

Addis Ababa University
School of Graduate Studies
Addis Ababa Institute of Technology
Department of Chemical Engineering

Design and Optimization of Molasses Treatment Plant to Reduce Scale Formation in Ethanol Production

(The Case of Metahara Sugar Factory Ethanol Plant)

By

Teshale Firdissa

October, 2012
Addis Ababa

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A Thesis Submitted to the Research and Graduate School of Addis Ababa University, Addis Ababa Institute of Technology, Department of Chemical Engineering in Partial Fulfillment of the Requirements for the Attainment of the Degree of Masters of Science in Chemical Engineering Under Process Engineering Stream.

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Acronyms

3-D	Three dimensional
ANOVA	Analysis of variance
Brix	Percentage by weight of the solid in a pure sucrose solution
CCD	Central composite design
cP	Centipoises
CPU	Condensate polishing unit
Db	Bundle diameter
E.D.T.A	Ethylene diamine tetra acetic acid
ICUMSA	International commission for uniform methods of sugar analysis
PPM	parts per million
RSM	Response surface methodology
SASTA	South African sugar technologists association
SD	Standard deviation
TEA	Triethanolamine
WHO	World health organization
WTP	Water treatment plant
XRD	X-ray powder diffraction
XRF	X-ray fluorescence

Abstract

Fouling in industrial heat exchangers leads to economic penalties. To overcome this problem, either cleaning of heat exchangers or reduction of the scaling is the two possible solutions. But, cleaning of heat transferring unit is an expensive exercise. Therefore, this study has been conducted with the objective to design and optimize molasses treatment plant to reduce scale formation in ethanol production.

The study has been conducted in such a way that, first scale samples collected from Metahara sugar factory ethanol plant distillation column and characterized physically and it is hard scale with an average thickness of 2.04cm and gray in color which shows that it is the result of crystallization. In addition to this, it has been characterized chemically to determine its composition and the scale is 63.87% composed of CaO. Then, to assess cause of this scaling, process water and the raw molasses has been characterized for their composition and pH which shows that process water is within a normal hardness and pH range. But, the molasses of Metahara sugar factory is with an average of 2.41% CaO which is abnormally high when compared to world average of 1.5% CaO % molasses. Therefore, the main cause of heat transferring units scaling in the plant is the CaO content of the molasses. To overcome this problem, treating the molasses with H_2SO_4 and heat is the best technology. Because, the reaction of CaO with H_2SO_4 at higher temperature give CaSO4 which is insoluble in water and easily separated by sedimentation. Experiments have been conducted with varying influential molasses clarification conditions and 100^OC temperature, 4 pH, 50^o brix and 2hours retention time have been determined as the optimum clarification process conditions. At these optimum conditions 54.43% of the CaO in the molasses has been removed. At these process conditions, 1.08CaO% molasses has been obtained which is too low when compared with world average of 1.5CaO% molasses.

Depending on the optimum conditions determined experimentally and the existing condition of the plant, molasses treatment plant process flow sheet has been proposed and the equipments for clarification plant have been designed in which case most of the equipments can be easily fabricated locally.

Finally, the plant is financially evaluated and its initial investment cost will be recovered fully within only eight operation months which makes the plant viable.

1. Introduction

1.1. Background

Fouling is a complex process, which usually involves various physical, chemical and biological processes. It is a process by which deposits settle and accumulate on heat transferring surfaces of heat exchangers. Fluids flowing in heat exchangers may contain dissolved substances, suspended matter or may carry substances that promote growth of biological organisms. As a result deposits may accumulate on a heat transfer surface leading to the formation of a layer which we call fouling. The thermal conductivity of the layer so formed is mostly very low and, therefore, its presence on a heat transferring surface tends to increase the resistance to heat flow.

Consequences of fouling in process industries include increased energy consumption, results in extra maintenance and cleaning costs, and loss of production opportunities to stop operation and clean the unit. In general, fouling in industrial heat exchangers leads to economic penalties.

Out of many types of fouling, scaling of heat exchangers is the most common type of fouling we face in process industries which refers to the formation of solid deposits on a heat transfer surface, arising primarily from dissolved inorganic salts present in the flowing fluid. This problem poses challenges to both designers and operators of heat exchangers in many process industries. The main physical mechanism responsible for deposit formation here is crystallization processes in which dissolved salts in the fluid crystallizes and deposit on the surface of heat exchangers.

Manufacturing of ethanol from sugar cane molasses is one example of an industry where scaling of heat exchangers surfaces is experienced. The manufacture of ethanol from sugar cane molasses involves three important processes, namely, molasses treatment, fermentation and distillation processes. These processes involve a number of heat transferring equipments which will be the limiting factors if fouled. In addition to these processes, ethanol plant also includes evaporation plant to reduce the volume of vinasse produced where multiple effect evaporators employed. All these processes are energy intensive processes. Beside these, ethanol plants mostly work in collaboration

with sugar factories where energy is the very prominent factor for profitability of the factories. For this reason, efficient energy utilization is of great importance in this plant. To achieve efficient utilization of energy, ethanol plants are designed with high energy integration between process units. This arrangement is, however, limited by the problem of fouling.

Almost all ethanol plants experience scaling of pre-heaters, distilleries and evaporators; but the extent of scaling varies from plant to plant, within a season and from season to season for individual equipment. These encrustations are formed from the combined effects of several processes involving inorganic and organic molecules or ions.

The possible causes of the scaling are impurities in molasses or process water. The impurities deposit onto heating surface areas of heat exchangers. Because heating surface areas have a higher temperature at their surface than the surrounding fluid and provide nucleation sites for scale growth. Scale facilitates the corrosion of surfaces, restricts fluid flow and, because it has low thermal conductivity, its accumulation on metal surfaces hinder heat transfer across the tubes wall.

The type of the scale being formed depends on a number of variables such as quality of input materials and intermediate products, flow properties of the fluid, rate of evaporation, and process conditions of the system (*Rackenann, et al, 2010*).

1.2. Statement of the Problem

Ethanol production is an energy intensive process since it involves many thermal unit operations like pre-heaters, distillation columns and evaporators. One of the most important characteristics of any thermal unit operation is to ensure that it can perform its function properly and at adequate rate to ensure that the unit does not become the rate limiting step in the factory. Therefore, profitability of the plant depends on how efficiently it uses the available energy. However, as the heating surfaces covered with scale, the heat transfer coefficients decline, and if the units are heavily fouled it will not always meet the design production rates. As a result, the unit becomes the limiting factor for the production rate *(Rackemann, et al, 2010).* Therefore, fouling of heat transferring units in ethanol production is a big challenge for profitability of the plant.

This problem is particularly very series in ethanol plant of Metahara sugar factory that:

i. The scaling rate of heat transferring equipments is very frequent and as a result, the distilleries and evaporator units do not work properly for more than four days after cleaning. Therefore, the processes operation stops every four days for cleaning. But, Finchaa sugar factory ethanol plant operates for more than six months without any cleaning and process interruption.
ii. The scale deposited on heat transferring surfaces with in this short period of time is on average 2.04 cm thick which incurs extra resistance on heat flow and results in extra steam consumption. But, in Finchaa sugar factory ethanol plant thermal units; there is no even a scale with structured shape to measure. Most of the time scale phased in the plant is in molasses heaters which can easily cleaned without process interruption using standby units.
iii. Since the scale formed is hard scale, currently it takes a minimum of eight hours to clean which results in loss of production opportunity. Both chemical and mechanical cleaning mechanisms involved in removing this scale. But, in Finchaa sugar factory, the units are easily cleaned by boiling caustic soda in the units without mechanical scraping.
iv. There is incurring of additional cost and losses of production opportunity to clean these units.

In Metahara sugar factory ethanol plant, the problem is not only the financial expense. The big challenge that the plant currently faces is the risky of the workers cleaning the equipments. Both, the distillation columns and evaporator sets are not suitable for cleaning and the workers are in risk of accident. But, no research has been done to identify the cause of this problem.

Therefore, the aim of this thesis is to identify the main cause of this scaling problem and to suggest the possible preventive solution or reduction for the problem.

1.3. Objectives

- ***General Objective***

  The general objective of this study was to design and optimize treatment plant for the raw material responsible for scaling to reduce scale formation in ethanol production as much as possible.

- ***Specific Objectives***

  The specific objectives of the study were to:

  - Characterize the scale formed in heat transferring units of the plant.
  - Characterize the composition of raw molasses from sugar industry and process water to the plant.
  - Assess the main cause(s) of the scaling of heating surface of heat transferring units of the plant.
  - Suggest the possible solution for the problem of scaling in the plant.
  - Treat the raw material responsible for the scaling to reduce its scale causing component(s).
  - Design and optimize treatment plant to reduce scale forming components of the raw material.
  - Compute financial analysis of the proposed molasses treatment plant.

1.4. Significance of the Study

These days, the world is phasing acute shortage of energy. As a result, cost of energy is increasing alarmingly. In addition to these problems, global warming is increasing at rate which seems out of control. These are because of the non renewable source of energy we are currently depending on, which are also the main source of green house gases. As a result, the nature itself is calling for the generation to use alternative renewable sources of energy such as fuel ethanol from biomass.

Besides using renewable energy sources, efficient utilization of the already existing energy is the best and top rating both to overcome the shortage of energy and to reduce global warming.

Ethiopia is one of the countries working strongly against these problems. In Ethiopia, fuel Ethanol has been used as blend with gasoline in car engines for the last four years and there is good promotion these days. To cover this consumption locally, ethanol plants have been included in the plan of new sugar factories projects and expansion of the existing ones which are currently in progress. Therefore, we will have more than ten ethanol plants in near future.

Currently, we have only two ethanol plants except the small scale producers. One at Finchaa sugar factory and the other at Metahara sugar factory. But, the newly implemented plant at Metahara sugar factory is with big challenge due to scaling of heat transferring units.

Therefore, after successful completion of this study, the paper will help to solve the problem of scaling in the plant and ensures efficient utilization of energy. In addition to this, it will help as technical input for ethanol producers from molasses as a whole.

2. Literature Review

2.1. Introduction

Fouling is a general term that includes any kind of deposit of extraneous material that appears upon the heat transfer surface during the lifetime of the heat exchanger. Whatever the cause or exact nature of the deposit, an additional resistance to heat transfers is introduced and the operational capability of the heat exchanger is correspondingly reduced. In many cases, the deposit is heavy enough to significantly interfere with heat transferring across the tube wall and fluid flow through the tube and increase the pressure drop required to maintain the flow rate through the exchanger.

To overcome this problem, the designer must consider the effect of fouling upon heat exchanger performance during the desired operational lifetime and make provisions in his design for sufficient extra capacity to insure that the exchanger will meet process specifications up to shut down for cleaning. The designer must also consider what mechanical arrangements are necessary to permit easy cleaning of heat exchangers.

2.2. Types of Fouling

There are several different basic mechanisms by which fouling deposits may be created and each of them in general depends upon several variables. In addition, two or more fouling mechanisms can occur in conjunction in a given service.

Depending on the key physical, biological or chemical process essential to the particular fouling mechanism, it is common to classify fouling into six categories. These categories are precipitation fouling, particulate fouling, corrosion fouling, biological fouling, solidification fouling and chemical reaction fouling *(Kadmbini Gaur, 2006)*.

2.2.1. Precipitation Fouling

Precipitation fouling occurs when dissolved salts in the flowing fluid crystallize as the fluid becomes supersaturated with respect to a deposit forming material. The driving force in precipitation fouling is provided by the difference in chemical potential of the substance in the solution and that at the surface. Inorganic salts can exhibit either normal or inverse solubility tendency. Salts that exhibit normal solubility form deposits on sub-cooled surfaces, while those salts that have inverse solubility behavior form deposits on superheated surfaces. The most widely encountered form of precipitation fouling is that due to crystallization. Examples of industries where crystallization fouling is a problem include desalination plants, sugar factories, ethanol plants and pulp mills.

2.2.2. Particulate Fouling

In Particulate fouling particles that are suspended in the flowing fluid get deposited on the heat transfer surface. The source of the suspended solids could be corrosion products or crystallization products formed in the bulk, or just particles such as sand. Sometimes, particulate fouling and crystallization fouling have been observed to occur together (*M. G. Mwaba, 2003)*

2.2.3. Corrosion Fouling

Corrosion fouling is due to the chemical reaction between the heat transferring wall and the species in the fluid. In this case, the heat transferring surface is also a reactant. Corrosion products may act as catalysts influencing other fouling mechanisms acting as nucleation sites. For instance, deposited corrosion products may lead to roughening of the surface, which, in turn would act as nucleation sites and promote crystallization and sedimentation. Corrosion problems are encountered in cooling systems when river water is used as a cooling medium or in boiler plants where fine suspensions of black magnetite particles may circulate with the boiler feed water.

2.2.4. Biological Fouling

Biological fouling occurs when an organic film consisting of microorganisms and their products develop on a heat transfer surface. Biological fouling can also result from the growth of microorganisms in the fluid and a subsequent deposition on the surface. This type of fouling is common in cooling water systems and in milk factories.

2.2.5. Solidification Fouling

Solidification fouling occurs either due to the solidification of a pure liquid in contact with a sub-cooled surface, or the deposition of a high melting point constituent of a liquid in contact with a cold heat transfer surface. Examples of this can be found during the production of chilled water.

2.2.6. Chemical Reaction Fouling

Chemical reaction fouling occurs when deposits accumulate on a heat transferring surface as a result of a chemical reaction. In this type of fouling, surface temperature is an important parameter as it affects the reaction rate. Oxidation promoters are also of importance. The material of the heat transfer surface does not take part in the reaction though it may act as a catalyst. This type of fouling is found in petrochemical industries.

2.3. Fouling Processes

Fouling is a transient process that occurs in a sequence of five stages. These are: - initiation or delay period, mass transport, deposition, removal, and aging.

2.3.1. Initiation or Delay Period

The initiation or delay period is the time period that immediately follows the startup of the exchanger and may last from a few seconds to several days. It is the time when conditions conducive to deposition on the heat transfer surfaces are established. The duration of this phase depends on factors such as type of fouling, surface temperature and surface condition. For instance, particulate fouling has practically no induction period while crystallization fouling may have a delay period of several weeks. For inversely soluble salts, the delay period is also observed to vary inversely with surface temperature. This is because super-saturation and rate reaction increase with temperature. In most cases, the beginning of deposition is associated with an increase

in heat transfer. This happens because the surface becomes rough as deposits form on a previously smooth surface.

2.3.2. Mass Transport

The components that are responsible for deposit formation on the surface are originally either suspended or dissolved in the fluid. During this stage, deposit forming components are transported from the bulk fluid to the heat transfer surface. The driving force for transport is the difference in the concentration of the species in the bulk fluid and at the surface.

2.3.3. Deposition

When the species reach the heat transfer surface, they either settle there or react to form substances that finally stick to the surface. Deposition can either be controlled by diffusion or by adhesion. If the rate at which species are transported to the wall is much higher than the rate at which they are integrated into the crystal lattice, then the deposition is said to be adhesion controlled. If, on the other hand, the rate of integration is much higher than the rate of diffusion, then the deposition is said to be diffusion controlled.

2.3.4. Removal

As the deposit layer starts increasing, some parts of it may be removed by the action of fluid shear. The amount removed depends on the strength of the deposit layer.

2.3.5. Aging

A deposit layer on the wall undergoes an aging process with time. This process may either strengthen or weaken the deposits. Despite the efforts invested, the process of fouling is at present not very well understood. This makes it difficult to accurately predict the evolution of the fouling thermal resistance. As a result, the current practice in the design of heat exchange systems is to incorporate a fouling factor in the calculation of the overall heat transfer coefficient.

2.4. Ethanol Manufacturing

2.4.1. Process Description

i. Raw Material

Molasses is the most commonly used raw material for production of ethanol. It contains about 50% of the total sugar; of which 30 to 33% is sucrose and rest is reducing sugar *(Mott Mac Donald, 2010).*

Molasses is obtained from the production of white sugar by repeated crystallization of sucrose in the mother liquor. It is the final molasses that obtained from the last massecuite, which is commonly used for the production of ethanol. The final cane molasses in Ethiopian sugar factories is with a purity of 34 to 40% which is a big loss if multiplied with the amount of molasses obtained from the sugar production which is in the range of 3 to 4% on cane. These can be recovered by further crystallization by boiling of the final process. But, it is not economical to recover this loss with crystallization process. Therefore, ethanol production is used to recover this loss in the form of ethanol alcohol which is the best solution to the current shortage and price rise of energy.

Ethanol production from molasses consists of three major process steps. These are molasses treatment, fermentation, and distillation processes. In addition to theses main steps, evaporation for vinasses concentration is the very important plant which requires special attention.

ii. Molasses Treatment

This stage is used for the reduction of the level of impurities in the molasses. Molasses treatment results in decreased level of inhibitory substances like Ca, Cu, and Fe in the molasses solution which improves ethanol production and calcium compounds which highly affect the efficiency of the plant by scale forming on the heating surface areas of the equipments in the later processes.

The first process step in molasses treatment is dilution of the molasses from 80 - 86 ^{o}brix to 50 - 60^{o}brix to reduce its viscosity and therefore to facilitate heating. Then, the

next step is heating the diluted molasses to temperature of 60 to 65^{o}C which facilitates the reaction between calcium oxides and H_2SO_4. After preheating, its pH adjusted by addition of sulfuric acid (H_2SO_4) until pH becomes 4 to 5. Finally, the molasses heated to 95 to 100^{o}C in continuous operation.

Under the effect of both temperature and acidification, calcium sulfate ($CaSO_4$) precipitation, flocculation of long chain colloidal, and insolubilization of gums and waxes reactions takes place within the molasses.

$$CaO + H_2SO_4 \longrightarrow CaSO_4 \downarrow + H_2O$$

Then, the precipitated calcium sulfate is to be separated from the clear molasses by decantation processes.

iii. Fermentation

Fermentation is the breakdown or catabolism of organic compounds by micro-organisms under both aerobic and anaerobic conditions. Various bacteria and yeasts metabolize sugars into ethanol through different pathways using different enzyme systems. Alcohol fermentation is used for the industrial production of alcohols and alcoholic beverages.

Ethanol for use in alcoholic beverages, and the vast majority of ethanol for use as fuel, is produced by fermentation processes. When saccharomyces (brewer's yeast) species of yeast metabolize sugar in the absence of oxygen, they produce ethanol and carbon dioxide. The overall chemical reaction conducted by the yeast may be represented by the chemical equation.

$$\text{Sugar (Carbohydrate)} \xrightarrow{\text{Yeast}} \text{2Ethanol + 2Carbon Dioxide}$$

$$C_6H_{12}O_6 \xrightarrow{\text{Yeast}} 2C_2H_5OH + 2CO_2$$

The process of culturing yeast under conditions to produce alcohol is referred to as brewing. Brewing can only produce relatively dilute concentrations of ethanol in water; concentrated ethanol solutions are toxic to yeast *(Kadmbini Gaur, 2006).*

iv. Distillation

Distillation process of fermented beer is the next very important step in production of alcohol after fermentation. Distillation is a method of separating mixtures based on differences in volatility of components in boiling liquid mixture. It is a physical separation process.

Once the alcohol is produced, it should be purified to the required quality. This is done by distillation process. This step consumes a considerable amount of energy and is also a deciding factor in the quality and profitability of ethanol produced. Hence, in line with the demand of the industry, efforts have always been exerted to minimize requirement of energy and to improve the basic quality of alcohol produced. Ease of operation, reliability, lower down time and flexibility of operations are other parameters considered during the design of distillation columns.

Energy-Saving by Using Multi-Pressure Distillation Plants

In ethanol production plant, multi-pressure distillation columns are most commonly used. The advantages of these plants are: Lower steam consumption, lower scale formation, reduced by-product formation in the mash column.

