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**SYRUP CLARIFICATION USING FLOTATION SYSTEM WITH
OPTIMIZED DOSAGES OF PHOSPHATE AND CATIONIC
FLOCCULANT: THE CASE OF WONJI SUGAR FACTORY**

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master
of Science in Biochemical Engineering

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Syrup clarification using flotation system with optimized dosages of phosphate and cationic flocculant.

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List of Acronyms.....IX

PWS.....plantation white sugar

DOE.....design of experiments

ICUMSA.....International Commission
for Uniform Methods of Sugar Analysis

USD.....United states dollar

GTP.....Growth and Transformation Plan

MWh.....Megawatt per hour

TCD.....Tons of cane per day

DAF.....Dissolved air flotation

DS.....Dry solids

CD.....Drag coefficient

CHM.....Crystal habit modifiers

CCD.....Central composition design

CFD.....Computational flood dynamics

SASTA.....South African Sugar Technology Association

VHP.....very high pool

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ABSTRACT

Syrup is a clarified juice evaporated to approximately 65% dry solids in a stepwise evaporation process. This concentrated syrup is needed to clarify further before the final fractionation. All Ethiopian sugar factories are designed for the production of plantation white sugar (PWS) by double sulphitation system which is the main source of an increased residual sulphur dioxide in the final product. There is a significant interest in many sugar producing countries towards producing a higher quality plantation white sugar with lower color and lower residual sulphur dioxide content. A sugar with a lower color and lower residual sulphur dioxide values is achieved by replacing the syrup sulfitation process with syrup phosphatation and flocculation. The study was conducted to optimize the syrup clarification as the result of the effect of Talodura and Phosphate on reducing color, turbidity and viscosity using flotation system and there by modifying or reducing the sulfate content in the sugar. This increased sulfate is due to syrup double sulfitation during syrup clarification at Wonji Sugar Factory. Since degree of clarification is dependent on the dose of Phosphate and Talodura flocculant, optimization of the doses was carried out against color, turbidity and reduction of viscosity. Design Expert 7 and JMP13 software were used to determine the common optimum doses. The range of levels of the P_2O_5 used was 117.8 - 680 mg/L, and that of the Talodura was 7.2 - 12.8 mg/L. The optimum levels, 668 mg/L of P_2O_5 and 12 mg/L of Talodura gave color and turbidity values of 9772 and 4669 ICUMSA respectively and a viscosity reduction of 39 %. Practicing the above optimum conditions at Wonji Sugar Factory could increase productivity and sugar quality.

Keywords: *Color, Phosphate, Syrup clarification, Talodura, Turbidity, Viscosity,*

CHAPTER 1 INTRODUCTION

1.1 Background of the study

The production of raw sugar from sugarcane consists of a series of units of operations, which begins with the extraction of the cane juice from the cane stalks and subsequent removal of the non-sugars. This process is summarized in figure 1. 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. The limed juice is then allowed to settle out suspended particles in a clarifier. Following the juice cleaning process the clear or clarified juice is then evaporated to approximately 65% dry solids (DS) in a stepwise evaporation process. Then the juice, which is now concentrated syrup, is formed and need to be further clarified before put through a final fractionation of sugars from non-sugars by crystallization in vacuum pans via evaporation and concentration and in crystallizers by cooling. (Broadhurst, 2002)

It is expected that the increasing interest in the production of both plantation white sugar and raw sugar of high quality will focus attention on raw syrup quality in the factory. Having identified undesirable impurities of raw syrup, steps can be taken in the factory to reduce the levels of these impurities in the pan feed syrup. The nature of impurities determines the methods of clarification to choose. In the case of process generated colorants', preventative measures such as inhibition of color formation by juice sulphitation are likely to prove increasingly attractive. Levels of other impurities such as insoluble and gums which, although present in relatively small quantities, affect sugar quality and factory recovery can be reduced at reasonable cost by clarification of the raw syrup. The removal of such impurities has proved attractive to factories producing plantation white sugar. Improvements in recovery indicated from the viscosity reducing effect of syrup clarification; is also likely to generate interest in the industry. (Bennett, *et.al* 1977)

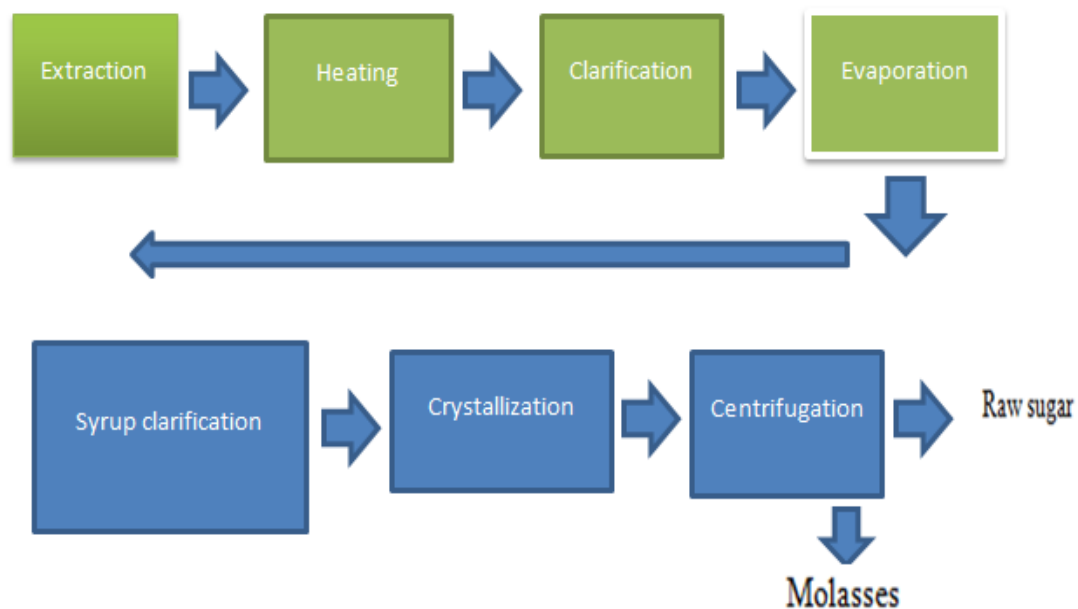


Figure 1.1 Process of the cane juice from the cane stalks and subsequent removal of the non-sugars, Broadhurst, 2002.

They are two ways of obtaining low color syrup that leads low color sugar. One way of obtaining low color sugar which is conventional is operating sulfitation on evaporator syrup (syrup taken from evaporator after clarified juice evaporation). Lime or lime saccharate is added, and then sulfur dioxide. Adding sulfur dioxide on syrup is called double sulfitation because ones sulfur dioxide is added to the juice clarification to achieve better color of sugar juice. By this time Ethiopian sugar factories are designed and working for production of plantation white sugar (PWS) by double sulphitation system which produces the traces of sulfur remain in these food product (sugar) and hazardous to human health.

In double sulfitation system the raw juice is heated to 75°C and pre limed to PH 9.2. Sulfur dioxide is first applied which neutralizes the alkalinity reacting with lime and forming calcium sulphite precipitate in the clarification process. In the second phase sulfur dioxide is again added in syrup treatment to PH 5.4 to reduce the viscosity of the syrup and massequite and improve molasses exhaustion. But the treated syrup is left acidic during its retention time in take case and the crystallization process in vacuum pan is carried out in turn affects sugar recovery. The treatment of the syrup with SO₂ is known also to reduce sugar color by just 6-15% (kulkami, 2009)

Syrup sulphitation also doesn't remove suspended solids and impurities like bagacillo and colloidal matter that may have escaped screening process, which adversely affect the crystallization, curing of massecuite and quality of sugar. This realization encouraged the development of an alternative technology that would avoid at least syrup sulfitation and help in producing good quality PWS sugar. (Bennet, 1971)

The second method which is new technology or alternative technology is Syrup clarification using flotation process. The basis of this process is based on the Phosphoflotation and froth flotation, conveniently termed as 'phosphoflotation' process applied in sugar refineries. Since the syrup liquor is very viscous, at about 65°Brix, clarification is done by flotation. Air is used to aerate the flocculated particles so that they float and are removed at the top of the clarifier as scum. The treated syrup is drawn from the bottom of the clarifier and sent to vacuum boiling pans to crystallize out the sugar. The mechanism involves physical capture of the air bubbles within the flocs and intermolecular attractions across the air/liquid interface. Scum can be floated off with bubbles in the clarifier. The degree of separation achieved depends on the surface properties of the solid particles.

Laboratory and factory scale trials on syrup clarification conducted by sugar research institute of Australia dated back 1960 assess the benefits of phosphitation clarification of syrup to improve the sugar quality. It was demonstrated that a process of heating syrup 76°C to 86°C and addition of phosphoric acid and lime would cause precipitation of calcium phosphate scum that included fats, waxes, proteins and ash constituents. This is done by investigated the use of specialty chemicals like Talofloc (cationic color removal agent) and Taloflote (polyacrylamide flocculant). A similar flocculant, Talodura was subsequently developed for use in syrup clarification.

Like other Ethiopian sugar factories Wonji Shoa Sugar Factory is also using the syrup double sulfitation even though two types of syrup clarification plants; syrup clarifier using flotation method and that of clarifier using sulfitation were planted. The second method which is syrup clarification using flotation system has installed in Wonji case and has many advantages over that of syrup sulfitation but it doesn't start working in this sugar factory yet.

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The efficiency of syrup clarification using flotation system highly depends on optimized dosages of factors like: flocculants added and phosphates to get good results on reduction of color, turbidity and viscosity. The variability in the composition of the juice as a result of differing geographical location, cane variety and seasonal influence as well as the conditions to which the cane is subjected during harvesting and transportation makes the nature of the research to be area specific; hence, there is no universal dose of phosphate and flocculent so as to produce the best possible quality clear syrup. Each factory is therefore essentially unique and adopts a system of clarification based on their own process with modifications usually determined by a combination of research and experience.



Figure 1.2 Wonji syrup clarification plants

1.2 Statement of the problem

Increased export prospects, increasing consumer awareness for hygiene and the changing habits by small packs are becoming more popular and are changed from time to time. Save for the right price consistently superior quality sugar is vital to securing a long-term advantage for the sugar industry. The insoluble matters content with large variations makes the sugar unsuitable for consumption by specialty consumer. Sugar cane juice is composed of various constituents like chlorophyll, xanthophyll, antherocynines & cynines etc. Most of them are removed during processing but some of them passes through syrup like colloidal substances, color causing impurities, gums, dextran, polysaccharides, bagacillo, in organic precipitates etc. This increases viscosities & resulting losses. The presence of sulfur di-oxide, calcium oxide, ash & reducing sugars makes it unacceptable for export purpose. Poor keeping quality and low color removal are common problems for double sulphitation.

There is also loss which is higher when double sulphitation is practiced to make mill-white sugar, due to the low pH reached in the syrup sulphitation stage. Syrup sulphitation is the process in which the pH of the syrup is reduced to a value of about 5, or in extreme cases, to as low as 4. Because of the high sensitivity of observed color to pH the resulting low pH syrup has lower color and, in addition, some insoluble material is dissolved under these acid conditions. However, the sugar produced from such low pH syrup has poor keeping quality and the color increases rapidly during storage. Furthermore, process losses through inversion are high. (Bennett, *et.al* 1977)

Sulfur dioxide (SO₂) is toxic gas. When it is used during the manufacture of any food product residual traces of sulfur remaining in such food product is hazardous to human health. In the sulphitation process, the use of sulfur burner is difficult as it causes the toxic (SO₂) to be released into atmosphere, leading to serious environmental pollution because of this potent greenhouse gas. It can also create health problems for the workers handling the sulfur burners. The cost of repair of sulfur burner plant is so high due to corrosion effect of sulphur. (Biotech, 2009)

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Syrup sulphitation end up significant amounts of sulfur and hence it affects the fermentation of the molasses by inhibiting the growth of the yeast. Moreover, traces of the sulfur that gets into the alcohol make it unsuitable for use as a fuel supplement, liquor, and pharmaceutical industries, unless further refinements are carried out. Thus the use of SO₂ in syrup does not provide any significant benefit. Further, whatever benefit does result lasts only for a short period of time. (Bennett, *et.al* 1977)

Currently, all Ethiopian sugar factories were designed for the production of plantation white sugar (PWS) by double sulphitation system which is the main source for the increased residual sulphur dioxide in the final product. There is significant interest in many sugar producing countries towards producing a higher quality plantation white sugar with lower color and lower residual sulphur dioxide content due to this residual sulphur dioxide is harmful in consumption. (Mohammed, 2013)

This realization prompted the development of an alternative technology that would avoid at least syrup sulphitation and help in producing good quality sugar. One option to replace the second sulfitation process is to use syrup clarification based on the phosphoflotation process. The phosphoflotation process can reduce color compounds that are produced during the factory processes. Such color and color precursor groups include melanoidins, caramels and alkaline degradation products of fructose and glucose. This research project was initiated to investigate the best working dosages of Talodura flocculant and phosphate on the benefits and methods of improving syrup clarification and to look at the results thus far in the review of syrup clarification as a possible technology for better sugar quality, specifically sugar color, reduced turbidity, viscosity.

1.3 Objectives

1.3.1 General objectives

- To study syrup clarification system using flotation process with optimized phosphate and cationic flocculants in Wonji Sugar Factory.

1.3.2 Specific objectives

- To analyze the raw syrup from Wonji Sugar Factory prior to clarification.
- To conduct the syrup clarification process using flotation system on the laboratory scale.
- To determine the dosage of phosphate and cationic flocculants that should be added for better clarification.
- To analyze the clarified syrup (color, turbidity, viscosity reduction) with the syrup clarification technology.
- To Optimize the effect of phosphate and cationic flocculants using central composite design using the DOE and JMP software.

1.4 Significance of the Study

The syrup clarification process is low cost solution both from the capital costs point of view as well as sugar operational costs in relation to the gains to be made by the sugar refinery factories. Syrup clarification system using flotation process ends with: Improvement in sugar quality with lower ICUMSA value and lower SO₂ contents, reduction in viscosity of syrup which in turn improves the pan flour working and these results in better exhaustion of molasses, increased boiling house capacity, reduction of final molasses % cane, rise in purity from unsulphered syrup to clear syrup. Which means: Faster boiling, leading to increased pan equity, faster purging to increased centrifugal capacity, reduction in non-sugars % leading to lower final molasses quantity and rise in purity, leading to higher boiling house recovery.

CHAPTER 2 LITERATURE REVIEW

2.1 The Sugar Industry general overview

Sugar is produced from cane and beet in over 130 countries in which sugar produced from sugarcane contributes about 65 to 70 % of global production. Brazil, India and China are leading countries and 85 percent of production was contributed by the top 15 producer countries. Moreover, in the last 50 years these countries were leading the industry. Ethiopia is one of sugar producing country from sugarcane and contributes about 0.18 % of the global sugar production. 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. (Girum Asfaw, 2015)

Commercial sugar production in Ethiopia was started in 1954 with the establishment of Wonji Sugar Factory. Since then, sugar is produced from irrigated and semi-mechanized sugarcane farms owned by the sugar estates and some out growers' scheme. Currently Ethiopia has about 45,000 ha of cultivated sugarcane farm that supplies cane only for three operating sugar factories (Wonji, Metahara and Finchaa) to produce annually about 460,000 tons of sugar. Finchaa and Metahara also produce about 20,000,000 and 15, 000, 000 liters of ethanol respectively and blended at 10 % with benzene for transport sector. The sugar industry is self-sufficient in term of its thermal and electric demand from cogeneration. The sugar industry contributed to the country's socioeconomic benefit by creating more than 28,000 employees. (Girum Asfaw, 2015)

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 on the three sugar state, namely Wonji, Metahara and Finchaa. Moreover, a new factory in Afar regional state, Tendaho Sugar factory, has begun to produce raw sugar as raw material for back end factory for refined production. The

countries five years Growth and Transformation Plan (GTP) which was launched in 2003 E.C. has given paramount emphasis to the sugar industry which demands huge technology development, dissemination and manpower training. At the end of the five years, it is planned to produce 2,250,000 tons of sugar and out of this to export 1,246,000 tons by establishing eight or nine huge sugar factories. The plan also targeted to produce 304,000 m³ ethanol and 606,943 MWh electric powers from cogeneration. (Girum Asfaw, 2015)

2.2 General overview of Wonji Sugar Factory

The factory is found at Oromiya regional state near Nazareth city at 110 kilo meters 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 two factories constructed by the Holland Company known as H.V.A had a capacity of producing 750,000 quintals of sugar a year. The sugarcane plantation land of these two factories was 7,000 hectares out of which 1,000 had been planted by out growers.



Figure 2.1 Satellite image of wonji sugar factory

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.

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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 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 new ethanol plant planned to be built, will have a capacity of producing 12,800 meter cube. The Factory is currently contributing 20 megawatt electric powers to the national grid in addition to satisfying its own demand which is around 11 megawatt. Its agricultural expansion project is currently being carried out around the areas known as Wakie Tiyo, Welenchiti and North Dodota areas. The factory with the help of this agricultural expansion project will have 16,000 hectares of sugarcane plantation field in total.



Figure 2.2 Wonji shoa sugar factories.

The total cane cultivation field of the factory has currently reached 12,800 hectares. And, the 7,000 hectares of the factory's sugarcane field cultivated with the agricultural expansion project is owned by out grower farmers of the surrounding area. There are 32 sugarcane growers association; which has in total 9,100 member farmers. The Factory, beyond

supplying the farmers with selected seeds, and rendering professional as well as technical support to them, has made irrigable land available to all. (Whayman and Crees, 1974)

2.3 Clarification as a unit operation

The sugar cane juice as expressed from the cane contains not only sucrose but also numerous other dissolved substances, as well as cellulose or woody fiber. Sugar cane juice is an extremely complex liquid medium, containing many organic and inorganic constituents in soluble, suspended or decant and suspended/colloidal form. The percentage of sugar (polarization) in the cane varies from 8 to 16 per cent and depends on a great extent on the variety of cane, its maturity, the condition of the soil, the climate and agricultural practices followed. Cane sugar for human consumption is produced by means of clarification of sugar cane juice. A critical step in the manufacture of any sugar (raw, plantation white, or refined) is clarification of the sugar juice. Clarification is the process of removing the constituents of the juice other than sucrose and at the same time minimizes loss of sucrose and color formation. Clarification is therefore an essential step to obtain high yields and high quality sugar. Several clarification methods are currently used including cold liming, hot liming and fractional liming with double heating, liming while boiling, calcium saccharate treatment and Java method. (Hugot, 1986)

Sulphur dioxide (SO₂) has been used for centuries to minimize color in food processing and fruit and vegetable storage. Sugarcane processors throughout the world use SO₂ to produce plantation white sugars. It consists of SO₂ absorption by the hot limed juice, reducing its basic pH to about 7.0. To improve floc formation, soluble phosphate is added to the juice. The soluble phosphate produces an insoluble calcium phosphate primary floc that traps other suspended impurities. In the cane sugar factory, the major role of sulfur dioxide has been to make white sugar rather than raw sugar through inhibition of color forming reactions including enzymatic browning reactions. However, periodic spikes in sulfur prices and sugar quality issues have stimulated efforts to reduce or even eliminate its use. With that in mind, a carbonation process has been tested and compared with standard sulfitation and defecation. Besides eliminating the use of sulfur, carbonation would also provide a means to utilize and take away some of the excess CO₂ that may be available cost-free in some sugar factories from molasses or juice fermentation. Among sugar cane processors worldwide, there is mixed interest in usage of sulfitation. (Godshall, 2002)

In Ethiopia, all sugar factories employ sulphitation process for the manufacture of plantation white sugar (PWS). In the United States (US), sulfitation has rarely been used in cane raw sugar factories since the 1950's. Today, there is renewed interest in the effectiveness of sulfur dioxide as a color retardant as many US factories are considering the production of high quality low color raw sugar to be sold as a food grade sugar . To improve decolorization without using an excessive amount of lime that would raise scale problems, phosphatation can be supported by a flocculating agent. Rapid flocculation and sedimentation of suspended particles in primary cane sugar juice is achieved using a high molecular weight anionic polymer flocculant (Doherty *et al.*, 2003).

Flocculation is the agglomeration of fine particles suspended in solution in to a flocculent mass. Flocculation removes insoluble suspended particles and colloidal impurities by aggregating them into flocs. A typical size range for pre-flocculation impurities in mill-extracted mixed juices at Louisiana raw sugar factories is 0.1 - 22 microns. In many cane sugar producing countries, the standard sugar product has a very low color in the range 80 to 250 IU. This sugar which is used in Ethiopia is commonly referred to as plantation white sugar (PWS). On the other hand, the standard for white (refined) sugar is considerably higher, requiring a color below 45 IU for EU No 2 or even 22.5 IU for grade 1 white sugar (Rein, 2008). The methods employed to produce PWS usually involve sulphitation of the juice and/or the syrup (Steindl, 2005). Plantation white sugar has been produced at raw sugar mills for many years without refining or re-crystallization (Rein, 2008).

2.3.1 Object of clarification

The term clarification is defined as a process by which all insoluble and some soluble impurities are removed from the juice or syrup. These impurities impart dark color to the juice and contain sucrose, reducing sugars, organic and inorganic matter in the solution. It also contains insoluble matter in suspension such as bagacillo (fine bagasse) and soil. The main object of clarification of mixed juice is as follows: Removal of maximum non sugars; elimination of suspended and colloidal impurities; removal of color forming compounds; to obtain brilliant, light colored, transparent clear juice free from any suspended impurities. (Whayman and Crees, 1974)

To obtain high quality clarified juices or syrups, removal of components other than sucrose should be maximized, and losses of sucrose and formation of color should be minimized.

