocity of milk of lime in the piping must be greater than 1 m/sec. centrifugal pumps are used, for milk of lime. Copper or brass parts are not resistant to alkalinity and they should be avoided from lime station [12].

2.3.1.4 Preparation of Lime Saccharate

Although the term "sucrate", officially designates chemical combinations with sucrose, "saccharate" is a term widely known and used in the sugar industry and has been adopted.

In the reaction between calcium oxide and sucrose (milk of- lime and sugar solutions), it has been established that there are three possible structures, viz. mono-, di- and tri- calcium saccharate depending on the chemical and physical conditions under which the reaction is conducted [10, 18].

Of the three, mono-calcium saccharate is the most soluble (especially at low temperatures) which in aqueous sugar and milk-of-lime solutions exhibits the properties of a true salt.

During the formation of lime saccharate the lime reacts with sucrose to form three possible structures: mono-calcium ($C_{12}H_{22}O_{11}CaO$), di-calcium ($C_{12}H_{22}O_{11}.2CaO$) and tri-calcium ($C_{12}H_{22}O_{11}.3CaO$) saccharates, depending on the chemical and physical conditions. The probable reaction mechanism for Saccharates is shown (in Figure 6). In order to ensure that the highly soluble mono-calcium saccharate is formed, it is important to maintain the two conditions a slight excess of sucrose and a temperature below $58^{\circ}C$ during preparations. Of the three, mono-calcium saccharate is the most soluble form hence providing a higher proportion of calcium ions readily available for interaction with inorganic phosphate ions [19].

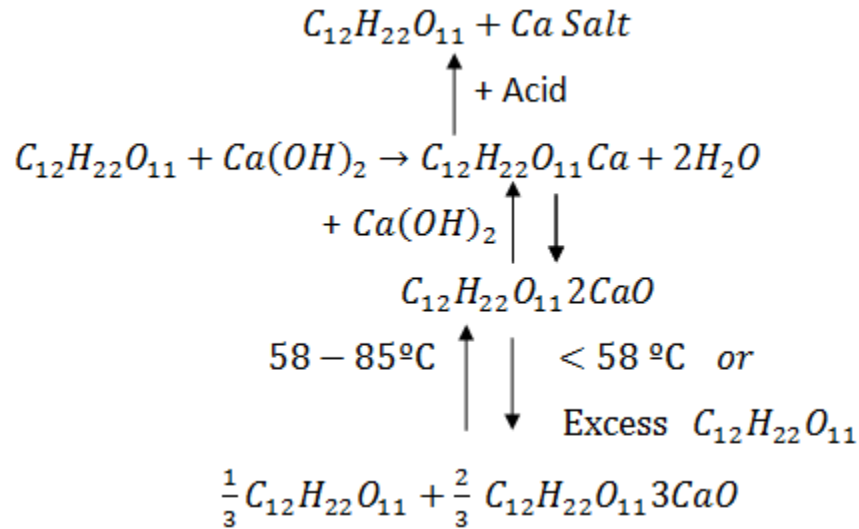


Figure 6: Probable Saccharate Reaction Mechanism [9]

From the stoichiometry a ratio of sucrose to calcium oxide of 6.1: 1 is required, in practice a ratio of 7: 1 is used thereby maintaining the slight excess of sucrose required [9]. In a factory there are many sources of sucrose that can be used to produce the required saccharate solution, from filtrate through to syrups. Evaporator syrup was finally adopted as it gave good clear juice clarity and required only a small volume for the sucrose level required. At the 7: 1 ratio, using 68° brix evaporator syrup and 15° Bx milk-of-lime, it was found that the pH of the resulting saccharate solution was in the range of 11.0 - 11.5. Hence, by controlling the saccharate pH at 11.0, excess sucrose is present and the formation of the mono-calcium saccharate is guaranteed [8, 10].

For preparation, syrup and milk-of-lime solutions are fed into the mixing tank which is sized for a retention period of 5 minutes to provide sufficient contact time for the saccharate to form. The syrup is fed at a fixed rate into the mixing tank and the milk-of-lime flow addition (Figure 7) is controlled by the pH of the saccharate solution, being at a pH of 11.0. The resulting saccharate solution overflows to a storage tank from where it is pumped through a circulating ring main by means of a conventional centrifugal pump. High and low set points in the storage tank actuate the addition of the syrup and, together with the pH controller; the saccharate is automatically made up. Saccharate is dosed from the ring main into the mixed juice line at a point prior to the intermediate juice pump after the primary heating stage. All excess saccharate returns to the storage tank, where a nozzle fitted to the discharge provides sufficient agitation to the solution in storage [22].

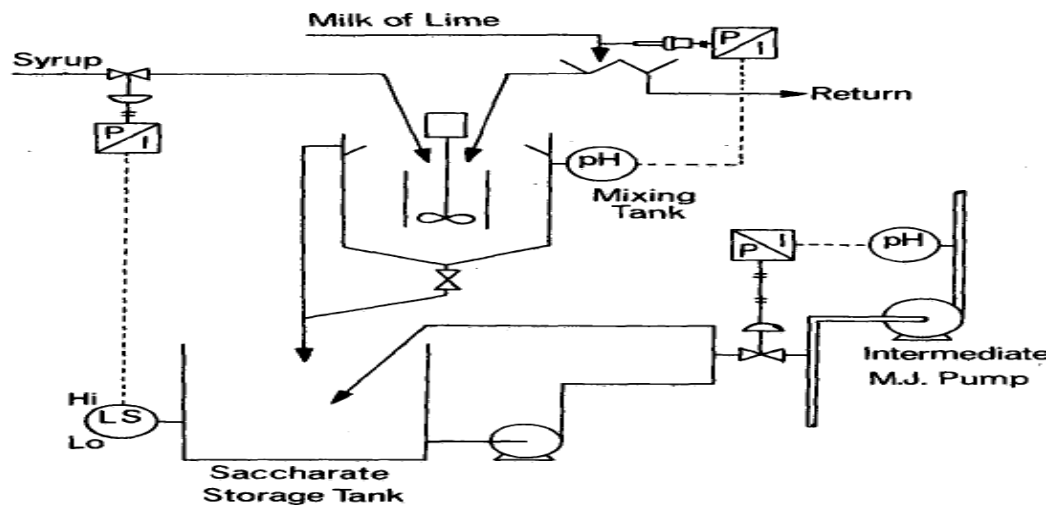


Figure 7: Saccharate Preparation and Dosing System [10].

A concern with lime-saccharate preparation is that syrup is exposed to conditions of very high pH and there will be some degradation of reducing sugars accompanied by an increase in the organic acid concentration. This possibility has been examined and it is concluded that it is desirable that the temperature in the lime-saccharate mixing tank be maintained below 58°C and that the residence time be minimized [13].

2.3.1.5 Comparison of MOL and Lime Saccharate

The composition of the lime mixture has a significant effect on the operation of the clarification system. Milk of lime gives the densest floc and mud but more turbidity while mixtures using

increasing proportions of juice and syrup give lighter, slower settling flocs, but less turbidity [13, 23]

The lime reaction can be made even more rapid if a system of saccharate liming is installed. The presence of sucrose causes a remarkable increase in lime solubility, and can increase it 100-fold. The solubility of lime in juice increases with its sugar content and decreases with increasing temperature, at 80°C, 2.5 to 3 g sucrose will dissolve in 100 g juice containing 10 to 12 g sucrose /100 g juice. Saccharate reactions in the juice are much faster and a superior clear juice is obtained. Other advantages of using lime saccharate over milk of lime include improved pH control and improved filter cake porosity. The advantages become more obvious when conditions become more difficult to achieve an acceptable clarification standard. It is more difficult to quantify the benefits particularly if only basic quality parameters are measured. Sophisticated schemes for the preparation of syrup or juice saccharate are now widely used [19].

2.3.1.6 Benefits of Lime Saccharate Clarification

Lime Saccharate liming gave a clearer juice and improved purity drop across the clarification station than hot liming with M.O.L. There are a number of inherent advantages when pumping, piping and storing calcium saccharate in contrast to the milk-of-lime suspensions, which is difficult to handle even under the most favorable conditions [24]. With saccharate solution centrifugal pumps may be used, pipe blockages are negligible and agitation of storage tanks can be minimal. An additional advantage that saccharate has over milk of lime is that of pH control, resulting in a steadier limed juice pH with fewer fluctuations [14]. Less clear juice/ syrup turbidity can also be achieved by the liming process with lime saccharate (Figure 8).

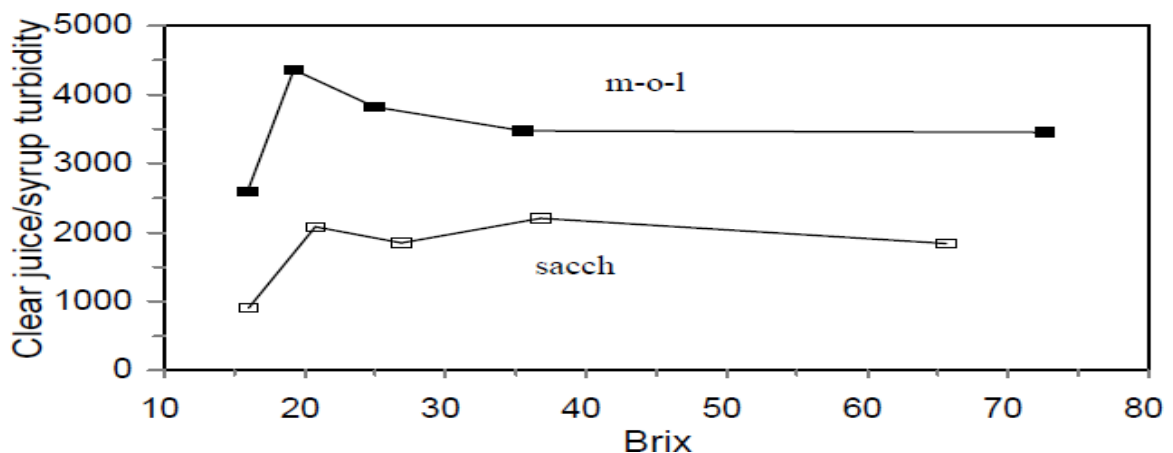


Figure 8: CJ/ Syrup Turbidity Versus Brix, Simulated Evaporator Effect [15].

2.3.2 Role of Phosphoric Acid in Juice and Additions of Phosphate

Phosphoric acid occurs in the cane as both soluble phosphates in the juice and in combination as protein in the cell material. The latter compounds being insoluble, only the soluble phosphates take part in the defecation. They react with the lime and form a precipitate that constitutes an important part of the floc produced in the juice by the lime [13]. The organic phosphate is in the form of a complex with organic compounds containing about 10 % phosphate. Most of the organic phosphate material is in the colloidal form, and is unavailable for formation of calcium phosphate precipitate flocs [19]. If the phosphate content is less than 200 to 300 mg P_2O_5 /kg juice, it is beneficial to make additions of inorganic phosphate (phosphoric acid, superphosphate, etc.) to raise the juice phosphate level to above 250- 300 mg/kg so that satisfactory clarification can be achieved when the cane juice contains about 300 mg/kg phosphate (as P_2O_5) [26]. The color removal from raw juice is also improving with the phosphate level as shown (in Figure 9).

The benefits of maintaining an optimum level of phosphate in juice are Greater colloidal elimination, less calcium in clarified juice, faster mud floc formation, with more rapid settling and better clarification with lighter colored clarified juice [22].

Disadvantages of too much phosphate addition can be: higher chemical costs, higher lime consumption and higher mud volume and hence higher filter mud sugar loss[11].