Distillation columns could be operated, on a similar principle to that of multiple-effect evaporators, to save energy. Such a 'multi pressure' scheme is particularly interesting for energy integration of the plant. Here, usually, the mash column is operated under vacuum and is heated by overhead alcohol vapors from the rectifying column. Thus, steam supply to the mash column is saved. Similarly, other columns are also operated 'in-pair' using overhead vapors from one to heat the other. There could be nearly a 50% saving in energy due to this integration. It was also observed that the level of impurities in alcohol from such plants is far lower, compared to plants with column operating at normal pressure *(G B Deshpande, 2002).*

Simplified Ethanol manufacturing process from Molasses is schematically shown in the following material flow chart *(Figure 2.1).*

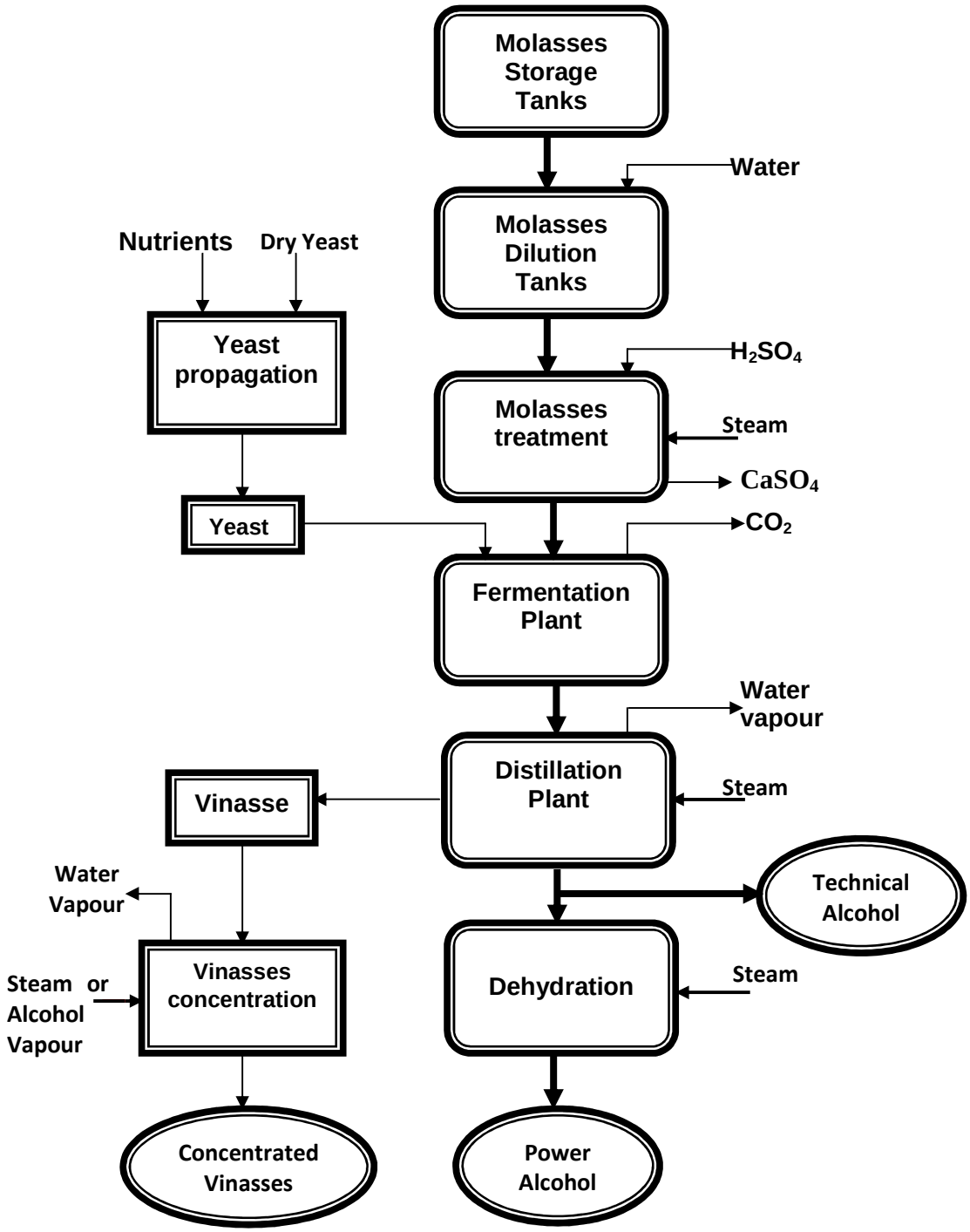


Figure 2.1:- *Process flow sheet of ethanol production from molasses*

v. Evaporation for Vinasse Concentration

Vinasse is a residue that results as by-product from alcohol distilleries in production of ethanol from molasses. From practical exposure, it is assumed that to produce 1-litr of alcohol from molasses, about 12-litrs of vinasse is produced. Because of this large volume production, disposal of vinasses is a headache for almost all ethanol plants. As a result, these liquor can therefore be processed into added-values animal feeds by concentration and, if necessary, drying and crystallization, precipitation of certain seals (e.g. potassium, sodium) *(GEA Wiegand, 1997).* In some ethanol plants, it also concentrated, mixed with filter cake from sugar factory and digested with bacteria. After full digestion, it is applied to cane field as fertilizer.

2.4.2. Fouling in Ethanol Manufacturing Process

In ethanol plants, impurities in raw materials which are either molasses or process water deposit onto heating surface areas of heat transferring units; because heating surface areas have a higher temperature at their surface than the surrounding juice and provide nucleation sites for scale growth. Scale facilitates the corrosion of surfaces, restricts fluid flow and, because it has low thermal conductivity, its accumulation on metal surfaces hinder heat transferring across the tubes wall.

The type of the scale being formed depends on a number of parameters, including the concentrations of scale-forming ions in molasses and intermediate products, the amount of dissolved and suspended solids, and the pH and flow properties of the solution, the rate of evaporation, the quality of input materials, and the operating temperature and pressure of the system (*Rackenann, et al, 2010*).

It has been discussed that different heat exchangers such as pre-heaters, distillation columns, and evaporators are involved in ethanol plants. These units are highly affected by fouling of heat transferring surface area which can be caused by different conditions such as raw material quality, nature of the unit, operating conditions, and so on. To overcome this problem, the designers and operators of the units have been conducted different studies and recommended different possible solutions.

i. Molasses Composition and Fouling

Composition of molasses varies from country to country and from factory to factory within the same country and from season to season with in the factory. Furthermore, scaling of heating surface depends on the type and amount of the compositions of molasses.

Different authors give different compositions of molasses. For example, KBK chemical engineers pvt. LTD, in India has been reported two typical compositions of Indian molasses as given in *Table 2.1* below.

Table 2.1:- *Typical analysis report of Indian cane molasses*

Sr. No.	Particulate	Test value	
		Sample A	**Sample B**
1	Brix	81.00	88.00
2	Moisture content (%)	21.51	16.70
3	Total suspended solid (%)	3.83	5.4
4	Total dissolved solid (%)	74.66	77.7
5	pH of molasses	4.17	4.2
6	Reducing sugar, percent by mass	22.68	23.18
7	Total reducing sugar	56.26	55.66
8	Total fermentable sugar percent by mass	50.22	50.13
9	Calcium content, gms/100^{o}brix	2.40	2.15
10	Fermentable/ non-fermentable ratio	2.05	1.81
11	Carbonated ash (%)	9.25	10.50
12	Sulphate (% of ash)	12.26	13.57
13	Nitrogen (% of molasses)	0.982	0.992
14	Potassium (% of ash)	16.5	15.27
15	Sodium (% of ash)	0.93	0.93
16	Chlorides (% of ash)	13.32	14.24
17	Phosphates (% of ash)	0.32	0.26
18	Total organic volatile acids mg/lit.	3500	2700

Source: *- KBK Chemical Engineering pvt. LTD, Maharashtra, 2009, India*

In Germany, Hubert Olbrich has been reported as the world average of molasses composition as follows in *(Table 2.2).*

Table 2.2:- *Average composition of cane molasses*

constituent	Cane molasses (%)
water	**20**
Organic constituent	72
➢ **sugars**	**62**
• saccharose	32
• Glucose	14
• Fructose	16
• Invert sugar	---
• raffinose	---
➢ **Non sugar**	**10**
• Nitrogenouse material, free and bound acids, soluble gummy substances	10
➢ **Inorganic constituents(ash)**	**8**
• SiO_2	0.5
• K_2O	3.5
• CaO	1.5
• MgO	0.1
• P_2O_5	0.2
• Na_2O	---
• Fe_2O_3	0.2
• Al_2O_3	---
• Soda and carbonate residue(as CO_2)	---
• Sulfate residue(as SO_3)	1.6
• Chloride	0.4

Source: *Hubert OLBRICH, 2006*

According to Schuumans & Van Ginneken, it is difficult to predict the exact composition of the molasses. It is influenced by soil and climatic conditions, variety and maturity of cane and the processing conditions in the factory. For his reason, only ranges with indicative averages of the composition can be estimated as follows *(Table 2.3).*

Table 2.3:- *Typical molasses specification*

constituent	Cane
Total Sugars	46-52%
Sucrose	30-40%
Reducing Sugars	15-20%
Unfermentable Sugars	2 - 4%
Non-Sugar Organic Matter	9-12%
Nitrogen components as protein (6.25 * N)	2-3%
Betaine	---
Glutamic Acid	---
Non-nitrogen bodies	---
Soluble gums/other carbohydrates	---
Organic acids	---
Crude Ash	8-11%
Sodium (as Na)	0.1-0.4%
Potassium (as K)	1.5-4.0%
Calcium (as Ca)	0.4-0.8%
Phosphorus (as P)	0.6-2.0%
Chloride (as Cl)	0.7-3.0%

Source: - *Schuumans & Van Ginneken, as sited on, Design and feasibility study of an ethanol distillery in Guyana by Eduardo Algodoal Zabrockis Manlio F. Coviello, 2009*

ii. Scaling and Column Internals

The phenomenon of scaling is attributed to precipitation of calcium salts in the presence of ethanol and higher temperature. Both these parameters reduce solubility of calcium salts, thus causing deposition. Bubble-caps were used in all the columns in the

distillation plants, initially installed. However, it was observed that with variation in composition of molasses, there were instances when the fermented mash had very high levels of calcium salts, which precipitated and deposited on the trays of the mash column. Columns with sieve trays had the disadvantage of not being able to operate at low turndown. Thus, 'hyperstat' grid trays were developed after considerable hydraulic studies. These trays offered the advantage of easy cleaning while ensuring high efficiency as well as lower downtime than sieve-trays. These trays have been used in several plants and have been found to be very good from the point of view of ease of cleaning. The hyperstat trays also had the advantage of horizontal flow of vapor, thus sweeping the tray surface as well as ensuring a longer path for vapor through liquid to achieve better mass transfer *(G B Deshpande, 2002).*

iii. Scaling in Evaporators

Vinasse contains all the nutrients of the raw materials except for their fermented starch and other sugars: i.e. they contain proteins, fat, fiber, minerals etc. in greater concentrations than were present in the original raw material molasses. Therefore, the problem of scaling is common in evaporators concentrating of vinasse.

a. Fouling and Temperature

The thin vinasses resulting from alcohol distilleries typically have a concentration range of between 5 and 10 % total solid. The final concentration that can be achieved depends on the type of raw material being processed, the qualities achieved by mechanical separation (the amount of suspended versus dissolved solids), and the fermentation process.

Viscosity of the concentrated liquor is normally the measure that determines the supper concentration limit. The concentrate quality, dried vinasses quality and fouling behavior are largely influenced by the temperatures within the evaporator. Temperatures of between 50℃ and 105 ℃ are used. The properties of vinasses from the same raw material can differ significantly due to seasonal variations, and are affected by the method of pretreatment *(GEA Wiegand, 1997).*

b. Fouling and Evaporator selection

Evaporator selection is normally determined by the required concentration ratio, the evaporation rate, the type of heating or heat recovery system, and in particular, by the viscosity and fouling characteristics of the vinasses. Falling film evaporators are used for low viscosities of up to about 100cP and large evaporation rates. For higher concentration ranges, forced circulation evaporators are used, handling viscosities of up to 1000 cP, for example, Where the product has a tendency to scale or foul, e.g. in the case of a vinasses containing calcium sulphates, forced circulation evaporators are commonly used. Therefore, falling film and forced circulation evaporators are used for the concentration of vinasses.

2.5. Effect of Fouling on Heat Transfer

The scales which are formed on heat transferring surfaces are materials normally of relatively low thermal conductivity when compared with the construction materials of the heat exchangers. The relative heat conductivity through various materials in comparison with scale taking copper which is known to be very good conductor of heat as unity is given below *(Table 2.4).*

Table 2.4:- *Relative heat conductivity through various materials*

Material	$\frac{\boldsymbol{Heat\ conductivity\ of\ Material}}{\boldsymbol{Heat\ Conductivity\ of\ Coppper}}$
Copper	1.00
Aluminum	0.546
Brass	0.275
Steel	0.118
Water	0.0019
Air	0.0000763
Scale	0.002

Source*: - D.P. KULKARNI,* Sugar Manufacture in India

This clearly shows the role played by scale in impeding the heat transfer from heating medium to boiling liquid when deposited on the surface of the heat transferring area.

In other case, different scalants have different thermal conductivity depending on the composition of the scalant contains. *Table 2.5* shows typical thermal conductivity values for commonly encountered scales.

Table 2.5: -*Thermal conductivity of common scalants.*

No	**Scaling material**	**Thermal conductivity *(W/mK)***
1	Calcium carbonate	0.9-2.9
2	Calcium sulfate	1.1-2.3
3	Calcium phosphate	2.6
4	Magnesium phosphate	2.3

Source: - *M. G. Mwaba, 2003*

Due to their low thermal conductivity, deposits forming on heat transfer surfaces increase the resistance to heat flow. The result is a reduction in the overall heat transfer coefficient of the equipment. To maintain the process temperatures of the juice in the heaters and to evaporate the required amount of water in the evaporators, it is necessary to raise the steam temperature. This requires raising the steam pressure which incurs additional cost. Raising the steam pressure is usually a temporary measure and with time maintaining the required process conditions becomes increasingly difficult. The heat transfer equipment is then shut down for cleaning.

As noted above the effect of fouling is to form solid deposit on the surface through which heat must be transferred by conduction. If we knew both the thickness and the thermal conductivity of the fouling so formed, we could treat the heat transfer problem simply as another conduction resistance in series with the wall. In general, we know neither of these quantities and the only possible technique is to introduce the additional resistance as fouling factors in computing the overall heat transfer coefficient.

Fouling effects inside the tube usually causes no particular problem if allowance has been made for the reduction in heat transfer and the small increase in flow resistance. However, fouling on the outside of finned tubes can be a more complicated matter, because in extreme situations there is a possibility that the finite thickness of the fouling layer can effectively close off the flow through the fins. On the other hand, finned

surfaces are sometimes found to be more resistant to fouling than plain surfaces (*Moore, 1974)* the reasons for this are not well established, though it may be that the expansion and contraction of the surface during normal operational cycles tends to break off brittle fouling films. Caution is advised, however, in applying finned tubes to services known to be significantly fouling.

High finned tubes are commonly used only with air and other low pressure and relatively clean gases. In such cases, fouling could occur is mostly dust deposition, which can easily be removed by blowing.

2.6. Materials Selection for Fouling Equipments

Potential fouling problems may influence materials selection in one or more ways. Most obvious perhaps is the minimization of corrosion type fouling by choosing a material of construction, which does not readily corrode or produce voluminous deposits of corrosion products. If chemical removal of the fouling deposit is planned, the material selected must also be resistant to attack by the cleaning solutions.

Secondly, biological fouling can be largely eliminated by the selection of copper-bearing alloys, such as 70-30 copper-nickel alloy. Generally, alloys containing copper in quantities greater than 70% are effective in preventing or minimizing biological fouling.

Thirdly, some types of fouling can be controlled or minimized by using high-flow velocities. If this technique is to be employed, the possibility of metal erosion should be considered as it is important to restrict the velocity and/or its duration to values consistent with satisfactory tube life. Some metals, such as titanium or stainless steels, can be quite resistant to erosion by the high velocity effluent. Recently, a new copper-nickel alloy containing nominally 83% copper, 17% nickel and 0.4% chromium has been developed by the international nickel company. This alloy is similar to the other copper-nickels relative to its corrosion resistance, but, however, has a much greater resistance to velocity attack.

2.7. Removal of Fouling

If fouling cannot be prevented from forming, it is necessary to make some provision for its periodic removal. Some deposits can be removed by purely chemical means, e.g., removal of carbonate deposits by chlorination. The application of chemical cleaning techniques is a specialized art and should be undertaken only under the guidance of a specialist. However, since chemical cleaning ordinarily does not require either removal of the equipment or disassembly of the piping if properly designed, it is the most convenient of the cleaning techniques in those cases where it can be used.

There are a number of techniques for mechanical removal of fouling. Scraping or rotary brushing are limited to those surfaces that can be reached by the scraping tool easily; a problem that is eased on the shell side by the use of large clearances between tubes and/or the use of rotated square tube layout. It should be noted that scraping should not be used on finned tubes. Use of very high velocity water jets is very common both inside and outside the tubes; though for the shell side the jets will not be very effective deep inside a large tube bank.

For situations where there is a high premium for maintaining a high degree of cleanliness, e.g., large power plant condensers, it may be possible to install a system for the continuous on stream cleaning of the interior surfaces of the tube. The new technologies utilize slightly oversized, sponge rubber balls which are continuously recirculated through the tubes on a random basis. As the balls pass through the tubes, they remove the accumulation of scale or corrosion products. A mesh basket in the outlet piping collects the balls and a ball pump reinjects them into the entering water flow. The type of balls having an abrasive secured to the outer surface should be used only with great caution as continuous abrasive action may shorten tube life due to the removal of the protective corrosion film formed in copper and copper base alloys.

2.8. Scale Characterization

Scale from different equipments and different areas consists of many different components and its composition can best be determined using a combination of techniques. Applicable techniques include atomic absorption spectrophotometry, x-ray powder diffraction (XRD), x-ray fluorescence (XRF), ion exchange/high performance chromatography, thermogravimetry/differential thermal analysis and electron microscopy *(Crees et al., 1992 and 1993).*

Typical analyses of scales from some Indian factories producing plantation white sugar by sulphitation are presented in *Table 2.6*

***Table 2.6**:- Scale composition in Indian sugar factories*

No.	***Component***	***Deccan***	***North India***
1	Organic matter	7-12%	35-38%
2	Silica SiO_2	25-50%	0.30-0.4%
3	Fe_2O_3, Al_2O_3	2.5-10%	0.2-4.0%
4	CaO	12-25%	30-40%
5	SO_4	1 -10%	21-30%
6	Phosphate	1.5-10%	1.1-10.0%

***Source**: - D.P. KULKARNI,* Sugar Manufacture in India

2.9. Hypotheses and Questions

The possible causes of fouling in ethanol plant heat transfer units are the raw materials of the plant which are either molasses or process water. But, modern water treatment plant has been provided in ethanol plant of Metahara sugar factory to overcome this problem which shows that, the possible cause for the problem could not go beyond the main raw material molasses. Therefore, this paper will give special attention to the quality of input molasses to the plant.

The possible composition of molasses that is responsible to cause fouling in ethanol plant heat transfer units is calcium oxide (CaO). The molasses from Metahara sugar factory is expected to be with high calcium oxide (CaO) content which results in the scaling of heat transfer units in ethanol plant. This comes from low quality of the lime used in clarification of mixed juice for production of plantation white sugar. This problem is a big challenge not only for the ethanol plant, but also for the sugar factory evaporation plant. To solve this problem, two options have been thought; the first option is to solve at source so that the molasses that comes to the plant is with low calcium oxide content. To do this, we have to replace the poor quality quick lime being used with good quality of lime. But, currently unless otherwise we import from abroad, there is no option to obtain good quality quick lime in Ethiopia. Therefore, this option is not feasible to immediately solve the existing problem. The second option is molasses treatment. This option is to treat the molasses once it comes with high CaO content which will be considered in this thesis.

At the end of the study, the paper will answer the questions:-What is the main cause(s) of fouling in ethanol plant?, Is there any means to solve this problem in economical way?, Is the proposed technology applicable in the existing plant set up?, Can the technology solve the existing problem permanently?, Is it easily adaptable to the existing setup of Ethanol Plant?, and all other related questions.

3. Materials and Methods

3.1. Characterization of the Scale of Heat Transferring Units

Before going to the solution one has to know the problem and the cause of the problem. Even if the severity of the scaling already known, the source of the problem has not been identified. Therefore, characterization of the scale helps to direct attention towards the component(s) responsible for the formation of the scaling and to assess the source of the compound(s). For this reason, the scale deposit first collected dry from distillation column of Metahara sugar factory ethanol plant by mechanical scrapping before the unit is boiled with caustic soda for cleaning. Then, it is re-sampled and the sample of the scale characterized both physically and chemically.

3.1.1. Materials

Materials used in this experiment are, scrapper, the sample scale collected from heat transferring units of Metahara sugar factory ethanol plant, measuring ruler, x-ray fluorescence (XRF).

3.1.2. Methods

i. Physical Characterization

The deposit collected from distillation column of the plant first characterized physically in such a way that seeing visually, touching and trying to break it. In addition to this, the scale samples re-sampled randomly and measured for thickness using measuring ruler. In this case, ten samples randomly selected and measured carefully and the average thickness of the samples calculated.

ii. Chemical Characterization

In this experiment, the deposit sample characterized at the Ethiopian ministry of mines laboratory of geochemical using x-ray fluorescence (XRF) method with the ultimate aim to describe the type of scale in heat transferring equipments.

External laboratory has been used since the sugar factories do not have such a sophisticated laboratory for scale characterization.

3.2. Characterization of Raw Molasses

Composition of molasses varies from country to country and from factory to factory within the same country and from season to season with in a factory depending on the type of cane, soil character, cane age, fertilizer used, chemicals used in processing sugar production, etc... Furthermore, characteristics and rate of scaling of heating surface depends on the type and amount of the compositions of molasses. Out of many, the main composition of molasses that highly contribute for fouling is CaO content which precipitates as calcium salts up on treatment with heat and acid. The sample molasses collected from input to the ethanol plant analyzed for pH, brix, CaO content, MgO content and density as follows.