Proteinaceous and waxy matter, some silica acid (hydrated SiO_2), and sesquioxides can be removed by heating, while liming neutralizes acids, forms calcium phosphates, and coagulates colloidal particles. Colloids are known to be responsible for higher or lower turbidity of sugar products and to have an adverse effect on the entire process (Rodriguez *et al.*, 1977).

Cane juice is a poly dispersed irreversible colloidal suspension in which the suspended particles carry a large negative charge. According to established theory of colloid stability, small particles are attracted one another by Van der Waals forces and therefore always tend to aggregate together but they are kept apart by electrostatic forces arising from their electrical charges. The measure of these repellent force is called Zeta potential and has been defined as a measure of net electrical potential (in millivolts) carried by particles in size ranges of 10 \AA to $10 \mu\text{m}$. The aggregation process is aided by the addition of simple electrolytes like $\text{Ca}(\text{OH})_2$ to the juice. The negatively charged colloidal calcium phosphate is formed by liming. This interaction results in coagulation and sedimentation of the particles (Rein, 1977).

2.3.2 Chemical reactions of clarification

The chemical reactions that occur during cane juice or syrup clarification are not fully understood. It is fundamental however that those reactions with lower free energy content would take place preferentially, with reactions requiring lower energy completing first. Defecation as an example is the most used method of clarification; therefore in looking at the reactions in clarification, defecation will be the clarification method of choice. The solubility of calcium oxide in water is about 0.12% at 25°C , but it is greatly increased in a solution of sucrose. The solubility however decreases with an increase in temperature. Calcium hydroxide being a relatively strong base of a divalent metal ionizes in solution to give CaOH^+ and OH^- . (Saska, 2002)

The secondary ionization is low, with less than 10 % of calcium as Ca^{++} . The reaction of lime and phosphate in juice or syrup precipitate calcium phosphate. This reaction is rather complex due to the reactions of phosphoric acid, calcium hydroxide, and the presence of other organic and inorganic compounds. Calcium phosphate reaction rate has been shown to be very low and the precipitate formed in two forms, tri-calcium phosphate in sucrose solution containing 0.3-0.5 % calcium oxide $\text{Ca}_3(\text{PO}_4)_2$, and calcium hydrogen phosphate

CaHPO₄. The formation of calcium hydrogen phosphate has been shown to have a faster reaction rate, and as it approaches completion the rate of the formation of tri-calcium phosphate increases. The rates of both reactions are greatly increased at high temperatures and result in an increase in the hydrogen ion (H⁺) concentration, which has been suggested as a contributor to the drop in the pH observed when juice is heated. (Honig, 1963)

Approximately 80-90% of the phosphate present in juice is precipitated with lime. It was shown that at a pH of about 8.5, about 99% of the phosphate present in juice are precipitated. Other calcium salts are precipitated in clarification; these may include sulfate, aconitate, and oxalate, tartrate, and citrate salts. These salts are normally precipitated in small quantities, but variations do occur depending on the quality of the juice. The sulfate content of cane juice is highly variable and approximately 20% is removed by liming to pH in the range 7-8 (Rundel, 1977).

The organic acids in juice are responsible for the natural pH of the juice (5.2 - 5.4) as well as the buffering capacity of the juice, which is mainly due to the juice aconitic acid content. The presence of other organic acids such as lactic, formic, acetic, propionic, and butyric acids are generally a result of microbial or chemical decomposition of sugars (Saska 2002). Another component of cane juice is silica. Silica is present in the juice in the form of dissolved silica, colloidal or suspended silica or as silicates. On average it is 0.42% of solids in mixed juice. Most of the suspended silica is removed by liming (Honig, 1963).

2.4 Syrup clarification using the floatation method

Syrup clarifiers use the floatation method unlike the juice clarifiers, which utilize a settling method. The settling method would not be possible with syrup because of the high density and viscosity. The mechanism of syrup clarification involves the trapping of air bubbles within the flocs and intermolecular attraction across the air/liquid interface. Syrup clarification occurs by heating the syrup, then aerating it to trap the fine particles, which are finally coagulated by a low molecular weight flocculant. The scum will float to the top of the clarifier where it is scraped off and returned to the mixed juice tank. The factors that directly influence the syrup clarifier are temperature, flocculant mixing and dosage, air and syrup flow rates. (Rundel, 1977)

Syrup clarification using flotation system with optimized dosages of phosphate and cationic flocculant.

Syrup clarification is an old technology that is being used to good effect especially in South Africa, Australia, Belize, India and Mauritius. It was first tried in South Africa in 1974 at Noodsberg with the following results: improved sugar quality, reduction in massecuite viscosities, no boiling house improvements. This process was discontinued at Noodsberg because the emphasis was not on quality. At Tonga at Hulett Sugar Limited, Felixton several trials were undertaken and they have shown good results with respect to; insoluble solids, color reduction, better boiling house recoveries. (Hon- Jun, 1990)

Then trials were undertaken at Belle Vue Sugar Mill in Mauritius with the following results; sugar quality was improved, massecuites were found to be less viscous and easier to cure, a 67% reduction in the syrup turbidity, no improvements on final molasses, there was an increase in color. In 1960 the Sugar Research Institute of Australia commenced its first syrup clarifier project and has since constructed syrup clarifiers in Australia, India and China to give a higher quality raw sugar. Syrup clarification is being done at Tower Hill Sugar Mill to reduce the insoluble solids for direct consumption sugars. Guysuco provided drawings and additional information for the syrup clarifier that was built at Tower Hill Mill in 2001 and a 73% reduction in turbidity was reported in 2001.

There are a few key parameters, which must be controlled before proper results can be obtained. Those key parameters are; air supply, heating of syrup, syrup flow, flocculant dosage and concentration, air supply. Air is applied to the syrup clarifier by air diffusers. The air is used for two reasons in the clarifier. Aerating the syrup is done so that the air bubbles cling to the precipitates in the syrup and it aids floating the floc to the top of the syrup clarifier. When starting up the clarifier the air must be added at a higher rate (15-20 p.s.i) than during operations. This is to create bubble formation at the top of the clarifier. It was found that excess air promotes faster scum formation. During operations the air should be regulated so that the minimum air is used to float the floc to the top of the clarifier and produce the lowest possible turbidity. This range is between 5-15 p.s.i. (Rein and Cox, 1987)

Heating of the syrup is essential to the coagulation of the flocs. A shell and tube heater, which uses 2nd vapor as the heating agent, heats the syrup. Studies from (Rein and Cox, 1987) have shown that changes in temperature will affect the turbidity removal of the syrup

and it peaks at a temperature of about 85°C, hence no specific trials were undertaken. (Rundel, 1977)

The flow of syrup is very important to obtain constant turbidity from the clarifier. Excess flow or low syrup brix conditions will cause syrup to overflow into the scum take off and returned to the mixed juice tank, thereby affecting the performance of the juice clarifier. There will be an increase in color and the juice clarifier will also become disturbed. If the syrup flow is not maintained within a range the ratio of syrup to flocculants will change and hence the turbidity will be affected unless there is an automatic link between the syrup flow and flocculent dosage. If the station is manned then the operator will need to change the flow of flocculant to get the desired turbidity, but it would be best if a flow controller is installed to more accurately control the flocculant dosage as the flow changes. At present a flow controller is not installed but one is being acquired to monitor the flow and ultimately control the dosage. (Hon- Jun, 1990)

The flocculant dosage and concentration affects the clarity of the syrup and this was evident from the scum at the top of the clarifier. The best results were obtained at concentrations of 0.1% and dosage of 15 ppm on brix. The flocculants used was Talodura with other flocculants. The sequence of air and flocculants additions affected the operation of the syrup clarifier. It was found that better results were obtained when the syrup was aerated before the addition of flocculants, but syrup clarifiers at other factories operate with the reverse. The flocculants is added into the syrup line by the use of a variable speed mono pump just before a specially designed mixer situated about 6 feet before the clarifier. The mixing system for the flocculants is very important because if there are lumps in the flocculants, it will affect clarification. It must be noted strict guidelines should be followed before the flocculent can work effectively. These include the mixing temperature and the aging of the flocculent before usage. The flocculent is mixed by air with a funnel used to distribute the flocculent at small quantities into the mixing tank, but this inevitably creates lumps. A new flocculant mixing system equipped with a venturi is being installed to improve flocculant mixing. (Rundel, 1977)

An SMRI turbidity meter is installed to monitor the turbidity as it changes. This is displayed on a chart recorder, which also records the temperature of the syrup going into the clarifier. These results can be downloaded to a computer for analysis. This is done on

daily basis. The laboratory does a turbidity analysis on none clarified and clarified syrup on alternate hours so that the reductions can be monitored. Also an insoluble solids analysis is done on a shift basis for the composite sugar samples.

Major components of the syrup clarifier station, includes;

- Clarifier
- Syrup heater
- Air diffusers
- Syrup pump
- Flocculant Tank
- Flocculant pumps
- Inline Turbidity meter and Recorders
- Inline mixer

In addition, improvements in the final molasses purities will result in increased sugar production, for example it is estimated that if the final molasses purity drops two unit this factory should recover a further hundreds tons of sugar per year, which is equivalent to huge money per year increased revenue. With the addition of lime and phosphates to the syrup better clarification will be achieved because of the formation of more agglomerates, which will further trap the insoluble particles and hence a greater reduction in color and insoluble solids will result. (Pottage, 1977)

2.4.1 Syrup clarification process

Syrup clarification is not a standard operation in all raw sugar mills. It is becoming more widely used and gradually replaces the double sulphitation process, particularly in the production of sugars for direct consumption, either to remove suspended solids or color or both. Because of the viscosity and greater density of the syrup, it is not possible to settle out the fine suspended solids. Flotation clarification does, however, work effectively when applied to syrup, without any sophisticated process requirements. The aerated phase is stable and does not require the extensive use of chemical to form and stabilize the scum layer as, for instance, flotation in mineral processing requires. As an alternative to filtration, flotation clarification can be considered as a simpler and cheaper option. It can be augmented with either sulphitation or phosphatation to achieve particular sugar quality criteria. Normally, the color index of clarified syrup is from 1600 to 1800 IU depending on

some factors such as cane varieties, qualities of sugarcane, capacity of factory, etc. If factories would like to have good quality sugar products, they have to meet such color index. (Rein, 2007)

Flotation clarification is a process which has found extensive use in water treatment and in the mineral processing industry. The process has also been used for many years in sugar refining in the form of phosphitation. Until recently flotation separation has received little fundamental attention. Schofield (2001) remarked as follows: "The lack of fundamental design criteria in 1991 painted a rather depressing picture of DAF (dissolved air flotation) design expertise and whilst DAF had existed as an art form far-over 30 years, as a science it was much less developed".

It has since been the subject of more intensive study using CFD techniques. Application of flotation clarification in raw sugar mills was pioneered by Tate and Lyle (Bennett *et.al*, 1977). The process was substantially improved by the development of efficient polyacrylamide flocculants and a number of installations clarifying syrup have been installed throughout the world. Systems have been installed in Hawaii, Taiwan, Louisiana, The Philippines, India, Colombia, South Africa, China, Mauritius and many other countries. It is attractive because it is a simple process carried out in inexpensive equipment. Subsequently flotation clarification has been applied to filtrate from rotary vacuum filters as well. As an alternative to filtration, flotation clarification can be considered as a simpler and cheaper option. It can be augmented with either sulfitation or phosphatation to achieve particular sugar quality criteria. In this process, very fine suspended is agglomerated and floated to the surface by fine air bubbles. (Bennett *et.al*, 1977)

Separation by flotation does not depend so much on size and relative density of particles being removed as it does on their surface properties. The process can be considerably enhanced through the use of appropriate chemicals. In the mining industry selective flotation of particular types of particles is possible through the addition of chemicals which change the surface properties. The use of flocculants in flotation has a substantial effect on the process, leading to mechanical entrapment of air bubbles in the floe particles and greatly assisting separation.

The mechanisms involved in the formation and flotation of floc particles are complex. Little work has been done to elucidate the mechanisms involved, and the process has evolved through empirical investigations to a viable process. Optimization invariably requires onsite testing using the particular syrup to be treated. An important aspect therefore is the method for a suitable laboratory test to simulate the process in practice and optimize conditions which may vary depending on location. (Rein, 2007)

2.4.2 Benefits of syrup clarification

Syrup clarification is characterized by the stable scum which is obtained. The process is simple, requires little supervision and the operating cost is low since it requires only the use of flocculent and may not require any additional chemicals. A further advantage is that the scum can be directed back to raw juice or perhaps to clarifier mud. If the latter option is employed, care must be taken to prevent an increase in the pol of the filter cake, but this can be minimized by optimizing the operation. The major benefits to be obtained from syrup clarification are an improvement in sugar quality and a reduction in massecuite viscosities. (Haarof and Edzwald, 2001)

The advantages of this application are greater when the quality of cane being processed is poor. From being in the position where the mill was regularly unable to produce VHP sugar in South Africa, Empangeni mill with syrup clarification was able to produce consistently good quality sugar meeting VHP specifications and for the first time was able to achieve good molasses exhaustion (Rein 1987). Although these benefits should help to achieve an improvement in overall sugar recovery, the small improvements anticipated have never been proven in the face of normal recovery variations. The best way of assessing the efficiency of syrup is still from turbidity removal results. A large number of syrup samples tested from many different mills have always shown the potential to achieve a reduction in turbidity of 80 to 95%. (Rein, 1987).

2.5 Principals involved in syrup clarification

2.5.1 Effect of operating parameters

Clarification of syrup from a raw sugar mill leads to a very stable scum layer and a high turbidity removal can be achieved merely with the addition of polyelectrolyte flocculants. Microscopic examination shows that the majority of the particles in unqualified syrup are in the range 1-10 μ m. In the scum the floc sizes are very much larger, comprising air bubbles and solid particles held together by the flocculent. Laboratory trials show that there is no significant purity improvement and that the ash removal is small. In addition, the improvement in syrup color is small. Perhaps because of the high syrup color however, the removal of turbidity is dramatic. The use of anionic flocculants, high molecular mass polyacrylamides is essential. The effect of flocculent dosage rate on turbidity removal is shown in Figure below. (Edzwald, 2001)

This indicates that a dosage of around 15 mg/kg DS is optimum. With very poor quality syrups, higher dosage rates of up to 30 mg/kg DS are required for best results. It has also been established that polyelectrolytes with a higher degree of hydrolysis and lower molecular mass give better results in this application. This generally means that the optimum flocculent for syrup clarification will be different to that used in juice clarification. Clarification of refinery melt on the other hand is more efficient if flocculent with a low degree of hydrolysis is used (Rein, 1988).

Temperature was found to have a significant effect on turbidity removal. This is shown in Figure below which indicates that a progressive improvement is obtained up to 85 °C after which the effect of temperature levels off. From Figure it can also be inferred that turbidity removal is independent of the Brix and viscosity of the syrup. The viscosity of 65 brix syrup is; about 60 % higher than that of the 60 brix syrup. See in next Figure. Therefore, viscosity values in the range encountered do not have any effect on this process, and the better results at higher temperatures are not due to viscosity reduction but due to the effect on the formation of flocs or on the intermolecular attractions across air/liquid interfaces. Other work confirms that the viscosity of the syrup does not affect the removal process (Rein *et al.* 1987).

Syrup clarification using flotation system with optimized dosages of phosphate and cationic flocculant.

Results of tests on boiling both clarified and unclarified syrup in the laboratory are described by Rein et al. (1987). The viscosities of molasses produced were measured and the results are shown in Figure. The viscosity of the clarified syrup and molasses after boiling was lower by up to 25%. A reduction in molasses viscosity is a significant advantage, since the viscosity affects centrifuging and the ultimate molasses exhaustion is generally controlled by the viscosity of massecuite. (Edzwald, 2001)

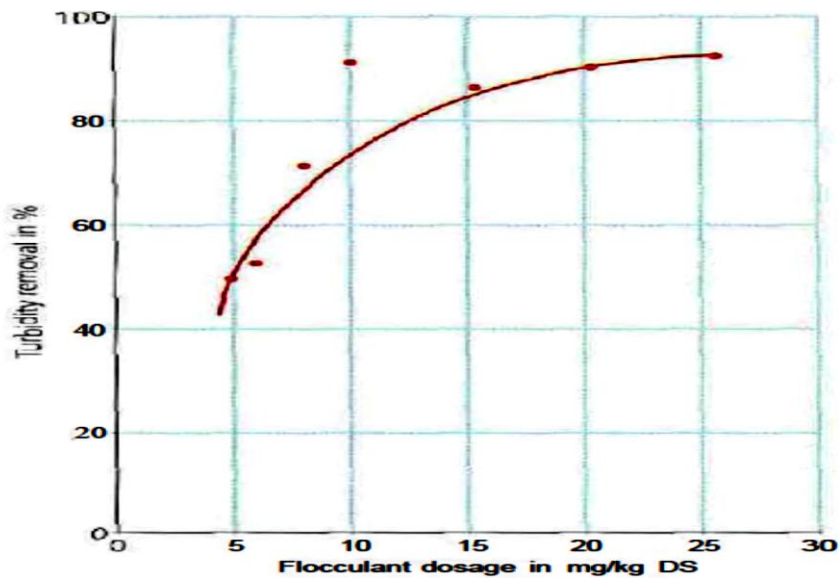


Figure 2.3 Turbidity removals in syrup as a function of flocculent dosage.

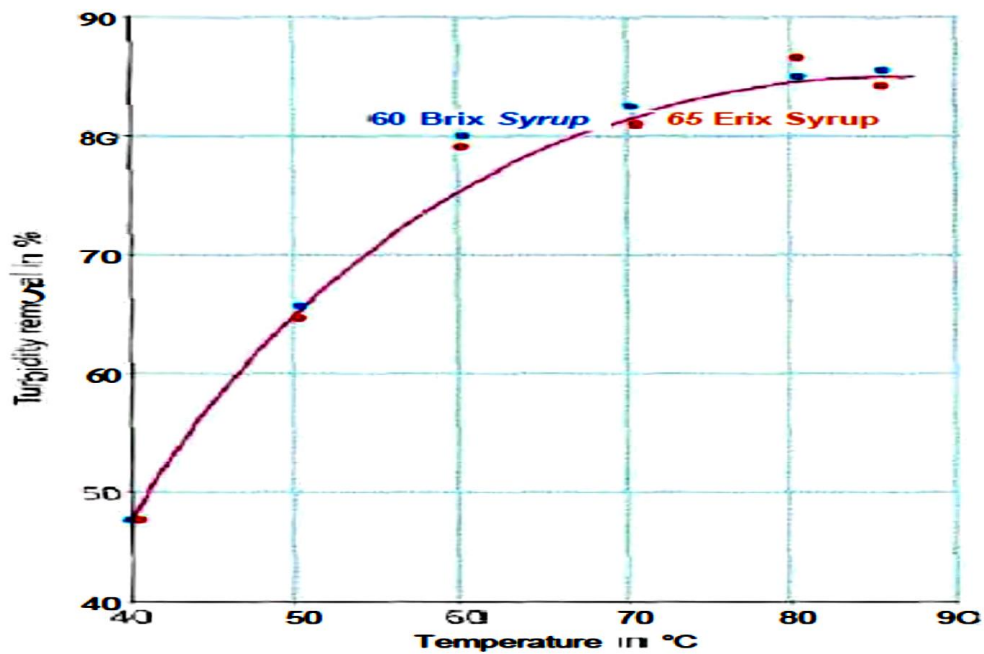


Figure 2.4 Effect of temperature on turbidity removal.