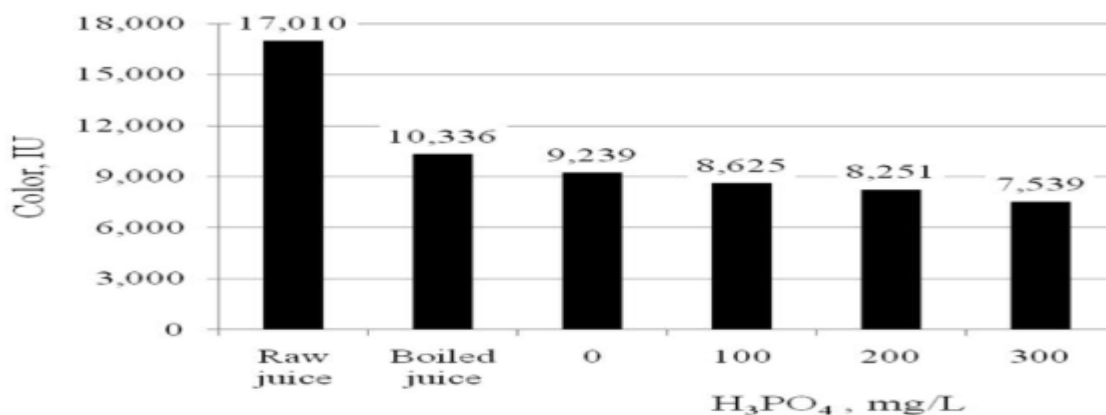


Figure 9: Color of Raw Juice by Hot Liming and Addition of Phosphoric Acid [13]

2.3.3 Role of Flocculants

Although reaction time is considered to be an important element in the reaction of lime (longer reaction times lead to improved floc formation, better settling rate, lower turbidity, less increase

in residual calcium and lower final mud volume) more emphasis is placed on throughput and reduced clarifier residence time. This has been aided by the availability of commercial flocculants. The functions of good flocculant includes increasing the settling rate of insoluble solids, decreasing mud volumes, producing good clarity (low turbidity) clarified juice and good filterability of mud, with good clarity of filtrate [27].

There are a multitude of flocculants available and the choice is dependent on several factors. Two of the main parameters are the degree of hydrolysis and the molecular size. The degree of hydrolysis for the commonly used partially hydrolyzed polyacrylamide flocculants shown in Figure 10 is defined as:

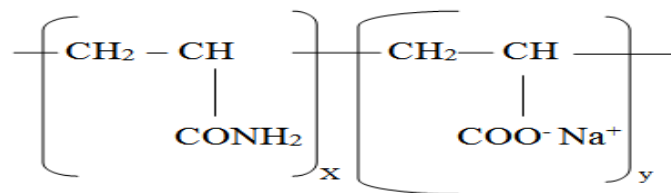


Figure 10: The Chemical Composition of Partially Hydrolysed Polyacrylamides [17]

The importance of flocculant especially in the modern rapid clarifiers is mandatory to control and accelerate mud coagulation and settling its effect is a binding effect for the already formed flocs as a result of chemical reactions as shown in Figure 11.

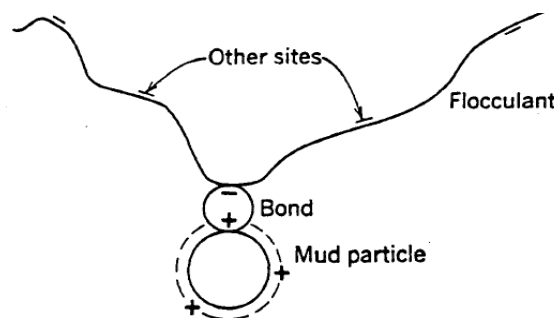


Figure 11: Secondary Floc Formation [16]

2. 4 Chemistry of Juice Clarification

2.4.1 Colour Removal in Juice Clarification

The quantity, quality and type of pigments and colorants in juice are dependent upon: the variety and maturity of sugar cane, climatic condition, agricultural practices (use of nitrogenous fertilizers) stored by plant as amino acids, cut to crush delays , amount of trashes incorporated into the crushed cane, soil condition and juice extraction practices [17, 28].

The colour of raw juice ranges from 10,000 to 20,000 IU with the variations reflecting effects of different cane cultivars, cane conditions and the varied quantities of tops and green leaves crushed with the clean billets [13]. Removal of cane sugar colorants can also be practiced by membrane filtration, ion exchange resins, packed carbon beds and oxidation reactions [29, 25] although not yet practiced in Ethiopian sugar factories.

2.4.2 Chemical Reactions in Juice Clarification

In the sugar cane industry, effective clarification of juice is necessary for the efficient and economical production of high quality raw sugar. A variety of chemical and physical reactions occur during the clarification process and these include: coagulation/precipitation of amorphous calcium phosphate, denaturation of proteins, gums, pectin and waxes; adsorption of waxy-like materials and suspended solids with precipitated inorganic non-sucrose components, precipitation of organic and inorganic salts and flocculation of macro-flocs via particle bridging of calcium phosphate flocs, impurities and copolymer flocculant [7]. Inversion of sucrose due to the effect of both pH and temperature, degradation of reducing sugars to organic acids caused by high pH and temperature and formation of colour species through enzymatic and non-enzymatic reactions between natural colourants, colour precursors and sugars are also the other main probable reactions occurring in juice clarification considered as side effects and needs attention of the clarification processer [16].

A wide range of chemical and physical reactions takes place in the juice. They can be classified as: those due to pH change, changes in Ca^{2+} concentration and the increase in temperature. These reactions can be subdivided into chemical reactions and physical reactions. The major chemical reaction is that of the Ca^{2+} cation with the phosphate ion to form phosphate' intermediates and to precipitate tri-calcium phosphate $\text{Ca}_3(\text{PO}_4)_2$. In cane juice reaction two common precipitate formations are known, the formation of $\text{Ca}_3(\text{PO}_4)_2$ and CaSO_3 (in Table 3). The CaO content of clear juice is a function of CaO content of mixed juice, Organic acids present in the original juice and acids formed in the clarification process. It would also depend on the clear juice pH or the amount of lime added [30].

The major physical reactions for the formation of flocs are based on $\text{Ca}_3(\text{PO}_4)_2$ and protein, surface charge effects vary the effective density of the flocs. Colloids formed from denatured proteins generally have a net negative surface charge effect, which controls, the efficiency of coagulation. Coagulation onto floc particles is influenced also by the presence of multivalent cations (Ca^{2+} , Al^{3+} , etc) and the use of flocculants. [11, 31].

Table 3: The Main Chemical Reactions in Juice Clarification [1].

Lime –Phosphate reaction	
$3\text{Ca}(\text{OH})_2 + 2 \text{H}_3\text{PO}_4 \rightarrow \text{Ca}_3(\text{PO}_4)_2 + 6\text{H}_2\text{O}$	Tri-calcium phosphate
Milk of lime and sulphur reactions	
$\text{Ca}(\text{OH})_2 + \text{H}_2\text{SO}_3 \rightarrow \text{CaSO}_3 + 2\text{H}_2\text{O}$	Calcium sulphite

2.4.2.1 Mechanism and Chemical Aspects of Juice Clarification

It has been shown that particulate matter in raw juice has a negative charge, the outer layer being proteinaceous and with a large percentage being mucoid, in which protein is coagulated with a polysaccharide. The electrostatic repulsion between these particles ensures that spontaneous flocculation of the suspension does not take place [33].

The charge lies in the ionizable groups of this outermost adsorbed layer and can be measured in terms of the charge particles (Zeta potential). Reducing the Zeta potential to zero (the isoelectric point) will result in optimum flocculation. This is achieved partially by the introduction of calcium ions in the form of lime when adjusting the pH. The reaction of organic matters with lime an increase lime consumption and reduces the effect on the lowering of the Zeta potential. Under these conditions clarification could be improved by the addition of calcium chloride [11]. The mechanism of primary floc formation involves the *in situ* precipitation of calcium phosphate. The Ca^{2+} ions adsorbed at the juice particle surfaces act as nuclei for this precipitation and the impurities become incorporated into the coagulum with the calcium phosphate acting as bridges between the impurity particles (Figure 12),

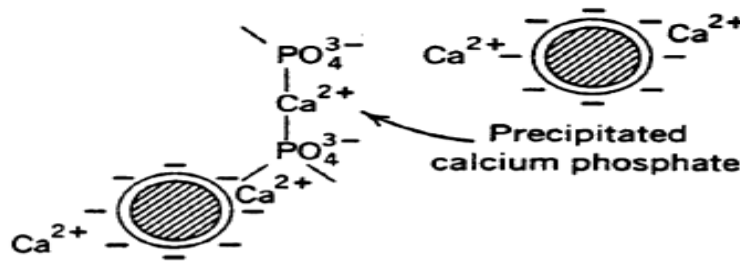


Figure 12: Calcium Phosphate Bridging [17]

The success of the primary flocculation is dependent upon the extent of the calcium phosphate precipitation and, therefore, on the concentration of the calcium and phosphate ions. Both the optimum calcium and phosphate concentrations increase with the age of the cane [17].

In the commercial process lime addition is determined by pH considerations rather than by calcium concentration and it is assumed that, since the calcium (and magnesium) content after liming is always in excess of that required for complete inorganic phosphate precipitation, the calcium requirement is always satisfied. It is generally accepted that phosphate levels of approximately 300 ppm are required for good clarification, and dosing with 80 % commercial phosphoric acid is done when levels are low and processing and clarification problems are experienced. At present dosing is gauged empirically. Much attention is given to pH control since values below seven results in losses due to sucrose inversion while values above eight lead to degradation of reducing sugars which increase colour formation [18, 35].

2.5 Juice Clarification Processes

2.5.1 Variants of defecation clarification procedures

There are many variants of the simple defecation process used throughout the cane sugar industry. Some of these listed recently are shown in Table 4.

Table 4: Detail of Typical Defecation-Clarification Methods [9]

Cold liming: Raw juice at less than 45 °C, lime saccharate (or milk of lime) to pH = 7.8 heated to 102 °C, add flocculant , and clarify.
Warm liming: Raw juice at less than 45 °C, lime saccharate (or milk of lime) to pH = 6.0 heated to 76°C, lime saccharate or milk of lime to pH = 7.8 heated to 102°C , flash to 100°C, add flocculant, and clarify.
Intermediate Liming: Raw juice , heated to 76 °C , lime saccharate (or milk of lime) to pH = 7.8, heat to 102 °C, flash to 100°C , add flocculant , and clarify
Hot liming: Raw juice , heated to 76 °C , heat to 102 °C, lime saccharate (or milk of lime) to pH = 7.8, , flash to 100°C, add flocculant , and clarify

Raw juice coming from the juice extraction is generally at a pH around 5.5. In cold liming it is generally limed to a pH of at least 7.2 and sometimes up to 8.3. The juice is then pumped through the primary heaters to an intermediate tank feeding pumps for the secondary heaters that heat the juice to a few degrees above its atmospheric boiling point [18].

2.5.1.1 Practical Procedures for Defecation Clarification

The defecation procedures, mostly used are the following:

2.5.1.1.1 Cold liming

The juice coming from the mills is, generally at a pH in the neighborhood of 5.5. It is usually limed to a pH of 7.2 but may be taken as high as high 7.3. It is then pumped to the heaters in order to bring the juice to just above its boiling point during its passage. i.e to 102°C minimum[16]. On leaving the heater, the juice passes into a flash tank and return to its corresponding boiling point with release of vapor, It passes immediately afterwards to the continuous clarifier where its pH drops to a value normally in the range of 6.8 to 7.2. Cold liming is sufficient for treatment of noble canes and for manufacture of raw sugar. The clarifiers give a negligible amount of scum [18, 34].

2.5.1.1.2 Intermediate liming

Here the first lime addition is after the intermediate warm juice tank at 75°C. into the 'eye' of the secondary juice pump as seen in Figure 13. The pH control setting is set about 0.2 to 0.3 units of pH higher than the desired clarified juice pH. Flocculent is added in the feed launder of the clarifiers. In some intermediate liming installations, the tank provided as a buffer between the first and second stage of the heating is deliberately designed to approximate a "plug flow" characteristic with a residence time of up 10 to 40 minutes. This buffer enables time for the natural amylase enzymes in the juice at its natural pH, to break down a substantial fraction of the starch present in the juice [7]. The juice temperature is controlled to a temperature (in the range 70 to 80 ° C) which is optimal for starch reduction being a compromise between the higher temperatures requires for rapid solubilization of starch granules and the lower temperature which avoids thermal destruction of the amylase. The clarification is improved at the same time. There would without doubt be some sucrose degradation by heat and invertase activity in this process. But this is difficult to quantify, and the advantages of the modification are seen to dominate this disadvantage [11, 20].