3.2.1. Materials

i. Sample

The sample used in this characterization is cane molasses which is collected from ethanol plant of Metahara sugar factory.

ii. Apparatus

The equipments used to conduct this study were, refractometer, measuring cylinders of 5ml, 50ml, 100ml, 2000ml conical flask of 250 ml, beakers of 250ml, funnel, burette of 100ml, volumetric flasks of 100ml, pH meter, digital weighing balance (precision, ±0.0001 gm), what-man filter paper (No 6).

iii. Reagent

Chemicals used in the study were basic lead acetate, potassium ferro cyanide, potassium iodide, E.D.T.A, distilled Water, ammonia solution, ammonium molbdet, erichrome black T, ethanol alcohol and triethanolamine, pH buffer solutions 4.00 and 7.00.

3.2.2. Methods

i. Determination of Raw Molasses pH

First the pH meter is calibrated inserting the electrode of the meter in to the known pH standard buffer solutions of 4.00 and 7.00pH and setting the reading to proper pH range. Then, the pH of the standard solutions checked on display that the meter is correctly reading. Finally pH of the sample molasses read for 45 days every day and the average pH for Metahara sugar factory molasses is obtained.

ii. Determination of Raw Molasses Brix

The well mixed sample molasses diluted to 5^{o}brix using distilled water by simple mass balance. The diluted molasses sample clarified by basic lead acetate and filtered using what man filter paper No 6. The clear sample collected and poured on to the refractometer prism and its brix read. Then, the refractometric reading multiplied by the dilution factor to represent the brix of the raw molasses. Similarly, this is done every day for 45 days and the average brix of the raw molasses of Metahara sugar factory measured.

iii. Determination of Raw Molasses Density

To determine the density of raw molasses, the molasses sample is well mixed by mechanical agitator. Putting 2000ml measuring cylinder on precision weighing balance the balance tarred to make the reading zero. Then, the molasses poured carefully in to the cylinder until the level becomes at 2000ml mark. Repeating this experiment three times and recording the weight, density of the raw molasses had been calculated as follows:

$$Density\ of\ raw\ molasses = \frac{Mass\ of\ the\ molasses\ sample}{Volume\ of\ the\ molasses\ sample}$$

The average weight of 2000ml raw molasses has been calculated as 262.26gm. Substituting the results obtained:-

$$\rho' = \frac{262.26gm}{200ml} = 1.3113\ gm/ml$$

But, according to *E. Hugot*, the molasses normally contains fine air bubbles entrained during the fugalling process and also picked up by friction every time the molasses is discharged in a fine stream into a tank *(E. Hugot, 1986).* Generally, it is estimated that the included air represents 5-17% of the volume of the molasses. In our case since the molasses is kept undisturbed for a long time, assuming that the included air is only 7%, the true density of the molasses becomes:-

$$\rho = \frac{262.26gm}{\left(200 - \frac{7}{100} \times 200\right)ml} = \mathbf{1.41\ gm/ml},$$

Which is in line with the recommendation of E. Hugot, that says 'true density of molasses is generally the order of 1.4 - 1.5 *gm/ml.*

iv. Determination of Calcium oxide Content of Raw Molasses

Calcium oxide is the main compound responsible for formation of heat exchangers scaling. To determine calcium oxide content of molasses, 1gm of raw molasses weighed correctly and mixed with 100ml of distilled water. Then, taking 5ml of the prepared solution, diluted further by adding 45ml distilled water to bring the total volume of the solution to 50ml. To use an indicator, first 2ml of buffer solution has been added to the solution. Then, 3-4 drop of erichrome black T indicator added. When pink red colour appears, the solution titrated by EDTA solution up on agitating the solution by magnetic agitator until the pink red colour changed to olive green colour. Finally the volume of titrate recorded and calcium oxide % molasses calculated as follows (ICUMSA method).

$$CaO\%\ molasses = volume\ \text{of titrate} \times \frac{100\text{ml}}{1\text{gm} \times 50\text{ml}} \times \frac{\text{molecular weight of CaO(gm)}}{10{,}000} \times 100$$

v. **Determination of Magnesium Oxide content of Raw Molasses**

To determine MgO percent raw molasses, 1gm of raw molasses weighed correctly and mixed with 100ml of distilled water. 5 ml aliquot of the sample solution added into a 100 ml conical flask and neutralized with potassium hydroxide using litmus paper to monitor the pH. The sample was dilute to 50ml with distilled water and 10 ml of the 50% triethanolamine solution and 2 ml of buffer solution added. Then, 3-4 drop of eriochrome black T indicator added and titrated with EDTA solution to a pure blue endpoint. The titration repeated every day for 45 days and the average result of this repetition is recorded. Finally, MgO% molasses is calculated as follows (ICUMSA method)

$$MgO\ \% = titrate\ volume \times \frac{100ml}{1g \times 50ml} \times \frac{molecular\ wheit\ of\ MgO}{1000} \times 100$$

3.3. Characterization of Process Water

If not well treated, process water can cause the savior scaling of heating surface area of the heat transferring units. Specially, if hard water is used as process water, there could be the deposition of calcium and magnesium compounds which are the hardness causing compounds of water. To assess the cause of the scaling in the plant characterization of process water also has been done as follows.

3.3.1. Materials

i. Apparatus

Apparatus used in this study are; 500 ml erlenmeyer flask, 100ml burette, 100ml and 1000ml volumetric flask, Digital weighing balance (precision, ±0.0001 gm), measuring cylinder, funnels, pH meter, magnetic stirrer and stirrer bar, beaker of 500ml.

ii. Reagent

Chemical reagents used in this study are; triethanolamine (TEA), ammonia buffer solution, eriochrome black T indicator solution, ethylene diamine tetra acetic acid (EDTA), pH buffer solutions 4.00 and 7.00.

3.3.2. Methods

i. Determination of Process Water pH

First, the pH meter calibrated using the 4.00 and 7.00 pH buffer solutions while stirring at a constant rate. Calibrations have been done at the beginning of each day using fresh buffer solutions. Then, the sample is allowed to cool to room temperature. Finally, the pH of the sample has been measured while stirring at a constant rate, allowing at least one minute for the reading to stabilize. This test has been done for one week every day and the average pH reading of the test has been recorded.

ii. Determination of Total Hardness of Process Water

Hardness in water is caused by dissolved calcium and, to a lesser extent, magnesium. It is usually expressed as the equivalent quantity of calcium carbonate ($CaCO_3$). Depending on pH and alkalinity, hardness above about some limit level can result in scale deposition, particularly on heating surface *(WHO, 2006).* Therefore, total hardness of process water sample collected from the plant analyzed by Complex metric titration.

The method is based on the chelating of EDTA, i.e. the reaction between EDTA and calcium and magnesium ions in the water. The result is expressed as the total calcium and magnesium concentration in ppm $CaCO_3$.

The sample water first filtered and 50 ml of the filtered water sample pipette into a 250 ml erlenmeyer flask. After adding about 2 ml of buffer solution, 3-4 drop of erichrom black T indicator solution added. After the appearance of wine red color, the solution is titrated with 0.01M EDTA from the burette until a blue end point is reached by the disappearance of the last purple coloration. Then, the total hardness has been calculated as follows:-

$$\textit{Total hardness (as ppm } CaCO_3\textit{)} = \textit{Titration volume (ml)} \times 20$$

3.4. Assessment of the Cause(s) of the Scaling of Heat Transferring Units

The possible cause(s) of scaling in ethanol plant is the impurities in the raw materials of the plant which are molasses and/or process water. To know the root cause of this scaling problem, first, the scale sample collected from the plant characterized physically and chemically to know its composition and to direct attention to the compound(s) responsible for the formation of the scale. Then, the raw materials of the plant which are molasses and water are characterized to know their composition. Depending on the characterization of the scale sample the compound(s) responsible for the scaling of the heat transferring units has been determined. Finally, from the characterization of both raw materials molasses and process water, the possible source of this scaling compound(s) is assessed.

3.5. Selection of the Best Technology for Molasses Treatment

Depending on the characteristics of the molasses, there are a number of technologies of molasses treatment for ethanol production. In this study, out of these technologies, two options had been thought to solve the problem that the plant currently faces depending on the practical exposure of the problem. The first option is to solve the problem at source in sugar production process so that the molasses that comes to the plant is with low scale causing compounds. The second option is molasses treatment. This option is to treat the molasses to remove the scale causing compounds once it comes with high scale causing compounds content. Comparison and contrast of these two options has been done to select the best technology for the case of Metahara sugar factory ethanol plant depending on the existing condition of the plant.

3.6. Molasses Treatment to Reduce Scale Forming Components

3.6.1. Materials

i. Sample

The major sample used during the experiment is cane molasses which is collected from ethanol plant of Metahara sugar factory. To be representative, the sample is collected from the inlet to the plant with big jar, agitated thoroughly and re-sampled for the tests conducted. The sample collected kept in refrigerator until the next experiment conducted.

The other sample used to conduct this study is dilution water which is used to adjust the brix of the molasses to the required value. To be fair and make similar with the factory operation, the dilution water for this purpose is collected from ethanol plant which is used for dilution in the plant also.

ii. Apparatus

The equipments used to conduct this study where, refractometer, measuring cylinders of 5ml, 50ml, 100ml, 1000ml, 2000ml, conical flask of 250 ml, beakers of 25ml, 250ml and 800ml, funnel, micro pipette of 5ml, burette of 100ml, volumetric flasks of 100ml and 1000ml, pH meter, Digital weighing balance (precision, ±0.0001 gm), what man filter paper (No 6).

iii. Reagents

Chemicals used in the study where sulfuric acid , basic lead acetate, potassium ferrocyanide, potassium iodide, E.D.T.A, distilled water, ammonia solution, ammonium molbdet, erichrome black T, ethanol alcohol and triethanolamine.

3.6.2. Methods

i. Factors Affecting Molasses Treatment

Removal of CaO from molasses can be affected by different factors such as pH, temperature, brix, retention time, flocculent usage, flow velocity and other minor factors. But, none of these factors equally contribute to the scaling of heat transferring surface. Depending on their relative effect, the first experiment of this study has been considered only three factors that have significant influence on molasses clarification which are pH, temperature and brix of the molasses. Therefore, the study has been carried out at various levels of these three factors. That is, three factors: temperature (80-100 ^{0}C), PH (4-5), and brix (50- 60) each at three levels with three replicates, and one response CaO% molasses in clear diluted molasses a total of 60 runs has been conducted. These ranges of the factors have been selected by practical experience of the process and then conducting pre-experimentation tests during proposal preparation.

ii. Experimental Design

To conduct this experiment and optimize these variables response surface with central composite design has been used**.** Because**,** response surface methodology, is a collection of mathematical and statistical techniques that are useful for the modeling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimize this response *(Douglas C. Montgomery, 2001).* The response surface methodology (RSM), based on statistical principles, can be employed as an interesting strategy to implement process conditions that drive to optimal removal of CaO from molasses by performing a minimum number of experiments. Therefore, in this work, optimization of process conditions (brix, temperature, and pH) using RSM for removal of CaO from molasses had been carried out and the influence of process variables on CaO removal analyzed using CCD experiments. To do these, design expert 7.0.0 software package has been employed.

Table 3.1:- *Experimental design using design expert (RSM of CCD)*

Run Order	Run Number	Temperature [^{o}C]	pH [pH]	Brix [^{o}Brix]	CaO before treatment (%) molasses	CaO after treatment (%) molasses	CaO removed (%)
14	1	90.00	4.50	60.00			
13	2	90.00	4.50	50.00			
8	3	100.00	5.00	60.00			
12	4	90.00	5.00	55.00			
2	5	100.00	4.00	50.00			
18	6	90.00	4.50	55.00			
17	7	90.00	4.50	55.00			
6	8	100.00	4.00	60. 00			
7	9	80.00	5.00	60.00			
16	10	90.00	4.50	55.00			
9	11	80.00	4.50	55.00			
4	12	100.00	5.00	50. 00			
19	13	90.00	4.50	55.00			
3	14	80.00	5.00	50.00			
15	15	90.00	4.50	55.00			
20	16	90.00	4.50	55.00			
10	17	100.00	4.50	55.00			
5	18	80.00	4.00	60.00			
11	19	90.00	4.00	55.00			
1	20	80.00	4.00	50.00			

iii. Experiment One

Determination of Optimum Process Conditions for Molasses Treatment

The experiment was carried out in such a way that, first the sample of raw molasses collected from input to the ethanol plant; then, the collected molasses analyzed for CaO content, brix and density. Depending on the initial brix, the molasses was diluted to the required different brixs by treated water as shown in the *Table 3.1* above by simple mass balance. Then, pH of the diluted molasses was corrected to the required value by addition of acid drop by drop up on agitation.

Finally, the molasses was heated up to the required temperature according to the experimental design output and then allowed to settle.

iv. Experiment Two

Determination of Optimum Retention Time

Using longer retention time of settling ensures best precipitation of the residue. But, it increases the size of the equipments to be used in the treatment plant and may results in unnecessary initial investment cost. To overcome this problem, optimization of retention time is very important. Therefore, the retention time of settling has been optimized using the best results of the above experiments.

The molasses treated with best conditions of the above experiment filled with measuring cylinder of 2000ml volume and the volume of precipitated mud measured and recorded every 10 minutes. In this case, the response variable is mud volume which decreases with increasing retention time *(Figure 3.1).*



Figure 3.1:- *Experimental set up to determine optimum retention time*

4. Result and Discussion

4.1. Characterization of the Scale in Heat Transferring Units

Result

i. Physical Characterization

The scale sample collected from the plant first characterized physically. When seen visually, it is with gray colour and seems brittle which can easily break. But, it is hard scale that even difficult to remove it from the surface of the heat exchangers. In addition to this, the scale randomly re-sampled and its thickness measured and up to *3cm* thick scale has been observed. Ten samples collected randomly and their thickness measured carefully. An average of 2.04cm thick scale has been deposited with in 4 operation days *(Table 4.1).*

Table 4.1:- *Thickness of Scale Samples Collected from Distillation Column*

Sample Number	1	2	3	4	5	6	7	8	9	10	**Average**
Thickness (cm)	1.2	2.5	2.9	2.8	0.8	0.5	3.1	2.7	1.0	2.9	**2.04**

ii. Chemical Characterization

Chemical characterization of scale shows the constituent compounds of the scale in percents. This exactly shows which compound(s) is responsible for the scaling. Therefore, the composition of sample scale characterized using x-ray fluorescence (XRF) at the laboratory of Ethiopian ministry of mines and the analysis result has been summarized as follows *(Table 4.2).*

Table 4.2: - *Composition of scale samples collected from distillation column*

No	Constituent	% Scale
1	Silicon dioxide (SiO_2)	2.92
2	Aluminum oxide (Al_2O_3)	0.52
3	Iron oxide (Fe_2O_3)	0.39
4	Calcium oxide (CaO)	63.87
5	Magnesium oxide (MgO)	1.51
3	Sodium oxide (Na_2O)	0.95
4	Potassium oxide (K_2O)	0.08
5	Titanium dioxide (TiO_2)	0.01
6	Manganese oxide (MnO)	0.02
7	Phosphors pentoxide (P_2O_5)	0.24
8	Loss on ignition (LOI)	29.49
	Total	**100**

Discussion

From physical observation, the deposit is clearly a scale which is formed due to crystallization which in most cases results in hard scale. This shows that the type of fouling encountered in the plant is precipitation fouling. In addition to these, the thickness of the scale observed is abnormally thick which has a capacity to incur extra resistance to the heat flow across the heat transferring surface. On average, the thickness of the scale formed in distillation column in four operation days after cleaning is *2.04cm* which is too thick and can increase the resistance to heat flow due to their low thermal conductivity *(Figure 4.1).*

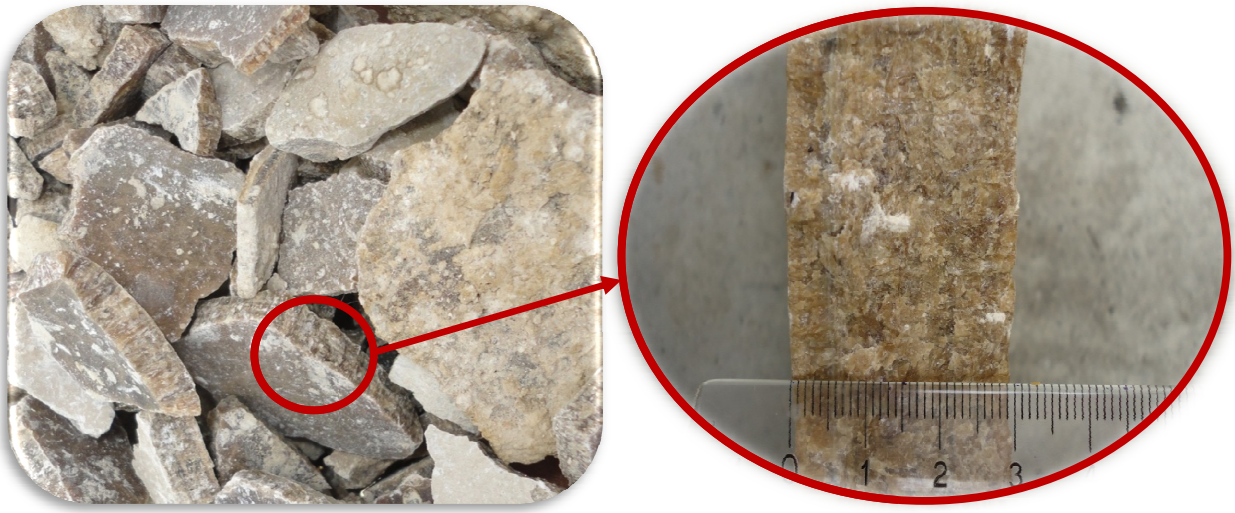


Figure 4.1: *- Thickness measurement of sample scale from distillation column*

In other case, from the x-ray fluorescence (XRF) analysis result, it can be seen that the scale so formed is 63.87% CaO which shows that the main component responsible for the scaling in the plant is calcium oxide compounds. The next major component of the scale is loss on ignition (LOI), which is with 29.49% scale. These, are, mostly organic compounds which can be damaged by ignition and moisture content. Other constituents are relatively too low and not statistically significant.

4.2. Characterization of Raw Molasses

Result

The above experiments have been done every day for 45 days and the average results of the experiments summarized as below (*Table 4.3)*.

Table 4.3: - *Characterization of raw molasses*

Characteristics	Results
Density(kg/m^3)	1.41
Refiractometric brix (^{O}brix)	84
pH	5.24
CaO% raw molasses	2.41
MgO % raw molasses	0.16

Discussion

From these values of molasses characteristics, it can be seen that CaO content of Metahara sugar factory molasses is 2.41% raw molasses (SD of 0.23) which is too high when compared with world average of 1.5% raw molasses *(Hubert OLBRICH, 2006).* But, when we see other components like MgO, there is no significant difference.

In addition to this, other parameters of the molasses like density, pH and brix, all the results are in the permissible range and no abnormal result has been observed

4.3. Characterization of Process Water

Result

The test result of water sample collected from the ethanol Plant of Matahara sugar factory has been summarized as follows *(Table 4.4).*

Table 4.4:- *Test result of process water sample*

Parameter	Result
pH	6.89
Total hardness*(mg $CaCO_3$/lt)*	64

Discussion

Different literatures recommend different level of total hardness limitation levels in process water. For example, according to world health organization, depending on pH and alkalinity, hardness above about 200 mg $CaCO_3$/lt can result in scale deposition, particularly on heating surface *(WHO, 2006)*. As presented on South African water quality guidelines, water with total hardness of 0 - 300 mg $CaCO_3$/lt will not cause or cause minor scaling in the heat exchangers *(Department of Water Affairs and Forestry, 1996)*. Similarly for Ethiopia, as reported for WHO as country report in 2004-2005, the permissible level of total hardness for process water is 300 mg $CaCO_3$/lt *(Dagnew Tadesse et, al, 2010).* For the level of pH, both WHO guideline and Ethiopian guideline recommended the range of 6.5 to 8.5 pH.

As it can be seen from the test results compared with the recommended results of different literatures, there is no problem of water quality as process water in ethanol plant of Metahara sugar factory.

4.4. Assessment of the Cause(s) of the Scaling of Heat Transferring Units

From the analysis result of the scale collected from the plant, the possible composition of raw materials that is responsible to cause fouling in the plant heat transfer units is calcium oxide (CaO); because, 63.87% of the scale is composed of CaO. On other hand, from the characterization of raw molasses, it can be seen that the molasses from Metahara sugar factory is with high calcium oxide (CaO) content. But, when we see the other raw material process water, it is soft water with total hardness of 64 mg $CaCO_3$/lt which is well below the recommendation of different literatures and could not cause scaling.

Therefore, these results indicate that the main source of heat transferring units scaling in the plant is the raw material molasses which is with high CaO content. Therefore, the next tax is how to reduce the CaO content of the molasses to overcome the problem of scaling.

4.5. Selection of the Best Technology for Molasses Treatment

The problem of scaling is a big challenge not only for the ethanol plant, but also for the source of molasses, sugar factories evaporation and crystallization plants. To solve this problem, two options had been thought; the first option is to solve at source so that the molasses that comes to the plant is with low calcium oxide content. From assessment of the source of CaO at the sugar factor, it has been seen that the quick lime used for clarification of mixed juice in the factory is as low as 60% CaO. But, good-quality lime should test 90 - 95% of CaO *(E. Hugot, 1986).* Therefore, to solve the problem at source, we have to replace this poor quality quick lime being used in sugar factory with good quality lime. But, currently unless otherwise we import from abroad, there is no option to use good quality quick lime in Ethiopia. The only local supplier of quick lime currently is caustic soda factory at Ziwayi. Beside this, it is not economical to import this bulk product from abroad. Therefore, this option is not feasible to immediately solve the existing problem of the plant.