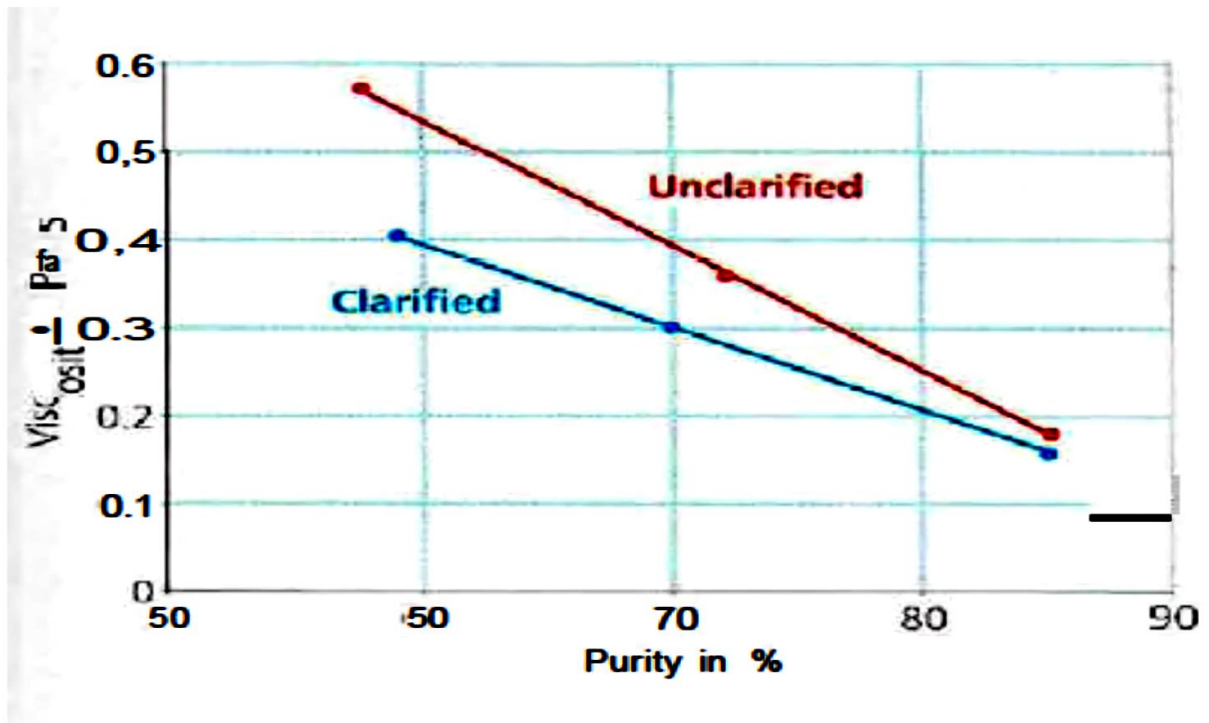


Figure 2.5 Viscosity of syrup and molasses (adjusted to 73 Brix and 40°C) with and without syrup clarification. (Rein, 1988)

2.5.2 Effect of added chemicals

The original Tate and Lyte patent claimed that it is essential to form a primary floc of calcium phosphate prior to forming a secondary floe with the addition of air and flocculent. Phosphate addition rates of around 300 mg P₂O₅/ kg DS are recommended. Other work has shown that the process can be operated without phosphate addition (Rein *et.al* 1987) and that addition of lime and phosphate does not improve the results compared to the standard process adding only flocculent. (Bennet *et al*, 1980)

Steindl and Doherty (2005) showed in laboratory tests that color removal is less than 10 % and is affected by the final PH. They showed that increasing the P₂O₅ dose from 250 to 500 mg/kg DS gave no benefit. However a number of installations do use phosphoric acid and lime. One of the problems in using additional phosphate in practice is the drop in pH which occurs as the reaction of calcium and phosphate goes to completion. A pH drop of about 0.5 units can be allowed for, but the danger of incomplete reaction leads to the possibility of post-precipitation and additional turbidity generation. Instead of using air, gassing with CO₂ and SO₂ has been tried (Rein, 1988). Use of CO₂ proved to have no advantage, but & significant improvement could be obtained with SO₂ gassing, (i.e.Sulflotation). In this case, best results were obtained by adding 0.3 kg lime/100 kg DS and 300 mg phosphate/kg DS and gassing with SO₂ to a pH between 6.0 and 6.5 before flotation. (Rein, 1988).

2.5.2.1 The application of cationic flocculants as decolorizing agents

Cationic surfactants (Bennett et al., 1971) can be used to precipitate colorants and other anionic impurities from sugar liquors. They have a strongly basic center coupled with a long chain hydrocarbon residue. The cationic center serves only as a means of attaching the hydrocarbon to the impurity or colorant anion. It is the hydrocarbon that renders the colorants repellent to water and which causes the color molecule to be precipitated from solution. The relationship between the molecular structure of cationic surfactants and their activity as color precipitants have been studied extensively. The most active cationic surfactants were found to be the di alkyl quaternary ammonium compounds containing two C₆ or two C₁₈ hydrocarbon chains. One product that has been developed for the sugar industry is Talofloc (dioctadecyl dimethyl ammonium chloride). The mode of interaction of Talofloc (Bennett, 1982) with colorant molecules is shown in Figure below. (Bennett *et al.*, 1971)

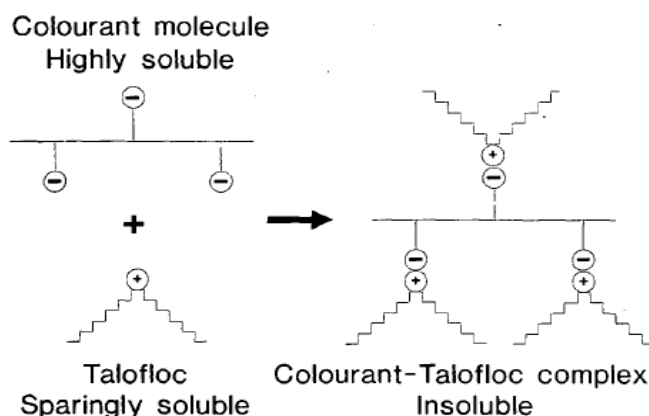


Figure 2.6 Mode of interaction of Talofloc with colorant.

Bennett *et al.* (1971) also found that color can be precipitated from solution with the use of primary or secondary amines. The addition of 100-200 ppm on cane of Talomel (acyclic di methylamine polymer) to a syrup clarifier was found to increase the de colorization by 20-30%. Residual Talomel in final A-sugar should be found below detectable levels. (Trot, 1988)

Talocarb (dimethylamine polymer), an FDA approved color precipitant, when dosed to final carbonated liquor immediately before filtration at a dosage rate of about 200 ppm on liquor solids, was found to increase the de colorization over carbonatation by 25-30%. Talocarb reacts with negatively charged color molecules, neutralizing their charges and causing precipitation. The precipitated color is subsequently removed during flotation or filtration. Talocarb in the addition of the flocculants improves the color of both the carbonated liquor and the liquor from the secondary acrylic resin station by about 20%. In pilot plant work on melt phosphatation, found that the refined sugars produced from melt treated with either polyamines or dioctadecyl dimethyl ammonium chloride were of similar quality and could meet the specifications needed for the soft drink and food industries. (Mochtar, 1989)

In South Africa, Matic *et al.* (1977) found that the addition of cationic flocculants during melt phosphatation improved liquor de colorization as well as phosphate and starch removals. Rein (1988) found that the addition of 10 ppm of cationic flocculent improves color removal during refinery sweet water clarification. Getaz and Bachan (1989), in their

Syrup clarification using flotation system with optimized dosages of phosphate and cationic flocculant.

work on syrup sulphitation/clarification, found that the addition of a water treatment flocculants (polyacrylamide) improved the de colorization quite significantly. Polyamines (copolymers of dimethyl amine and epichlorohydrin) and other chemicals with cationic properties are used extensively as flocculants in the clarification of potable water. (Getaz and Bachan, 1989)

In the clarification according to Baxter *et al.* (1992), flocculants destabilize colloidal matter by the formation of physical bridges between two or more particles, uniting the solid particles into a random three-dimensional structure which is loose and porous. In the sugar industry these cationic chemicals do not act as flocculants as described above but behave more as decolorizing agents.

Flotation clarification of syrup has been in operation at a few South African mills over the past 20 years. The original motivation was to enable production of VHP quality sugar at mills that received poor quality cane. Use of flotation clarification processes has subsequently been extended to meet like Reduction of insoluble matter in direct consumption brown sugars; Further reduction of VHP sugar color and Low-cost purification of melt in a back-end refinery. (Bennett *et al.*, 1971)

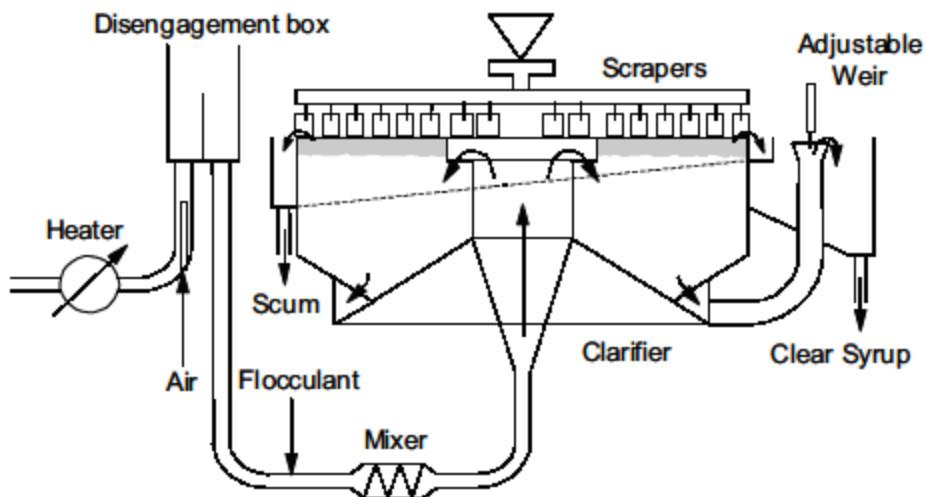


Figure 2.7 Typical flotation vessels.

2.5.3 Effect of aeration of syrup

Separation of particles either in clarification by settling or by flotation clarification is determined by the terminal velocity of the particle. This is obtained by equating drag and buoyancy forces. Using the *Stokes law* relationship for the drag coefficient for spherical particles of diameter d at low *Reynolds* numbers ($C_D = 24/Re$), the equation for terminal velocity U_t is:

$$U_t = \frac{\Delta\rho \cdot g \cdot d^2}{18\mu}$$

Where $\Delta\rho$ is the difference in density. The viscosity of syrup μ is considerably higher than that of juice, which means that separation by settling is more difficult in syrup. The density is also higher, so that the density difference between liquid and solid is insufficient to achieve settling in practice. However in flotation, the density of the aerated floc is low and the density difference is large, making separation feasible. Work reported by *Echeverri and Rein* (2006) suggests that the density difference is of the order of 800kg/m^3 and the average floc velocity 1.4mm/s (5m/h) from equation the average floc size is $183\mu\text{m}$. Considerable variation around these average values was observed. In practice the particles being floated are not spherical and *Haarof and Edzwald* (2001) report that the constant in equation is higher than 18 and could be as high as 33. Thus the numerical value of the terminal velocity will be affected by both the shape and size of the aggregates. Since the terminal velocity is proportional to particle diameter squared, it is desirable to achieve large floc sizes. Three methods of aeration are possible: (*Doherty, 2005*)

1. Electro flotation: Uses electrolysis at submerged electrodes to produce very small bubbles less than $50\ \mu\text{m}$.
2. Dissolved air flotation (DAF) where bubbles are produced by aerating under pressure ($450\text{-}500\ \text{kPa}$) and releasing the pressure on the supersaturated solution. Bubble sizes are generally very uniform with an average size between 20 and $60\ \mu\text{m}$.
3. Dispersed air flotation where air is dispersed mechanically and entrained into the liquid. Bubble sizes may be somewhat larger and display a wider size range.

Electrolysis is generally not practical on a full scale. Experience in water treatment and sugar refining has indicated that dissolved air flotation gives better results than the simpler aeration by dispersed air flotation (Saranin, 1972). In refining, claims that the air bubbles are occluded within the calcium phosphate flocs as they form, and so must be small and preferably $< 30 \mu\text{m}$. Thus calcium phosphate formation and aeration should take place simultaneously and not sequentially. In the case of syrup clarification, larger bubbles are quite adequate since there be a total absence of calcium phosphate floc, and the attachment of bubbles to particles is clearly by a different mechanism. (Honjun, 1990)

When processing syrup, dissolved air flotation shows no advantage and if anything, gives worse performance than dispersed air flotation (Rein *et al.* 1987). This is evidence of the stable foam formed in this application is the interests of simplicity and cost, dispersed air flotation is a better option. Zeng Sixian *et al.* (1998) have shown that an improvement in turbidity of the clarified liquor is possible by applying ultrasonic vibration to the liquor after the addition of flocculent. With the low and variable solids load in syrup, instead an air to solids ratio is not meaningful. An air to syrup ratio of $0.04 \text{ m}^3/\text{m}^3$ syrup is commonly used. (Rein *et al.* 1987)

2.5.3.1 Dissolved Air Flotation (DAF Flotation)

Flotation is described as a gravity separation process in which gas bubbles attach to solid particles to cause the apparent density of the bubble-solid agglomerates to be less than that of the water, thereby allowing the agglomerate to float to the surface. (Baxter *et al.* 1992),

Dispersed air flotation involves the formation of bubbles by diffusers, spargers, and other mechanical means. Large bubbles are formed and can be effective in treating suspensions containing large particles such as mineral separation and industrial waste treatment. Dispersed air flotation is generally unsuitable for liquid or syrup treatment as the bubble size is large and because of high turbulence and use of undesirable frothing and surfactant chemicals. However, the French Ozoflot® system applies ozone-rich air as a pretreatment oxidation process for waters high in algae using diffusers to achieve dispersion. (Doherty, 2005)

In dissolved air flotation, air bubbles are produced by the reduction in pressure of a water stream saturated with air. The three main types of dissolved air flotation are *vacuum flotation*, micro-flotation, and pressure flotation. (Alemayehu, 2000)

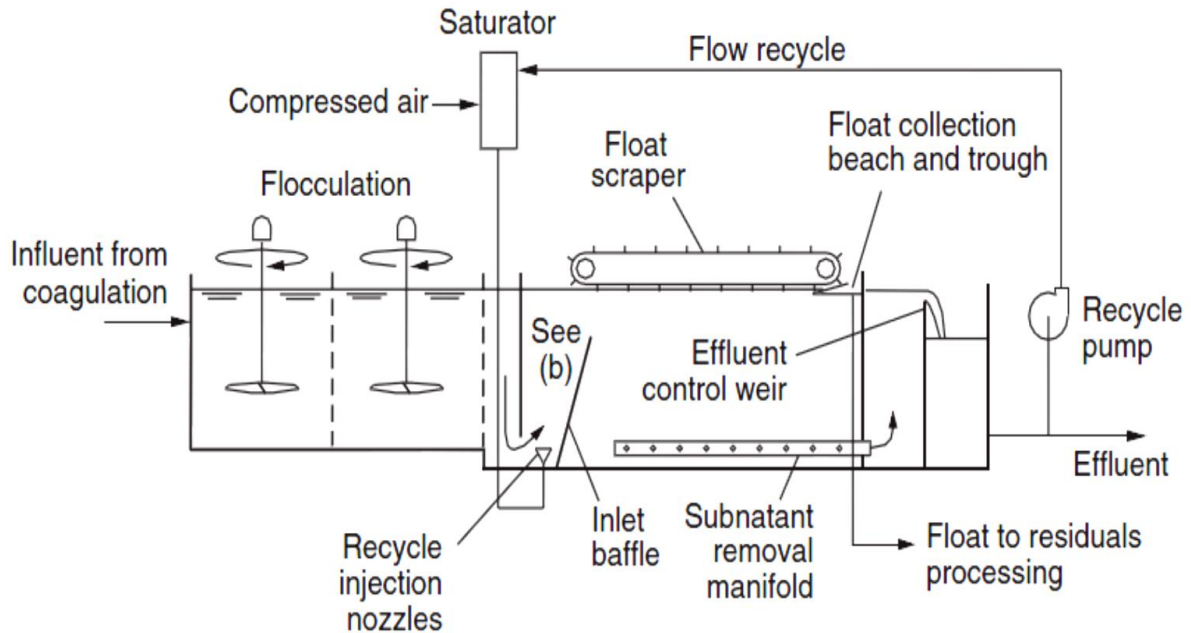


Figure 2.8 DAF Process Schematic

Factors that affect DAF performance are as the followings: Proper coagulation, should produce destabilized flocs, floc characteristics, small and low-density floc is preferred, bubble size and rise velocity, 10-100 mm floc bubble size, laminar flow regime, air loading, ensure dense bubble cloud, floc-bubble attachment, important to know the mechanisms for floc-bubble attachment, solubility of gases, ensure sufficient air delivery. (Alemayehu, 2000)

2.6 Harmful effects of SO₂ consumption with sugar

Sulphur dioxide has traditionally been used in food processing and produces storage to minimize color formation due to browning reactions associated with amino acids interacting with invert sugars in the Maillard reaction. Sugar beet processors routinely use sulphur dioxide in process streams for the same purpose. Among sugar cane processors worldwide there is mixed interest in usage of sulfitation. In the United States, sulfitation has rarely been used in cane raw sugar factories since the 1950's. Today, there is renewed interest in the effectiveness of sulfur dioxide as a color retardant as many US factories are considering the production of high quality low color raw sugar to be sold as a food grade sugar. (Anonymous, 1996)

Under normal ambient temperature and pressure, sulphur dioxide is a colorless, pungent smelling, nonflammable gas. In very low concentrations this gas can cause extreme eye and respiratory irritation, thus must be used in a controlled environment. The Egyptians and Romans burned sulfur to form sulfur dioxide (SO₂) as a means of sanitizing wine-making equipment and today SO₂ is used to treat most light colored dehydrated fruit and vegetables to prevent undesirable enzymatic and non-enzymatic “browning” reactions. Sulfur dioxide provides the added benefit of acting as a food preservative and functions as an antioxidant. Sulfite additive has been used extensively in the food industry to retard Maillard reactions. (Weeny, 1981)

The two main groups of reaction between sugars, ascorbic acid and their dehydration products and bisulfite, are primarily the hydroxy sulfonate and organo sulfur compounds. Browning reactions, of whatever type, are caused by the formation of unsaturated, colored polymers of varying composition. Compounds that engender browning usually contain a carbonyl or potential carbonyl grouping (Hodge, 1953). Browning can be inhibited by compounds that block or eliminate or combine with carbonyl groups. The multiplicity of studies regarding browning reaction theories is reviewed thoroughly in Hodge’s (1953) review article. The purpose of sulfiting purified and clarified thin juices are 1) to control juice color formation; 2) to improve the boiling properties of the juices; and 3) reduce the excess alkalinity (Ginnis, 1982).

Two methods of sulfuring are: by sulfur stove, burning elemental sulfur for production of sulfite and bubbling sulfur dioxide through process streams and produced during these processes is the undesired sulfate ion that can interfere with crystallization causing an increase in molasses purity and production. The oxidation of sulfite to sulfate is greatly retarded as the sugar concentration is increased. Sulfitation can control juice color by interfering with chromophoric molecular groups include carbonyl (ketones), carbonyl (aldehydes), carboxyl, and amido. “These compounds are characterized by an electron imbalance, an electronically excited state, a molecular resonance, an absorption of specific bands of transmitted light, and to the beholder, color” (Ginnis, 1982). Color compounds in cane and beet sugar products include naturally occurring pigments along with a large heterogeneous variation of color compounds produced during processing.

It has been estimated that for a 98.5° pol raw sugar, colorants account for approximately 15-20 % of the weight of non-sugars. In granulated refined sugar the estimate is approximately 30 ppm (Clarke, 1988).

In the cane sugar factory, the major role of sulfur dioxide has been to make white sugar rather than raw sugar through inhibition of color forming reactions. This is achieved by addition of SO₂ to the alkenic double bond in an α , β -unsaturated carbonyl intermediate as well as to the carbonyl group, which yields β -sulfonated aldehydes that are of comparatively low reactivity in reactions leading to the production of browning compounds by the Maillard reaction and degradation of invert sugars (Shore, et al., 1984). Sulfur dioxide also has the ability to inhibit or retard enzymatic browning reactions. Sulfur dioxide added as 300-500 ppm to raw beet juice resulted in minimal (5%) color reduction (Shore, et al., 1984). Onna and Sloane (1978) reported that 300 ppm decreased color in syrup and whole raw sugars by about 25% with crystal color reduced by 46%. Final refined granulated sugar from this process had 35% less color. (Shore, *et al.*, 1984)

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

In cane and beet processing, there are many variations in procedure for adding sulfur dioxide. There is cold sulfitation with SO₂ added to cold raw juice then limed; alkaline sulfitation where juice is limed then sulfited and again sulfite added to syrup prior to pan boiling. Hot sulfitation is where juice is heated first then sulfited and limed; this method is used to reduce the solubility of calcium sulfite. Other modifications of these procedures are used according to plant capabilities etc.

In Northern Europe, a method of combining sulfitation with preliming of diffusion juice was developed. Small additions of SO₂ to an acidic (PH 5.5-6.0) diffusion juice improved filtration and sedimentation, as well as reduced juice color development. Effect on sucrose recovery was not discussed. Indonesian cane processors have developed a similar process using sulfitation with lime with the production of a high standard quality white consumption sugar for export (Marches, 1953).

This plantation white sugar is the result of two sulfitation procedures, first at original clarifier when added with lime and second as syrup sulfitation prior to vacuum pan. Sulfitation in Louisiana is a very old process, possibly originating with French or English settlers (Spencer, et al., 1945). Cold raw juice was pumped through a sulfur tower with a countercurrent of sulfur dioxide to produce a fairly good, irregular, near or off-white sugar. By the late 1930's use of sulfur dioxide was on the decline and was then mainly used for production of direct consumption molasses. This study was undertaken to determine the effect of sulphur dioxide on model and real cane process streams. This work is part of SPRI's continuing research on determining the effect of invert and pH on sucrose recovery and color formation. (Andrews, 2002)

2.7 Carbonatation and Phosphatation process

It is now almost universal for sugar refineries to use either carbonatation or phosphatation process to clarify the melt liquor. These chemical processes, as well as removing the finely divided particles of insoluble and semi-colloidal matter, also eliminate significant amounts of color and other non-sucrose impurities which would otherwise have to be removed at greater expense in the subsequent decolorization or crystallization processes. Recent improvements to the traditional refining processes using new chemicals, techniques and equipment are described and discussed below. (Bennett *et al.*, 1971)

Basically, the process consist of precipitating insoluble calcium phosphates of variable composition in hot melt liquor by first adding phosphoric acid, or an acid phosphate, followed by calcium hydroxide, either as slurry with water (milk of lime) or dissolved in sugar syrup as lime sucrate, to give a final pH of 7.2 – 7.4. This treatment produces a calcium phosphate floc that is filtered with difficulty. Consequently, air flotation is commonly used to separate the precipitated solids from the liquor; such systems are called

frothing clarifiers. During the flocculation and in the course of rising through the liquor, the floccules collect most of the fine suspended impurities in the solution. Impurities such as gums, waxes, and fine are swept from the liquor and appear at the surface as scums. In this manner a rather complete separation of the precipitate and impurities is obtained without resorting to settling or filtration. The scums are then removed from the liquor surface by a skimming device. (Moodley, 1993)

2.7.1 Phosphatation process

One important modification to the phosflotation process is the application of color precipitants, like talofloc or colorgone to refinery remelt liquors whereby anionic high molecular weight color and other impurities are precipitated and subsequently removed as a flotation scum. Also the replacement of the conventional clarifiers' type Jacobs or Williamson with modern, new circular design, high yield clarifiers has greatly improved the performance of the phosflotation process. Another advance is the extensive application of highly efficient polyacrylamide flocculants e.g. taloflote, which not only speeds up clarification, but also strengthens the floc against shearing forces mainly during the de sweetening stage. (Bennett *et al.*, 1971)

2.7.1.1 Color removal:

While phosphatation generally achieves a decoloration in the range of 25-30%, the addition of these color precipitant or cationic surfactants, increases the efficiency of color removal to a high level of about 70%. (Moodley, 1993)

2.7.1.2 Removal of insoluble solids:

While particles of size under 200 micron are, as a rule, successfully enmeshed in the floccules and are removed in the process, insoluble solids such as bagacillo and fluff of over 200 micron have poor floatability characteristics. Consequently, if not separated by prescreening of the melter liquor, they are carried over with the clarified liquor, imparting to it a cloudy appearance. Furthermore, if present in sufficient quantity they seriously impede liquor flow over the char, by forming a mat on the surface layer. Removal of 50-70% of solids present in the original melt is normally obtainable by the process. (Moodley, 1993)

2.7.1.3 Secondary precipitation:

Formation of floc in phosphate-clarified liquor is usually referred to as the secondary precipitation. The occurrence of this floc has been reported by a number of observers. It, of course, creates problems in the processes subsequent to clarification. In a reasonably well conducted flocculation process the residual P₂O₅ is well under 70 ppm and occurrence of secondary precipitation is not likely. But if something can happen, early or later will it happen. (Bennett *et al.*, 1971)

2.7.1.4 Removal of ash:

Removal of soluble inorganic constituent from melter liquor is one of the objectives of clarification. However, the level of removal obtained by any one of the three conventional methods of clarification is only marginal. Phosflotation, it has been reported by various writers, removes from nil to 20% of ash in the original liquor.