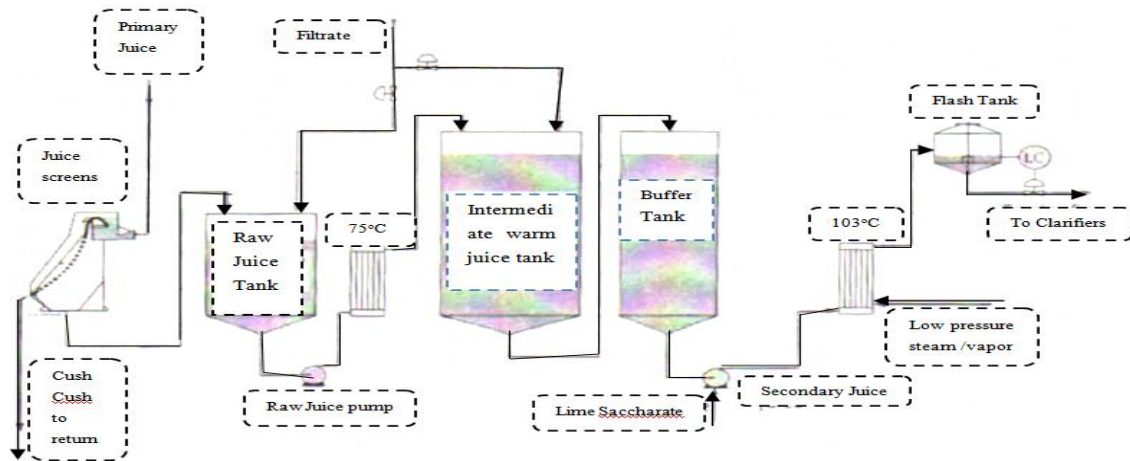


Figure 13: An Intermediate Liming Scheme for Cane Juice [11]

2.5.1.1.3 Hot liming

Here the lime saccharate (or milk of lime) is added just before the flash tank. The pH control setting is set about 0.2 to 0.3 units of pH higher than the desired clarified juice pH. The achievement of good pH control is technically more difficult with hot liming but it is reported to achieve the best quality clarified juice with the disadvantage of more voluminous muds, particularly with saccharate addition [13, 20].

2.5.1. 2 The Juice heating and its effect in juice clarification

Defecation clarification is usually carried out by a combination of the addition of lime Ca(OH)_2 , to raise the pH value from 5.3 to 7.2-8.0. The Ca(OH)_2 , can be in the form of milk of lime, lime-juice mixture or lime-syrup saccharate. Heating in stages to the boiling point with flashing is to remove entrained or dissolved air [33].

The main precipitant is calcium phosphate which forms the basis of floc that adsorbing much of the other precipitating materials. The physical elimination of impurities is not complete and depending on the pH value of the juice after the treatment the residual Ca^{2+} content may be higher than its content in the original juice [6]. The fact that floc formation can be initiated by heating alone indicates that the effect of temperature has a significant part to play in clarification. This is attributed primarily to protein coagulation. It is generally believed that superheating is not advantageous and that temperatures just above the boiling point (103°C) are the maximum for good practice [22].

In hot lime clarification, the sugarcane juice is first heated and natural flocs form by coagulation of colloids, particularly proteins (Figure 14). The heated juice is treated with lime to form even larger flocs through calcium phosphate bridges. The created flocs subsequently precipitate in clarification tanks. Precipitation is aided by polyanionic acrylamide flocculants which agglomerate and add weight to the flocs, thus increasing their rate of precipitation [8].

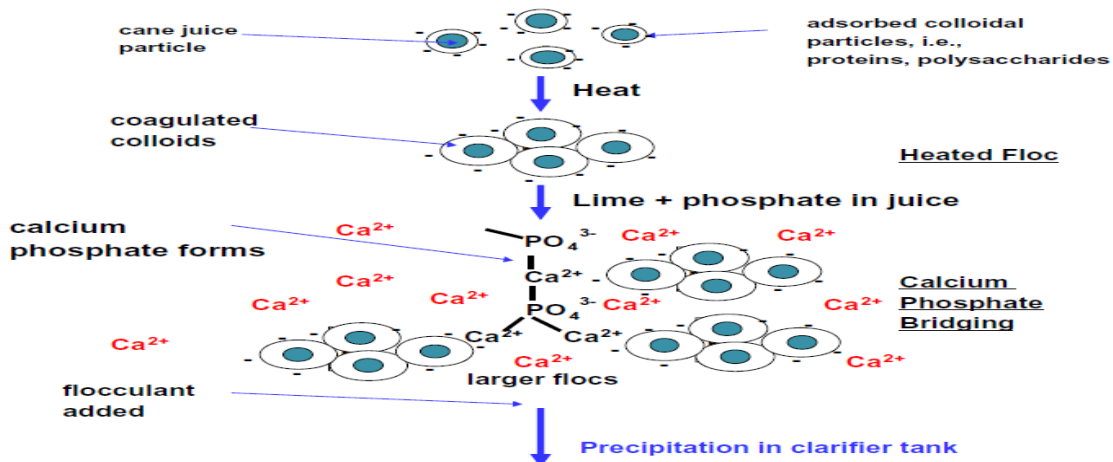


Figure 14: Effect of Hot Lime Clarification and Calcium Phosphate Bridging [8]

2.5.1.3 pH effects and its control

Clarification control involves primarily the control of juice pH, which is affected by juice and lime now, and juice temperature. The basic type of control used in clarification is continuous closed loop control of pH, assisted by other loops for juice flow smoothing and heater temperature control. On-line measurement of pH used to be carried out manually using colorimetric test papers but now sophisticated electronic methods using glass and reference electrodes have been developed sufficiently to enable almost universal adoption for juice pH measurement [18].

They are now relatively easy to maintain and calibrate using standard pH buffer solutions typically selected for pH values of 4.0, 7.0 and 12. Used with automatic liming addition valves and regulators. They have led to substantial improvements in clarification. Control of pH is almost universally carried out using a standard control loop where lime addition.

To control the pH of the limed juice, signals from the pH probe are used to control the flow of lime via a controller and actuator. The pH probe has to be located at a point where the lime and juice is properly mixed not too close or too far from the lime addition point. This helps to prevent erratic changes in juice pH and provides for better pH control [18, 36].

Milk of lime addition has traditionally been carried out through an automatic adjusted splitter box delivering into a juice mixing tank, with the pH measurement taken on the juice outlet. To minimize valve blockages it is good practice to have a fully re-circulating stream of lime mixture [6].

2.5.2 Juice clarifiers

When the juice has undergone the desired treatment it must be allowed to settle in order to separate the clear juice from the precipitate formed in the body of the juice. The settling or subsidence is carried out in continuous settlers or clarifiers. There are different types of clarifiers in operation these days. The Dorr clarifier, which was the most widely used, is a large cylindrical tank provided with a central shaft rotating very slowly (12 cycle per hour) and carrying scrapers of sheet metal that slowly brush the bottom of each compartment. As seen in figure 15, a central tube connects the upper parts of the various compartments. The incoming juice passes from the central tube into the several compartments by ducts that lead it across the annular space in which the muds descend. The mud that deposits in each is moved slowly towards the center where it falls by an annular passage to the bottom of the vessel, descending along the length and on the exterior of the central tube. The clarified juice is drawn off from each compartment by pipes at the upper part close to the side wall of clarifier to a "juice box" in which the output from each compartment may be regulated by means of a sliding tube on the end of the pipe; this fixes the discharge level relative to the level of juice in the clarifier [11].

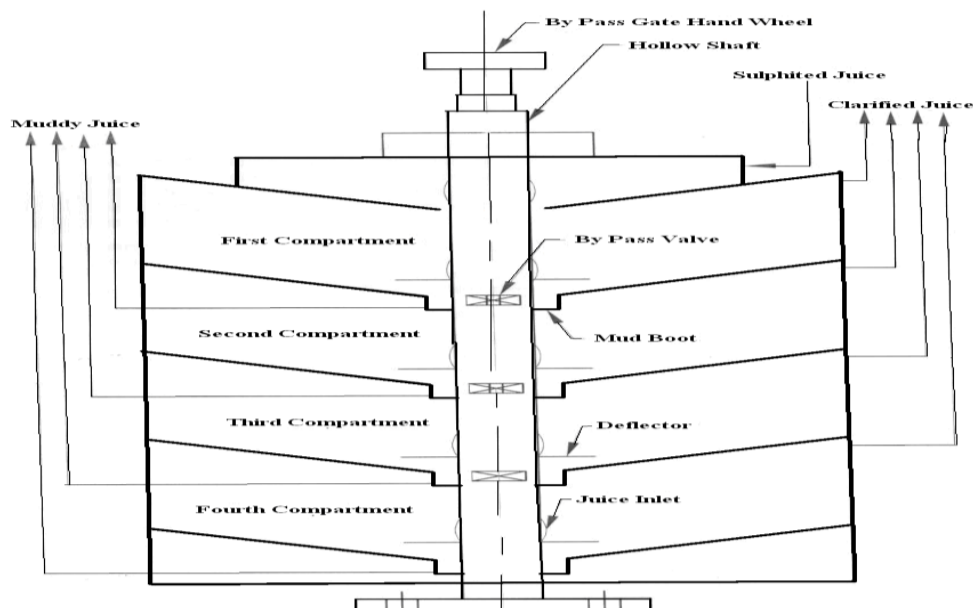


Figure 15: Dorr- Clarifier [10]

The other currently becoming popular is single tray rapid clarifier which was pioneered by the SRI (Sugar Research Institute, Australia), in the 1970s, and has been very successful (Figure 16). It is simpler and considerably cheaper than the multi-tray types for the same juice throughput [11].

Juice from the flash tank enters into a feed chamber and is split in both directions into the annular feed launder. The juice overflows through notches into the feed well and is deflected laterally into the separation region of the vessel.

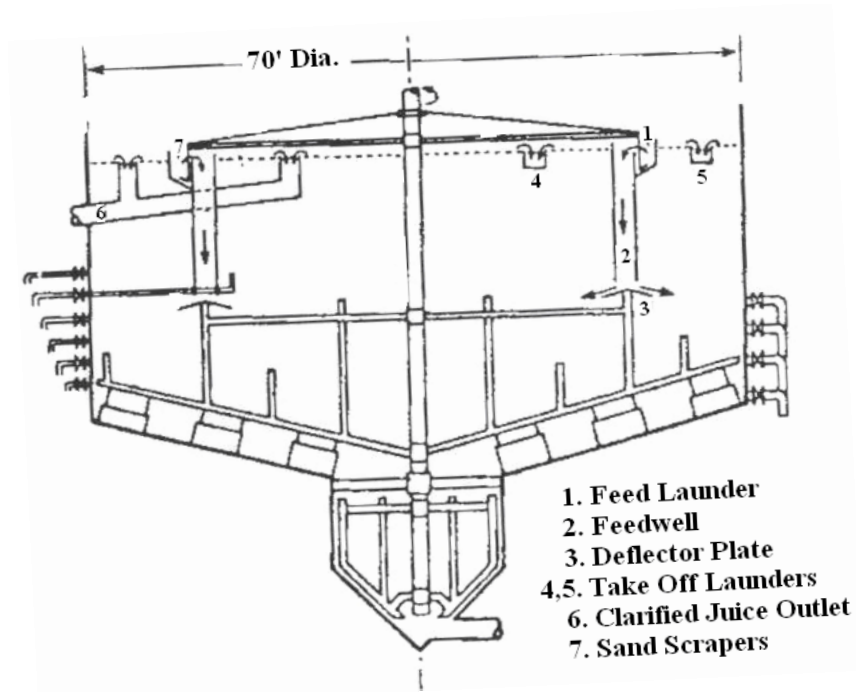


Figure 16: SRT Rapid Clarifier [10]

The design embodies the most positive multipoint feed arrangement that could operate on a continuous basis without causing floc damage from localized high velocity or high turbulence regions. The "New Generation SRT juice Clarifier Design" features a new feeding system with a single feed point and simple clarified juice removal utilizing a perforated plate. [6, 11].