The second option is molasses treatment. This option is, once the molasses comes with high scale causing compounds content, to treat it to remove the scale causing compounds which had been conducted in this study.

4.6. Molasses Treatment to Reduce Scale Causing Components

Experiment One

4.6.1. Determination of Optimum Process Conditions for Molasses Treatment Result

The treated molasses allowed to settle *(Figure 4.2)* and the clear molasses collected by decantation and analyzed for CaO content and the following results has been obtained.



Figure 4.2: - *Settling of treated molasses.*

The laboratory results of the experiment have been collected depending on the run order recommended by the software and tabulated as in the *Table 4.5* below. The experiments are conducted and these results are collected according to the experimental design output of the software to minimize equipment and human error of the experiment.

Table 4.5: - *Present CaO removed after molasses treatment*

Run Order	Run Number	Temperature [^{o}C]	pH [pH]	Brix [^{o}brix]	CaO before treatment (%) molasses	CaO after treatment (%) molasses	CaO removed (%)
14	1	90.00	4.50	60.00	**2.07**	**1.51**	**27.05**
13	2	90.00	4.50	50.00	**1.87**	**1.07**	**42.78**
8	3	100.00	5.00	60.00	**2.37**	**1.77**	**25.32**
12	4	90.00	5.00	55.00	**2.03**	**1.44**	**29.06**
2	5	100.00	4.00	50.00	**2.37**	**1.08**	**54.43**
18	6	90.00	4.50	55.00	**2.51**	**1.31**	**47.81**
17	7	90.00	4.50	55.00	**2.73**	**1.54**	**43.59**
6	8	100.00	4.00	60. 00	**2.83**	**1.74**	**38.52**
7	9	80.00	5.00	60.00	**2.28**	**1.73**	**24.12**
16	10	90.00	4.50	55.00	**2.57**	**1.68**	**34.63**
9	11	80.00	4.50	55.00	**2.38**	**1.73**	**27.31**
4	12	100.00	5.00	50. 00	**2.63**	**1.3**	**50.57**
19	13	90.00	4.50	55.00	**2.24**	**1.55**	**30.80**
3	14	80.00	5.00	50.00	**2.43**	**1.54**	**36.63**
15	15	90.00	4.50	55.00	**2.31**	**1.64**	**29.00**
20	16	90.00	4.50	55.00	**2.37**	**1.66**	**29.96**
10	17	100.00	4.50	55.00	**2.54**	**1.59**	**37.40**
5	18	80.00	4.00	60.00	**2.53**	**1.72**	**32.02**
11	19	90.00	4.00	55.00	**2.57**	**1.32**	**48.64**
1	20	80.00	4.00	50.00	**2.51**	**1.59**	**36.65**

Discussion

From over view of the results, the maximum removal of CaO has been occurred at temperature of 100^{O}C, pH of 4 and brix of 50^{O} at which CaO removed becomes 54.43%. In other case, the minimum removal of CaO has been recorded at temperature of 80^{O}C, pH of 5.00 and brix of 60^{O} at which CaO removed becomes only 24.12%.

In order to determine the optimal levels of each variable for maximum CaO removal, response (% CaO removed) contour plots and 3-D response surfaces of the results obtained were constructed by plotting the response (% CaO removed) on the Z-axis against two independent variables, while maintaining other variables at their optimal levels which is helpful for understanding both the main and the interaction effects of these two factors. The response surfaces can be used to predict the optimum range for different values of the test variables and the major interactions between the tests variables can be identified from the circular or elliptical nature of the contours. The contour plots and 3-D response surfaces plots based on independent variables were obtained using the software package design expert 7.0.0 as follows.

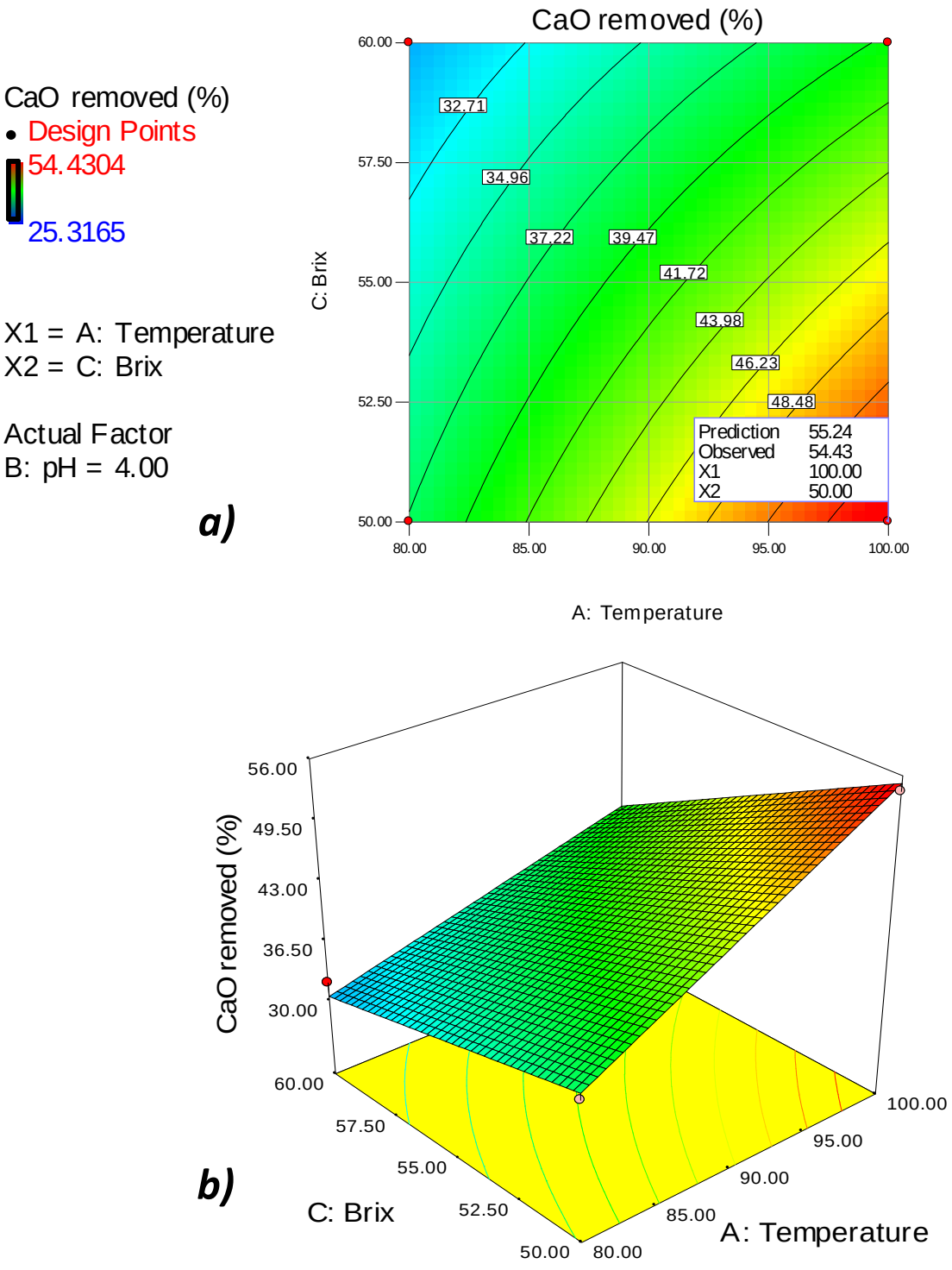


Figure 4.3: - *The effect of temperature and brix on % CaO removed from molasses at 4pH* ***a)*** *Contour plot b****)*** *3-D surface plot*

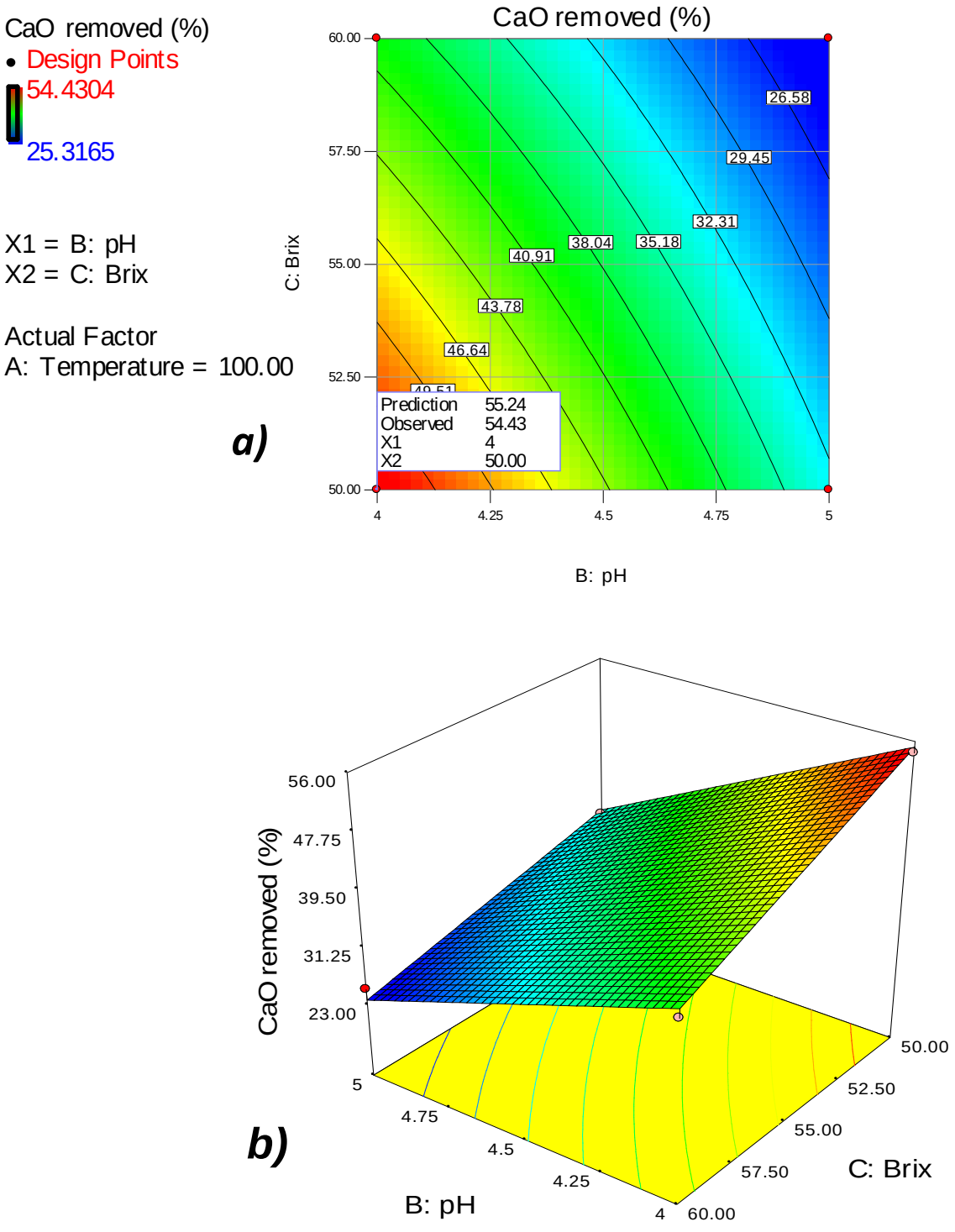


Figure 4.4: - *The effect of pH and brix on CaO removal from molasses at 100^{o}C*

a) *Contour plot* ***b)*** *3-D surface plot.*

The above Figs.4.3 and 4.4 **a*)*** contour and ***b)*** 3-D plots show interaction effects of temperature, pH and brix on the response variable of present CaO removed from molasses. The circular natures of the contours shows that the interaction effects between the test variables are not significant and therefore optimum values of the test variables can be easily obtained.

From the figures above, it can be seen that, as one goes from lower temperature to higher temperature within the given range of the temperature, CaO removed (%) from the molasses also increases. This means, increasing temperature of the molasses treatment favors removal of CaO from the molasses. In other case, as one move from lower pH to higher pH within the given range, CaO removed highly decrease, which shows that increasing pH of the molasses negatively affects CaO removal from molasses. Similarly, as one moves from lower brix to higher brix, CaO removed from the molasses highly decrease. These show that, unlike temperature, the effect of pH and brix on molasses treatment is inversely proportional that lowering pH and brix favors CaO removal from molasses.

From the optimization of these factors, it has been observed that at lower brix of 50^{o}, higher temperature of 100^{o}C and lower pH of 4 the maximum CaO has been removed, which 54.43% of the CaO in the molasses. At these process conditions 1.08 CaO % molasses has been obtained which is very low when compared with the world average of 1.5% *(Hubert OLBRICH, 2006)*. Therefore, these points have been selected as best process conditions of the significant factors for molasses treatment.

i. Development of Regression Model Equation

The model equation that correlates the response ($pecent\ CaO\ removed$) to the molasses clarification process variables, temperature, pH and brix in terms of actual value was given below

$$\boldsymbol{CaO\ removed}\ (\%) = \mathbf{105.58} + \mathbf{0.41T} - \mathbf{8.48p} - \mathbf{1.24B}$$

Where: - T = Temperature of the molasses (^{o}C)

p = pH of the molasses

B = Brix of the molasses (^{o}brix).

From this model equation it can be seen that both brix and pH negatively affect CaO removal where as temperature affects positively. Even if their effects are relatively different, the individual effects of all factors are significant. But, the interaction effects, and effects of all more than 1st order terms are zero and this terms has not been included in the model equation.

iii. Effect of Individual Process Variables

a. Effect of temperature on CaO removal from molasses

The experimental result shows that percent CaO removed from molasses increases with increasing temperature from 80^{O}C to 100^{O}C *(Figure 4.5).*

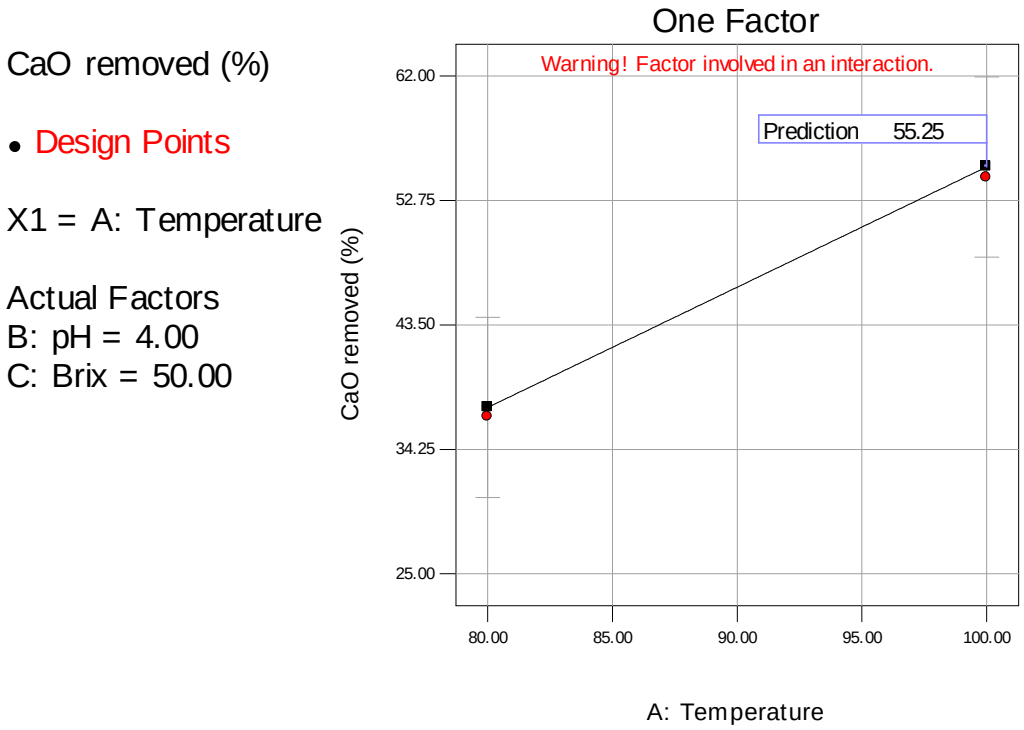


Figure 4.5: - *Effect of temperature on present CaO removed from molasses.*

The graph shows that increasing reaction temperature of CaO and H_2SO_4 favors formation of $CaSO_4$ which can easily removed by decantation. It seems experimentally that increasing temperature further will increase removal of CaO and decrease CaO % molasses. But, it is not practical that heating the molasses further more than 100^{O}C requires extra steam and design of special equipments working under higher pressure which are additional cost. Because, It is not the same to heat up the molasses by 10^{O}C

below boiling point of water (100^{O}C) and heating the molasses by 10^{O}C above boiling point of water. In addition to these, heating the molasses more than 100^{O}C could caramelize the sugar in molasses and reduce ethanol yield. In addition to these, at the temperature more than 100^{O}C, the water content of the molasses evaporates and the brix of molasses further increase which negatively affects the clarification process. Therefore, the best molasses clarification temperature to remove CaO from molasses is 100^{O}C.

b. Effect of pH on CaO removal from molasses

Unlike temperature, percent CaO removed from molasses is inversely proportional with pH that it increases with decreasing pH. This shows that using excess H_2SO_4 consumes the maximum CaO in the molasses. Similarly, as it can be seen from figure 4.6, further decrease in pH below 4 seems further decreases in the CaO % molasses; but, the same problem that lower pH means higher H_2SO_4 consumption which is extra cost. In addition to this, yeast could not resist pH of less than 4 and therefore 4pH is the ideal condition for molasses clarification.

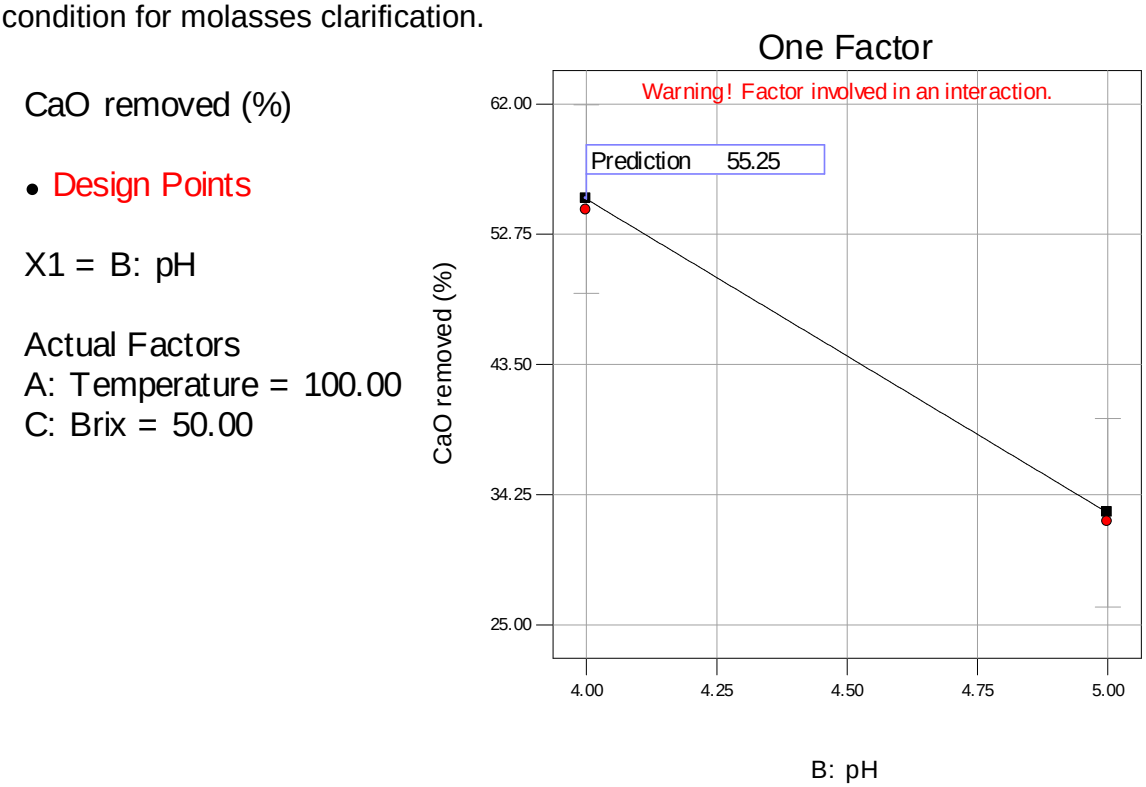


Figure 4.6: - *Effect of pH on present CaO removed from molasses.*

c. Effect of brix on CaO removal from molasses

Figure 4.7 shows that there is a decrease in percent CaO removed from molasses with increasing in brix of the molasses. This is because; lower brix favors the removal of $CaSO_4$ by sedimentation since it reduces viscosity of the molasses and facilitates the reaction by increasing circulation of material. Even if lower brix favors CaO removal, there is a limitation that diluting the molasses further requires extra steam to heat the molasses up to $100^{O}C$ and then to cool it down to $32^{O}C$ which is required in fermentation process for yeast life. On other case, our main objective is energy saving. Therefore, it is not economical to dilute the molasses below 50^{O}brix. In addition to these, diluting the molasses below 50^{o}brix will result in larger size of the equipments to be use in molasses treatment plant which is extra cost.