2.7.1.5 Sucrose inversion:

Exposure of liquor to temperatures ranging from 85 to 99 °C, depending on the type of clarifier used, during the flotation period leads to inevitable inversion of sucrose. Most observers reported inversion of the order of 0.01%. Scums from phosphatation systems are generally sent to secondary clarifiers to reduce their sugar content. Two or three stage flotation separators, using polyacrylamide flocculating agents as mentioned, permit countercurrent de sweetening, more or less without filtration equipment. (Schuman, 200)

Nevertheless refineries using modern Phosphatation/Flotation process still have to deal occasionally with some immanent drawbacks of the system, including high sugar losses, cloudy clarifier liquors and wet scums muds of difficult disposal. Most operators of the process admit having witnessed production of both excellent and poor liquors from a given installation. With the notable exception of one or two refineries, conventional phosphatation-flotation is found in practice to be a sensitive process. Relatively minor changes can have a catastrophic effect on flotation characteristics, leading to the appearance of heavy carry-over in the clarified liquor. If flotation is incomplete, the liquor not only looks bad but is poor in quality and needs to be filtered before it becomes acceptable for the char or ion exchanger treatment. The history of phosphatation for clarification of refinery liquors may be summarized as follows. (Bennett *et al.*, 1971)

The advantages of phosphatation were recognized in the very early days of sugar refining, but it was slow to receive acceptance because of the difficulties of floc separation. The reasons for the interminable evaluator debate may lie in the fundamental and inherent difference that exists between phosflotation and the two other processes carbonatation and diatomite filtration. This difference is that flotation, unlike diatomite filtration or carbonatation filtration, has no element of positive separation of the insoluble solids. Infiltration of the liquor, if the liquor passes through filter cake, it is free of solids of a certain size. If not it does not pass through filter cake. In flotation the liquor passes through a clarifier irrespective of whether complete or nil separation of coagulum is obtained. (Smith and Schuman, 2000)

2.7.2 Carbonatation Process

Refinery carbonatation has been used for over 100 years for the refining of raw sugar. It is a cheap and robust process. The process consists of adding slurry of calcium hydroxide in water to the raw melt solution. Then carbon dioxide gas is bubbled into the sugar solution in saturators, under controlled conditions of pH and temperature. Generally the carbon dioxide is added to the saturators in two stages, with the major part of the gassing carried out in the first saturator. The impurities are both absorbed by, and enmeshed in, the conglomerated particles of the calcium carbonate precipitated by the reaction of the carbon dioxide and calcium hydroxide.

New significant developments for the carbonatation process, patented by Putsch Co. in the last years, has brought the carbonatation, as the process of choice for updating existing installation or for new refineries. Namely the introduction of Richter Tubes as efficient gas distributors for carbonatation vessels and the utilization of modern Membrane Filter presses for single stage filtration of carbonated syrup have given the conventional carbonatation process an impulse to higher performance level. The ease of separation of impurity from carbonated liquor in refinery practice is determinate by the filterability of the precipitated CaCO_3 . Provided the design and operating conditions of the saturators follow well-known principles of crystallization processes, the carbonatation system is relatively insensitive to minor variations.

It is considerably more dependent on the quantity of lime precipitated in the liquor. For any liquor there is a particular lime dose at which the filterability will be greatest. The optimum lime dose varies from below 0, 4 % CaO on solids in some liquors to over 1,2 % CaO in others. Approximately 30 times more lime is precipitated as carbonate during carbonatation than as phosphate during phosphatation. (Steindl and Doherty, 2005)

Separation of the clear liquor and the calcium carbonate is done by pressure filtration. This filtration required expensive two-stage filtration plant for the separation and de sweetening of the calcium carbonate precipitate. Now day single stage filtration is state-of-the-art. A significant portion of the calcium carbonate cake is required to act as a filter aid and growth of a suitable filtering carbonate cake is as important as color removal. One of the main objectives of carbonatation is the removal of the impurities present in the raw sugar entering the refinery. These impurities will have negative effects on some of the unit operations in the refinery. Firstly certain impurities will have a profound effect upon the nucleation and growth process involved in the formation of the calcium carbonate conglomerate. As a consequence such impurities will impact upon the filtration processes in the refinery. Secondly the presence of another impurity will adversely affect the sugar crystallization process and lastly refined sugar quality will be influenced by this impurities.

Praxis have shown that carbonatation is very effective in the in the removal of the following impurities: Results of impurity removal from melt during carbonatation (1,10 % CaO addition on Brix): Color 55%,Turbidity 90%, Starch 93%, Gums 29%, Sulphates 86%, Phosphates 100%, Magnesium 67%. The following comments can be made regarding the results in the above: About 55% of the clour is removed, Most of the turbidity (90%), starch (93%), sulphates (86%) and phosphates (100%) are removed, a small amount of the gums is removed, and a high proportion of magnesium is also removed. (Smith and Schuman, 2000)

In addition, it has been shown that during carbonatation glucose, fructose and aconitic acid, if not precautions are taken, can be easily destroyed with increase in lactic acid and higher molasses losses. Basically reducing the contact time of raw melt with lime at high temperature noticeably reduces the invert sugar destruction. It has also been shown that carbonatation removed floc-forming impurities and it has generally been accepted that carbonatation refineries produce floc-free refined sugar.

The two main components responsible for formation of floc are proteins and polysaccharides, known as floc precursors, which are removed by carbonatation. In addition it is confirmed that color removal during carbonatation is a function of the melt color, amount of lime added and the final pH. (Steindl and Doherty, 2005)

2.7.2.1 Comparative quality

Being concerned with the problems of attaining maximum clarification at optimum costs, technologists inevitably ask which one of three processes of melt clarification - diatomite filtration, phosflotation or carbonatation - provides the best answer. This question arises in planning a new refinery or when the existing process becomes unacceptable either for technological or economic considerations. A complete answer to this question can only be obtained by going through a close economic analysis of the alternative involving such factors as cost of capital, labor, and materials used in the alternative processes, level of education of the available labor, size of the plant etc. In the present context we can consider only the technical effectiveness of the respective processes. Even though this appears to be a simple question it is not easily answered.

There have been changes from one process to another since the 1950's. Changes took place from diatomite filtration either to phosflotation or carbonatation. There were also changes from phosflotation to carbonatation. Of the newly built refineries the smaller sizes adopted, as a rule, phosflotation, while the larger ones preferred carbonatation. (Smith and Schuman, 2000)

2.7.3 Coagulation and Flocculation

With the increasing demand to achieve efficient and cost effective removal of color in the production of high quality white sugar, a number of processes and chemicals have been investigated. Cationic flocculants such as polyamine chemistries are an example of decolorizing agents used to precipitate colorants and other anionic impurities from sugar liquors (Bennett et al., 1971; Moodley, 1993). Cationic polymers can be used to bind and facilitate precipitation of color bodies from refinery melt liquor by way of the negatively charged color bodies being attracted to the positively charged polymer, thus forming an insoluble precipitate that can be easily removed from the refinery melt. (Moodley, 1993)

In this work, polymers were evaluated under laboratory conditions, utilizing refinery melt liquor that was subjected to various refining processes. These include (i) carbonation where lime and carbon dioxide gas (recovered from boiler flue gas) form a calcium carbonate precipitate that absorbs color particles, (ii) sulphitation, where sulphur dioxide gas is reacted with lime to produce a calcium sulphite precipitate which adsorbs to the color bodies, and (iii) phosphatation whereby lime and phosphoric acid are reacted together to form a calcium phosphate precipitate, which absorbs and entraps the colour bodies. The colour bodies are then removed either by filtration or by flotation in an air flotation unit using a high molecular weight anionic flocculant to enhance the separation of the solids from the melt liquor. (Bennett *et al.*, 1971)

The cationic polymeric decolourisation agent is used to enhance rather than replace the refining processes. Benefits include a greater performance efficiency as well as enhanced colour removal during periods of exceptionally high colour loading.

Phosflotation (Phosphatation-flotation) is a widely practiced method for the defecation of a raw sugar melt. The process involves the coagulation of impurities with a calcium phosphate precipitate followed by the flotation of this coagulum to yield a clear liquor underflow. In recent years, a number of new materials have been introduced in order to improve the efficiency of the process. An upgrading in the through put of flotation clarifiers have been achieved by the application of high molecular weight anionic polyacrylamides as flotation aids. Due to their long chain length and negative charge in solution, these polymers build up large flocs which can be floated at a much enhanced velocity. This ensures a high throughput of turbidity free liquor. (Shephard, 1977)

One of the important developments has been the introduction of the Talofloc process which aims at achieving a large measure of de colorization during defecation. A cationic surfactant (Talofloc) is added prior to the precipitation of phosphate and the final aerated suspension of calcium phosphate coagulum is flocculated by the addition of an anionic polyacrylamide (Taloflote). The advantage of obtaining considerable de colorization in the phosphatation process lies in the greater economy that can be achieved in the subsequent decolorizing stage." The purpose of this study was to investigate the degree of impurity removal that can be achieved with the aid of cationic flocculants. In addition, the effect on the process of a polyacrylamide flotation aid was investigated. (Shephard, 1977)

2.7.3.1 Coagulation:

Coagulation is the step where colloidal particles (similar to spheres of a diameter of less than 1 micrometer) are destabilized. Coagulation comes from the latin word 'coagulare' which means 'to agglomerate'. Coagulation is the result of the addition of chemical reagents to liquid suspensions where the dispersed colloidal particles are assembled in larger aggregates called flocs or microflocs. Coagulation is an intermediary step, but it is essential to the physico-chemical treatment process of juice and syrup. This is the first step in the elimination of colloidal particles and its main function is to destabilize the particles. This destabilization is essentially the neutralization of the electrical charge present on the surface of the particle thus facilitating the agglomeration of the colloids. (Moodley, 1993)

Colloids are insoluble particles suspended in water. Their small size (less than 1 micron) makes the particles extremely stable. They can have different origins: Mineral: silt, clays, silica, hydroxydes and metallic salts and Organic: humic and fulvic acids, color, surfactants. Micro-organisms such as bacteria, plankton, algae, and viruses are also considered as colloids. The stability and consequently the instability of suspended particles is a factor of different attraction and repulsion forces: (Runggas, 1977)

- Van der Waals forces
- Electrostatic forces
- Universal attraction
- Brownian motion

Coagulation is both a physical and a chemical process. The reactions between particles and coagulant will allow the formation of aggregates and their subsequent sedimentation. Cationic coagulants neutralize the negative charge of colloids and form a spongy mass called microflocs. The coagulation mechanism can be summarized of the two; charge neutralization which is corresponds to the lowering of the electrical charges that have a repulsion effect on the colloids and aggregation of the particles.

2.7.3.2 Flocculation:

Flocculation is the step where destabilized colloidal particles (or the particles formed during the coagulation step) are assembled into aggregates. The flocculation step can only operate on a water/wastewater where the particles are already destabilized. It is the logical step following coagulation. (Bennett *et al.*, 1971)

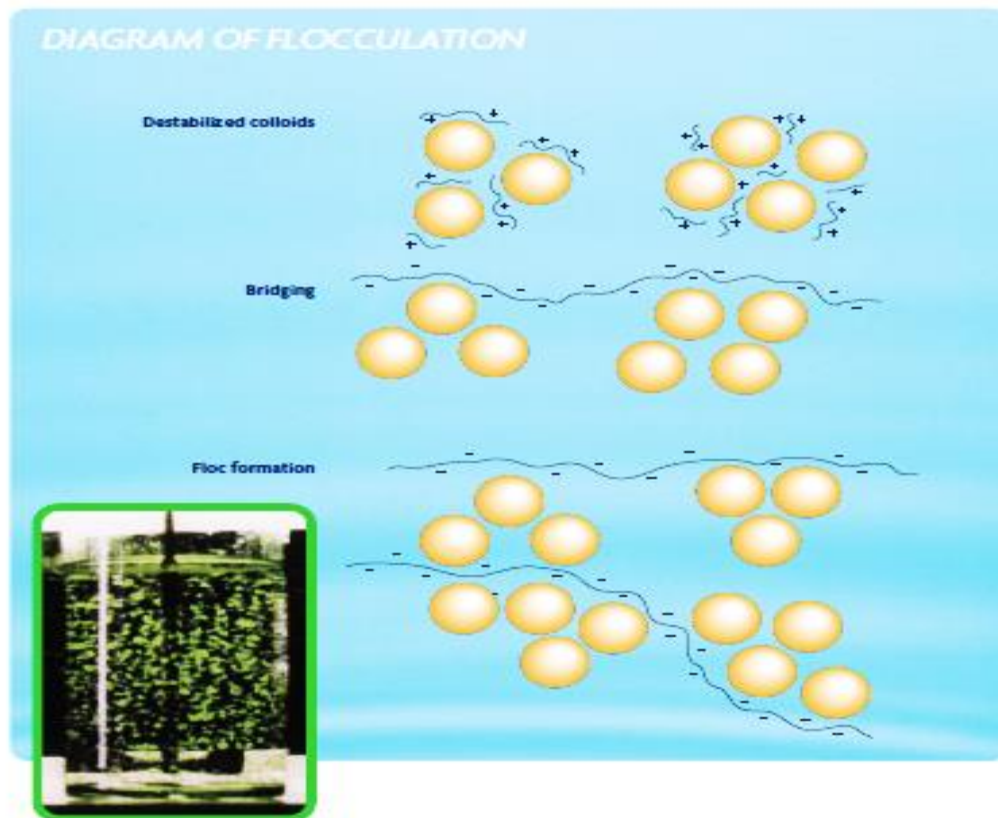


Figure 2.9 diagram of flocculation

2.7.3.3 Destabilized particles:

The origin of destabilized particles is various and depends mainly on the origin of the water to be treated. They can come from an initial coagulation step. The charge (+ or -) brought by the flocculants will be selected according to the nature of destabilized particles in the water. In general the selection follows the pattern as: Anionic flocculants (-) for mineral particles and Cationic flocculent (+) for organic particles. (Runggas, 1977)

2.7.3.4 Flocculation mechanism:

Flocculants, with their very high molecular weights (long monomer chain) and their charge content, fix the destabilized particles and aggregates along the polymer chain. There follows, during the flocculation step, an increase in the size of the particles present in the water phase resulting in the formation of flocs. The type of bonds between the destabilized particles and the flocculant are mainly ionic bonds and hydrogen bonds. Amongst the 800 different flocculants of the Flopam range, two main categories of flocculants can be distinguished.

2.8 Froth flotation fundamental principles

Froth flotation is a highly versatile method for physically separating particles based on differences in the ability of air bubbles to selectively adhere to specific mineral surfaces in mineral/water slurry. The particles with attached air bubbles are then carried to the surface and removed, while the particles that remain completely wetted stay in the liquid phase. Froth flotation can be adapted to a broad range of mineral separations, as it is possible to use chemical treatments to selectively alter mineral surfaces so that they have the necessary properties for the separation. It is currently in use for many diverse applications, with a few examples being: separating sulfide minerals from silica gangue (and from other sulfide minerals); separating potassium chloride (sylvite) from sodium chloride (halite); separating coal from ash-forming minerals; removing silicate minerals from iron ores; separating phosphate minerals from silicates; and even non-mineral applications such as de-inking recycled newsprint. It is particularly useful for processing fine-grained ores that are not amenable to conventional gravity concentration. (Klimpel, 1995)

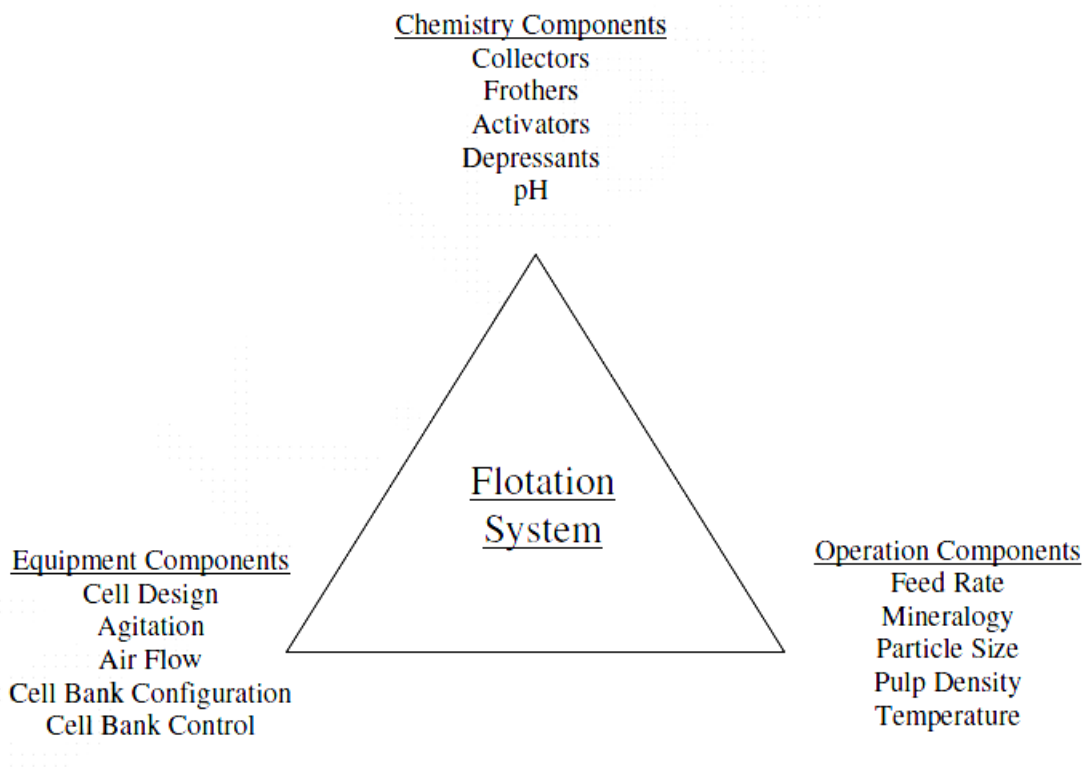


Figure 2.10 The flotation system includes many interrelated components, and changes in one area.

Froth flotation is a good example of an engineering “system”, in that the various important parameters are highly inter-related, as shown in Figure 2.11. It is therefore important to take all of these factors into account in froth flotation operations. Changes in the settings of one factor (such as feed rate) will automatically cause or demand changes in other parts of the system (such as flotation rate, particle size recovery, air flow, pulp density, etc.) As a result, it is difficult to study the effects of any single factor in isolation, and compensation effects within the system can keep process changes from producing the expected effects. This makes it difficult to develop predictive models for froth flotation, although work is being done to develop simple models that can predict the performance of the circuit from easily-measurable parameters such as solids recovery and tailings solid content (Klimpel, 1995).

2.8.1 Types of Flotation

Different methods of producing gas bubbles give rise to different types of flotation processes. These are electrolytic flotation, dispersed air flotation, and dissolved air flotation. The basis of electrolytic or electro flotation is the generation of bubbles of hydrogen and oxygen in a dilute aqueous solution by passing a DC current between two electrodes. The application of electrolytic flotation has been restricted mainly to sludge thickening and small wastewater treatment plants in the range 10 to 20 m³/h and has limited application to drinking water treatment. (Saranin, 1972)

2.8.2 Hydrophobicity/hydrophilicity

The basis of froth flotation is the difference in wet abilities of different minerals. Particles range from those that are easily wet able by water (hydrophilic) to those that are water-repellent (hydrophobic). If a mixture of hydrophobic and hydrophilic particles are suspended in water, and air is bubbled through the suspension, then the hydrophobic particles will tend to attach to the air bubbles and float to the surface, as shown in Figure 3. The froth layer that forms on the surface will then be heavily loaded with the hydrophobic mineral, and can be removed as a separated product. The hydrophilic particles will have much less tendency to attach to air bubbles, and so it will remain in suspension and be flushed away (Whelan and Brown, 1956).