CHAPTER THREE

3. Materials and Methods

3.1 Materials

Equipments and instruments used for the experiments were Volumetric flasks, Erlenmeyer flasks, Conical flasks, Buchner funnel, Microprocessor pH meter (Type HANNA pH 211, Cambridge, England), Electronic balance (type ABJ 320-4, Cambridge, England), Mixed juice heater with stirrer (locally prepared pan), Rudolph Research Analytical (USA) Automatic Refractometer (Model J157) for Brix measurement, Rudolph Research Analytical(USA) Saccharimeter(Model AP880) for pol determination and spectrophotometer(Model CE 1011, Cambridge, England) for absorbance measurement.

Chemicals and Reagents:

Chemicals and reagents used were Lead acetate Basic anhydrous 99% from LOBA CHEMIE PVT.LTD (Mumbai, India), Erichrom black T indicator LOBA CHEMIE PVT.LTD (Mumbai, India) , Ethylene Diamine tetra Acetic acid, disodium salt 99% from LOBA CHEMIE PVT.LTD (Mumbai, India), Ammonium buffer solution (Ammonium chloride-amonium hydroxide buffer), Ammonium oxalate monohydrate 99% $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, (Mumbai, India), 0.1M NaOH and 0.1M HCl.

3.2 Sample Preparation

For the study, MOL, $\text{Ca}(\text{OH})_2$ of 15 degree Baume was first prepared by taking calcium oxide, CaO from Wonji Shoa Sugar Factory. Using the same MOL, lime saccharate (SACCH) was prepared by mixing 200 mL of milk of lime with 110 mL syrup by controlling the pH in the range of 11.0 to 11.5 to guarantee the formation of mon-calcium saccharate. About nine litres of mixed juice samples have been collected from juice extraction plant (Wonji Shoa Sugar Factory), made composited and divided in equal portions for both MOL and SACCH testing. The juice was heated, limed for MOL and SACCH, degassed by gentle boiling and settled at 100 °C in the 1000 mL measuring cylinder for 30 minutes, using 5 mg/L of a conventional polyelectrolyte flocculant and clear juices were obtained and collected for further analysis.

3.3 Analytical Methods

The effectiveness of juice clarification were measured for settling rate and mud volume and analyzed for quality of Clear Juice like color, Calcium oxide content, turbidity and pH.

3.3.1. Determination of the Settling Rate

1000 mL graduated cylinder was filled with the treated juice. Then, timing the settling rate was started as soon as the sample showed the first sign of separation (a very thin layer of clear juice above the solids starts to occur). The settling rate is the height of the settled solid in one minute [36]. The distance travelled by the mud (cm) divided by the total time (s) consumed was considered as the settling rate.

3.3. 2. Mud Volume

1000 mL measuring cylinder was placed on a platform and filled with the treated juice. Soon after filling, a timer was started and the height of the precipitate at 15 minutes was recorded as final mud volume. Using the clear juice from the cylinder after treatment by MOL & SACCH, the ICUMSA colour, turbidity and total calcium was analyzed as described below.

3.3.3 Brix Determination

Following the ICUMSA method [38], Brix was determined by refractometric method. The juice was poured from sample can to the 100 mL flask and kept in a cooling water bath to bring its temperature near to 20 °C After the sample was sufficiently cooled, it was taken out from the cooling water bath and then, two to three drops of sample was added to the refractometer prism and the reading taken.

3.3.4 Pol Determination

Following the ICUMSA method, approximately 100 mL of the juice sample was poured in to the flask. 1 g basic lead acetate was added and shaken vigorously then allowed to stand for 30 seconds to permit flocculation of the precipitate. It was filtered through a fluted filter paper held in the funnel, which rests directly in the beaker and then the saccharimeter reading was taken. Finally, Pol% of the juice sample was calculated based on refractometer brix reading of the juice sample and saccharimeter reading from Table 7, Appendix D.

3.3. 5 Determination of the Colour of Juice

The color of the juice samples was determined following the ICUMSA procedure [17].

A diluted solution of sample was prepared to be tested, (5⁰ brix solution). For the brix of clear juice 16.7, a 5⁰ brix solution was prepared by weighing $100/16.7 \times 5 = 29.94$ g of clear juice, made up to 100g, mixed and filtered. The pH was adjusted to 7.0 +/- 0.1 using HCl or NaOH. The absorbance was measured in 1 cm cell at 420 nm against water as reference. The same procedure was followed all treatments.

The ICUMSA colour will be measured according to

$$\text{ICUMSA Color} = \frac{\text{Abs}}{bC} \times 1000 \dots \dots \dots \text{EQ 3}$$

Where: Abs = Absorbance at 420 nm, b = Cell length in cm and

C =Concentration of total solids in g/mL as determined by refractometer

3.3.6 Determination of Calcium and Magnesium in Juice

The concentration of calcium and magnesium in primary, mixed or clarified juice was determined by complexiometric titration against EDTA solution. Calcium was precipitated out of the juice solution by potassium oxalate: subsequent titration against EDTA gave magnesium concentration in the juice.

For determination of CaO + MgO concentration, 50 mL of juice sample was pipetted into a 100 mL volumetric flask and made up to mark with distilled water. Then, 10 mL of this solution was added into a 200 mL Erlenmeyer flask and diluted to about 50 mL with distilled water. Further 2 mL ammonium buffer solution and 8 drops of Erichrome black T indicator were added. The solution was stirred with a magnetic stirrer and titrated against standard EDTA solution until the pink color of the solution first changes to light green.

For determination of MgO concentration, 100mL of the juice sample was pipetted into a 200 mL volumetric flask, with the addition of 25 mL of 5% ammonium oxalate solution, and made up to mark with distilled water. The solution was mixed thoroughly and allowed to stand for 1 hour to ensure complete precipitation of the calcium oxalate. 10mL of the two solutions were pipette into a 250 mL Erlenmeyer flask and diluted to about 50 mL with distilled water. Then 2 mL ammonia buffer solution and 8 drops of Eriochrome black T indicator were added. The solution was then stirred with a magnetic stirrer and titrated against standard EDTA solution until the pink color of the solution first changes to lights green.

Calculation:

$$\text{CaO in juice} = \frac{0.57(a - b)}{C} \times 1000 \dots \dots \dots \text{EQ 4}$$

1ml standard EDTA = 0.574mg CaO = 0.413MgO

Titre for CaO + MgO determination = a mL

Titre for MgO determination = b mL

Aliquot of diluted juice used for titration = C mL

$$\text{MgO in juice} = \frac{0.413(b)}{C} \times 1000 \dots \dots \dots \text{EQ 5}$$

For 10mL of diluted aliquot used for the analysis the above formulas be reduced to:

CaO in juice = 57.4 (a-b) MgO in juice = 41.3 (b)

3.3.7 Determination of Turbidity in Clarified Juice

The turbidity of clarified juice is a measure of the effectiveness of the clarification process. The ICUMSA Colors of Unfiltered and filtered samples were measured at 420nm and the difference between the readings was taken as the turbidity of the sample.

For determination of turbidity of clarified juice, a 2⁰ - brix solution was prepared from the original brix of the clarified juice determined. The amount of clarified juice 2⁰ - brix solution was weighed in a beaker and made up to 100 g with distilled water. This solution was divided into equal portions into two 100 mL beakers. The first portion of the sample was taken and filtered through Buchner funnel with whatman No 5 filter paper. Then the pH of the filtrate was adjusted to 7.0 ± 0.2 using either 1M NaOH or 1M HCl and absorbance (A₁) was measured in 1cm- cell at 420 nm against a distilled water blank.

$$\begin{aligned} \text{ICUMSA}_{420\text{nm}} \text{ Color C 1} &= \frac{A_1}{1\text{cm} \times \text{concentration of total solids}} \times 1000 \dots \dots \text{EQ 6} \\ &= \frac{A_1 \times 1000}{1 \times 2 \times 1.00602/2} = \frac{A_1 \times 1000}{0.0201} \end{aligned}$$

The 2nd portion of the sample was taken (not filtered) and the pH was adjusted to 7.0 ± 0.2 using NaOH or HCl and absorbance (A₂) was measured in 1cm cell at 420 nm against distilled water blank.

$$\text{ICUMSA}_{420\text{nm}} \text{ Color C 2} = \frac{A_2}{1\text{cm} \times \text{total solids conc. g/mL}} \times 1000 \dots \dots \dots \text{EQ 7}$$

Expression of the result

$$\text{Turbidity of clarified juice} = \text{C 2} - \text{C 1} = \frac{(A_2 - A_1)}{0.0201} \times 1000 \dots \dots \dots \text{EQ 8}$$

3.4 Data Analysis

All the calculated data were statistically analyzed by RCBD (Randomized complete block Design) SAS system to determine the significance among treatments of different response variables.

CHAPTER FOUR

4.1 Results and Discussion

By using the milk of lime and lime saccharate previously prepared, the juice liming procedures were carried out for three pH ranges of 8.0, 8.5 and 9.0 at laboratory level for composited mixed juice qualities (Purities) in triplicates for each pH range. For both milk of lime and lime saccharate prepared at laboratory level, juice liming treatments were done at the same 1st heating temperatures of 76°C , the same 2nd heating temperature (up to boiling) and equal concentration of 5 mg/L flocculants added for each treatment. During all treatments by milk of lime and lime saccharate for different mixed juices collected from Wonji sugar factory, settling rate and mud volume were measured differently. Furthermore, clear juice color, turbidity values and CaO content in clear juice for each treatment for milk of lime and lime saccharate were measured following their respective laboratory procedures and the values calculated for comparison as presented in Table 5 and Figures 16, 17 and 18.

Table 5 : Average Analysis Results for Response variables

pH level	Type	CJ Purity (%)	settling rate (cm/min)	mud volume (cm ³)	ICUMSA color (IU)	Turbidity (TU)	CaO content (ppm)
8	MOL	91 ± 0.2	11 ± 0.1	175 ± 1.7	3763 ± 4.7	38 ± 0.11	888 ± 4.7
8	SACCH	92 ± 0.15	12 ± 0.2	144 ± 2.8	3182 ± 83.9	30 ± 1.6	624 ± 8.8
8.5	MOL	87 ± 0.2	12 ± 0.5	241 ± 2.5	4550 ± 58.1	65 ± 2.5	665 ± 26.9
8.5	SACCH	89 ± 0.1	12 ± 0.1	208 ± 1.7	3803 ± 102	29 ± 2.2	584 ± 23.0
9	MOL	84 ± 0.1	12 ± 0.4	115 ± 2.0	7001 ± 81.0	180 ± 1.6	738 ± 11.8
9	SACCH	85 ± 0.2	12 ± 0.2	107 ± 0.33	5607 ± 27	111 ± 3.3	611 ± 6.5

Values in the Table means (±SD) of three replicates, SD – standard deviation

At different pH treatments of pH 8.0, 8.5 and 9.0, for composited mixed juice samples ; color, turbidity and CaO content in their clear juice was recognized differently in which higher values recorded for MOL liming treatment compared to Saccharate liming for the same Mixed juice quality, the same 1st heating & 2nd heating temperature and the same flocculant dosing.

4.1.1 ICUMSA Color (IU)

The colour of raw (mixed) juice ranged from 10,000 to 20,000 IU with the variations reflecting effects of different cane cultivars, cane conditions and the varied quantities of tops and green leaves crushed with the clean billets. The relative decolourisation, defined as $100 \times (\text{Colour of raw juice} - \text{Colour of clarified juice}) / \text{Colour of raw juice}$ for defecation by hot liming, averaged 32% (6,800 to 13,600 IU) ; sulphitation and carbonation were nearly equally efficient in terms of colour removal, with decolourisation of (5500 to 11000 IU) and 42%, respectively [11].

In this research work, only defecation by hot liming was considered at different pH treatments for comparing the effect of saccharate liming over milk of lime without juice sulphitation.

As it was observed in Table 5 ICUMSA color data, the color for lime saccharate treated clear juice was with lower ICUMSA color compared to the MOL treated clear juice , indicating that saccharate liming has good efficiency in color removal in mixed juice clarification compared to the conventional milk of lime liming process.