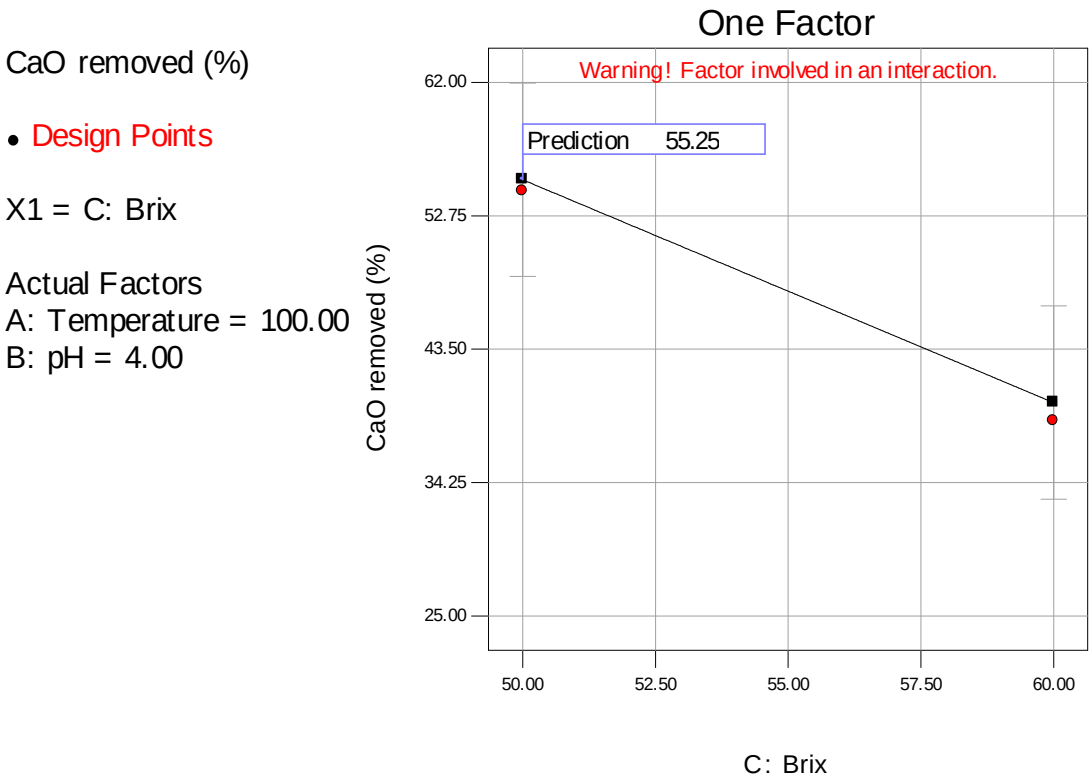


Figure 4.7: - *Effect of brix on present CaO removed from molasses.*

ii. Interaction Effect Between Process Variables

Interaction between Process Variables can affect the performance of clarification plant. But, as it already seen, in this case, the interaction effects of the process variables are not significant. In this section, these effects are going to be seen statistically and graphically *(Figure 4.8)* as follows:-

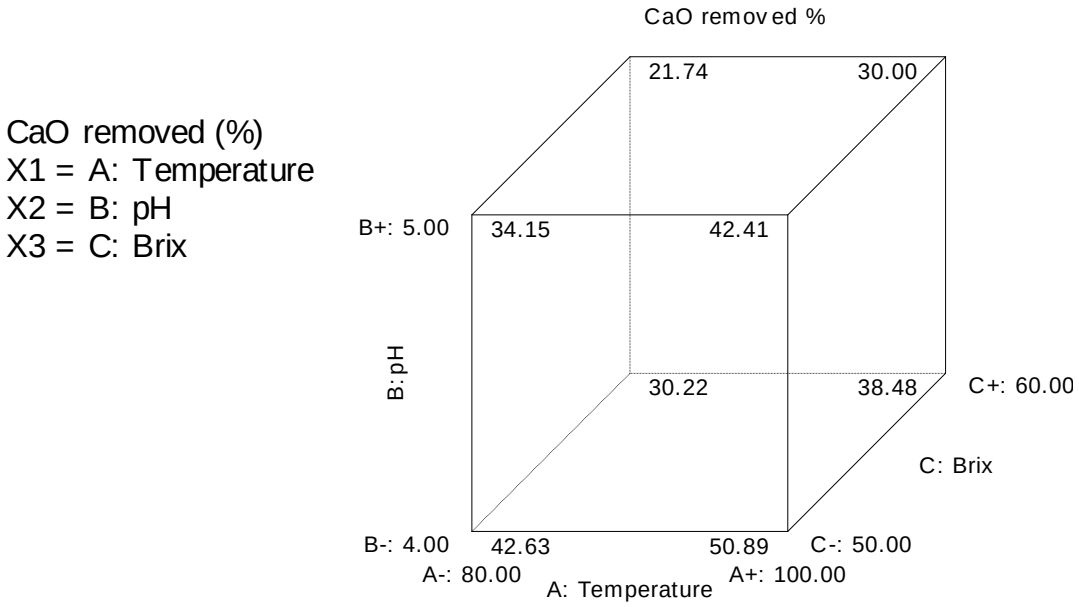


Figure 4.8:- *Cubic representation of interaction effects of temperature, pH and brix on present CaO removed from molasses.*

a. $\boldsymbol{Temperature - pH\ interaction\ effect}$

$$= \frac{1}{4 \times 2}(38.48 - 30.22 - 50.89 + 42.63 + 30.00 - 21.74 - 42.41 + 34.15) \quad = \mathbf{0}$$

This result shows that temperature-pH interaction has no effect on percent CaO removed from molasses. This is shown graphically in figure 4.9 below. From the graph, it can be seen that the lines are almost parallel that shows there is no significant interaction effect between the two factors.

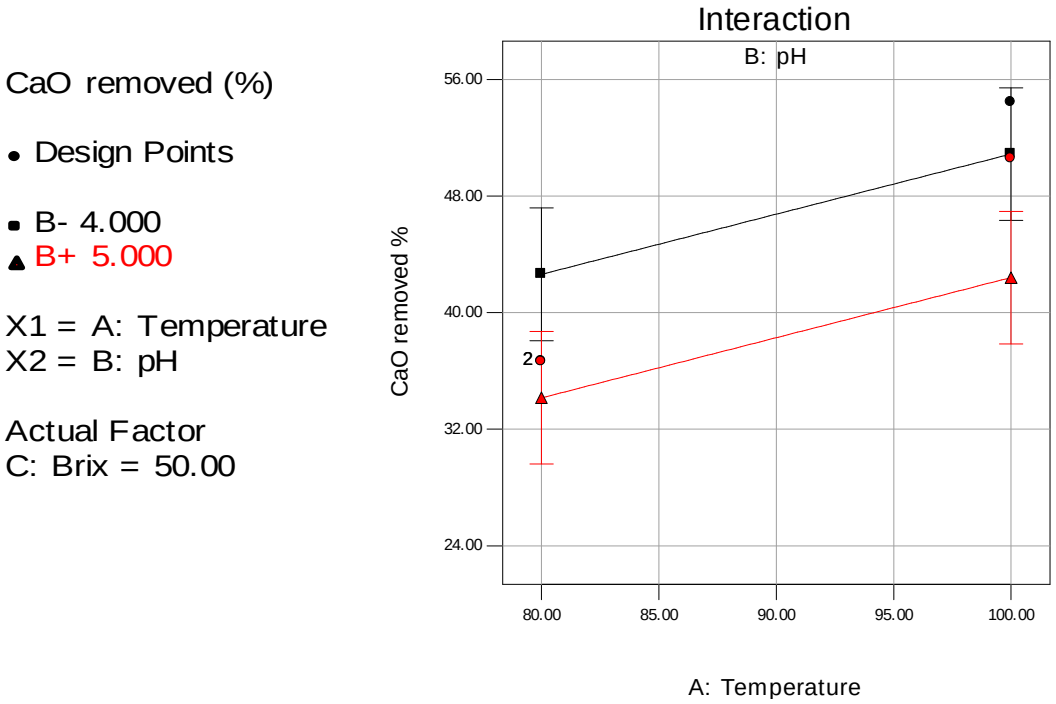


Figure 4.9: - *Temperature-pH interaction effect on percent CaO removed from molasses*

b. $\boldsymbol{Temperature - brix\ interaction\ effect}$

$$= \frac{1}{4 \times 2}(42.63 - 50.89 + 30.22 - 38.48 - 34.15 + 42.41 - 21.74 + 30) \ = \mathbf{0}$$

Similarly, temperature-brix interaction has no effect on percent CaO removed from molasses. This is shown graphically in figure 4.10 below. In this graph also, the lines are almost parallel which shows that there is no interaction effect between temperature and brix of the molasses.

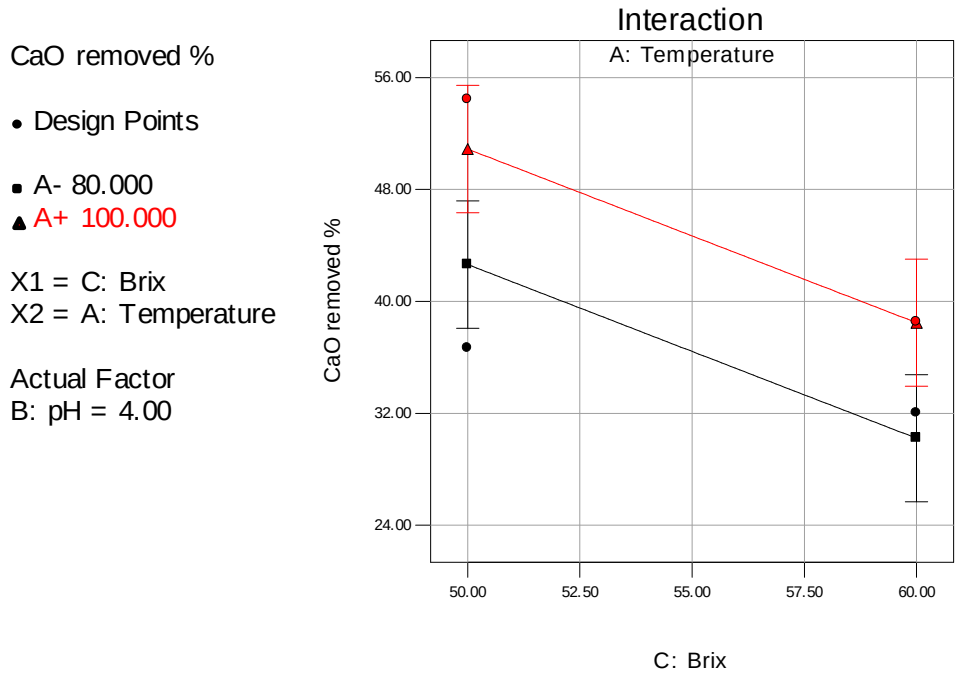


Figure 4.10: - *Temperature-brix interaction effect on percent CaO removed from molasses*

c. $\boldsymbol{pH - brix\ interaction\ effect}$

$= \frac{1}{4\times2}(42.63 + 50.89 - 30.22 - 38.48 - 34.15 - 42.41 + 21.74 + 30) \ = \mathbf{0}$

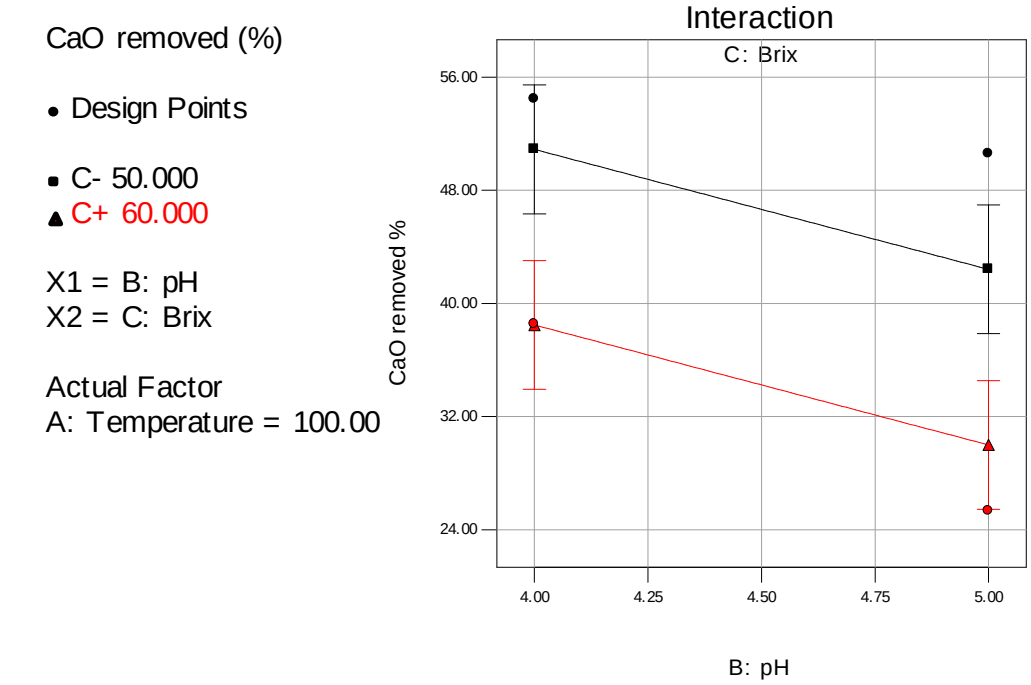


Figure 4.11: - *pH-brix interaction effect on percent CaO removed from molasses*

pH-brix interaction also has a no effect on percent CaO removed from molasses. As shown in *figure 4.11 above, the lines are parallel lines which indicated that the interaction effect of the factors is zero.*

iv. Optimization of Process Variables

Our interest is to maximize the removal of CaO content from raw molasses as much as possible so that the possibility of scale formation minimized. The results above have shown that the three molasses clarification influential process variables affect the removal of CaO from molasses. But, the effects of the interactions between the factors are not statistically significant. Therefore, the next step is to optimize the process variables in order to obtain the highest removal of CaO (higher percent of CaO removed) using the model regression developed.

Using the optimization function in Design Expert soft ware package, it was predicted that at the conditions; 100^{O}C temperature, 4pH media and 50^{O}brix dilution results in the optimum (maximum) percent of CaO removed which is 55.24. In order to verify this prediction, experiments were conducted and the result of 54.43% CaO in the molasses has been removed which well agree with the predicted value.

Therefore, this study shows that, the maximum CaO removal from molasses is obtained at higher temperature *(100^{o}C),* lower pH *(4)* and lower brix *(50^{o})* at which 54.43% CaO in the molasses removed. At these process conditions, CaO % molasses becomes 1.08 which is very interesting since it is too low when compared with the world average of 1.5 CaO %molasses *(Hubert OLBRICH, 2006)*.

Experiment Two

4.6.2. Determination of Optimum Retention Time

Result

This experiment has been conducted for seven days once every day and the average results of the experiment tabulated below *(Table 4.6).*

Table 4.6:- *Mud volume % molasses*

Retention Time [minutes]	0	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160	170	180
Mud volume [%]	100	84	70	59	50	42	37	33	29	26	23	20	18	17.5	17	16.5	16	16	16

This data has been plotted using excel spread sheet to determine the optimum retention time as follows *(see the following Figure 4.12).*

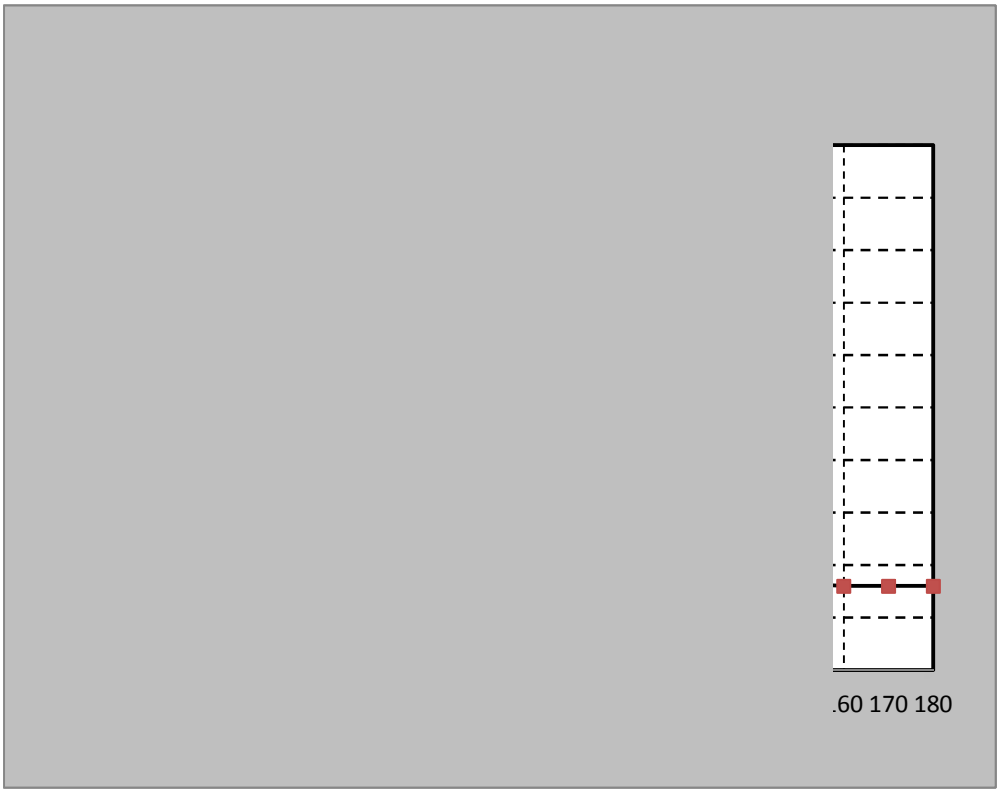


Figure 4.12: - *Effect of retention time on mud volume*

Discussion

From the graph, it can be seen that, mud volume is decreasing with increasing retention time. In other case the minimum mud volume is our interest. But, after 120 minutes, there is no significant decrease in mud volume with increasing retention time. Therefore, 120 minute is chosen as the optimum retention time with 18% of mud volume.

5. Design of Molasses Clarification Plant

5.1. Process Description

For ethanol plant integrated to sugar factory, as in most cases, molasses obtained from the sugar factory by centrifugal separation of the last massecuite, is pumped from sugar factory to the ethanol plant, and stored in bulk molasses storage tanks for the next processes. The storage tanks are of stainless steel having capacity for storage for more than two months operation. This is to give enough time for impurities in molasses to settle as much as possible.

The raw molasses that comes from crystallization plant contains impurities like the nutrients, carbon, nitrogen, vitamins and minerals that boost the growth of the fermenting micro-organisms, yeast. However, alongside these, the raw molasses also contains substances such as inorganic solid matters like calcium and magnesium salts, and other impurities derived from the sugar crop itself or from the sugar production process, that inhibit the micro-organisms growth, and can lead to difficulties in the downstream process, like yeast separation by centrifuge and scale formation in heaters and distillation column. To overcome these problems, these impurities must be separated from the molasses as early as possible, mostly by settling. In order to facilitate settling of impurities, molasses clarification processes which contains the activities such as dilution, pre-heating and addition of sulfuric acid (acidification) and final heating of the molasses to be undertaken.

To reduce viscosity of the molasses so that facilitate heating of molasses and aid proper mixing with sulfuric acid, the raw molasses is diluted to the optimum 50^{o}brix with treated or semi treated water or condensate from sugar factory, and then preheated to temperature of 65^{o}C using steam. The molasses must then be acidified with sulphuric acid to pH of about 4. As a result of the acidification, the calcium, magnesium and other inorganic salts in the molasses react with sulphuric acid and form precipitates as calcium and magnesium sulphates which can easily be separated during the subsequent settling process.

In addition to facilitating clarification process, acidification and preheating of raw molasses helps to deactivate some undesirable microorganisms, especially bacteria. Acidification also facilitates inversion (hydrolysis) of sucrose in to glucose and fructose which are fermentable forms of simple sugars.

To reduce investment cost of the clarification plant, pre-dilution, pre-heating and acidification can be done in a single steam jacketed tank fitted with agitator. Steam is admitted in to the jacket and condensed, while controlled amount of raw molasses, sulphuric acid and dilution water are mixed in the tank with the aid of agitator.

After adjusting pH with sulfuric acid, the molasses is then heated to the optimum temperature of 100^0C in shell and tube heat exchangers, using dry saturated steam to facilitate reaction of CaO with H_2SO_4 further, to coagulate impurities and to sterilize the molasses by inactivating undesirable microorganisms. After this final heating, the impurities in the molasses are made to settle in molasses decanters. The final sludge from the decanter is mixed with vinasses and filter cake, digested with bacteria and used as fertilizer for cane fields.