Particles can either be naturally hydrophobic, or the hydrophobicity can be induced by chemical treatments. Naturally hydrophobic materials include hydrocarbons, and non-polar solids such as elemental sulfur. Coal is a good example of a material that is typically

naturally hydrophobic, because it is mostly composed of hydrocarbons. Chemical treatments to render a surface hydrophobic are essentially methods for selectively coating a particle surface with a monolayer of non-polar oil. (Kawatra, 1987)

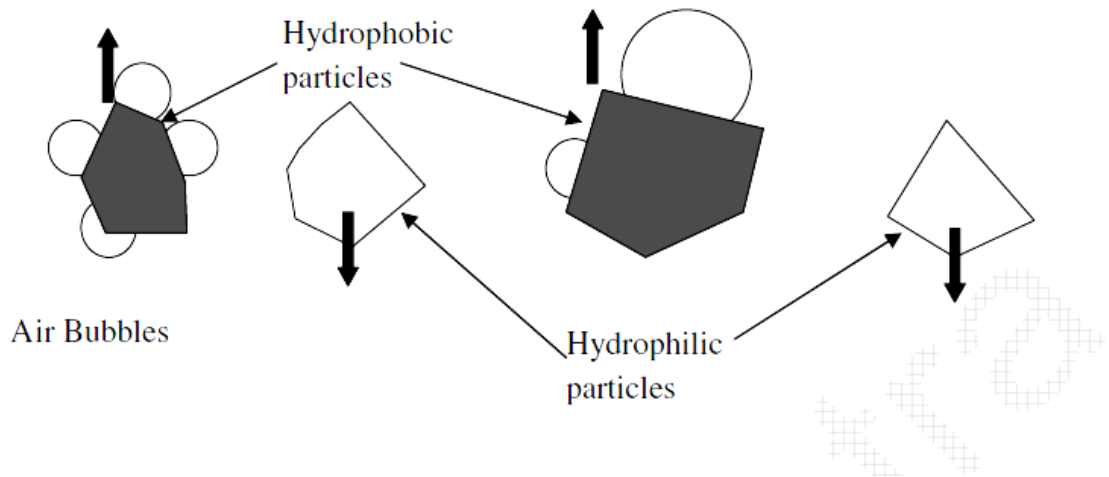


Figure 2.11: Selective attachment of air bubbles to hydrophobic particles.

The buoyancy of the bubbles then carries these particles to the surface, leaving the hydrophilic particles behind. The attachment of the bubbles to the surface is determined by the interfacial energies between the solid, liquid, and gas phases. This is determined by the Young/Dupre Equation,

$$\gamma_{lv} \cos \theta = (\gamma_{sv} - \gamma_{sl})$$

where γ_{lv} is the surface energy of the liquid/vapor interface, γ_{sv} is the surface energy of the solid/vapor interface, γ_{sl} is the surface energy of the solid/liquid interface, and θ is the “contact angle”, the angle formed at the junction between vapor, solid, and liquid phases, as shown in Figure 4. If the contact angle is very small, then the bubble does not attach to the surface, while a very large contact angle results in very strong bubble attachment. A contact angle near 90° is sufficient for effective froth flotation in most cases. (Eisele, 1987)

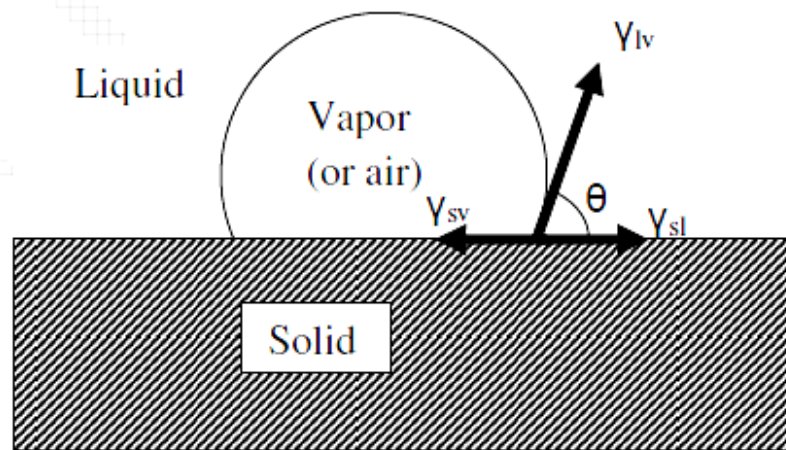


Figure 2.12: Contact angle between and air bubble and a solid surface immersed in liquid.

2.8.3 Particle/Bubble Contact

Once the particles are rendered hydrophobic, they must be brought in contact with gas bubbles so that the bubbles can attach to the surface. If the bubbles and surfaces never come in contact, then no flotation can occur. Contact between particles and bubbles can be accomplished in a flotation cell such as the one shown schematically in Figure below. (Eisele, 1987)

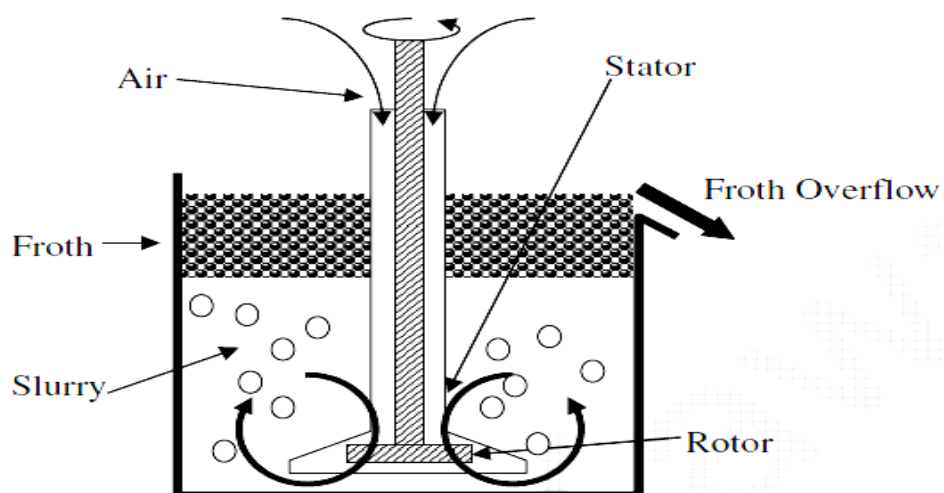


Figure 2.13: Simplified schematic of a conventional flotation cell.

The rotor draws slurry through the stator and expels it to the sides, creating a suction that draws air down the shaft of the stator. The air is then dispersed as bubbles through the slurry, and comes in contact with particles in the slurry that is drawn through the stator. Particle/bubble collision is affected by the relative sizes of the particles. If the bubbles are large relative to the particles, then fluid flowing around the bubbles can sweep the particles past without coming in contact. It is therefore best if the bubble diameter is comparable to the particle diameter in order to ensure good particle/bubble contact. (Eisele, 1987)

2.8.4 Collection in the Froth Layer

Once a particle and bubble have come in contact, the bubble must be large enough for its buoyancy to lift the particle to the surface. This is obviously easier if the particles are low density (as is the case for coal) than if they are high-density (such as lead sulfide). The particle and bubble must remain attached while they move up into the froth layer at the top of the cell. The froth layer must persist long enough to either flow over the discharge lip of the cell by gravity, or to be removed by mechanical froth scrapers. If the froth is insufficiently stable, the bubbles will break and drop the hydrophobic particles back into the slurry prematurely. (Kimpel, 1995)

However, the froth should not be so stable as to become persistent foam, as foam is difficult to convey and pump through the plant. The surface area of the bubbles in the froth is also important. Since particles are carried into the froth by attachment to bubble surfaces, increasing amounts of bubble surface area allows a more rapid flotation rate of particles. At the same time, increased surface area also carries more water into the froth as the film between the bubbles. Fine particles that are not attached to air bubbles will be unselectively carried into the froth along with the water (entrainment); excessive amounts of water in the froth can result in significant contamination of the product with gangue minerals. (Kawatra, 1987)

2.8.5 Reagents

The properties of raw mineral mixtures suspended in plain water are rarely suitable for froth flotation. Chemicals are needed both to control the relative hydrophobicity of the particles, and to maintain the proper froth characteristics. There are therefore many different reagents involved in the froth flotation process, with the selection of reagents depending on the specific mineral mixtures being treated. (Glembotskii *et al.* 1972)

2.8.5.1 Collectors:

Collectors are reagents that are used to selectively adsorb onto the surfaces of particles. They form a monolayer on the particle surface that essentially makes a thin film of non-polar hydrophobic hydrocarbons. The collectors greatly increase the contact angle so that bubbles will adhere to the surface. Selection of the correct collector is critical for an effective separation by froth flotation. Collectors can be generally classed depending on their ionic charge: they can be nonionic, anionic, or cationic. The nonionic collectors are simple hydrocarbon oils, while the anionic and cationic collectors consist of a polar part that selectively attaches to the mineral surfaces, and a non-polar part that projects out into the solution and makes the surface hydrophobic. Collectors can either chemically bond to the mineral surface (chemisorption), or be held on the surface by physical forces (physical adsorption). (Eisele, 1987)

2.8.5.2 Chemisorption:

In chemisorption, ions or molecules from solution undergo a chemical reaction with the surface, becoming irreversibly bonded. This permanently changes the nature of the surface. Chemisorption of collectors is highly selective, as the chemical bonds are specific to particular atoms.

2.8.5.3 Physisorption:

In physisorption, ions or molecules from solution become reversibly associated with the surface, attaching due to electrostatic attraction or van der Waals bonding. The physisorbed substances can be desorbed from the surface if conditions such as pH or composition of the solution changes. Physisorption is much less selective than chemisorption, as collectors will adsorb on any surface that has the correct electrical charge or degree of natural hydrophobicity. (Glembotskii *et al.* 1972)

2.8.5.4 Nonionic Collectors:

Hydrocarbon oils, and similar compounds, have an affinity for surfaces that are already partially hydrophobic. They selectively adsorb on these surfaces, and increase their hydrophobicity. The most commonly-floated naturally-hydrophobic material is coal. Addition of collectors such as fuel oil and kerosene significantly enhances the hydrophobicity of the coal particles without affecting the surfaces of the associated ash-forming minerals. This improves the recovery of the coal, and increases the selectivity

between coal particles and mineral matter. Fuel oil and kerosene have the following advantages over specialized collectors for froth flotation: 1) they have low enough viscosity to disperse in the slurry and spread over the coal particles easily, and 2) they are very low-cost compared to other compounds which can be used as coal collectors. (Kawatra, 1987)

In addition to coal, it is also possible to float naturally-hydrophobic minerals such as molybdenite, elemental sulfur, and talc with nonionic collectors. Nonionic collectors can also be used as “extenders” for other collectors. If another, more-expensive collector makes a surface partially hydrophobic, adding nonpolar oil will often increase the hydrophobicity further at low cost.

2.8.5.5 Anionic Collectors:

Anionic collectors are weak acids or acid salts that ionize in water, producing a collector that has a negatively-charged end that will attach to the mineral surfaces, and a hydrocarbon chain that extends out into the liquid, as shown in Figure below. (Eisele, 1987)

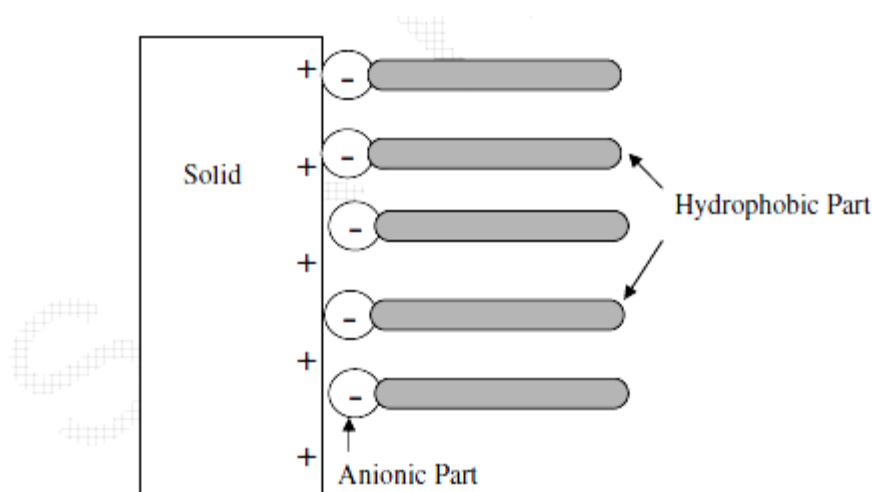


Figure 2.14: Adsorption of anionic collector onto a solid surface.

The anionic portion is responsible for the attachment of the collector molecule to the surface, while the hydrophobic part alters the surface hydrophobicity. (Kawatra, 1987)

CHAPTER 3 MATERIALS AND METHODS

3.1 Site of the experiment

The experiment was held at Wonji Shoa Sugar Factory's laboratory. The laboratory is found at Oromiya Regional State near Nazareth City at 110 Kilometers from Addis Ababa. Any research related to the sugar cane production and sugar processing technologies are held mainly in this laboratory.

The experiment was conducted based on syrup produced from the mixed cane varieties and taken from the factory as a sample. The syrup clarification experimental work and the determination of the response variables were done at the research laboratory service of the station.



Figure 3.1 Wonji Sugar Factory

3.2 Materials

Sample for the experiment was:

- Raw syrup from evaporator

The equipment and materials:

- Measuring cylinder,
- Conical flask,
- PH meter,
- Stirrer
- Precision refractometer, Buchner funnel,
- spectrophotometer,
- 1cm cell,
- Whatman No. 5 filter paper
- membrane filters
- glass electrode
- 1-liter beaker
- Volumetric flask

Chemicals and Reagents:

- Talodura,
- Phosphate,
- CaCO_3
- NaOH solution,
- HCl solution,
- Kieselguhr filters aid.
- Sodium thiosulphate
- Lime saccharate
- Potassium dichromate
- Potassium iodide solution (For standardization)

3.3 Sample Preparation

Syrup of 16 L was collected from evaporator for one run. Laboratory scale experiment was conducted on syrup clarification by Talodura process in contrast to the conventional syrup sulphitation system. The experiment was conducted on samples of syrup collected from the final effect of evaporators, at five levels of phosphate concentration (as Hussein Mohammed, 2013 states the gap is good if the dosages start from a hundred and seven hundreds,) (117.8, 250, 350, 450, 550 and 682.8mg/kg) using phosphoric acid of food grade neutralized with lime saccharate to PH 7.0 and treated with Talodura solution of concentration 7.2, 8, 9, 10, 11 and 12.8mg/kg of solid. The experiment conducted was analyzed using central composition design (CCD) and JMP13.

Talodura flocculants solution of 0.1% strength was prepared from powder by feeding in to spray water of 10-55°C and mixed by stirring. The solution then kept for a minimum of 2 hours after preparation to allow complete hydration of the polymer. The thick syrup from the last effect of evaporator was heated to 85°C and then treated with each level combinations of phosphoric acid and the PH was adjusted to 7.0 using lime saccharate. The treated syrup was aerated in the system that ensures the correct size distribution and volumetric concentration of the air bubbles. The aerated syrup is dosed with solution of Talodura as per the CCD run order.

The secondary flocculation of primary flocs and air bubbles were developed. The flocculated syrup was now kept in clarifier of 1 Liter graduated measuring cylinder for 20 minutes. Such treatment was done for the rest CCD combinations of phosphate and Talodura. The flocculated impurities separate as floc scum, which was removed from the surface of the syrup by scraping mechanism.

The samples of syrup clarified by Talodura process was compared with that of the one treated by sulphitation method and subjected to laboratory analysis for the following parameters: Color, turbidity, reducing sugars, conductivity ash, insoluble matter, residual SO₂, viscosity of the syrup suspended matter, lime salts and purity of syrup.

3.4 Analytical methods

The quality of syrup like color, sulfur dioxide content, and turbidity was calculated as the following.

3.4.1 Color:

The ICUMSA color method 4 using a wavelength of 420nm was applied for testing the color of light colored syrup, as usually made on clarified juice to measure effectiveness of clarification. Apparatus used for the purpose were; spectrophotometer equipped with 10, 5 and 1cm cells, membrane filters of 47mm diameter, pore size 0.45 μm , precision refractometer and reagents used was 0.1M TEA solution and 0.05M HCl, 0.05M NaOH.

Procedure: A diluted solution of sample to be tested, (50 brix solution) was prepared. For the brix of syrup was 65, then 100g of 50 brix solution was weighed $100/65 \times 5 = 7.69\text{g}$ of syrup, made up to 100g and mixed. The pH of the solution was adjusted to 7.0 ± 0.2 with TEA buffer solution and mixed. (The use of TEA buffer solution is better than a 1M HCl or 1M NaOH solutions). The solution was filtered through a membrane filter with pore size 0.45 μm . The solution was placed in an optical cell and measure absorbance, at 420nm in a spectrophotometer using distilled water as reference standard of zero color. (*The cell length was chosen so that the instrument reading was between 20-80% transmittance and 0.1, 0.7 absorbance.*)

e) The result was expressed as the following.

$$\text{ICUMSA 420 color unit} = \frac{\text{Absorbance} \times 1000}{b \times c}$$

Where: b. Cell length (cm)

c. Concentration of total solids (gm/ml)

3.4.2 Turbidity

The turbidity of clarified juice or syrup is a measure of the effectiveness of the clarification process. The ICUMSA Colors of unfiltered and filtered samples was measured at 420nm and the difference between the readings was the turbidity of the sample. Apparatus used were: Precision refractometer, pH meter, Buchner funnel, spectrophotometer, 1cm cell, Whatman No. 5 filter paper and the reagents were NaOH 1M solution, HCl 1M solution, Kieselguhr filter aid.

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Procedure: The original brix of the clarified syrup was determined and prepared a 65 brix solution. The original brix = 60, then for 100g of 65 brix solution, the weight of the original clarified syrup taken for dilution = $6.5/60 \times 100 = 10.833\text{g}$. The amount of clarified syrup was weighed out necessary to make 65 brix solutions (in this case 10.833g of clarified syrup) in a beaker and made up to 100g with distilled water. The solution was divided into equal portions in two 100ml beakers. The first portion of the sample was taken and filtered through Buchner funnel with Whatman No 5 filter paper using kieselguhr filter aid. The first 10ml running was discarded. The pH of the filtrate was adjusted to 7.0 ± 0.2 using either 1M NaOH. Absorbance (A1) in 1cm- cell at 420nm was measured against distilled water blank.

$$\text{ICUMSA 420 Color } C_1 = \frac{A1 \times 1000}{1\text{cm} \times \text{concentration of total solids } \left(\frac{\text{g}}{\text{ml}}\right)}$$

Concentration of total solids (g ml^{-1}) = Brix x true density/100. The 2nd portion of the sample (do not filter) was taken and adjusted to the pH to 7.0 ± 0.2 using NaOH. Absorbance (A2) was measured in 1cm cell at 420nm against distilled water blank.

$$\text{ICUMSA420 Color } C_2 = \frac{A2 \times 1000}{1\text{cm} \times \text{total solids concentration } \left(\frac{\text{g}}{\text{ml}}\right)}$$

The result was expressed as the following:

$$\text{Turbidity of Clarified syrup} = C_2 - C_1 = \frac{A_2 - A_1 \times 1000}{0.201}$$

3.4.3 The pH

PH of sugar solution (50g/100g concentration) was determined using glass electrode attached to pH meter after calibration at pH 4.00, 7.00 and 9.00 at 20°C following ICUMSA method GS1/2/3/4/7/8-23 (1994)

3.4.4 Sulphur Dioxide (SO₂).

The Iodometric method is convenient for routine factory control for clear juice, syrup as well as plantation white sugar which is accurate enough for the purpose and the analysis, take little time. SO₂ exists as sulphurous acid (H₂SO₃) in aqueous solutions. Starch solution forms an intense blue absorption compound with the presence of Iodine. When titrating with iodine in the presence of starch the end point is determined from the appearance of permanent blue color with excess of one drop of Iodine solution. The method was used for clear juice, syrup and plantation white sugar for routine factory control. Reagents used for

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this specific experiment was: 0.01N iodine solution, starch solution, HCl (1:3), 0.1N sodium thiosulphate solution, potassium dichromate, 20% potassium iodide solution (For standardization)

Procedure: 200ml of syrup sample was taken and diluted by adding 400ml distilled water. The burette was filled with this diluted syrup solution. 25ml of 0.01N iodine solution was pipette into porcelain dish and 5ml of (1:3) diluted HCl solution was added. The Iodine solution with the diluted syrup sample from the burette was titrated till the brown color begins to disappear. Then a few ml of starch solution was added and continued titration till the blue color disappears. The volume of syrup taken for titration was read (ml) from the burette.

The result was calculated as the following.

From the reducing and oxidizing property of H_2SO_3 and I_2 respectively,

$$1\text{ml } 0.01 \text{ N I}_2 \text{ oxidizes} = 0.32\text{mg SO}_2$$

$$25\text{ml } 0.01 \text{ N I}_2 \text{ oxidizes} = 25 \times 0.32 \text{ mg SO}_2$$

$$V \text{ ml diluted syrup (burette reading) oxidizes} = 25 \times 0.32\text{mg SO}_2$$

$$600\text{ml diluted syrup} = \frac{600}{V} \times 25 \times 0.32\text{mg SO}_2$$

$$\begin{aligned} 1\text{lit. (1000ml) undiluted syrup} &= \frac{1000}{200} \times \frac{600}{V} \times 25 \times 0.32 \text{ mg SO}_2 \\ &= 24000/V \text{ mg SO}_2, \end{aligned}$$

Where: V is the burette reading of diluted syrup.