As observed in Figure 17, with increasing pH for each treatments of pH 8.0, 8.5 and 9.0, the ICUMSA color were found increasing accordingly for both milk of lime and lime saccharate cases. In practice, that is due to color formation for heating the treated juice to boiling point at higher pH values without neutralization. Theoretically, higher pH values and high temperature with high retention time are a risk for reducing sugar (glucose and fructose) destruction resulting in formation of organic acids and further forming coloring products and impurities in the clear juice.

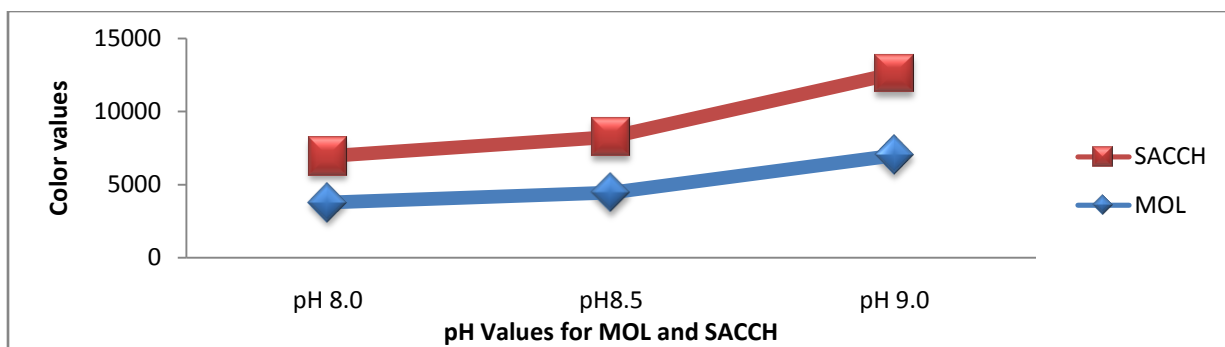


Figure 17: Color Comparison for MOL and SACCH

4.1.2 Turbidity values

For mixed juice samples treated at different pH values pH 8.0, 8.5 and 9 for both MOL and lime saccharate in the same operating conditions, the response parameters for their clear juice turbidity has been observed significantly different. For lime saccharate 30 ± 1.6 , 29 ± 2.2 and 111 ± 3.3 TU were found whereas 38 ± 0.11 , 65 ± 2.5 and 180 ± 1.6 TU were the turbidity values for the same samples respectively (Table 5). The data has indicated that saccharate liming has good efficiency in turbidity removal in mixed juice clarification compared to the conventional milk of lime liming process.

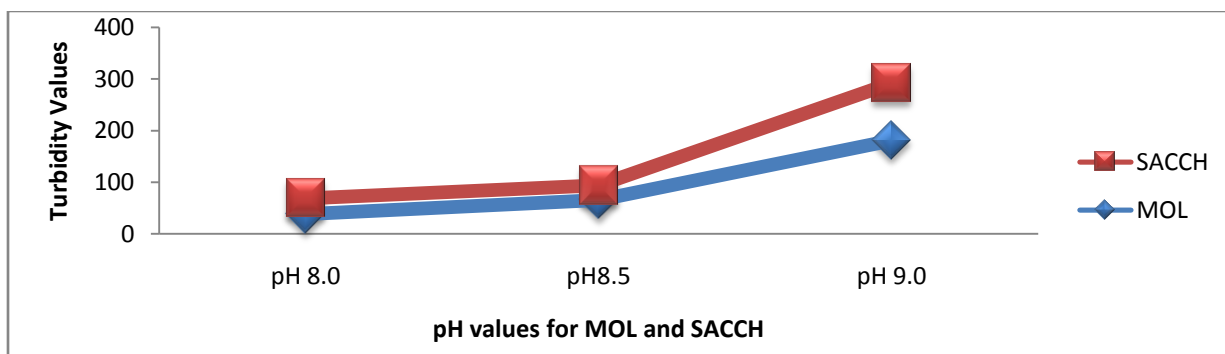


Figure 18: Turbidity Values Comparison for MOL and SACCH

In Figure 18, it was seen that with increasing pH for each treatments of pH 8.0, 8.5 and 9.0, the turbidity values were found increasing accordingly for both milk of lime and lime saccharate cases. In practice, that is due to impurities formation for heating the treated juice to boiling point at higher pH values without neutralization. Theoretically, higher pH values and high temperature with high retention time are a risk for reducing sugar (glucose and fructose) destruction resulting in formation of organic acids and further forming impurities in the clear juice.

4.1.3 CaO Content

For mixed juice samples treated at different pH values pH 8.0, 8.5 and 9 for both MOL and lime saccharate in the same operating conditions, the response parameters for their clear juice CaO content has been observed significantly different. For lime saccharate 624 ± 8.8 , 584 ± 23.0 and 611 ± 6.5 ppm CaO content were found whereas 888 ± 4.7 , 665 ± 26.9 and 738 ± 11.8 ppm were the CaO contents for the same samples respectively as recorded in Table 5. The data has indicated that saccharate liming has good efficiency in CaO content removal in mixed juice clarification compared to the conventional milk of lime liming process.

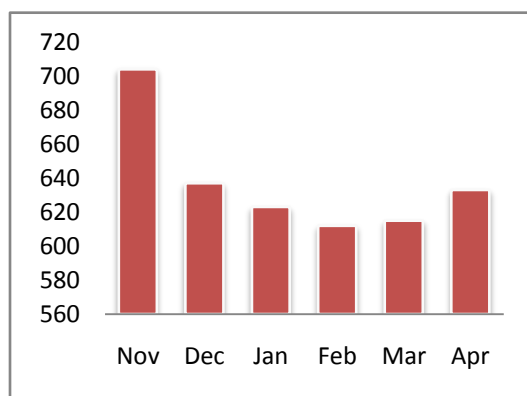
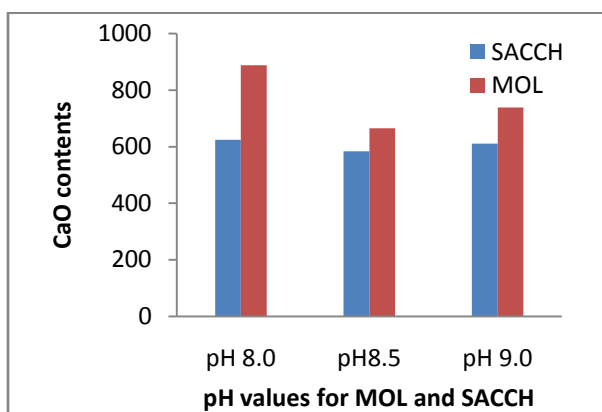


Figure 19: Cao Content in CJ for MOL and SACCH Figure 20: CaO content in CJ for Wonji (2019/2020)

In Figure 19, when comparing SACCH & MOL treatments, the CaO content for the SACCH was seen with lower values compared to the MOL treatments, indicating that SACCH liming has better performance in juice clarification compared to MOL liming defecation technique.

When comparing CaO content in clear juice for Wonji sugar factory (with mixed juice sulphitation in practice) of six months campaign 2019/2020 (data taken from quality control department) in Figure 20, compared to the CaO content in clear juice for SACCH liming even without mixed juice sulphitation were recorded similar in the range of 600 to 700 ppm for most treatments. This indicates how much mixed juice liming by SACCH has significant effect in reducing CaO content in clear juice.

In practice, lower CaO content in clear juice is appreciated from juice clarification point of view since higher CaO content in clear juice is one of the main causes for immediate fouling of juice evaporators resulting in poor performance of evaporators and finally resulting factory shut down for cleaning activities.

4.1.4 Settling Rate and CJ purity

In Table 5, it has been observed that almost for the three pH treatments option pH 8.0, 8.5 and 9.0, for the mixed juice treatment by milk of lime and lime saccharate, there was no significant difference for the settling rate and CJ purity in almost all treatment options, although SACCH treatments has shown better performance.

4.2 Data Analysis

All replicated data were statistically analyzed by SAS system to determine the significance among treatments of different response variables.

Table 6: ANOVA results Summary

Response Parameter	Mean	Type	F-Value	Pr >F	Coefficient of variation
Settling Rate	9.87	MOL	0.3	0.08686	18.5621
	10.05	SACCH			
CJ Purity	73.40	MOL	0.2	0.09026	17.9423
	74.37	SACCH			
Mud Volume	146.08	MOL	11.9	0.03115	21.8188
	127.30	SACCH			
Turbidity	74.56	MOL	40.8	0.0083	39.7963
	46.48	SACCH			
ICUMSA Color	4097.96	MOL	20.0	0.02004	24.4028
	3355.81	SACCH			
CaO Content	637.16	MOL	33.5	0.0109	20.7820
	511.01	SACCH			

As seen in Table 6, the SAS system has shown ICUMSA color, turbidity, Mud volume and CaO content for the CJs treated with SACCH compared to MOL-treated CJs have indicated that the model terms are significantly different for the values of "Prob > F" less than 0.05 for each treatments where as for CJ purity and Settling rate, the CJs treated with SACCH compared to MOL-treated CJs has indicated that the model terms are not significantly different for the values of "Prob > F" greater than 0.05. Distribution of Mud volume, distribution of ICUMSA color, distribution of turbidity and distribution of CaO content statistical data in Appendix C 3 , Appendix C 4, Appendix C 5 and Appendix C 6) have also clearly indicated that the SACCH treated CJ has lower values compared to CJ treated with MOL.

CHAPTER FIVE

5 Conclusion and Recommendation

5.1 Conclusion

The result of this research work has clearly indicated that saccharate liming juice clarification has advanced efficiency in improving clear juice color, turbidity, CaO content in clear juice and settling rate as compared to the conventional liming system. The statistical data analysis has shown that less ICUMSA color, less mud volume, less turbidity and less CaO content for the CJs treated with SACCH compared to MOL-treated CJs and similarly since the values of "Prob > F" for these parameters have shown less than 0.05, the model terms are significantly different. The good efficiency values obtained with SACCH compared with MOL were caused by the higher % Color removal, the higher % turbidity removal and the higher % CaO removal with SACCH.

The concrete change in the main juice clarification efficiency parameters, clear juice color, turbidity and CaO content in clear juice have great impact on overall operation of the factory. The performance parameters such as boiling house recovery, loss in final molasses and sugar quality are also affected by these parameters.

The most remarkable finding of the research lies on the significant reduction on CaO content in clear juice which has direct impact on performance of Juice evaporators and reduction in clear juice color by the use of lime saccharate instead of milk of lime which can directly improve the final product color.

This study also indicated that for a sugar factory in need of producing sugar without sulphitation, the use of lime saccharate is the best liming processes to be chosen for good quality sugar. Juice sulphitation is mainly applied for bleaching purpose. The use of lime saccharate instead of MOL reduces more colour in clear juice and therefore it can minimize the risk of highly off colored sugar in case of SO₂ gas generation plants failure like Wonji and other Sugar Factories in Ethiopia.

5.2 Recommendation

By implementation of lime saccharate juice clarification on a factory basis without extra investment with simple existing milk of lime line arrangement, the factory can achieve the most incredible benefits. In this case, the existing milk of lime preparation plant can be used for the preparation of lime saccharate with installation of instrumental devices to control the flow of syrup to the preparation tanks to acquire the right mono calcium saccharate. To achieve better clarification results, parameters like the desired density of lime saccharate, the desired concentration and temperature of syrup, the correct mixing time, and stability in the flow of juice need to be controlled.

This research work has focused only on comparison of MOL and SACCH in the defecation process. It is known that Sulphitation and Carbonation can further improve these efficiency parameters. Therefore, the factory can achieve more remarkable results by the use of lime saccharate together with the conventional juice sulphitation and these findings can also be applicable to other sugar factories in Ethiopia practicing juice sulphitation for production of plantation white sugar. In most of Ethiopian sugar factories including Wonji Shoa Sugar Factory, applying juice sulphitation, SO_2 gas generation failure is a recurring problem. Therefore, it is recommended to use lime saccharate liming process instead of Milk of lime (MOL) liming.

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APPENDICES

Appendix -A: Sugar Industry Terminology

Absolute Juice – All water containing all soluble (dissolved) solids from the cane. It thus equal to (cane – Fiber.)

Bagasse – The residual obtained from crushing cane. Its components are fiber, pith, water, solids, lost sucrose all water insoluble in the cane.