The clear molasses obtained from the decanter is called supernatant or treated molasses cooled to 32^oC using plate heat exchanger. The cooling water used in the heat exchanger going to be used as dilution water in dilution- preheating-acidification tank to recover back the energy from the clean molasses.

The proposed simple process diagram of the molasses clarification plant has been given in figure 5.2 below.

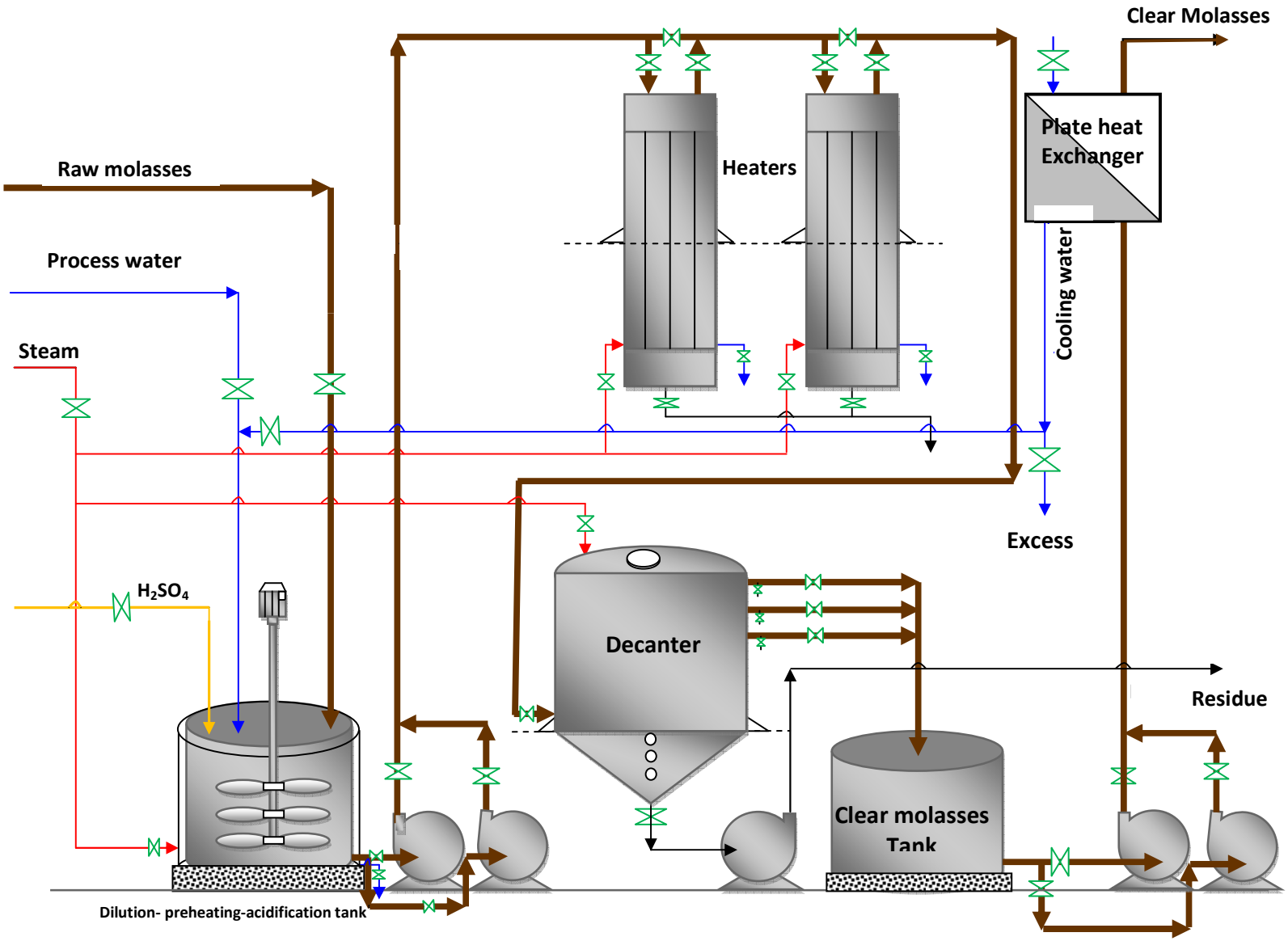


***Figure 5.1**: - Proposed molasses treatment plant*

5.2. Equipment Design

The design of each equipments included in the plant and that can be fabricated locally has been done in detail by using the design method in *chemical engineering design* by *Coulson and Richardson's volume 6*. But, the equipments that cannot be fabricated locally have been specified and are to be purchased from abroad. No detailed design has been included for these equipments.

5.2.1. Dilution -Acidification-Preheating Tank

The simplest way to transfer heat to a process or storage vessel is to fit an external jacket or an internal coil. But, in this case since we are going to use agitator internally, an internal coil type could not be our choice. Therefore, externally jacketed type vessel is going to be used for this purpose. In addition to this, to reduce investment cost, Per-dilution, pre-heating and acidification can be done in a single steam jacketed tank fitted with agitator. Steam is admitted in to the jacket and condensed, while controlled amount of raw molasses, sulfuric acid and dilution water are mixed in the tank with the aid of agitator.

The most commonly used type of jacketed vessel consists of an outer cylinder which surrounds part of the vessel. The heating medium circulates in the annular space between the jacket and vessel walls and the heat is transferred through the wall of the vessel. Circulation baffles are usually installed in the annular space to increase the velocity of the liquid flowing through the jacket and improve the heat transfer coefficient. The spacing between the jacket and vessel wall will depend on the size of the vessel, but will typically range from 50 mm for small vessels to 300 mm for large vessels *(Coulson & Richardson's, Volume 6, 2005).*

i. Material Balance

From the practical operation, the molasses flow rate to the plant is = $6m^3/h$

From laboratory analysis result brix of the raw molasses is = 84 ^oBrix

$$After\ dilution\ from\ 84^o brix\ to\ 50^o brix = \frac{6m^3/h\ \times 0\ .84}{0.5} = 10.08m^3/h$$

Therefore, the material flow in and out of the tank is *$10.08m^3/h$.*

From this, amount of dilution water going to be used is:

Mass of dilution water =Total masses of material inflow – Mass of molasses

$$Q_w\ (m^3/h)=10.08m^3/h - 6.00\ m^3/h=4.08\ m^3/h$$

Since the dilution water to be used here is that comes from cooling of clear molasses, it initial temperature is at 30^{o}C.

ii. Dimension of the Tank

Let the tank holds the diluted molasses for 20 minutes. Then, from the flow rate of the diluted molasses volume of the tank required is:-

$$\text{volume of the tank} = 10.08\frac{\text{m}^3}{\text{h}} \times \frac{\text{h}}{60\text{munte}} \times 20\text{minute} = 3.36\text{m}^3$$

$$\text{Assuming } 5\% \text{ safety margin} = 3.36 \times \frac{5}{100}\text{m}^3 = 0.168\ \text{m}^3$$

$$\text{Therefore total volume of the tank} = 3.36\text{m}^3 + 0.168\text{m}^3 = 3.528\text{m}^3$$

$$From\ the\ geometry\ of\ the\ tank: Volume, V = \pi r^2 h$$

From physical space of the plant let the height of the tank be h=2m.

$$\text{Then, } 3.528m^3 = \pi \times r^2 \times 2m$$

$$r = \sqrt{\left(\frac{3.528}{\pi \times 2}\right)}\ \text{m}$$

$$r = 0.75m$$

$$D = 2r = 1.5m$$

Where: - r= radius of the thank and

D= diameter of the tank

The dimension of the tank has been shown in the figure below schematically.

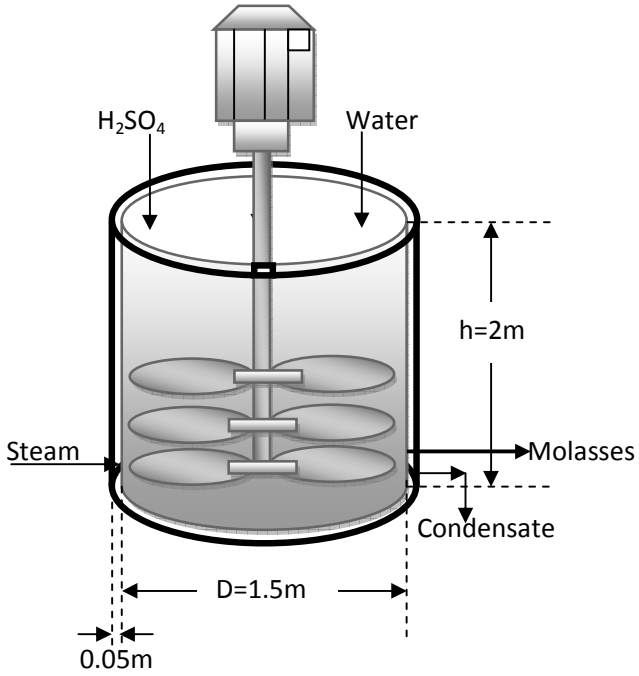


Figure 5.2: - *Dilution -acidification-preheating tank*

iii. Energy Balance

The rate of heat transfer from the jacket to the molasses will be given by:

$$\frac{dQ}{dT} = UA(T_s - T) \ldots\ldots\ldots\ldots\ldots 1$$

Where: - *dQ* = the increment of heat transferred in the time interval *dt*,

U = the overall heat transfer coefficient,

T_s = the steam saturation temperature,

T = molasses temperature.

Steam to ethanol plant is with pressure of 3.5 kg/cm^2 at which saturation temperature is 148^{o}C. (i.e. T_s = 148^{o}C).

Molasses initial temperature has been measured for 45 days once every day and the average value is 28^{o}C. whem this molasses mixed with dilution water which is at 30^{o}C, the final temperature of the diluted water become:-

$$4.08\,{}^{m^3}/_{h} \times 30^{o}C + 6\,{}^{m^3}/_{h} \times 28^{o}C = 10.08\,{}^{m^3}/_{h} \times T$$

$$T = 29^{o}C$$

Which is to be preheated to 65^{o}C *(i.e. T_1 = 29^{o}C & T_2 = 65^{o}C)*

The increase in the molasses temperature *dt* is related to the heat transferred *dQ* by the energy balance equation:

$$\boldsymbol{dQ = WC_p dt} \ldots\ldots\ldots\ldots\ldots \mathbf{2}$$

Where: - *W = mass of molasses in the tank,*

C_p = specific heat of molasses

t = heating time (seconds)

Equating equations *1* and *2* we have:-

$$WC_p \frac{dt}{dT} = UA(T_s - T)$$

Integrating this equation: $\int_0^t dt = \frac{WC_p}{UA} \int_{T_2}^{T_1} \frac{dT}{(T_s - T)}$

$$A = -\frac{WC_p}{Ut} \ln\left(\frac{T_s - T_2}{T_s - T_1}\right) \ldots\ldots\ldots\ldots\ldots 3$$

From Hand book of Cane Sugar Engineering by *E. Hugot*;

For molasses: C_p = 2.43kJ/kg

U = 0.37 W/m^2.^{o}C

t= 20 minutes = *1200 s*, which is heating time or retention time in the tank.

$$mass \text{of the diluted molasses in the tank} = \mathrm{V_m}\rho_m + V_w\rho_w$$

$$W = 1.428m^3 \times 1\,{}^{kg}/_{m^3} + 2.1m^3 \times 1.41\,{}^{kg}/_{m^3}$$

$$W = 4.389kg$$

Substituting these all values in *equation 3* the surface area of the jacket becomes:

$$A = 10.04m^2$$

Properties of molasses

From Hand book of Cane Sugar Engineering by *E. Hugot*; thermal conductivity of molasses at 60% sucrose and 50^{O}C, $U = 0.37\ kcal/mole/h/O_C$

The specific heat of molasses may be obtained with somewhat better precision than the simple formula C=1-0.006B, by means of the formula of Janovsky and Archangelsky.

$$\boldsymbol{C = 1 - [0.6 - 0.0018t + 0.0008(100 - P)]\frac{M}{100}} \ldots\ldots\ldots\ldots\ldots * \quad \textit{(E. Hugot, 1986)}$$

Where: - ***P*** = true purity (sucrose/dry substance) of the molasses = **38%**

M = dry substance % in the molasses = **84%**.

Molasses initial temperature= 65^{o}C

Molasses final temperature to be = 100^{o}C

t = temperature of the molasses, in ℃ $= \sqrt{29 \times 65} \approx \boldsymbol{43^{o}C}$

Then substituting these values in equation *:

Specific heat of a molasses, in kcal /kg, C_p =0.52 kcal /kg = 2.18kJ/kg.

$$heat\ load\ using\ diluted\ molasses, \dot{q} = \left(C_{p_m}\dot{m}_1 + C_{p_w}\dot{m}_2\right)\Delta T$$

$$= (2.18 \times 8.46 + 4.20 \times 4.08) \times (65 - 29) \times \frac{1}{3600}$$

$$\dot{q} = \boldsymbol{355.788}W$$

Properties of steam

- Type = dry saturated
- Pressure = 3.5kg/cm^2
- Temperature = 148^{O}C (from steam table)

Latent heat of dry saturated at 3.5kg/cm^2 and 148^{o}C, h_s=2,739.3485 kJ/kg

Assuming that the approach temperature of the heat exchanger to be 10^{O}C,

Vapour living the heat exchanger is at temperature = 110 ^{O}C at which absolute pressure= 1.46kg/cm^2.

Latent heat of vapor at 1.46 kg/cm^2 and 110^{o}C, h_v=2,739.3485 kJ/kg

Therefore, the heat load from the steam is given by:-

$$\dot{q} = c_p \dot{m}_s \Delta t_s + (\dot{m}_s h_s - \dot{m}_s h_v)$$

$$steam\ required, \boldsymbol{\dot{m}_s} = \frac{\dot{q}}{c_p \Delta t_s - (h_s - h_v)}$$

$$= \frac{355.788}{4.2 \times (148 - 110) + (2739.35 - 2691.66)} \times 3.6$$

$$m_s = \mathbf{6.18 kg/h}$$

ii. Dimension of the Jacket

Then to calculate the spacing of the jacket: $A = 2\pi rh$

Let height of the jacket be equal to that of the tank, i.e. *h=2m*

$$10.04m^2 = 2 \times \pi \times r \times 2m$$

Therefore, r = 0.8 m

Diameter of the jacket, D = 1.6 m

Spacing of the Jacket, $S = \frac{(1.6-1.5)}{2} = 0.05m = \mathbf{50mm}$

5.2.2. Molasses Heaters

Shell and tube heat exchangers in their various construction modifications are probably the most widespread and commonly used basic heat exchanger configuration in the process industries. The reasons for this general acceptance are several. The shell and tube heat exchanger provides a comparatively large ratio of heat transfer area to volume and weight. It provides this surface in a form which is relatively easy to construct in a wide range of sizes and which is mechanically strong enough to withstand normal shop fabrication stresses, shipping and field erection stresses, and normal operating conditions. There are many modifications of the basic configuration, which can be used to solve special problems. The shell and tube heat exchanger can be reasonably easily cleaned, and those components most subject to failure gaskets and tubes can be easily replaced. Finally, good design methods exist, and the expertise and shop facilities for the successful design and construction of shell and tube exchangers are available throughout the world. It can be easily fabricated locally in ordinary fabrication shops of the sugar factories.

This most commonly used type of heat transferring equipment, *i.e.*, shell and tube heat exchanger, is to be used in this process to heat the molasses, the design of which is the main subject of this section. Here, two similar units to be used such that when one unit is under operation the other standby to be isolated for cleaning. This is done simply by valve arrangement as shown in figure below.

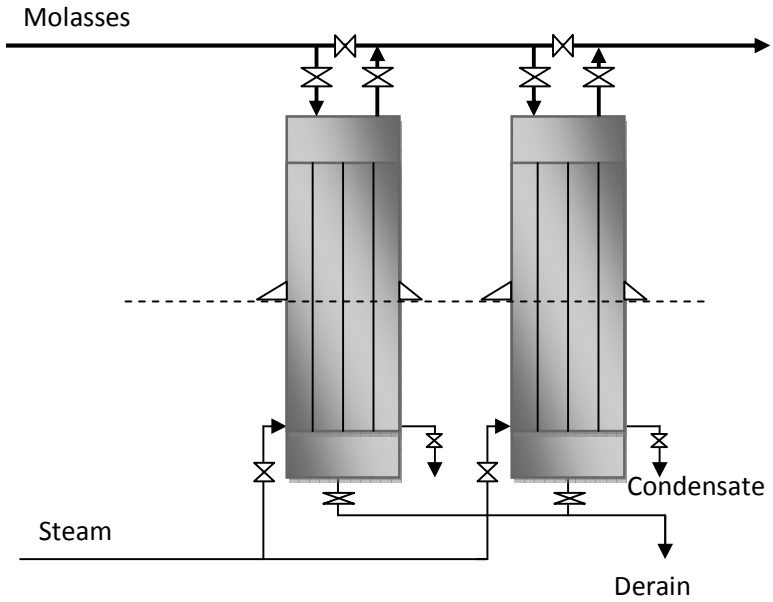


Figure 5.3: - *Schematic diagram of shell and tube molasses heater*

i. Mass Balance

To determine material flow in and out of the heat exchanger:

Refractometric brix of the molasses *Brix=84^{o}brix*

Flow rate=6 m^3/h

Density =ρ_m=1.41kg/m^3

$$\text{mass flow rate of molasses, } \dot{m}_1 = 6\,{}^{m^3}/_{h} \times 1.41\,{}^{kg}/_{m^3} = 8.46\,{}^{kg}/_{h}$$

$$dilution\ water\ to\ bring\ the\ molasses\ from\ 84^o brix\ to\ 50^o brix$$

$$Q = \frac{0.84 \times 6}{0.50} - 6 = 4.08\, m^3/h$$

$mass\ of\ dilution\ water$:-

$$\dot{m}_2 = Q \times \rho_w = 4.08\, m^3/h \times 1\, {}^{kg}/_{m^3} = 4.08\, kg/h$$

$$total\ mass\ flow\ rate,\ \dot{m} = \dot{m}_1 + \dot{m}_2 = 8.46\, {}^{\text{kg}}/_{\text{h}} + 4.08\, kg/h = \mathbf{12.54}\, kg/h$$

Diluted molasses volumetric flow rate, $Q_t = 10.08 m^3/h$

ii. Energy Balance

Properties of steam

Type = dry saturated (dryness factor, $x = 0$)

Pressure = 3.5kg/cm^2

Temperature = 148^{O}C (from steam table)

Latent heat of dry saturated at 3.5kg/cm^2 and 148^{o}C, h_s=2,739.3485 kJ/kg

Assuming that the approach temperature of the heat exchanger to be 10^{O}C,

Vapour living the heat exchanger is at temperature = 110 ^{O}C at which absolute pressure= 1.46kg/cm^2.

Latent heat of vapor at 1.46 kg/cm^2 and 110^{o}C, h_v=2,739.3485 kJ/kg

Properties of molasses

From Hand book of Cane Sugar Engineering by *E. Hugot*; thermal conductivity of molasses at 60% sucrose and 50^{O}C, $U = 0.37\ kcal/mole/h/O_C$

The specific heat of molasses may be obtained with somewhat better precision than the simple formula C=1-0.006B, by means of the formula of Janovsky and Archangelsky.

$$\boldsymbol{C = 1 - [0.6 - 0.0018t + 0.0008(100 - P)]\frac{M}{100}} \ldots\ldots\ldots\ldots\ldots * \quad \textit{(E. Hugot, 1986)}$$

Where: - ***P*** = true purity (sucrose/dry substance) of the molasses = **38%**

M = dry substance % in the molasses = **84%**.