3.4.5 Determination of Brix in syrup (dilution 1:3 m/m)

A 200 g of syrup was weighed out in a 1-liter beaker. Distilled water was added and brought to 600 g stirred and mixed well. About 200 ml of the diluted sample was filtered through fluted Whatman No. 91 filter paper. The 1st 20 ml of filtrate was rejected and sufficient filtrate in a beaker was collected. The refractometer Brix as close to 20°C as possible was determined. Expression of the result was Brix of syrup = refractometer reading x 3

3.4.6 Determination of Pol in Syrup Clarification

Determination of the Brix of syrup was as described above. About 200 ml (1:3) m/m diluted solution of syrup in a beaker was taken. Minimum quantity of Horne's dry basic lead acetate (about 0.5g/100 ml) was added and mixed well. Filtered through Whatman No.91 filter paper or equivalent, discarded the first 25ml of the filtrate was discarded and

the rest was collected. The clear filtrate was polarized without de leading and without delay at 20°C; in 200 mm pol tube and the pol reading was taken. From the brix obtained, the pol factor from table was found. Expression of the result was (pol %syrup) Pol % syrup = pol reading x pol factor x 3 was registered.

3.4.7 Determination of Soluble Phosphate content

Phosphate content of juice or syrup is the most important factor for efficient clarification. In sugarcane the phosphates are inorganic as well as organic. The inorganic phosphates exist as free phosphate ion taken part in juice clarification. Therefore, juice with adequate quantity of inorganic phosphate is desirable. If inorganic phosphate level in juice less than 300ppm w/v the juice cannot be properly clarified and addition of phosphate may be required. The amount of inorganic phosphate left in clarified juice should be not less than 10ppm, which converts calcium and magnesium into non-scaling form in the proceeding evaporation process. Hence this method is for determination of soluble orthophosphate. Principle involved calculating the syrup phosphate was: Ammonium molybdate reacts in an acid medium with dilute solutions of orthophosphate to form molybdophosphoric acid, which can be converted by reducing agent like stannous chloride or ascorbic acid to the intensely colored molybdenum blue.

Apparatus used for the experiments was: pH meter spectrophotometer, pipettes 50 ml beakers, 150 100ml, volumetric flasks of 50, 100ml and reagents and materials used were: 0.1M H₂SO₄ Potassium hydrogen phosphate, 0.1M Na OH ammonium molybdate solution, ascorbic acid Kieselguhr, Whatman No. 91, Phosphate in mixed Juice, clear Juice and syrup.

Procedures: A 100ml of syrup brix diluted to the juice level was mixed with some filter aid and filtered through Whatman No. 91 filter paper. A 50ml of filtered juice was pipette into a 100ml beaker and adjusted the pH with 0.1M H₂SO₄ or NaOH. Then it was transferred quantitatively to 100ml volumetric flask and made up to mark with distilled water. An aliquot of the diluted juice was pipette into a 150ml beaker. Distilled water was added to about 40ml. 4ml ammonium molybdate solution was added and mixed. A 0.1g ascorbic acid was added and covered with watch glass and boiled gently for exactly 1 minute. The solution quickly cooled and transferred into the solution of 50ml volumetric flask and made up to mark with distilled water. The optical density of the blue color was measured in

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spectrophotometer using 1cm cell at 650nm against a blank of distilled water. Corresponding to the optical density the P₂O₅ concentration was found from the standard curve.

3.4.7.1 Preparation of Standard Curve for phosphate (P₂O₅)

Stock Phosphate solution was prepared by dissolving 0.1916g potassium dihydrogen phosphate (KH₂PO₄) in a 1litre of water. This solution contains 100 mg P₂O₅/liter, i.e. 0.1mg P₂O₅/ml. Standard phosphate solution was prepared again by pipette 25ml stock phosphate solution and diluted to 250ml in a volumetric flask. This solution was contains 0.01mg P₂O₅/ml. For calibration 0, 5, 10, 15, 20 and 25ml standard phosphate was pipette solution into six 150ml beakers and added distilled water to about 40ml. To each beaker 4ml ammonium molybdate solution was added and mixed. 0.1gm ascorbic acid was added and covered with watch glass, heated to boiling and boiled for exactly 1min, cooled the solution quickly, transferred quantitatively to 50ml volumetric flasks and made up to mark with distilled water. These solutions were containing: 0, 0.05, 0.1, 0.15, 0.20, 0.25mg P₂O₅/50ml test solution. The optical density was measured of the blue color in a spectrophotometer using 1cm cell at 650nm against distilled water blank. In our case:

Mg. P ₂ O ₅	0	0.05	0.1	0.015	0.20	0.25
Optical density		0.01	0.3	0.315	0.4	0.48

Table 3.3 Calibration of phosphate concentration against its optical density

From the measured optical density of each test solution and phosphate concentration, a graph of optical density against P₂O₅ concentration was plotted by noticing whenever a new batch of reagent is used a standard curve should be prepared.

Expression of the result was like the following:

$$\text{Ppm P}_2\text{O}_5 \text{ in juice} = \frac{\text{mg P}_2\text{O}_5 / 50\text{ml} \times 2 \times 1000}{\text{Aliquot of distilled juice used (ml)}}$$

3.5 Experimental Design

The effect of two factors (phosphitation and flocculation dosages) on the optimization of syrup clarification was evaluated and Central Composite Design (CCD) for two-factors was employed to conduct the experiment. Central Composite Design (CCD) with 8 center points and a total run of 16 in triplicates was used at constant temperature of 85°C investigate the effect of levels of factors on the response variables. The main variables considered here are: Turbidity, color, sulphur dioxide content, reducing viscosity. Then the optimum clarification level combinations of the factors were determined. JMP™ Software was used to provide experimental designs, generate second degree polynomial models and make statistical evaluations. The experiment was conducted using a lower and upper real value of 7.2 and 12.8 pH values for Talodura flocculent and the lower real levels of Phosphitation was 117.2 and the upper real value will be 682.8 The lower and upper real values were coded as -1 and +1 respectively and that of the center points was coded as 0. The lower and upper axial points were coded by $-\alpha$ and $+\alpha$ respectively as shown in Table

Factors	Fixed Temp 85°C	Coded levels				
		$-\alpha$	-1	0	+1	$+\alpha$
P₂O₅	At fixed (PH) 7.0	≤ 117.8	117.8	400	682.8	≥ 682.8
Talodura		7.2	8.5	9.5	10.5	12.8

Table 3.1 Coded and corresponding actual value of the factors used in the central composite design.

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Condition phosp floccul	Condition phosp floccul	Condition phosp floccul
1. -1 -1	5. + α 0	9 0 0
2. -1 +1	6. - α 0	10 0 0
3. +1 -1	7. 0 + α	11 0 0
4. +1 +1	8. 0 - α	12 0 0
		13. 0 0
		14. 0 0
		15. 0 0
		16. 0 0
2² =full factorial design Nf=4	Trials at axial points Na=4	Trials at central points No =8

Table 3.2 Central composite design (CCD) for coded levels of the two factors
(phosphatation and flocculation)

3.6 Statistical analysis

The data was analyzed and modeled using the statistical software JMP13 (by SAS Institute Inc., Cary, NC, USA). Second degree polynomial models were generated. The significant terms in the models were identified by analysis of variance (ANOVA) for each response. Significance was judged if the probability level of the F -statistic calculated from the data was less than 0.05. The model adequacy was checked by R^2 , R^2_{adj} and, Lack of Fit test. The Tables of summary of fit, ANOVA, lack of fit and parameter estimates which were generated by the software were presented in the Appendix part. Super imposed contour plots were developed to search the optimum conditions for the three main responses, namely, turbidity, color, and viscosity reduction.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Results of the Syrup analysis from Wonji Sugar Factory

The raw syrup taken from the factory done by double sulfitation without any treatment has the following values for color, turbidity, viscosity, phosphate, viscosity and purity.

Sample	Sample	Parameters							
source	code	Pol (°Z)	Brix (%)	Purity (%)	Turbidity IU	Color (IU)	Viscosity (mpa.s)	SO ₂ ppm	P ₂ O ₅ ppm
Wonji	A	49.79	60.63	82.12	13731	17451	60	30	117.2

Table 4.1 Analytical results of syrup from Wonji Sugar Factory.

4.2 Results of syrup clarified at different level of combinations of phosphate and flocculation.

The results of experimental work from the laboratory and analytical data for response variables (Table) obtained are as follows. The results of each color, turbidity and viscosity reduction were filled as CCD order and the data analyzed using the JMP software are presented and discussed here under accordingly.

	Pattern	phosphate	talodura	color	turbidity	visc. reduction
1	--	-1	-1	14658	11534	54
2	--+	-1	1	12913	10316	53
3	+--	1	-1	11866	9767	52
4	++	1	1	9772	4668	45
5	a0	-1.414213562	0	10819	5217	51
6	A0	1.4142135624	0	10667	5883	49
7	0a	0	-1.414213562	10717	5488	51
8	0A	0	1.4142135624	10920	5501	55
9	00	0	0	13886	5545	51.5
10	00	0	0	13851	5515	51.8
11	00	0	0	14001	5670	51
12	00	0	0	13515	5730	50.9
13	00	0	0	13650	5670	52
14	00	0	0	13666	5730	51
15	00	0	0	13515	5630	51
16	00	0	0	13500	5560	51

Table 4.2 Average results obtained from syrup at different level combinations of phosphate and flocculation.

4.3 Color of clarified syrup

It was observed that the minimum and the maximum color values were 9772 and 14669 IU, respectively were gained after treatment with different dosages of the phosphate and talodura flocculant. This wide range of responses indicated that the color value was significantly affected by the dosage of phosphate and flocculants. For example, the combination 668 ppm phosphate with 12 ppm flocculants gave a color value of 9772 where as that of 117 ppm phosphate and 7.2 ppm flocculants gave a color of 14669 IU.

A quadratic model of color was developed as shown below: Final equation in terms of actual factors:

$$C = 13698.00000 - 506.74506 * t - 705.73933 * p - 87.25000 * t * p \\ - 1097.12500 * t^2 - 1059.37500 * p^2$$

Where C=Predicted color, t=talod, p=phosphate values.

The actual by predicted plot shows how well it was fitted. The actual values form a scatter of points around each mean curve. It shows the actual color values on the y-axis and the predicted values on the x-axis. The points were randomly distributed along the diagonal line with in 95% confidence limit region.

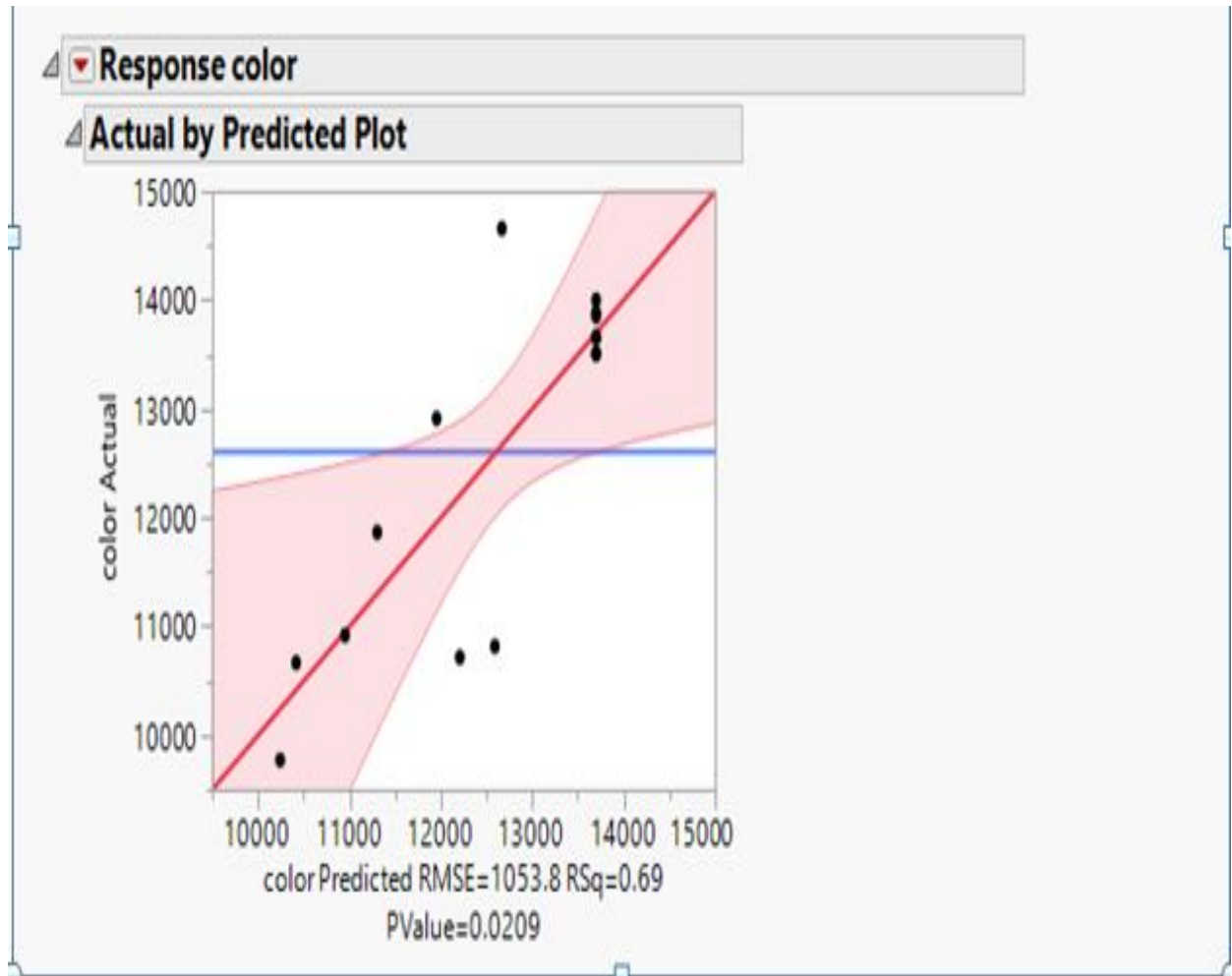


Figure 4.1 Diagonal lines within 95% confidence limit region.

As Appendix table 1.1 indicates that summary of fit for syrup was given by R^2 and Adj R^2 0.69460 and 0.52290 respectively. The R^2 reports that 80% of the variation in the response can be absorbed by fitting the model. One measure of goodness-of-fit is how well the points lie along the 45 degree diagonal line.

Design-Expert® Software
Color

Color points by value of

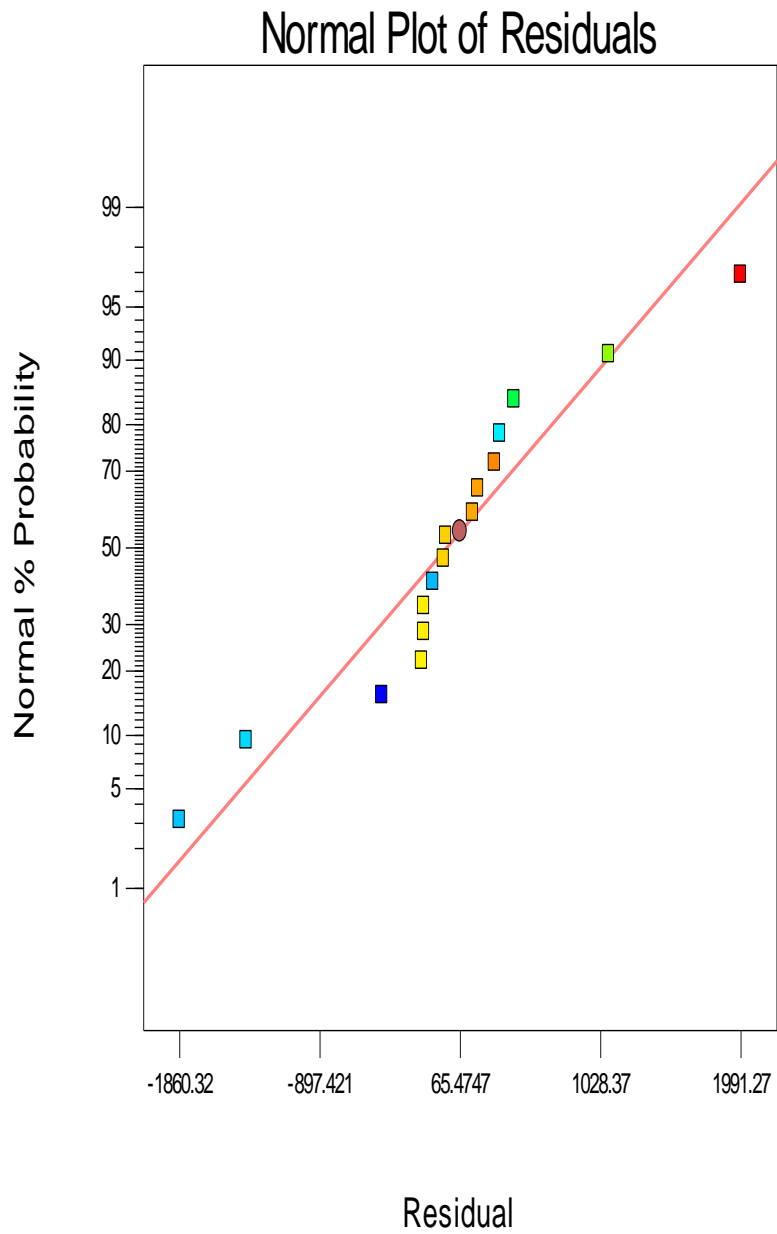
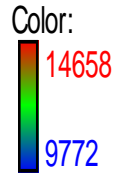


Figure 4.2 The actual by predicted plot for color points

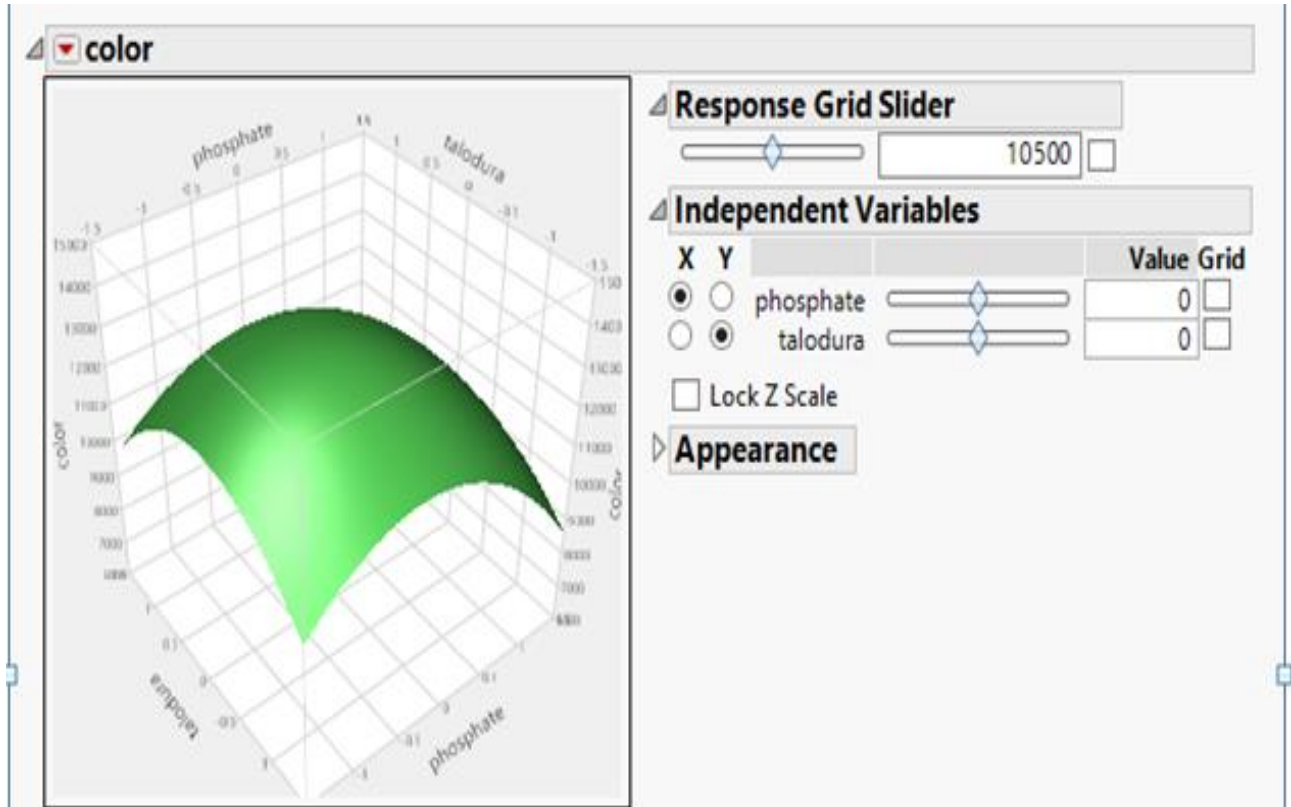


Figure 4.3 Response grid slider shows variation in color.

4.4 Turbidity of clarified syrup

It was observed that the minimum and the maximum turbidity values were 4669 IU and 11534 IU respectively. This wide range of responses indicated that the turbidity value was significantly affected by the dosage of phosphate and flocculant. For example, the combination 668 ppm phosphate with 12 ppm flocculant gave a turbidity value of 4669 where as that of 120 ppm phosphate and 12 ppm flocculant gave a turbidity of 11534 IU.