Cane – The raw material as delivered at the Factory weighbridge.

Clarified Juice – the Juice obtained after clarification and used as evaporator feed.

Diffuser Juice – The juice withdrawn from the cane or bagasse diffuser.

Fiber – the dry water insoluble component of cane. Natural fiber is the fiber with chemically bound Brix-free water present in its structure.

Hydrometer Brix – The percent by mass of soluble solid matter in a solution as indicated by a brix hydrometer..

Mixed Juice – The juice sent from the extraction plant to the boiling house.

Molasses – The mother liquor of massecuite separated from the crystal. It is distinguished by the same term as massecuite from which it was extracted. (A, B, C, molasses).

Plantation White Sugar– White sugar manufactured from basic raw material in a sugar mill for direct consumption

Pol:- The apparent sucrose content of a sugar product determined by direct or single polarization. Reading on the scale of polarimeter, indicating the apparent sucrose content of the sample to be analyzed. If the sample is a pure sugar solution, the Pol equals to sucrose percentage

Raw Sugar – The product of cane sugar factories which is an intermediate crystalline product resulting from the evaporation of water from sugar cane stalk juice.

Refractometer Brix – The percent by mass of soluble solid matter (sucrose & soluble non-sucrose) in a solution as indicated by a sugar refractometer.

Reducing Sugars – The reducing substances in the cane and its products calculated as invert sugar. (Glucose, Fructose)

Refined Sugar – High purity white sugar manufactured from remelted raw sugar.

Sucrose (Saccharose) – The pure chemical compound with the formula $C_{12}H_{22}O_{11}$. It is a true Pol, taking in to account the influence caused by the presence of other polarizing substances such as invert sugar.

Appendix – B Main equipment



Mixed Juice heater



Refractometer



Polarimeter



Spectrophotometer

Appendix –C: ANOVAs results of the response variables for the Milk of lime and lime saccharate clarification systems.

The SAS system

Class Level Information

Class Levels Values

Rep	2	1	2
Type	2	MOL	SACCH
pH	3	8.00	8.50 9.00

Number of Observations Read 12

Number of Observations Used 12

Dependent Variable: Purity

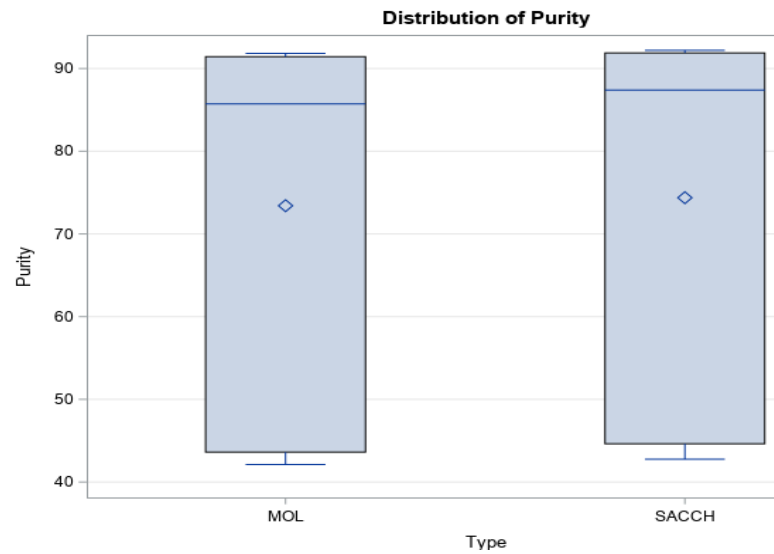
Source	DF	Type I SS	Mean Square	F Value	Pr > F	CoeffVar	Purity Mean
Rep	1	2518.072408	2518.072408	14.33	0.0068		
Type	1	2.832408	2.832408	00.2	0.09026	17.94236	73.89083
pH	2	1944.684717	972.342358	5.53	0.0362		

Purity LSD grouping

Type Estimate

SACCH 74.3787

MOL 73.4050



Appendix C 1: Distribution of Purity for MOL and SACCH

Dependent Variable: settling rate

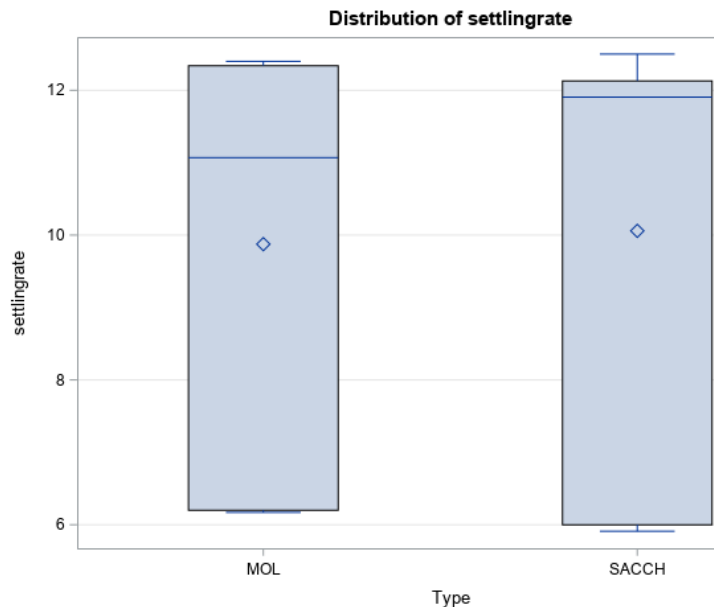
Source	DF	Type I SS	Mean Square	F Value	Pr > F	Coeff Var	Settling rate Mean
Rep	1	51.50163333	51.50163333	15.05	0.0061	18.56218	9.966667
Type	1	0.10083333	0.10083333	00.3	0.08686		
pH	2	17.87551667	8.93775833	2.61	0.1422		

Settling rate LSD grouping

Type Estimate

SACCH 10.0583

MOL 9.8750

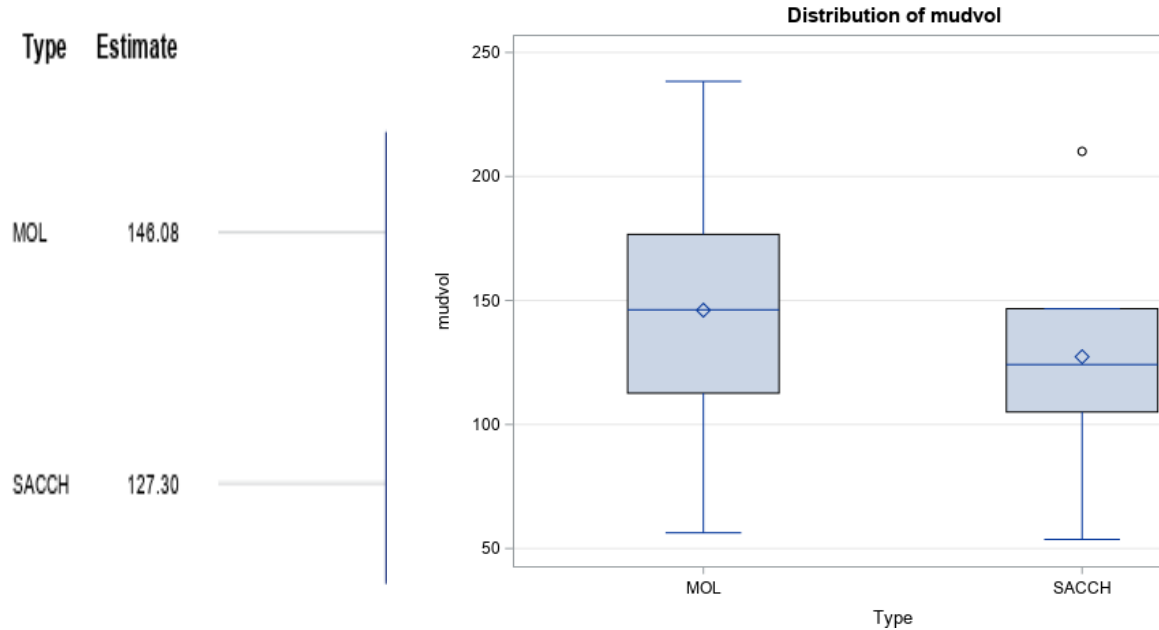


Appendix C 2: Distribution of settling rate for MOL and SACCH

Dependent Variable: mud volume

Source	DF	Type I SS	Mean Square	F Value	Pr > F	Coeff. Var	Mud vol Mean
Rep	1	9816.66403	9816.66403	11.04	0.0127	21.81882	136.6933
Type	1	1058.06520	1058.06520	11.9	0.03115		
pH	2	17774.45432	8887.22716	9.99	0.0089		

Mud volume LSD grouping

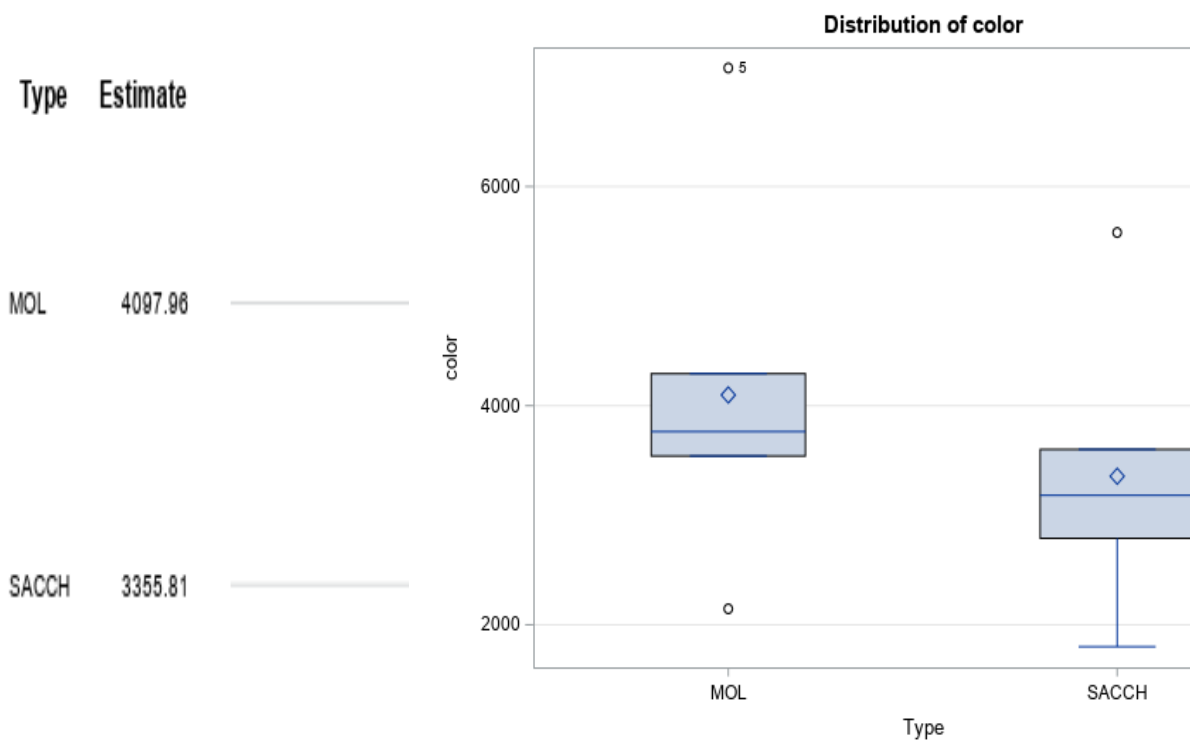


Appendix C 3: Distribution of mud volume for MOL and SACCH

Dependent Variable: ICUMSA color

Source	DF	Type I SS	Mean Square	F Value	Pr > F	Coeff. Var	color Mean
Rep	1	8532914.210	8532914.210	10.32	0.0148	24.40280	3726.885
Type	1	1652345.025	1652345.025	20.0	0.02004		
pH	2	6787094.689	3393547.345	4.10	0.0662		