Molasses initial temperature= 65^{o}C

Molasses final temperature to be = 100^{o}C

t = temperature of the molasses, in ℃ = $\sqrt{65 \times 100} \approx \boldsymbol{80^o C}$

Then substituting these values in equation *:

Specific heat of a molasses, in kcal /kg, C_p =0.58 kcal /kg = 2.43kJ/kg.

$$heat\ load\ using\ diluted\ molasses, \dot{q} = \left(C_{p_m}\dot{m}_1 + C_{p_w}\dot{m}_2\right)\Delta T$$

$$= (2.43 \times 8.46 + 4.20 \times 4.08) \times (100 - 65) \times \frac{1}{3600}$$

$$\dot{q} = \mathbf{366.468}W$$

$$\dot{q} = c_p\dot{m}_s\Delta t_s + (\dot{m}_s h_s - \dot{m}_s h_v)$$

$$steam\ required, \boldsymbol{\dot{m}_s} = \frac{\dot{q}}{c_p\Delta t_s + (h_s - h_v)}$$

$$= \frac{366.468}{4.2 \times (148 - 110) + (2739.35 - 2691.66)} \times 3.6 = \mathbf{6.36}\boldsymbol{kg/h}$$

$$Log\ mean\ temperature = \frac{(148 - 100) - (110 - 65)}{ln\left(\frac{148 - 100}{110 - 65}\right)} = 46.48^0C$$

Use one shell path and two tube path *(Appendix C):*

$$R = \frac{(148 - 110)}{(100 - 65)} = 1.09$$

$$S = \frac{(100 - 65)}{(148 - 65)} = 0.42$$

From graph of temperature correction factor for one shell path and two tube path at *R=1.09* and *S=0.42* approximately *(Coulson & Richardson's, volume 6, page-657)*

F_t=0.88

$$Therefore\ log\ mean\ temperature = 0.88 \times 46.48 = 40.9^oc$$

iii. Dimension of the Heat Exchanger

$$Total\ heating\ area, \qquad A = \frac{\dot{q}}{\Delta T_{lm}U} = \frac{366.468W}{40.9 \times 0.37} = 24.22m^2$$

From tube standard *(Perry page 10-72)* choose:

Pipe of: - *20 mm* outer diameter

16 mm internal diameter

2 mm wall thickness

2 m long

$$surface\ area\ of\ one\ tube = \pi Dl = \pi \times 0.02m \times 2m = 0.1257m^2$$

$$Number\ of\ tubes = \frac{Total\ heating\ area}{surface\ area\ of\ one\ tube} = \frac{24.22}{0.1257} = 192.65\ tubes \approx 192 tubes$$

$$Tube\ per\ path\ = \frac{192 tubes}{2 path} = 96\ tubes\ per\ path$$

As the shell-side fluid, steam, is relatively clean and cleaning not required use 1.25 triangular pitches.

$$Bundle\ diameter, D_d = d_o \left(\frac{N_t}{K_1}\right)^{\frac{1}{n_1}}\ , (Coulson\ and\ Richardon's\ volume\ 6\ page\ 649)$$

Where:- N_t = number of tubes,

D_b = bundle diameter, mm,

d_o = tube outside diameter, mm.

K_1 and n_1 read from table for 2-tube pass as: $K_1=0.249$

$n_1=2.207$

$$Db\ =\ 20 \times \left(\frac{192}{0.249}\right)^{\left(\frac{1}{2.207}\right)} = 406.62mm$$

Use outside packed heat and from graph, shell-bundle clearance =38mm

Shell diameter=$406.62\ mm$ +38mm=**444.62mm**

Note. Shell size could be read from standard tube count tables and nearest standard pipe sizes are **457.2 mm** (Perry page 10-72).

5.2.3. Molasses Decanter

Decanters are used to separate liquids where there is a sufficient difference in density between the liquids for the droplets to settle readily. Decanters are essentially tanks which give sufficient residence time for the droplets of the dispersed phase to rise (or settle) to the interface between the phases and coalesce. In an operating decanter there will be three distinct zones or bands: clear heavy liquid; separating dispersed liquid (the dispersion zone); and clear light liquid.

Decanters are normally designed for continuous operation. A great variety of vessel shapes is used for decanters, but for most applications a cylindrical vessel will be suitable, and will be the cheapest shape. For this purpose, a cylindrical vessel with conical lower end is to be used in this case.

Calculation of decanter volume

From the practical operation, the molasses flow rate to the plant is = 6m^3/h

Brix of the raw molasses is = 84 ^{o}brix

$$After\ dilution\ from\ 84^o brix\ to\ 50^o brix = \frac{6m3/h\ \times 0\ .84}{0.5}\ = 10.08m^3/h$$

Optimum retention time from experiment = *2 hours*

$$Therefore\ operating\ volume\ of\ the\ decanter = 10.08m^3/h\ \times\ 2h = 20.16m^3$$

$$5\%\ safety\ margine\ = \frac{5 \times 20.16}{100} = 1.008m^3$$

From the experiment to determine optimum retention time, the final mud volume is 18%. Therefore:-

$$18\%\ mud\ put\ (Dead\ volume) = \frac{18 \times 20.16}{100} = 3.6288m^3$$

$$Total\ volume\ of\ the\ decanter\ = 20.16 + 1.008 + 3.6288 = 24.8m^3$$

Calculation of dimension of the decanter

Design factors that need more evaluation in clarifier designs are steep tank bottom slope and very shallow side depth. An improperly designed clarifier bottom slope or side water depth can result in a large reduction of effective tank capacity compared with a good design. The recommended slope and side depth is 20^o to 40^0 and 2 m respectively *(B. G. Jones et. al. 2005).* In this design, 2m side depth has been selected as the.

From the experiment result to determine the optimum retention time, it has been seen that the minimum mud volume % molasses was 18%. Therefore, the mud put, which is the conical part of the decanter, should be 18% of the total volume so that the mud not to come up above the feed inlet. If the mud becomes above the feed point, the incoming material could disturb the mud which highly affects the decantation process.

Therefore:-

- the volume of the cylindrical part of the decanter,$V_1 = 24.8m^3 \times \frac{82}{100} = 20.34m^3$
- the volume of the conical part of the decanter, $V_2 = 24.8m^3 \times \frac{18}{100} = 4.46m^3$

$$From\ the\ geometry\ of\ the\ decanter\ V_1\ = \pi r^2 h_1 = 20.34m^3$$

From which r=1.8 m

$$D = 3.6m$$

$$V_2 = \frac{1}{3}\pi r^2 h_2 = 4.46\ m^3$$

From which h_2=1.31 m

$$Tan\ \theta\ = \frac{h_2}{r} = \frac{1.31}{1.8} = 0.73$$

$$\boldsymbol{\theta} = tan^{-1}(0.73)$$

$$\boldsymbol{\theta = 36^o}$$

This is in the recommended slop range of 20^o to 40^o.

The dimension of the decanter has been shown in the figure below schematically.

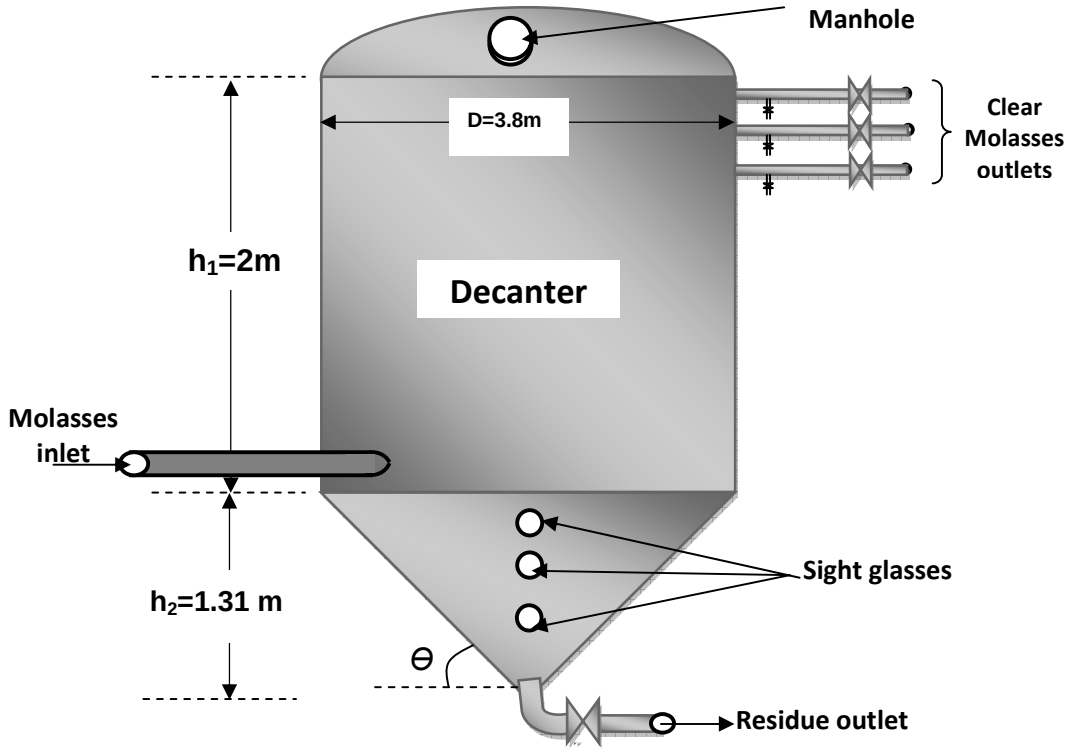


Figure 5.4: - *Decanter for molasses clarification*.

5.2.4. Clear Molasses Receiving Tank

i. Mass Balance

From the practical operation, the molasses flow rate to the plant is = $6m^3/h$

Brix of the raw molasses is = 84 ^{o}brix

$$After\ dilution\ from\ 84^o brix\ to\ 50^o brix = \frac{6m^3/h\ \times 0\ .84}{0.5} = 10.08m^3/h$$

Therefore, the material flow in and out of the tank is *$10.08m^3/h$*

ii. Dimension of the Tank

Let the tank holds the diluted molasses for 20 minutes. Then, from the flow rate of the diluted molasses volume of the tank required is:-

$$\text{volume of the tank} = 10.08\frac{\text{m}^3}{\text{h}} \times \frac{\text{h}}{60\text{munte}} \times 20\text{minute} = 3.36\text{m}^3$$

$$\text{Assuming } 5\% \text{ safety margin} = 3.36 \times \frac{5}{100}\text{m}^3 = 0.168\ \text{m}^3$$

$$\text{Therefore total volume of the tank} = 3.36\text{m}^3 + 0.168\text{m}^3 = 3.528\text{m}^3$$

$$From\ the\ geometry\ of\ the\ tank: Volume, V = \pi r^2 h$$

From physical space of the plant let the height of the tank be h=2m.

Then, $3.528m^3 = \pi \times r^2 \times 2m,$ r=0.75m

D=1.5m

The dimension of the tank has been shown in the figure below schematically.

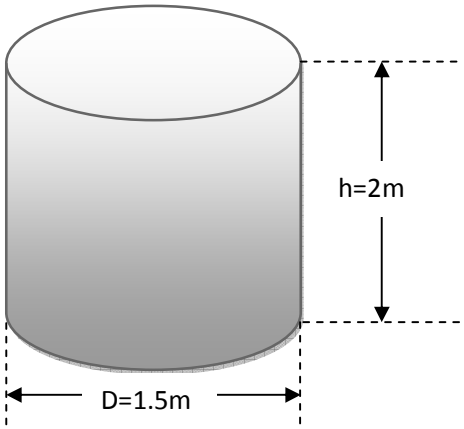


Figure 5.5: - *Clear molasses receiving tank*

5.2.5. Molasses Pumps

There are four with similar capacity centrifugal pumps in the proposed molasses clarification plant. Two of which are for Diluted and Acidified Molasses one operational,

the other stand by and the other two for clear Molasses similarly one operational, the other stand by. Mud Pump is a bit different special type centrifugal pump for pumping thick mud from the decanter. In this case, since mud removal is not continuous operation, no stand by pump is considered and it is only one pump for this purpose.

Pumps cannot be fabricated locally and therefore no detailed design of the pumps has been included. But, they have been specified to simply chosen from market as the following specifications *(Table 5.1).*

Table 5.1:-*List of pumps and their specification*

No	**Description**	**Type**	**Number**	**Capacity(m^3/h)**
1	Diluted and Acidified Molasses Pump	Centrifugal	2	12
2	Clear Molasses Pump	Centrifugal	2	12
3	Mud Pump	Special type centrifugal	1	6

5.2.6. Clear Molasses Cooler

Finally the output of this clarification process which is clear molasses is going to be fed to fermentation plant. But, at the end of this process, the molasses is heated up to the temperature of 100^{O}C. In other case, fermentation plant requires a temperature of 32^{O}C which is optimum temperature for the yeast to live and perform their function. Even if there is some ^{O}C drop in temperature on process, it could not go down to the required 32^{O}C temperature naturally. Therefore, heat exchanger should be included to cool down the molasses to the required temperature.

It is impossible to know how lower it could drop without using coolers theoretically unless it is practically evaluated. Rather, it depends on the atmospheric condition, retention time, agitation, etc. Therefore, without the knowledge of input and output specifications, it is difficult to design the heat exchanger. Here selection of heat exchanger has been made rather than designing it.

Plate heat exchangers are more flexible and it is easy to add or remove extra plates to adjust the heat exchanger to the required temperature. Therefore, plate heat exchanger is the best choice for this case. In addition to this, plate heat exchangers have the advantages of easier to maintain, Low approach temps can be used, as low as 1 ^{O}C, compared with 5 ^{O}C to 10 ^{O}C for shell and tube heat exchangers, more suitable for highly viscous materials and fouling tends to be significantly less in plate heat exchangers.

Therefore, plate heat exchanger with a maximum capacity to cool the molasses from 100^{O}C to 32^{O}C with cooling media of water at the initial temperature of 10^{O}C is going to be selected from market and purchased for this purpose.

Table 5.2: - *Specification of plate heat exchanger*

Fluid Group	Molasses		Water	
	Inlet	Outlet	Inlet	Outlet
Temperature (^{O}C)	100	32	18	30
Pressure (5bar)	5	5	5	5
Mass flow rate (kg/h)	12.54		41.11	

Energy Balance

From over all heat transfer: $q = \dot{m}c_p\Delta T$

Using that of the molasses: $q = 12.54 \times 2.43 \times (100 - 32) = 2{,}072.11W$

The, the amount of water required: $\dot{m} = \frac{q}{c_p\Delta T}$

$$\dot{m} = \frac{2{,}072.11W}{4.2 \times (30 - 18)} = \mathbf{41.11}\boldsymbol{kg/h}$$

6. Financial Analysis of Molasses Treatment Plant

Experimentally and engineering wise it has been seen that investing molasses clarification plant for the plant is feasible. But, its feasibility should be checked financially. In this section, the proposed project to be analyzed financially depending on the proposed and designed molasses clarification plant according to Max S. Peters, Klaus D. Timmerhaus and James c. Van Horne *(Max S. et.al (1991) James et.al (2004)).*

6.1. Investment Cost Estimation

In this cost some costs like land moving, land lease, building cost and other minor costs have not been included sine the plant is already existing and the only work know is the expansion work. But some civil work costs like foundation works of tanks and pumps and floor works has been included. In addition to this, except pumps and plate heat exchangers, all the equipments to be fabricated locally which highly minimize initial investment cost of the plant

Table 6.1: - *Initial investment cost of molasses clarification plant*

No	**Description**	**unit**	**quantity**	**Cost per unit (Birr)**	**Total cost (Birr)**
Equipment cost					
1	Dilution- preheating-acidification tank	pcs	1	83,200	83,200
2	Heaters	pcs	2	15,033.85	30,067.70
3	Decanter	pcs	1	131,002	131,002
4	Clear molasses Tank	pcs	1	28,600	28,600
5	Centrifugal Pumps	pcs	4	53,905	215,620
6	Special Centrifugal Pumps	pcs	1	27,348	27,348
7	Cooler	pcs	2	17,799.85	35,599.7
8	Civil work	Lamp sum	----	100,000	100,000
9	Contingence (15%)	Lamp sum	----	----	97,715.61
Total		----	----	----	**749,153.01**

6.2. Operating Cost Estimation

This cost is the cost encored due to day to day operation activity of the proposed clarification plant. In this case, overhead cost does not included as there is no additional overhead cost due to implementation of this plant. But, one operator and one assistant operator are required to operate the plant together with their requirements.

Table 6.2: - *Operating cost of molasses clarification plant*

No	**Description**	**unit**	**quantity**	**Cost per unit(Birr)**	**Total cost(Birr)**
Utility cost					
1	Steam	Ton	90.288	4,359.9	39,364.665
2	Water	m^3	295,992	5.6	1,675,555.2
3	Electricity	KWH	216,000	0.58	125,280
Sub-total		----	----	----	**1,840,199.865**
Man power					
1	Operator	Person	1	27,936	27,936
2	Assistant operator	Person	1	14,400	14,400
Sub-total			----	----	**42,336**
Protective device					
1	Goggle not colored	pcs	4	84.5	338
2	Head cover	pcs	4	9.90	39.6
3	Leather glove	pcs	4	47.00	188
4	Leather shoes	pcs	4	97.40	389.6
5	Soap 200 g	pcs	24	3.80	91.2
6	Woolen glove	pcs	4	16.96	67.84
7	Shirt and long trouser	pcs	4	55	220
Sub- total		----	----	----	**1,334.24**
Other costs					
1	Over time	day	44	235.2	10,348.8
2	incentive	year	1	7,056	7,056
3	Contingence (15%)	year	1	113,971.476	361,109.85
Sub-total		----	----	----	**378,514.65**
Total		----	----	----	**2,768,508.86**

In addition to the budget of the plant for 6,037.5 liters of H_2SO_4, additional 1,750,000 birr/ year is required for the purchase of H_2SO_4.

6.3. Cost to Clean the Scale

In the plant the scaling rate of heat transferring equipments is very frequent and as a result, the distilleries and evaporator units could not work properly for more than four days after cleaning. Therefore, the processes operation stops every four days for cleaning. In addition to this, since the scale deposited on heat transferring surfaces in this short period of time is very thick and hard scale, it takes a minimum of eight hours to clean the units which is 60 hours (2.5days) per month. During this time, all the workers of the plant kept idle and the cleaning activity done by other laborers paying additional payment. But, since the cost of alcohol recovered going to be considered, this cost is utilized to produce the recovered alcohol and will not be included in the cash flow separately.

Table 6.3: - *Monthly salary of Metahara sugar factory ethanol plant workers*

No	Job title	Grade	Formation	Monthly salary	2.5 days Salary
1	Ethanol head	19	1	6806	567.17
2	Process section head	17	1	4696	366.33
3	Biocompositing section head	16	1	5384	448.67
4	Maintenance section heads	16	1	3520	293.33
5	Process supervisor	13	3	13,188	1,098.99
6	Technical supervisor	13	1	4057	338.08
7	Quality control supervisor	13	1	4396	366.33
8	Instrument supervisor	13	1	3520	293.33
9	Electrical supervisor	13	1	4396	366.33
10	Store supervisor	12	1	2862	238.50
11	Distillery Forman	11	3	9,489	790.74
12	Biocompositing Forman	11	1	3341	278.42
13	Spare part Forman	10	1	2910	242.50
14	Finished product Forman	10	1	2862	238.50
15	Distillation operator	8	3	8,340	695.01

Table 5.3:- Continues…

16	Fermentation operator	8	3	8,340	695.01
17	Skilled welder mechanic	8	1	2780	231.67
18	Skilled electrician	8	1	2780	231.67
19	Secretary	8	1	1965	163.75
20	Skilled mechanic	8	3	4,890	407.49
21	Safety technician	8	3	6,984	582.00
22	Laboratory analyzer	8	3	4,890	407.49
23	Electric/instrument technician	8	3	6,984	582.00
24	WTP and CPU operator	7	3	6,984	582.00
25	Estate car driver	7	2	3,500	291.66
26	Wheel tractor driver	6	1	1520	126.67
27	Messenger	2	1	973	81.08
Total		-----	46	-----	**11,004.72**

***(Source: -** Metahara sugar Factory finance department)*

Before mechanical cleaning, scaled unit boiled with caustic soda solution to soften the hard scale and to make cleaning easier. This also encores an additional 20,816 Birr/year cost on the plant.

The other huge cost the factory pay for cleaning is loss of production opportunity. The production is interrupted every four days for a minimum of eight hour. This becomes 2.5 days per month. When this is multiplied with daily production of the plant which is 50,000 liters per day, there is a loss of opportunity to 125,000 liters per month. Assuming an average capacity utilization of 85% 106,250 liters of alcohol going to produced. The minimum current cost of ethanol is 8 birr/liter; therefore there is a loss of 850,000 birr/per month. Multiplying with 10 operation months, there is a loss of **8,500,000 birr/year** due to lose of production opportunity to clean the scaled heat transferring units. Therefore, due to implementation of molasses clarification plant, the factory going to save this huge money per year.

Other cost of cleaning of the scale is labour cost for cleaning paying 70 birr per cleaning for a minimum of five laborers which becomes 26,250 Birr/year.

6.4. Projected Cash Flow

This all costs are going to be summarized in the following section to show that whether the proposed project is feasible or not to implement.