A quadratic model of turbidity was developed as shown below: Final equation in terms of actual Factors.

$$Turbidity(T) = 5631.25 - 671.89 * t - 924.58 * p - 970.25 * t * p + 846.62 * t^2 + 818.87 * p^2$$

Where T=Predicted turbidity, t=talod, p=phosphate values.

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The actual by predicted plot shows how well it was fitted. The actual values form a scatter of points around each mean curve. It shows the actual color values on the y-axis and the predicted values on the x-axis. The points were randomly distributed along the diagonal line with in 95% confidence limit region.

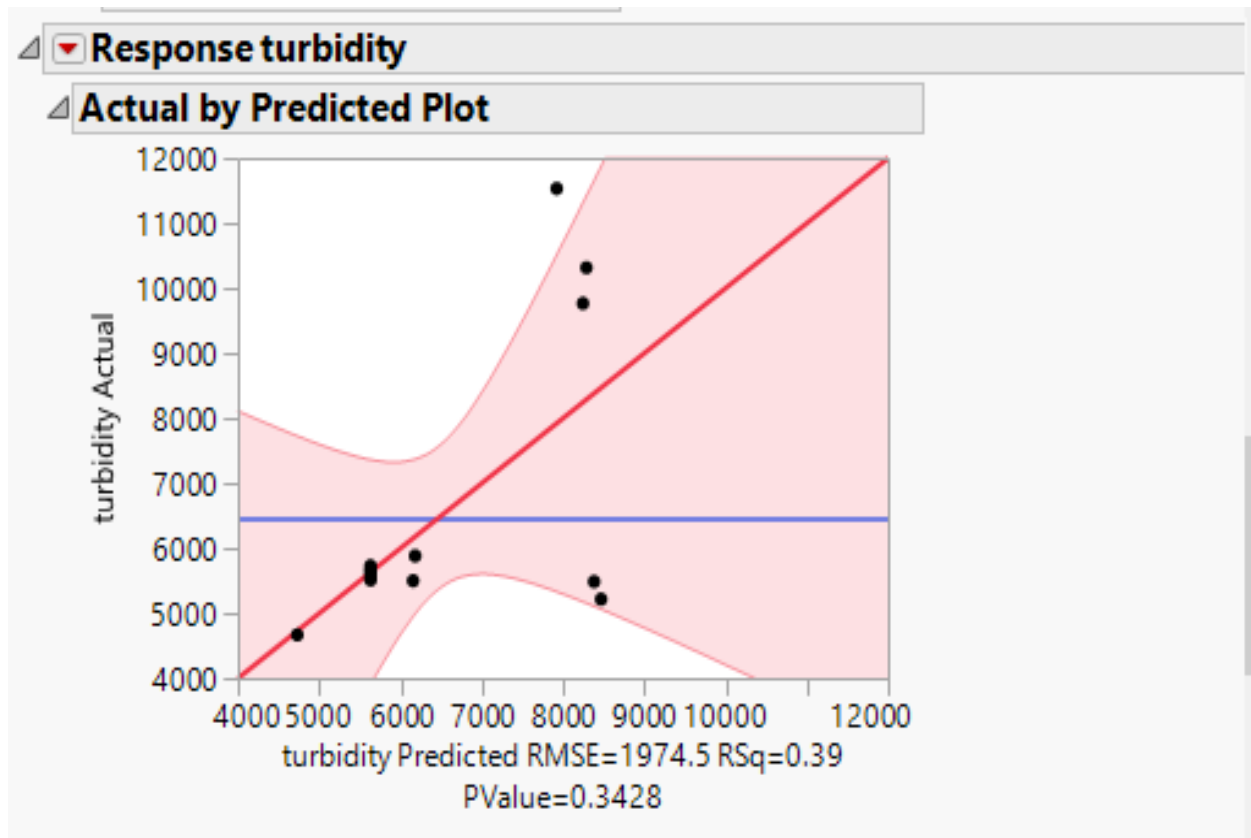


Figure 4.4 Diagonal lines within 95% confidence limit region.

As Appendix table 1.2 indicates that summary of fit for syrup turbidity was given by R^2 and Adj R^2 0.57460 and 0.392290 respectively. The R^2 reports that 70% of the variation in the response can be absorbed by fitting the model. One measure of goodness-of-fit is how well the points lie along the 45 degree diagonal line.

Design-Expert® Software
Turbidity

Color points by value of
Turbidity:
11534
4668

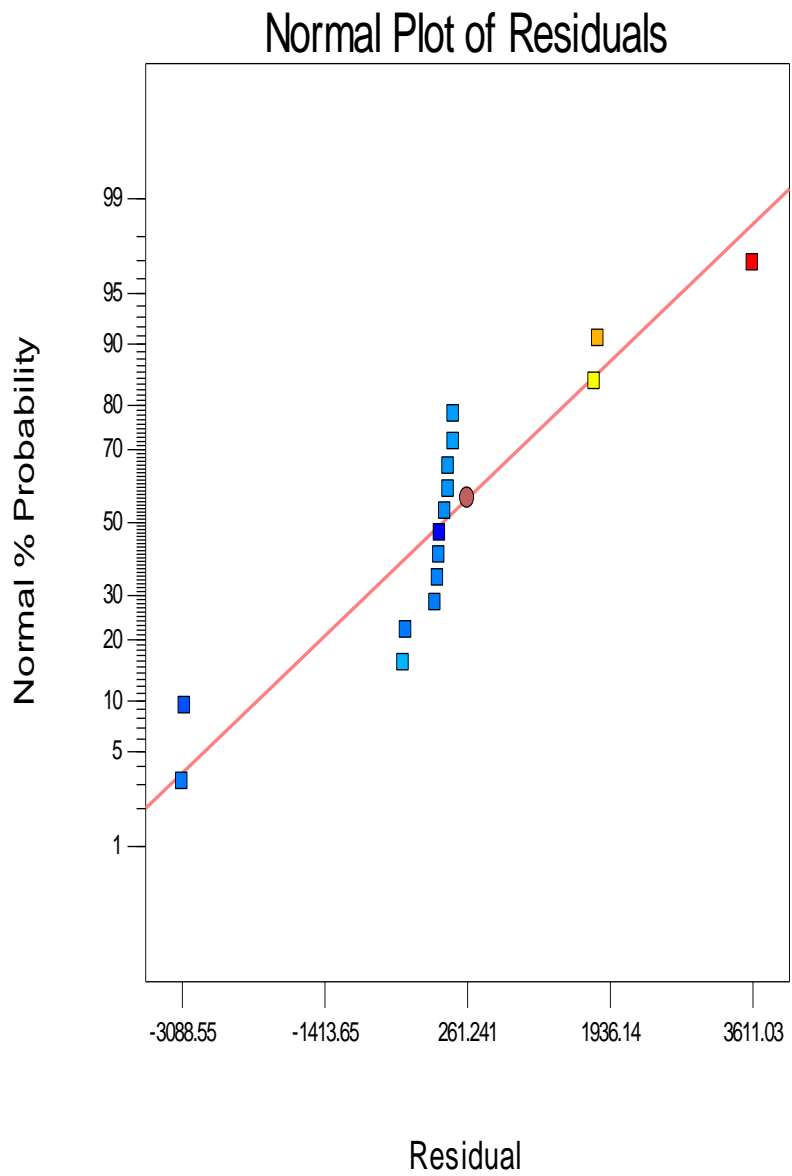


Figure 4.5 The actual by predicted plot for turbidity points.

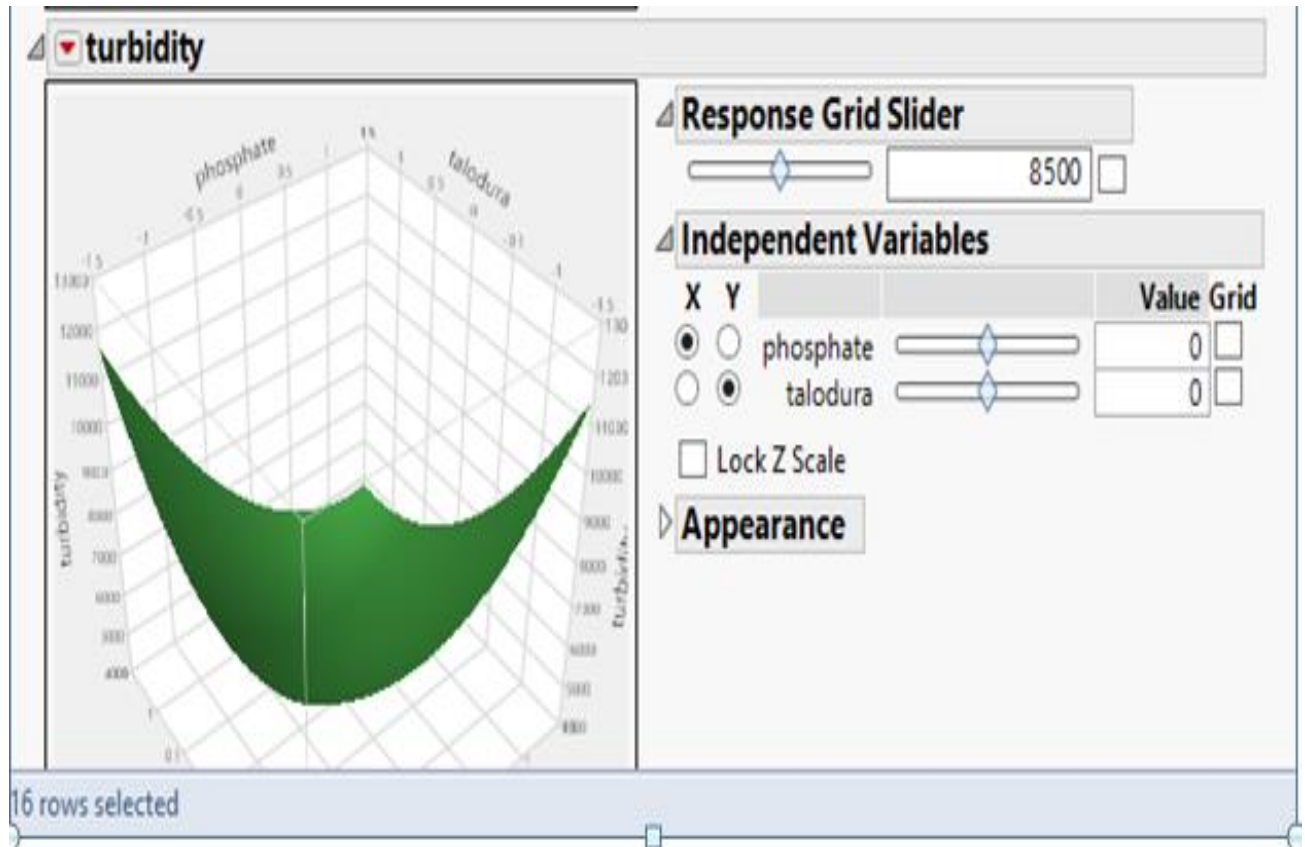


Figure 4.6 Response grid slider shows turbidity variation

4.5 Viscosity of clarified syrup

The minimum and the maximum viscosity values were 45 and 54 mpa.s respectively. This wide range of responses indicated that the viscosity value was significantly affected by the dosage of phosphate and flocculant. For example, the combination 668 ppm phosphate with 12 ppm flocculant gave a viscosity value of 45 where as that of 300 ppm phosphate and 8.5 ppm flocculant gave a viscosity result 54 mpa.s

The combined effect of phosphate and flocculant on the syrup viscosity was statistically significant with p - value 0.0029 (Appendix). The Prob > F = 0.2567 in the Lack of Fit (Appendix Table 1.3) suggested that the fitted model was adequate. On the other hand, higher levels of both phosphate and flocculant led to a low viscosity value.

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A quadratic model of turbidity was developed as shown below: Final equation in terms of actual Factors.

$$\text{Visc. reduction}(V) = 51.28 - 1.3 * t - 0.54 * p - 1.50 * t * p - 0.76 * t^2 + 0.74 * p^2$$

Where v=Predicted viscosity, t=talod, p=phosphate values.

The actual by predicted plot shows how well it was fitted. The actual values form a scatter of points around each mean curve. It shows the actual color values on the y-axis and the predicted values on the x-axis. The points were randomly distributed along the diagonal line with in 95% confidence limit region.

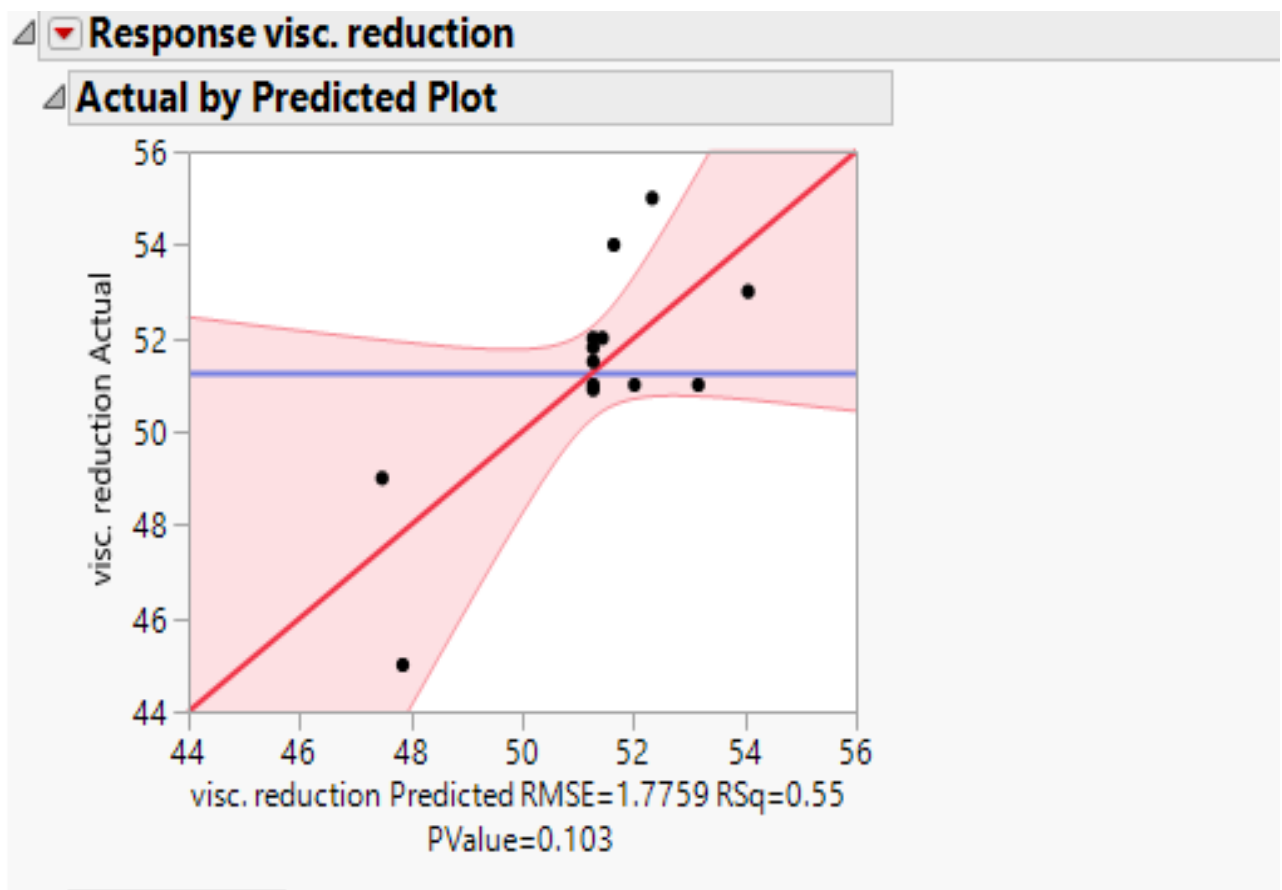


Figure 4.7 Diagonal lines within 95% confidence limit region.

Design-Expert® Software
Visc. reduction

Color points by value of
Visc. reduction:

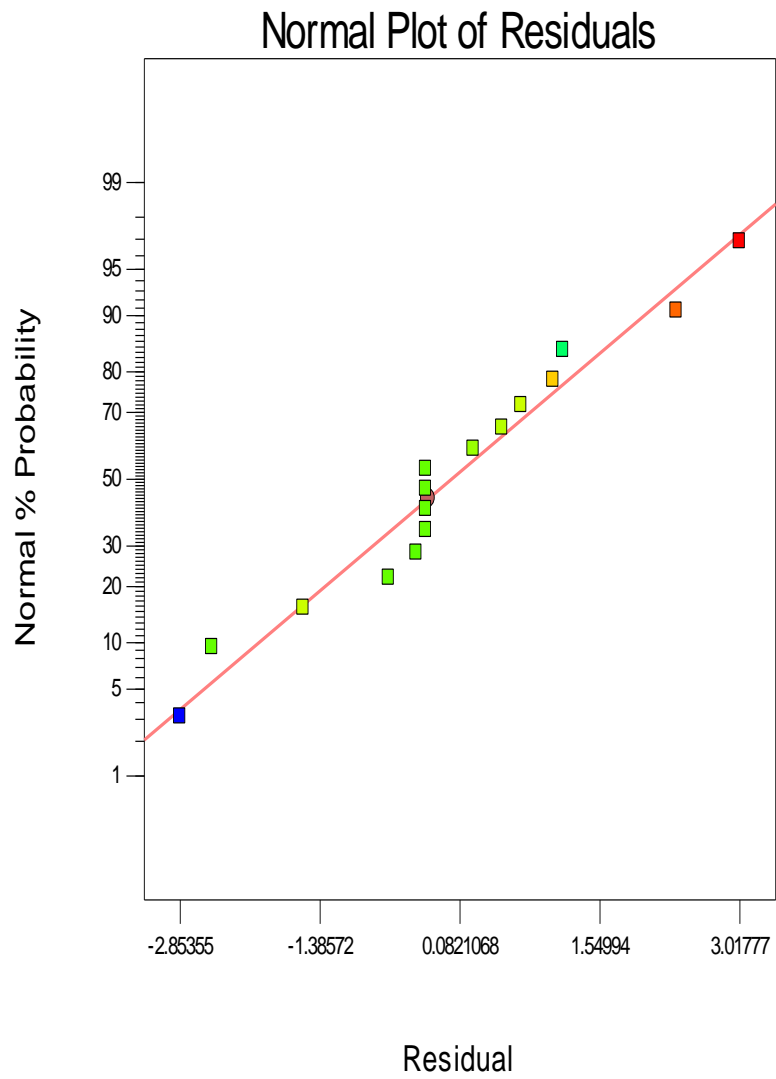
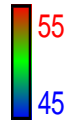


Figure 4.8 The actual by predicted plot for viscosity points

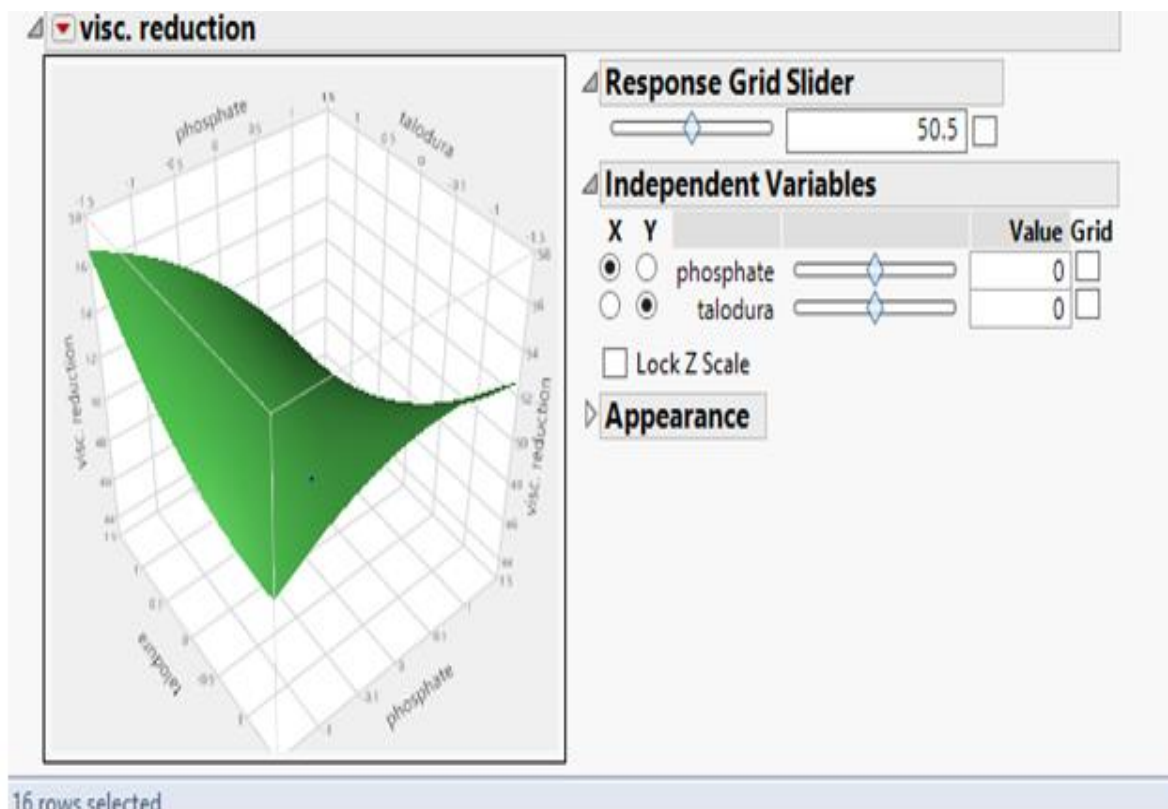


Figure 4.9 Response grid slider shows viscosity variation

4.6 Optimum point for combined color, turbidity and viscosity reduction

Optimization of Phosphate and the Talodura flocculant conditions is one of the most important stages in the development of clarified syrup leads clarified of sugar. Response surface methodology (RSM) is an effective optimization tool wherein many factors and their interactions affecting the response can be identified with fewer experimental trials than one factor at a time experiment.