ICUMSA color LSD grouping



Appendix C 4: Distribution of ICUMSA color for MOL and SACCH

Dependent Variable: turbidity

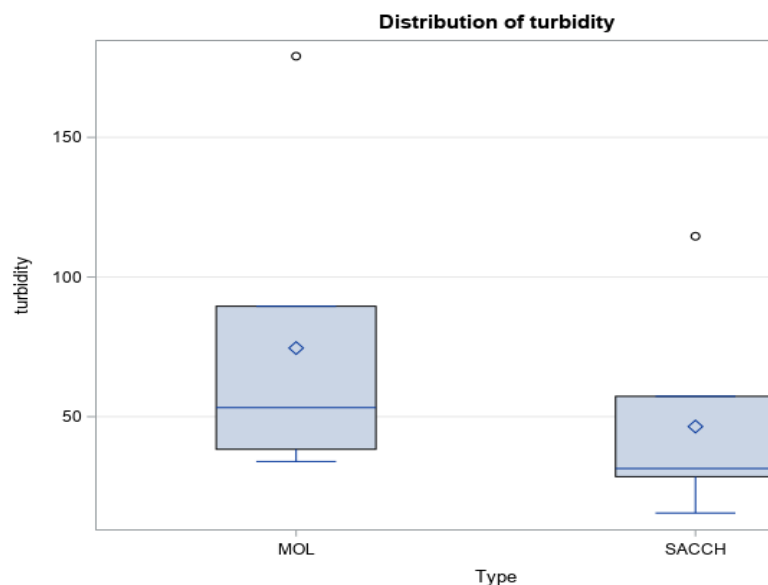
Source	DF	Type I SS	Mean Square	F Value	Pr > F	CoeffVar	turbidity Mean
Rep	1	3094.76201	3094.76201	5.34	0.0542	39.79634	60.51583
Type	1	2369.11101	2369.11101	40.8	0.00830		
pH	2	14780.32952	7390.16476	12.74	0.0046		

Turbidity LSD grouping

Type Estimate

MOL 74.5667

SACCH 46.4650



Appendix C 5: Distribution of turbidity for MOL and SACCH

Dependent Variable: CaO content

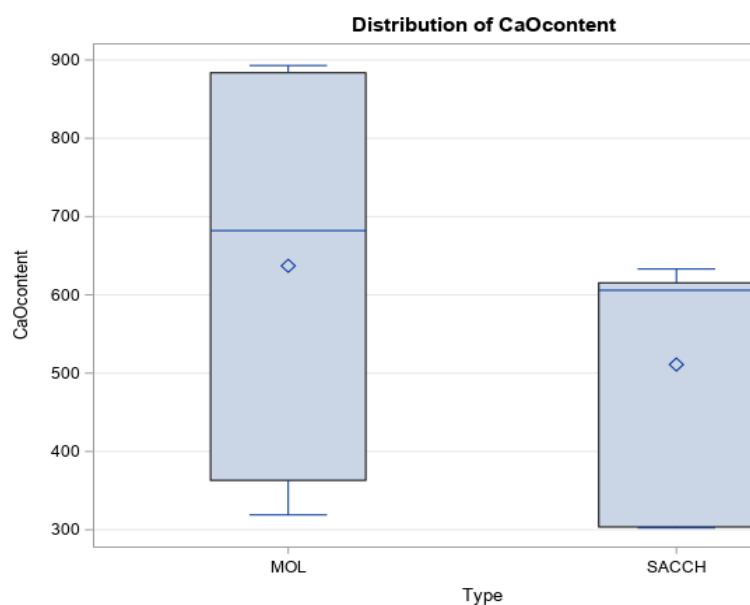
Source	DF	Type I SS	Mean Square	F Value	Pr > F	CoeffVar	CaO Mean
Rep	1	140041.4496	140041.4496	9.84	0.0165	20.78209	574.0833
Type	1	47746.5136	47746.5136	33.5	0.01097		
pH	2	201188.2917	100594.1458	7.07	0.0209		

CaO content LSD grouping

Type Estimate

MOL 637.16

SACCH 511.01



Appendix C 6: Distribution of CaO content for MOL and SACCH

Appendix D : Pol or Sucrose Factors According to Refractometer Solids (Brix values)

To obtain pol multiply the saccharimeter reading obtained from dry lead acetate clarification by the factor corresponding to the refractometer solids.

To obtain sucrose multiply the calculated sucrose reading by the factor:

Pol factor = 26

99.718 x a p. sp gr at 20°C/20°C

Example

Saccharimeter reading = 41.5

Refractometer solids (Ref Sol) = 11.50

Pol = 41.5 x 0.24920 = 10.34

Table 7: Pol or Sucrose Factors According to Refractometer Solids

Ref sol.	Pol factor									
	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.1	0.26064	0.26063	0.26062	0.26061	0.26060	0.26059	0.26057	0.26056	0.26055	0.26054
0.2	0.26053	0.26052	0.26051	0.26050	0.26049	0.26048	0.26047	0.26046	0.26045	0.26044
0.3	0.26043	0.26042	0.26041	0.26040	0.26039	0.26038	0.26037	0.26036	0.26035	0.26034
0.4	0.26033	0.26032	0.26031	0.26030	0.26029	0.26028	0.26027	0.26026	0.26025	0.26024
0.5	0.26023	0.26022	0.26021	0.26020	0.26019	0.26018	0.26017	0.26016	0.26015	0.26014
0.6	0.26013	0.26012	0.26011	0.26010	0.26009	0.26008	0.26007	0.26006	0.26005	0.26004
0.7	0.26003	0.26002	0.26001	0.26000	0.25999	0.25997	0.25996	0.25995	0.25994	0.25993
0.8	0.25992	0.25991	0.25990	0.25989	0.25988	0.25987	0.25986	0.25985	0.25984	0.25983
0.9	0.25982	0.25981	0.25980	0.25979	0.25978	0.25977	0.25976	0.25975	0.25974	0.25973
1.0	0.25972	0.25971	0.25970	0.25969	0.25968	0.25967	0.25966	0.25965	0.25964	0.25963
1.1	0.25962	0.25961	0.25960	0.25959	0.25958	0.25957	0.25956	0.25955	0.25954	0.25953
1.2	0.25952	0.25951	0.25950	0.25949	0.25948	0.25947	0.25946	0.25945	0.25944	0.25943
1.3	0.25942	0.25941	0.25940	0.25939	0.25938	0.25937	0.25936	0.25935	0.25934	0.25933
1.4	0.25932	0.25931	0.25930	0.25929	0.25928	0.25927	0.25926	0.25925	0.25924	0.25923
1.5	0.25922	0.25921	0.25920	0.25919	0.25918	0.25917	0.25916	0.25915	0.25914	0.25913
1.6	0.25912	0.25911	0.25910	0.25909	0.25908	0.25907	0.25906	0.25905	0.25904	0.25903
1.7	0.25902	0.25901	0.25900	0.25899	0.25898	0.25897	0.25896	0.25895	0.25894	0.25893
1.8	0.25892	0.25891	0.25890	0.25889	0.25888	0.25887	0.25886	0.25885	0.25884	0.25883
1.9	0.25882	0.25881	0.25880	0.25879	0.25878	0.25877	0.25876	0.25875	0.25874	0.25873
2.0	0.25872	0.25871	0.25870	0.25869	0.25868	0.25867	0.25866	0.25865	0.25864	0.25863
2.1	0.25862	0.25861	0.25860	0.25859	0.25858	0.25857	0.25856	0.25855	0.25854	0.25853
2.2	0.25852	0.25851	0.25850	0.25849	0.25848	0.25846	0.25845	0.25844	0.25843	0.25842
2.3	0.25841	0.25840	0.25839	0.25838	0.25837	0.25836	0.25835	0.25834	0.25833	0.25832
2.4	0.25831	0.25830	0.25829	0.25828	0.25827	0.25826	0.25825	0.25824	0.25823	0.25822
2.5	0.25821	0.25820	0.25819	0.25818	0.25817	0.25816	0.25815	0.25814	0.25813	0.25812
2.6	0.25811	0.25810	0.25809	0.25808	0.25807	0.25806	0.25805	0.25804	0.25803	0.25802
2.7	0.25801	0.25800	0.25799	0.25798	0.25797	0.25796	0.25795	0.25794	0.25793	0.25792
2.8	0.25791	0.25790	0.25789	0.25788	0.25787	0.25786	0.25785	0.25784	0.25783	0.25782
2.9	0.25781	0.25780	0.25779	0.25778	0.25777	0.25776	0.25775	0.25774	0.25773	0.25772
3.0	0.25771	0.25770	0.25769	0.25768	0.25767	0.25766	0.25765	0.25764	0.25763	0.25762
3.1	0.25761	0.25760	0.25759	0.25758	0.25757	0.25756	0.25755	0.25754	0.25753	0.25752
3.2	0.25751	0.25750	0.25749	0.25748	0.25747	0.25746	0.25745	0.25744	0.25743	0.25742
3.3	0.25741	0.25740	0.25739	0.25738	0.25737	0.25736	0.25735	0.25734	0.25733	0.25732
3.4	0.25731	0.25730	0.25729	0.25728	0.25727	0.25726	0.25725	0.25724	0.25723	0.25722
3.5	0.25721	0.25720	0.25719	0.25718	0.25717	0.25716	0.25715	0.25714	0.25713	0.25712
3.6	0.25711	0.25710	0.25709	0.25708	0.25707	0.25706	0.25705	0.25704	0.25703	0.25702
3.7	0.25701	0.25700	0.25699	0.25698	0.25697	0.25696	0.25695	0.25694	0.25693	0.25692
3.8	0.25691	0.25690	0.25689	0.25688	0.25687	0.25686	0.25685	0.25684	0.25683	0.25682