Individual optimum region for each of the responses, turbidity, color, and reducing viscosity was located earlier. This is because; turbidity, color, and viscosity are more influential in indicating the syrup clarification efficiency than the rest. Turbidity removal is considered as primary objective and turbidity measurement can be used with a high degree of confidence to measure the efficiency of clarification (Mkhize, 2003). The location of the best regions and the model developed for the individual parameters can be used to improve problems faced with regard to each parameter.

Design-Expert® Software

Desirability
1
0

X1 = A: A
X2 = B: B

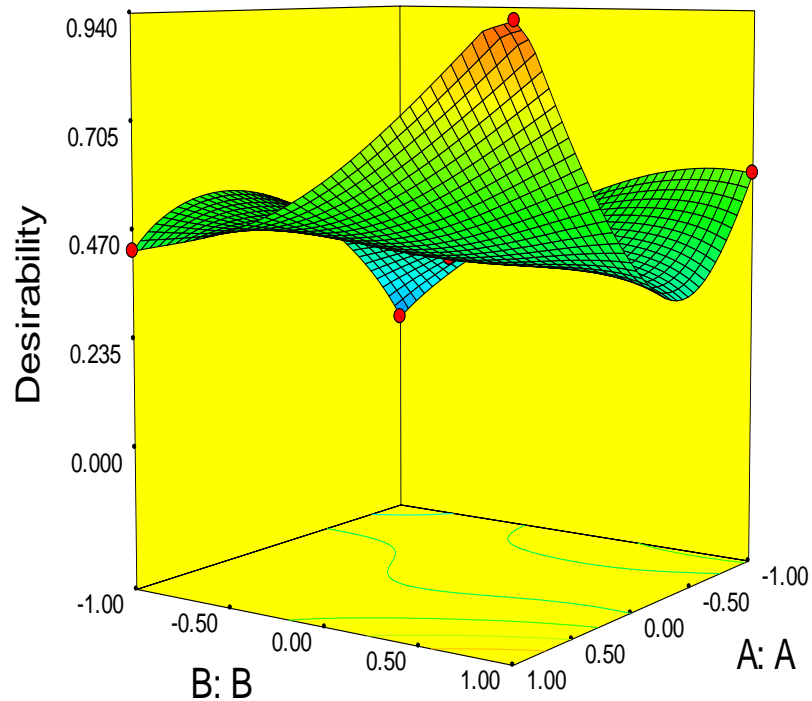


Figure 4.10 The desired point for optimum clarification

There is a need to superimpose the contour maps of the three responses in a single contour plot. The process of finding a region in which the responses are superimposed to provide the highest or lowest possible yield is known as optimization. The intersection point of two or more optimal contour lines defines the coordinates of the optimum level for each factor (Maximo, and Gacula, 1993). The following desirable ranges of responses need to be fulfilled in order to locate the common optimum point in Figure 4.10.

Turbidity: low values of turbidity are desirable; hence, one should use contour lines with predicted responses in the neighborhood of 4668 to obtain low turbidity value. The region bounded by 4668 contour lines was selected as the optimum region for turbidity.

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Color: The low value of color was bounded by contour lines 9772. This region selected as an optimum region for low color.

Viscosity reduction: The high value of Viscosity reduction was 45 and selected as an optimum region for Viscosity reduction.

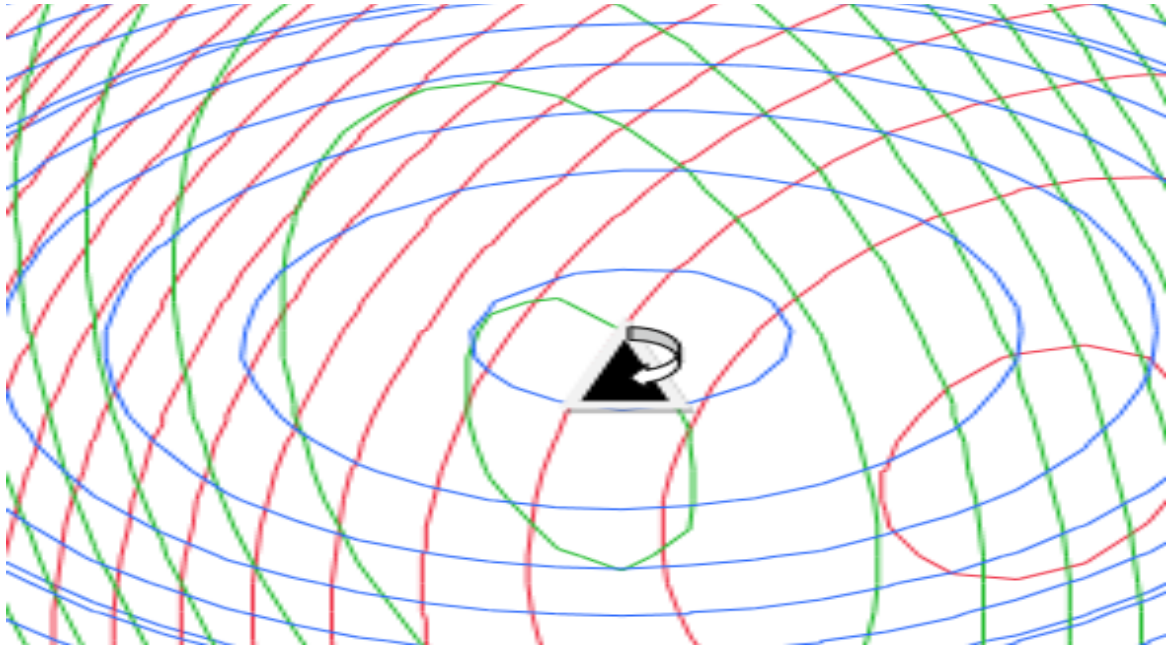


Figure 4.11 Superimposed contour plots for optimum point.

Therefore, using JMP optimization software, the optimum range for the three response combination was determined by choosing the intersection range that satisfied the three responses accordingly in the contour plotting graph. The mentioned three scenarios help to generate a common optimum region. The region obtained by superimposing the above response boundaries was depicted in the arrowed region of the superimposed contour map (Figure 4.10).

	Pattern	phosphate	talodura	color	turbidity	visc. reduction
4	++	1	1	9772	4668	45

Table 4.3 The optimum phosphate and talodura for syrup clarification.

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

All Ethiopian sugar factories are practicing production of plantation white sugar (PWS) by double sulphitation system. Sulfur dioxide (SO₂) is toxic gas. When it is used during the manufacture of any food product residual traces of sulfur remaining in such food product is hazardous to human health. The other technology of clarification is Syrup clarification using flotation process. The basis of this process is based on the Phosphoflotation and froth flotation, conveniently termed as 'phosphoflotation' process applied in sugar refineries. Since the syrup liquor is very viscous, at about 65°Brix, clarification is done by flotation. The flotation system uses chemicals like cationic flocculant (talodura) and phosphates to bring up impurities to surface of the syrup clarifier. For this operation proportionating the dosages of these chemicals is mandatory. By this research experiments; dosages of phosphate of 668ppm and 12ppm of talodura was approved. It is excellent to operate this flotation system with these chemical dosages for excellent clarity of sugar at Wonji Sugar Factory.

5.2 Recommendation

By the time this research was done Wonji Sugar Factory is using syrup sulfitation by missing juice sulfitation because of the failures of the system. This makes high ICUMSA values of color, turbidity and viscosity reduction on sample analyzed. Because of these high values of sample analyzed; the high change done, up to 70% is still not low color syrup. Secondly these experiments were done at the laboratory scale with laboratory materials and it is recommended that these experiments should be repeated with syrup clarification set up made for syrup clarification.

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APPENDICES

Appendix A. Table of Least Squares fit to results of color, turbidity and viscosity for clarified syrup

Appendix table 1. Model fitting to results of color for clarified syrup

Appendix Table 1.1 Summary fit for results of color for clarified syrup

RSquare	0.6900054
RSquare Adj	0.700081
Root Mean Square Error	155.1574
Mean of Response	794.6875
Observations (or Sum Wgts)	16

Appendix Table 1.2 ANOVA for results of color for clarified syrup

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Model	5	963277.3	192655	8.0027	0.0029*
Error	10	240738.2	24074		
C. Total	15	1204015.4			

Syrup clarification using flotation system with optimized dosages of phosphate and cationic flocculant.

Appendix Table 1.3 Lack of fit for results of turbidity for clarified syrup

Residual	1.000E+006	5	0.0030	0.3367		
Lack of Fit	1.111E+007	3	3.703E+006	99.66	< 0.0001	significant
Pure Error	2.601E+005	7	37153.14			
Cor Total	3.604E+007	15				

The Model F-value of implies the model is significant. There is only a 3.367% chance that a "Model F-Value" this large could occur due to noise.

Appendix table 2. Model fitting to results of turbidity for clarified syrup

Appendix Table 2.1 Summary fit for results of turbidity for clarified syrup

RSquare	0.791305
RSquare Adj	0.686957
Root Mean Square Error	852.1841
Mean of Response	7958.563
Observations (or Sum Wgts)	16

Syrup clarification using flotation system with optimized dosages of phosphate and cationic flocculant.

Appendix Table 2.2 ANOVA for results of turbidity for clarified syrup

Source	Sum of Squares	df	Mean Square	F Value	p value	Prob > F
Model	2.468E+007	5	4.935E+006	4.34	0.0232	significant
A-A	2.054E+00	1	2.054E+006	1.81	0.2086	
B-B	3.985E+006	1	3.985E+006	3.51	0.0907	
AB	30450.25	1	30450.25	0.027	0.8733	
A2	9.629E+006	1	9.629E+006	8.47	0.0156	
B2	8.978E+00	1	8.978E+006	7.90	0.0185	

The Model F-value of 4.34 implies the model is significant. There is only a 2.32% chance that a "Model F-Value" this large could occur due to noise.

Appendix Table 2.3 Lack of fit for results of turbidity for clarified syrup.

Residual	35.78	103.58	0.0022	0.5567	
<i>Lack of Fit</i>	<i>34.49</i>	<i>3</i>	<i>11.50</i>	<i>62.14</i>	<i>< 0.0001 significant</i>
<i>Pure Error</i>	<i>1.29</i>	<i>7</i>	<i>0.19</i>		
Cor Total	70.80	15			

Appendix table 3. Model fitting to results of viscosity for clarified syrup

Appendix Table 3.1 Summary fit for results of viscosity for clarified syrup

RSquare	0.722075
RSquare Adj	0.583112
Root Mean Square Error	0.171718
Mean of Response	0.56375
Observations (or Sum Wgts)	16

Appendix Table 3.2 ANOVA results of viscosity for clarified syrup

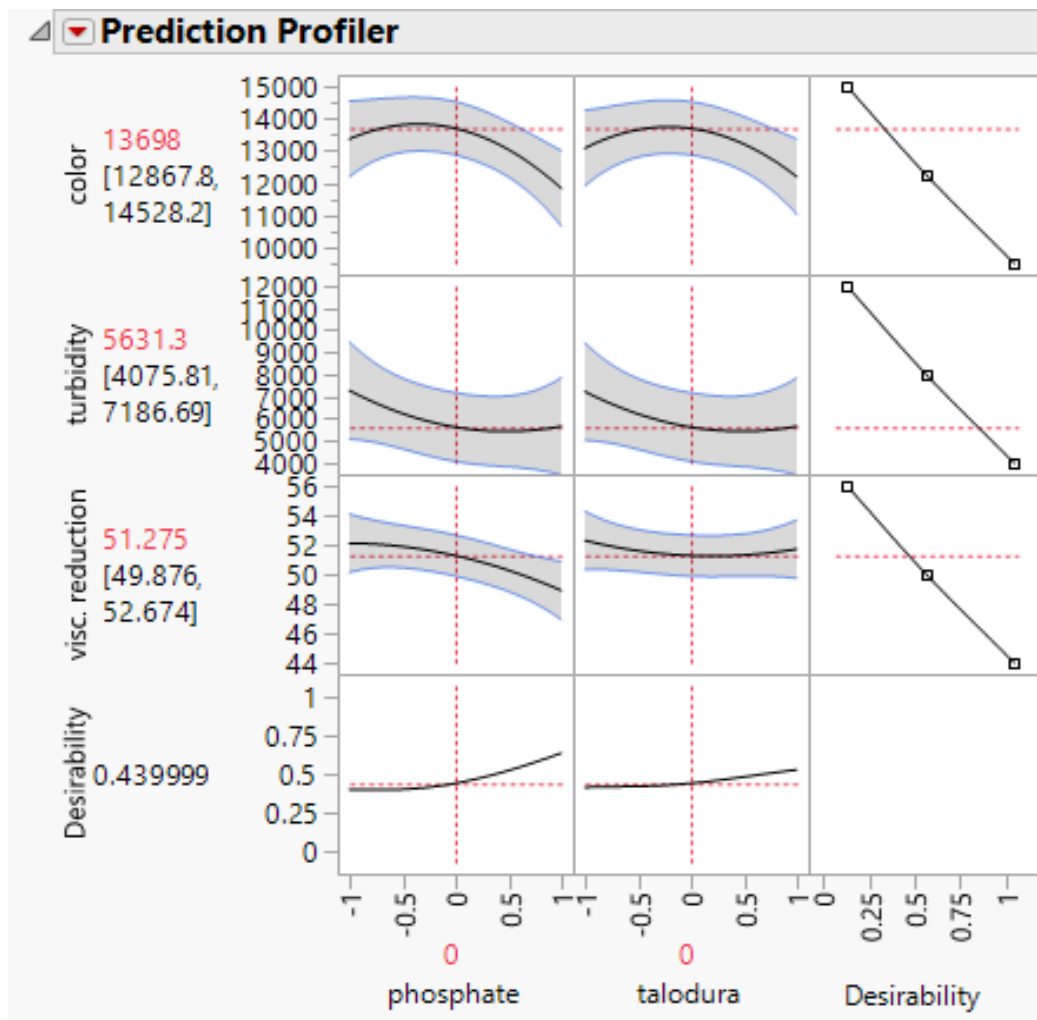
Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Model	5	75954.786	15191.0	8.3071	0.0025*
Error	10	18286.652	1828.7		
C. Total	15	94241.438			

Syrup clarification using flotation system with optimized dosages of phosphate and cationic flocculant.

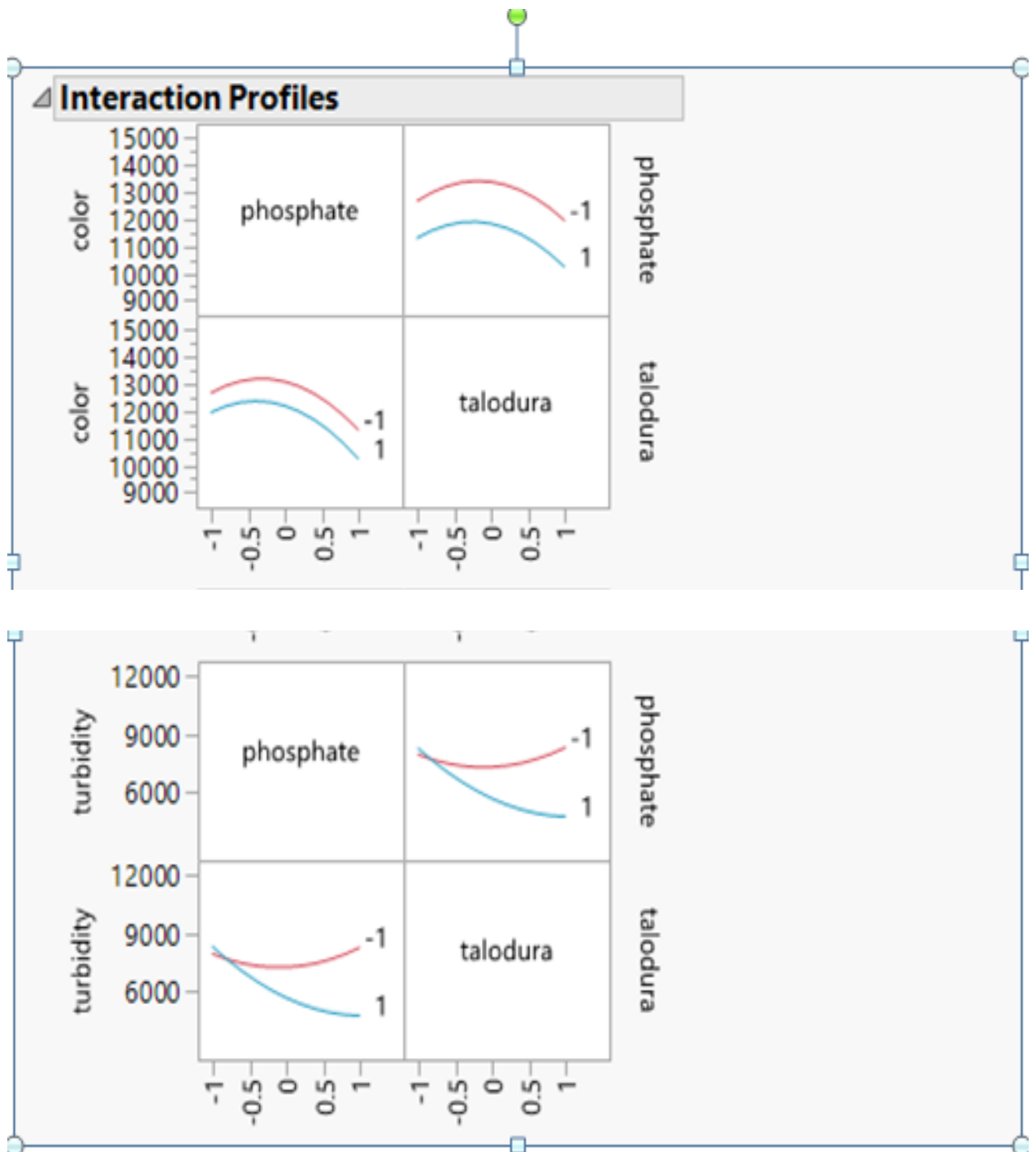
Appendix Table 3.3 Lack of fit for results of viscosity for clarified syrup.

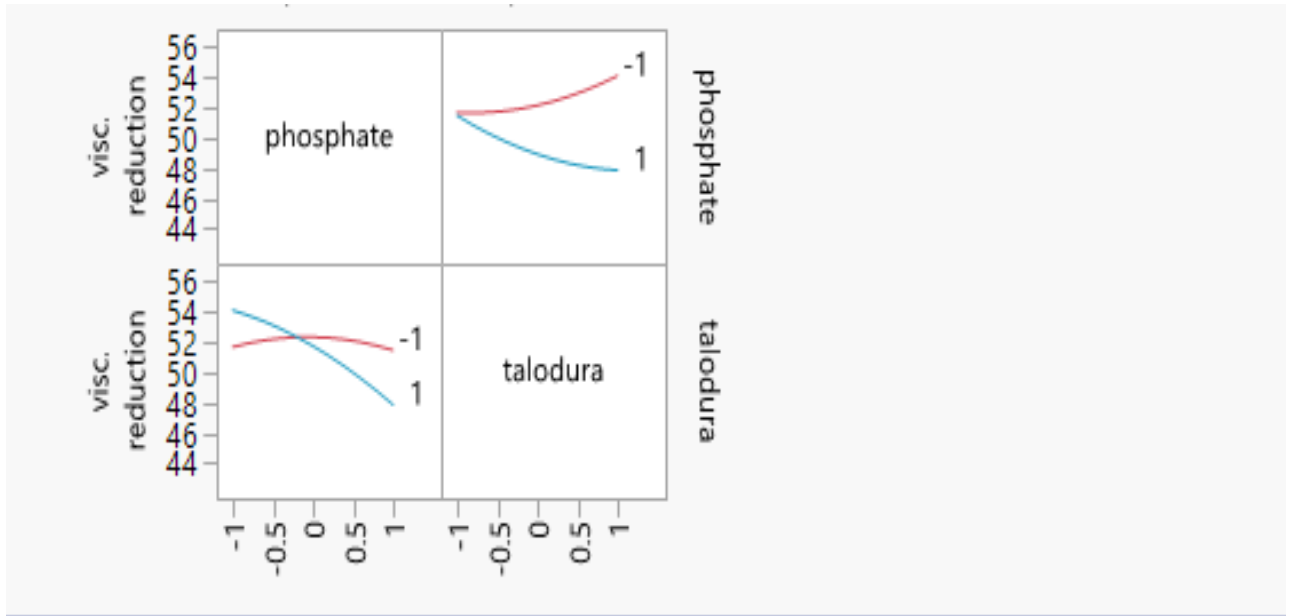
Residual	3.873E+007	10	3.873E+006	0.0029	0.2567
Lack of Fit	3.868E+007	3	1.289E+007	1859.65 < 0.0001	significant
Pure Error	48537.50	7	6933.93		
Cor Total	6.405E+007	15			

Appendix B. figures



Appendix Figure 1. Prediction profile





Appendix Figure 2. Interaction profiles

Appendix C. photos



Appendix Photo 1. Cane loading in the field



Appendix Photo 2. Flotation system syrup clarification plant

Syrup clarification using flotation system with optimized dosages of phosphate and cationic flocculant.



Appendix Photo 3. Flotation system syrup clarification plant



Appendix Photo 4. Sample of the syrup taken from wonji factory



Appendix Photo 5. The talodura flocculant



Appendix Photo 6. The CaCO₃ used to precipitate the phosphate