Ref sol.	Pol factor									
	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
4.0	0.25671	0.25670	0.25669	0.25668	0.25667	0.25666	0.25665	0.25664	0.25663	0.25662
4.1	0.25661	0.25660	0.25659	0.25658	0.25657	0.25656	0.25655	0.25654	0.25653	0.25652
4.2	0.25651	0.25650	0.25649	0.25648	0.25647	0.25746	0.25645	0.25644	0.25643	0.25642
4.3	0.25641	0.25640	0.25639	0.25638	0.25637	0.25636	0.25635	0.25634	0.25633	0.25632
4.4	0.25631	0.25630	0.25629	0.25628	0.25627	0.25626	0.25625	0.25624	0.25623	0.25622
4.5	0.25621	0.25620	0.25619	0.25618	0.25617	0.25616	0.25615	0.25614	0.25613	0.25612
4.6	0.25610	0.25609	0.25608	0.25607	0.25606	0.25605	0.25604	0.25603	0.25602	0.25601
4.7	0.25600	0.25599	0.25598	0.25597	0.25596	0.25595	0.25594	0.25593	0.25592	0.25591
4.8	0.25590	0.25589	0.25588	0.25587	0.25586	0.25585	0.25584	0.25583	0.25582	0.25581
4.9	0.25580	0.25579	0.25578	0.25577	0.25576	0.25575	0.25574	0.25573	0.25572	0.25571
5.0	0.25570	0.25569	0.25568	0.25567	0.25566	0.25565	0.25564	0.25563	0.25562	0.25561
5.1	0.25560	0.25559	0.25558	0.25557	0.25556	0.25555	0.25554	0.25553	0.25552	0.25551
5.2	0.25550	0.25549	0.25548	0.25547	0.25546	0.25545	0.25544	0.25543	0.25542	0.25541
5.3	0.25540	0.25539	0.25538	0.25537	0.25536	0.25535	0.25534	0.25533	0.25532	0.25531
5.4	0.25530	0.25529	0.25528	0.25527	0.25526	0.25525	0.25524	0.25523	0.25522	0.25521
5.5	0.25520	0.25519	0.25518	0.25517	0.25516	0.25515	0.25514	0.25513	0.25512	0.25511
5.6	0.25510	0.25509	0.25508	0.25507	0.25506	0.25505	0.25504	0.25503	0.25502	0.25501
5.7	0.25500	0.25499	0.25498	0.25497	0.25496	0.25495	0.25494	0.25493	0.25492	0.25491
5.8	0.25490	0.25489	0.25488	0.25487	0.25486	0.25485	0.25484	0.25483	0.25482	0.25481
5.9	0.25480	0.25479	0.25478	0.25477	0.25476	0.25475	0.25474	0.25473	0.25472	0.25471
6.0	0.25470	0.25469	0.25468	0.25467	0.25466	0.25465	0.25464	0.25463	0.25462	0.25461
6.1	0.25460	0.25459	0.25458	0.25457	0.25456	0.25455	0.25454	0.25453	0.25452	0.25451
6.2	0.25450	0.25449	0.25448	0.25447	0.25446	0.25445	0.25444	0.25443	0.25442	0.25441
6.3	0.25440	0.25439	0.25438	0.25437	0.25436	0.25435	0.25434	0.25433	0.25432	0.25431
6.4	0.25430	0.25429	0.25428	0.25427	0.25426	0.25425	0.25424	0.25423	0.25422	0.25421
6.5	0.25420	0.25419	0.25418	0.25417	0.25416	0.25415	0.25414	0.25413	0.25412	0.25411
6.6	0.25410	0.25409	0.25408	0.25407	0.25406	0.25405	0.25404	0.25403	0.25402	0.25401
6.7	0.25400	0.25399	0.25398	0.25397	0.25396	0.25395	0.25394	0.25393	0.25392	0.25391
6.8	0.25390	0.25389	0.25388	0.25387	0.25386	0.25385	0.25384	0.25383	0.25382	0.25381
6.9	0.25380	0.25379	0.25378	0.25377	0.25376	0.25375	0.25374	0.25373	0.25372	0.25371
7.0	0.25370	0.25369	0.25368	0.25367	0.25366	0.25365	0.25364	0.25363	0.25362	0.25361
7.1	0.25360	0.25359	0.25358	0.25357	0.25356	0.25355	0.25354	0.25353	0.25352	0.25351
7.2	0.25350	0.25349	0.25348	0.25347	0.25346	0.25746	0.25344	0.25343	0.25342	0.25341
7.3	0.25340	0.25339	0.25338	0.25337	0.25336	0.25335	0.25334	0.25333	0.25332	0.25331
7.4	0.25330	0.25329	0.25328	0.25327	0.25326	0.25325	0.25324	0.25323	0.25322	0.25321
7.5	0.25320	0.25319	0.25318	0.25317	0.25316	0.25315	0.25314	0.25313	0.25312	0.25311
7.6	0.25310	0.25309	0.25308	0.25307	0.25306	0.25305	0.25304	0.25303	0.25302	0.25301
7.7	0.25300	0.25299	0.25298	0.25297	0.25296	0.25295	0.25294	0.25293	0.25292	0.25291
7.8	0.25290	0.25289	0.25288	0.25287	0.25286	0.25285	0.25284	0.25283	0.25282	0.25281
7.9	0.25280	0.25279	0.25278	0.25277	0.25276	0.25275	0.25274	0.25273	0.25272	0.25271
8.0	0.25270	0.25269	0.25268	0.25267	0.25266	0.25265	0.25264	0.25263	0.25262	0.25261
8.1	0.25260	0.25259	0.25258	0.25257	0.25256	0.25255	0.25254	0.25253	0.25252	0.25251
8.2	0.25250	0.25249	0.25248	0.25247	0.25246	0.25245	0.25244	0.25243	0.25242	0.25241
8.3	0.25240	0.25239	0.25238	0.25237	0.25236	0.25235	0.25234	0.25233	0.25232	0.25231
8.4	0.25230	0.25229	0.25228	0.25227	0.25226	0.25225	0.25224	0.25223	0.25222	0.25221
8.5	0.25220	0.25219	0.25218	0.25217	0.25216	0.25215	0.25214	0.25213	0.25212	0.25211
8.6	0.25210	0.25209	0.25208	0.25207	0.25206	0.25205	0.25204	0.25203	0.25202	0.25201
8.7	0.25200	0.25199	0.25198	0.25197	0.25196	0.25195	0.25194	0.25193	0.25192	0.25191
8.8	0.25190	0.25189	0.25188	0.25187	0.25186	0.25185	0.25184	0.25183	0.25182	0.25181
8.9	0.25180	0.25179	0.25178	0.25177	0.25176	0.25175	0.25174	0.25173	0.25172	0.25171
9.0	0.25170	0.25169	0.25168	0.25167	0.25166	0.25165	0.25164	0.25163	0.25162	0.25161
9.1	0.25160	0.25159	0.25158	0.25157	0.25156	0.25155	0.25154	0.25153	0.25152	0.25151
9.2	0.25150	0.25149	0.25148	0.25147	0.25146	0.25145	0.25144	0.25143	0.25142	0.25141
9.3	0.25140	0.25139	0.25138	0.25137	0.25136	0.25135	0.25134	0.25133	0.25132	0.25131
9.4	0.25130	0.25129	0.25128	0.25127	0.25126	0.25125	0.25124	0.25123	0.25122	0.25121
9.5	0.25120	0.25119	0.25118	0.25117	0.25116	0.25115	0.25114	0.25113	0.25112	0.25111

Ref sol.	Pol factor									
	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
9.6	0.25110	0.25109	0.25108	0.25107	0.25106	0.25105	0.25104	0.25103	0.25102	0.25101
9.7	0.25100	0.25099	0.25098	0.25097	0.25096	0.25095	0.25094	0.25093	0.25092	0.25091
9.8	0.25090	0.25089	0.25088	0.25087	0.25086	0.25085	0.25084	0.25083	0.25082	0.25081
9.9	0.25080	0.25079	0.25078	0.25077	0.25076	0.25075	0.25074	0.25073	0.25072	0.25071
10.0	0.25070	0.25069	0.25068	0.25067	0.25066	0.25065	0.25064	0.25063	0.25062	0.25061
10.1	0.25060	0.25059	0.25058	0.25057	0.25056	0.25055	0.25054	0.25053	0.25052	0.25051
10.2	0.25050	0.25049	0.25048	0.25047	0.25046	0.25045	0.25044	0.25043	0.25042	0.25041
10.3	0.25040	0.25039	0.25038	0.25037	0.25036	0.25035	0.25034	0.25033	0.25032	0.25031
10.4	0.25030	0.25029	0.25028	0.25027	0.25026	0.25025	0.25024	0.25023	0.25022	0.25021
10.5	0.25020	0.25019	0.25018	0.25017	0.25016	0.25015	0.25014	0.25013	0.25012	0.25011
10.6	0.25010	0.25009	0.25008	0.25007	0.25006	0.25005	0.25004	0.25003	0.25002	0.25001
10.7	0.25000	0.24999	0.24998	0.24997	0.24996	0.24995	0.24994	0.24993	0.24992	0.24991
10.8	0.24990	0.24989	0.24988	0.24987	0.24986	0.24985	0.24984	0.24983	0.24982	0.24981
10.9	0.24980	0.24979	0.24978	0.24977	0.24976	0.24975	0.24974	0.24973	0.24972	0.24971
11.0	0.24970	0.24969	0.24968	0.24967	0.24966	0.24965	0.24964	0.24963	0.24962	0.24961
11.1	0.24960	0.24959	0.24958	0.24957	0.24956	0.24955	0.24954	0.24953	0.24952	0.24951
11.2	0.24950	0.24949	0.24948	0.24947	0.24946	0.25746	0.24944	0.24943	0.24942	0.24941
11.3	0.24940	0.24939	0.24938	0.24937	0.24936	0.24935	0.24934	0.24933	0.24932	0.24931
11.4	0.24930	0.24929	0.24928	0.24927	0.24926	0.24925	0.24924	0.24923	0.24922	0.24921
11.5	0.24920	0.24919	0.24918	0.24917	0.24916	0.24915	0.24914	0.24913	0.24912	0.24911
11.6	0.24910	0.24909	0.24908	0.24907	0.24906	0.24905	0.24904	0.24903	0.24902	0.24901
11.7	0.24900	0.24899	0.24898	0.24897	0.24896	0.24895	0.24894	0.24893	0.24892	0.24891
11.8	0.24890	0.24889	0.24888	0.24887	0.24886	0.24885	0.24885	0.24884	0.24883	0.24882
11.9	0.24881	0.24880	0.24879	0.24878	0.24877	0.24876	0.24875	0.24874	0.24873	0.24872
12.0	0.24871	0.24870	0.24869	0.24868	0.24867	0.24866	0.24865	0.24864	0.24863	0.24862
12.1	0.24861	0.24860	0.24859	0.24858	0.24857	0.24856	0.24855	0.24854	0.24853	0.24852
12.2	0.24851	0.24850	0.24849	0.24848	0.24847	0.25746	0.24845	0.24844	0.24843	0.24842
12.3	0.24841	0.24840	0.24839	0.24838	0.24837	0.24836	0.24835	0.24834	0.24833	0.24832
12.4	0.24831	0.24830	0.24829	0.24828	0.24827	0.24826	0.24825	0.24824	0.24823	0.24822
12.5	0.24821	0.24820	0.24819	0.24818	0.24817	0.24816	0.24815	0.24814	0.24813	0.24812
12.6	0.24811	0.24810	0.24809	0.24808	0.24807	0.24806	0.24805	0.24804	0.24803	0.24802
12.7	0.24801	0.24800	0.24799	0.24798	0.24797	0.24796	0.24795	0.24794	0.24793	0.24792
12.8	0.24791	0.24790	0.24789	0.24788	0.24787	0.24786	0.24785	0.24784	0.24783	0.24782
12.9	0.24781	0.24780	0.24779	0.24778	0.24777	0.24776	0.24775	0.24774	0.24773	0.24772
13.0	0.24771	0.24770	0.24769	0.24768	0.24767	0.24766	0.24765	0.24764	0.24763	0.24762
13.1	0.24761	0.24760	0.24759	0.24758	0.24757	0.24756	0.24755	0.24754	0.24753	0.24752
13.2	0.24751	0.24750	0.24749	0.24748	0.24747	0.25746	0.24745	0.24744	0.24743	0.24742
13.3	0.24741	0.24740	0.24739	0.24738	0.24737	0.24736	0.24735	0.24734	0.24733	0.24732
13.4	0.24731	0.24730	0.24729	0.24728	0.24727	0.24726	0.24725	0.24724	0.24723	0.24722
13.5	0.24721	0.24720	0.24719	0.24718	0.24717	0.24716	0.24715	0.24714	0.24713	0.24712
13.6	0.24711	0.24710	0.24709	0.24708	0.24707	0.24706	0.24705	0.24704	0.24703	0.24702
13.7	0.24701	0.24700	0.24699	0.24698	0.24697	0.24696	0.24695	0.24694	0.24693	0.24692
13.8	0.24691	0.24690	0.24689	0.24688	0.24687	0.24686	0.24685	0.24684	0.24683	0.24682
13.9	0.24681	0.24680	0.24679	0.24678	0.24677	0.24676	0.24675	0.24674	0.24673	0.24672
14.0	0.24671	0.24670	0.24969	0.24668	0.24667	0.24666	0.24665	0.24664	0.24663	0.24662
14.1	0.24661	0.24660	0.24959	0.24658	0.24657	0.24656	0.24655	0.24654	0.24653	0.24652
14.2	0.24651	0.24650	0.24949	0.24648	0.24647	0.25746	0.25746	0.24645	0.24644	0.24643
14.3	0.24642	0.24641	0.24640	0.24639	0.24638	0.24637	0.24636	0.24635	0.24634	0.24633
14.4	0.24632	0.24631	0.24630	0.24629	0.24628	0.24627	0.24626	0.24625	0.24624	0.24623
14.5	0.24622	0.24621	0.24620	0.24619	0.24618	0.24617	0.24616	0.24615	0.24614	0.24613
14.6	0.24612	0.24611	0.24610	0.24609	0.24608	0.24607	0.24606	0.24605	0.24604	0.24603
14.7	0.24602	0.24601	0.24600	0.24599	0.24598	0.24597	0.24596	0.24595	0.24594	0.24593
14.8	0.24592	0.24591	0.24590	0.24589	0.24588	0.24587	0.24586	0.24585	0.24584	0.24583
14.9	0.24582	0.24581	0.24580	0.24579	0.24578	0.24577	0.24576	0.24575	0.24574	0.24573
15.0	0.24572	0.24571	0.24570	0.24569	0.24568	0.24567	0.24566	0.24565	0.24564	0.24563