Table 6.4: *Projected cash flow*

Year	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Capacity utilization%	---	100	100	100	100	100	100	100	100	100	100
Cash in flow	**---**	**8,547,066**	**8,547,066**	**8,547,066**	**8,547,066**	**8,547,066**	**8,547,066**	**8,547,066**	**8,547,066**	**8,547,066**	**8,549,066**
Ethanol sales	---	8,500,000	8,500,000	8,500,000	8,500,000	8,500,000	8,500,000	8,500,000	8,500,000	8,500,000	8,500,000
Labor cost saving	---	26,250	26,250	26,250	26,250	26,250	26,250	26,250	26,250	26,250	26,250
Chemical saving	---	20,816	20,816	20,816	20,816	20,816	20,816	20,816	20,816	20,816	20,816
Salvage value	---	---	---	---	---	---	---	---	---	---	2,000
Cash out flow	**749,153.01**	**7,327,774.53**	**7,327,774.53**	**7,327,774.53**	**5,201,815.25**	**5,201,815.25**	**5,201,815.25**	**5,201,815.25**	**5,201,815.25**	**5,201,815.25**	**5,201,815.25**
Investment	**749,153.01**	---	---	---	---	---	---	---	---	---	---
Utility cost	---	**2,346,323.97**	**2,346,323.97**	**2,346,323.97**	**2,346,323.97**	**2,346,323.97**	**2,346,323.97**	**2,346,323.97**	**2,346,323.97**	**2,346,323.97**	**2,346,323.97**
Chemical	---	1,750,000	1,750,000	1,750,000	1,750,000	1,750,000	1,750,000	1,750,000	1,750,000	1,750,000	1,750,000
Factory overheads	---	426,993.64	426,993.64	426,993.64	426,993.64	426,993.64	426,993.64	426,993.64	426,993.64	426,993.64	426,993.64
Depreciation (15%)	---	755,623.15	755,623.15	755,623.15	755,623.15	755,623.15	755,623.15	755,623.15	755,623.15	755,623.15	755,623.15
Capital charges (35%)	---	1,763,120.67	1,763,120.67	1,763,120.67	---	---	---	---	---	---	---
Interest (12%)	---	604,498.52	604,498.52	604,498.52	---	---	---	---	---	---	---
Gross profit	**-749,153.01**	**1,219,291.47**	**1,219,291.47**	**1,219,291.47**	**3,345,250.75**	**3,345,250.75**	**3,345,250.75**	**3,345,250.75**	**3,345,250.75**	**3,345,250.75**	**3,347,250.75**

6.5. Feasibility Study

According to the projected income statement, the project will start generating profit in the first year of operation. Depending on the income statement, other indicators of profitability which show the viability of the project has been calculated as follows:

Pay Back Period

The investment cost and income statement projection are used to project the pay-back period as follows:

Year	0	1	2	3
Cumulative cash flow	-749,135.01	470,156.46	1,689,447.93	2,908,739.4
Yearly cash flow	---	1,219,291.47	1,219,291.47	1,219,291.47

$$Payback\ period = 0\ year + \frac{749{,}135.01}{1{,}219{,}291.47} \times 12\ months = 7.4\ months$$

$$\approx \mathbf{8}\ \boldsymbol{months}$$

This shows that, the plant initial investment cost will be fully recovered within 8 operation months. Therefore, implementing of clarification plant for Metahara sugar factory ethanol plant is financially feasible.

7. Conclusion and Recommendation

7.1. Conclusion

Ethanol plant is one of process industries where scaling leads to high economic penalties since it involves a number of heat exchangers. In this study, the problem of scaling of heat exchangers in ethanol plant of Metahara sugar factory, the cause(s) of the scaling problem and the possible solution for the reduction of the problem has been studied.

Deposit samples taken from distillation columns of Metahara sugar factory ethanol plant and characterized both physically and chemically. Physical characterization of the scale sample shows that the scale so formed in short period of time is too thick which measures up to 3cm and hard scale which cannot be easily removed. In addition to this, the composition of deposit samples analyzed using x-ray fluorescence to identify the composition of the scale and so that gives the indication to determine scale causing components of the raw material. From sample compositions investigated, it is found that CaO (63.87%) is the main scale causing component. This leads to the conclusion that crystallization of Ca compounds is the main cause for scaling of heat exchangers in ethanol plant. Beside this, organic particles are also found in the deposit sample which shows that particulate fouling also contributes to deposit formation.

From investigation of the cause of this scaling, since the plant is provided with water treatment plant and process water used in the plant is with good quality, the only source of this scaling is molasses. To ensure that really the cause of the scaling is molasses, the raw material molasses and process water characterized and the molasses found with abnormally high CaO (2.41%) content which most probably comes from poor quality of quick lime used for the clarification of mixed juice in production of plantation white sugar. But, quality of the process water used in the plant was very good which could not be the cause for the scaling. These ensure that the main cause of the scaling in the plant is the raw molasses input.

To overcome this problem, experiments have been conducted in order to study the clarification of molasses and how the various operational parameters of molasses clarification affect the removal of CaO from molasses. To conduct the experiment, three influential process variables temperature, brix and pH have been chosen. The experimental result shows that, good removal of CaO from molasses is obtained at higher temperature ($100^{O}C$), lower pH (4) and lower brix (50^{O}). At these optimum conditions, the maximum percent of CaO removed (54.43 %) has been obtained. At this process conditions 1.08 CaO % molasses has been obtained which is very low when compared with the world average of 1.5%

Moreover, an experiment has been conducted to determine the optimum retention time using the above optimum conditions and 2 hours has been chosen as the optimum retaliation time for the clarification of molasses.

Using the optimum operating conditions determined experimentally and the existing condition of the plant, molasses clarification plant has been proposed and design of the equipments to be used in the plant also done.

Finally, the proposed clarification plant financially analyzed and it is with payback period of only eight operation months which makes the implementation of the plant feasible.

7.2. Recommendation

The cost of ethanol production can be minimized by maintaining the optimum efficiency of the heat exchangers and reducing the amount of downtime necessary for cleaning. The profitability of the plant highly depends on the maintenance of clean heat transfer surfaces and efficient utilization of energy. But, the scaling of heat exchangers is the severe problem in Metahara sugar factory ethanol plant which highly affects the profitability of the plant.

Depending on the results obtained in this thesis, available resources and technical feasibility, the following recommendations are suggested:

- Knowledge of the costs involved in fouling is important in determining the severity of the problem. The total operational costs arising from fouling at the plant are not fully determined due to lack of information on some cost elements. It is recommended that Metahara sugar factory ethanol plant should consider implementing a system for determining fouling related costs so that severity of the scaling easily raveled.

- A fouling monitoring system should be implemented on all heat exchangers of the plant. Currently, some temperature sensors of heat exchangers in the plant do not work properly. With effective temperature sensors fitted on inlet and outlet of the heat exchangers, information can be collected and the fouling of the equipment evaluated easily. This information can be used for scheduling cleaning activities.

- Monitoring system of the quality of cleaning and cleaning procedure should be implemented. This is important in view of the fact that the condition of a heat transfer surface has a large effect on the initiation of scaling. If the scale formed is not completely removed during the cleaning time, it becomes the nucleation site for the new scale formation which facilitates scaling of the heat exchangers.

- For the long term solution of the problem, Metahara sugar factory ethanol plant should implement clarification technology to remove CaO from the process streams. The clarification method of mixed juice in production of plantation white sugar using milk of lime introduces CaO in to the process stream which comes to ethanol plant with molasses. Since CaO is mostly responsible for deposit formation on heat transfer surfaces, elimination of this component of molasses will greatly help in reducing the scaling problems in the factory.

- In order to obtain realistic results, experiments should be conducted at industrial scale at similar conditions as those prevailing in the actual process conditions. While fluid and thermal conditions can be reproduced in the laboratory, it is impractical to reproduce others, such as the condition of having the fluid pass through heat exchangers. It is therefore recommended that for future experiments the test section be installed in the factory as a bypass to the actual process.

8. References

1. ***Berkeley (2011)*** *Centrifugal Pumps Price Book CB1525 Supplement, Effective June 15, 2011*
2. ***C. P. East, W. O. S. Doherty, C. M. Fellows, and H. Yu (2010)*** *Characterization of sugar juice heat exchanger tube deposit, Surf. Interface Anal.*
3. ***Coulson & Richardson's (2005)*** *Chemical Engineering Design, Volume 6, 4th edition, university of Oxford, UK:*
4. ***Crees, O.L., Cuff, C. and Doherty, W.O.S. (1992)*** *Examination of evaporator scales from the far Northern regions of the sugar industry. Proc. Aust. Soc. Sugar Cane Technol.*
5. ***D.P. KULKARNI.*** *Cane Sugar Manufacture in India: The sugar technologists Association of India, New Delhi, India.*
6. ***D.W. Rackemann, W.O.S. Doherty and C.P. East (2010)*** *Development of descriptor tools for the characterisation of Australian sugar mill evaporator scale. Sugar Research and Innovation, Queensland University of Technology, Australia. Proc. Int. Soc. Sugar Cane Technol., Vol. 27, 2010.*
7. ***Dagnew Tadesse, Assefa Desta, Aberra Geyid, Woldemariam Girma, Solomon Fisseha, Oliver Schmoll (2010)*** *Rapid Assessment of Drinking Water Quality in the Federal Democratic Republic of Ethiopia, Country Report of the Pilot Project Implementation in 2004-2005, World Health Organization and UNICEF 2010*
8. ***Department of Water Affairs and Forestry (1996)*** *South African Water Quality Guidelines 2nd edition, Volume 3: Industrial Use. Edited by S. Holmes, CSIR Environmental Services; Pretoria, South Africa.*

9. ***Department of Water Affairs and Forestry (1996)*** *South African Water Quality Guidelines 2nd edition, Volume 1: Domestic Use. Edited by S. Holmes, CSIR Environmental Services; Pretoria, South Africa.*
10. ***Douglas C. Montgomery (2001)*** *Design and Analysis of Experiments, 5th. Arizona State University, Page 427.*
11. ***E. Hugot (1986)*** *Hand book of cane sugar engineering, 3rd edition, Elesevier science publisher company INC. The Netherlands*
12. ***Eduardo Algodoal Zabrockis, Manlio F. Coviello (2009)*** *Design and feasibility study of an ethanol distillery in Guyana.*
13. ***Eshetu S., Fikadu G., Emebet D., and Gossaye W. (2005)*** *Metahara Sugar Factory, Quality Control Laboratory Manual, Metahara Ethiopia.*
14. ***G B Deshpande (2002)*** *Over View of Continuous Alcohol Fermentation and Multipressure Distillation Technology, Praj Industries Ltd, Bavdhan, Pune - 411 021, India.*
15. ***G Naidoo, BM Schoonees, PM Schom (2005)*** *SASTA Laboratory Manual including the Official Methods, 4th Edition, July 2005. The South African Sugar Technologists' Association, South African.*
16. ***GEA Wiegand GmbH (1997)*** *Evaporation for Stillage Concentration, GEA Process Engineering Germany*
17. ***Hubert Olbrich (2006)*** *THE MOLASSES, Fermentation Technologist, Institut für Zuckerindustrie, Berlin (Germany).*
18. ***James c. Van Horne (2004)*** *Financial Management and Policy, 12th Edition, New Delhi, India*

19. ***Kadambini Gaur (2006)*** *Process Optimization for the Production of Ethanol via Fermentation. Thapar Institute of Eng'g & Technology, Patiala, India.*
20. ***Mott MacDonald (2010)*** *Molasses Based Fuel Ethanol (Bio-Fuel) Plant. Agro Industries Corporation Ltd Industrial Extension Bureau, India Gujarat.*
21. ***KBK Chemical Engineering PVT. LTD (2009)*** *Metahara Sugar Factory Ethanol Plant Project, Maharashtra, India.*
22. ***Max S. Peters, Klaus D. Timmerhaus (1991)*** *Plant Design and Economics for Chemical Engineers, 4th Edition, University of Colorado, USA*
23. ***Misheck G. Mwaba (2003)*** *Analysis of Heat Exchanger Fouling in Cane Sugar Industry. Technische Universiteit Eindhoven, the Netherlands.*
24. ***Moore I.A. (1974)*** *"Fin Tubes Foil Fouling for Scaling Services," Chem. Proc., 8 August 1974.*
25. ***Mott MacDonald (2010)*** *Molasses Based Fuel Ethanol (Bio-Fuel) Plant, Gujarat Agro Industries Corporation Ltd India*
26. ***R.J. Steindl (2010)*** *Clarification of Cane Juice for Fermentation. Sugar Research & Innovation, Queensland University of Technology, Australia.*
27. ***Robert H. Perry (1999)*** *Perry's Chemical Engineers' Handbook, 7th edition, The McGraw-Hill Companies, Inc., USA*
28. ***WHO (2006)*** *World Health Organization Guidelines for drinking-water quality [electronic resource].Volume. 1, Recommendations. – 3rd edition.*

9. Appendix

9.1. Appendix A

Laboratory Analysis Results

Expermental Design Run Sheet

(Round One)

	Run #1	**Run #2**	**Run #3**
Temperature	90°C	90°C	100°C
pH	4.5pH	4.5pH	5.0pH
Brix	60 ° Brix	50° Brix	60° Brix
CaO	1.54(%)	0.73(%)	1.88 (%)
	Run #4	**Run #5**	**Run #6**
Temperature	90°C	100°C	90°C
pH	5pH	4.0pH	4.5pH
Brix	55° Brix	50° Brix	55° Brix
CaO	1.45 (%)	1.43 (%)	0.98 (%)
	Run #7	**Run #8**	**Run #9**
Temperature	90°C	100°C	80°C
pH	4.5pH	4.0pH	5.0pH
Brix	55° Brix	60° Brix	60°Brix
CaO	1.51 (%)	1.76 (%)	1.82 (%)
	Run #10	**Run #11**	**Run #12**
Temperature	90°C	80°C	100°C
pH	4.5pH	4.5pH	5.0pH
Brix	55° Brix	55° Brix	50° Brix
CaO	1.64(%)	1.77(%)	1.65(%)
	Run #13	**Run #14**	**Run #15**
Temperature	90°C	80°C	90°C
pH	4.5pH	5.0pH	4.5pH
Brix	55° Brix	50°Brix	55° Brix
CaO	1.31(%)	1.65(%)	1.64(%)
	Run #16	**Run #17**	**Run #18**
Temperature	90°C	100°C	80°C
pH	4.5pH	4.5pH	4.0pH
Brix	55°Brix	55° Brix	60° Brix
CaO	1.51 (%)	1.44 (%)	1.76 (%)
	Run #19	**Run #20**	
Temperature	90°C	80°C	
pH	4pH	4.0pH	
Brix	55° Brix	50° Brix	
CaO	1.67 (%)	1.91 (%)	

Expermental Design Run Sheet

(Round Two)

	Run #1	**Run #2**	**Run #3**
Temperature	90°C	90°C	100°C
pH	4.5pH	4.5pH	5.0pH
Brix	60° Brix	50° Brix	60° Brix
CaO	1.35 (%)	1.22(%)	1.73 (%)

	Run #4	**Run #5**	**Run #6**
Temperature	90°C	100°C	90°C
pH	5pH	4.0pH	4.5pH
Brix	55° Brix	50° Brix	55° Brix
CaO	1.43 (%)	0.91(%)	1.57(%)

	Run #7	**Run #8**	**Run #9**
Temperature	90°C	100°C	80°C
pH	4.5pH	4.0pH	5.0pH
Brix	55° Brix	60° Brix	60°Brix
CaO	1.49 (%)	1.68 (%)	1.65 (%)

	Run #10	**Run #11**	**Run #12**
Temperature	90°C	80°C	100°C
pH	4.5pH	4.5pH	5.0pH
Brix	55° Brix	55° Brix	50° Brix
CaO	1.64 (%)	1.67(%)	0.82(%)

	Run #13	**Run #14**	**Run #15**
Temperature	90°C	80°C	90°C
pH	4.5pH	5.0pH	4.5pH
Brix	55° Brix	50°Brix	55° Brix
CaO	1.57 (%)	1.80 (%)	1.70(%)

	Run #16	**Run #17**	**Run #18**
Temperature	90°C	100°C	80°C
pH	4.5pH	4.5pH	4.0pH
Brix	55°Brix	55° Brix	60° Brix
CaO	1.77 (%)	1.71(%)	1.68 (%)

	Run #19	**Run #20**
Temperature	90°C	80°C
pH	4pH	4.0pH
Brix	55° Brix	50° Brix
CaO	1.63(%)	1.13(%)

Expermental Design Run Sheet

(Round Three)

	Run #1	**Run #2**	**Run #3**
Temperature	90°C	90°C	100°C
pH	4.5pH	4.5pH	5.0pH
Brix	100° Brix	50° Brix	60° Brix
CaO	1.64(%)	1.25(%)	1.70 (%)

	Run #4	**Run #5**	**Run #6**
Temperature	90°C	100°C	90°C
pH	5pH	4.0pH	4.5pH
Brix	55° Brix	50° Brix	55° Brix
CaO	1.44(%)	0.91(%)	1.37(%)

	Run #7	**Run #8**	**Run #9**
Temperature	90°C	100°C	80°C
pH	4.5pH	4.0pH	5.0pH
Brix	55° Brix	60° Brix	60°Brix
CaO	1.63(%)	1.79(%)	1.73 (%)

	Run #10	**Run #11**	**Run #12**
Temperature	90°C	80°C	100°C
pH	4.5pH	4.5pH	5.0pH
Brix	55° Brix	55° Brix	50° Brix
CaO	1.76(%)	1.76(%)	1.43(%)

	Run #13	**Run #14**	**Run #15**
Temperature	90°C	80°C	90°C
pH	4.5pH	5.0pH	4.5pH
Brix	55° Brix	50°Brix	55° Brix
CaO	1.76(%)	1.18(%)	1.57(%)

	Run #16	**Run #17**	**Run #18**
Temperature	90°C	100°C	80°C
pH	4.5pH	4.5pH	4.0pH
Brix	55°Brix	55° Brix	60° Brix
CaO	1.70(%)	1.63(%)	1.73 (%)

	Run #19		**Run #20**
Temperature	90°C		80°C
pH	4pH	4.0pH	
Brix	55° Brix		50° Brix
CaO	0.65(%)		1.72 (%)

9.2. Appendix B

Reagent Preparation

i. Ammonium Molybdate Solution

1. Dissolve 10gm of powdered ammonium molybdate tetra hydrate, $(NH_4)_6MoO_{24}.4H_2O$) (AR) in a hot distilled water.
2. Cool and make to the mark in a 100ml volumetric flask.
3. Filter through what man No 91 filter paper or equivalent (185ø).
4. Add 8M sodium hydroxide solution (Ca.8m) to increase pH to between 7 and 8.

ii. Buffer Solution (pH 10) for Total Hardness Determination

1. Add 142ml concentrated ammonia solution (AR) to 17.5gm ammonia chloride (NH_4Cl) (AR) 250 ml volumetric flask.
2. Dilute to mark with distilled water in a volumetric flask.

iii. Erichrome Black T Indicator

1. Add 1ml of sodium carbonate solution and 1.0gm of erichrome black T in to 100ml volumetric flask.
2. Dissolve by 30 ml distilled water and mix well.
3. Make to mark with isopropyle alcohol and mix.
4. Store in colored bottle.

v. Sodium Hydroxide (8 M)

1. Weigh 80gm sodium hydroxide (NaOH) (AR) pellets
2. Dissolve in distilled water.
3. Transfer into a 250ml volumetric flask,
4. Dilute almost to the mark.
5. Cool and make to the mark.

vi. EDTA solution (Di-sodium salt of ethylene diamine tetra acetic acid) or Merck quality:-

1. Weigh accurately 6.6473 g of E.D.T.A. into beaker.
2. Dissolve it in distilled water and make up the solution to 1000ml to obtain exactly M/56 solution 200 ml Ammonia of C.P. quality, 500 gm Lead sub acetate
3. Horn's dry lead 500 gm Potassium ferrocynide (merck quality) 100 gm Potassium Iodide C.P. quality 300 ml erichrome black T into a 100 ml volumetric flask and dissolve it in rectified sprit of absolute alcohol.
4. Make up the volume with the sane solvent and use it as indicator.

vii. EDTA (0.01M):-

1. Dissolve 1.8612gm of EDTA (AR) in distilled water in 500ml volumetric flask.
2. Dilute to the mark with distilled water

9.3. Appendix C

Physical Data

Table 9.1:-*Typical viscosity range of cane molasses*

Temperature(^{o}C)	Viscosity Range (cP)
10	20.000 – 40.000
15	10.000 – 25.000
20	5.000 – 10.000
25	3.000 – 5.000
30	2.000 – 3.000
35	1.500 – 2.500
40	1.000 – 2.000

Source: - *Schuumans & Van Ginnekent*

Temperature correction Factor

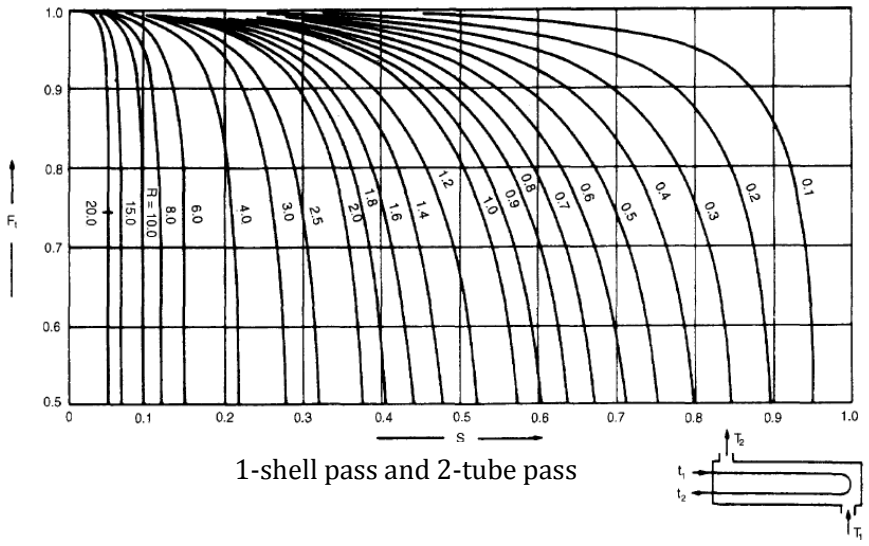


Figure 9.1: - *Temperature correction factor, split flow shell, 2 tube pass*

*(**Source: -** Coulson and Richardson's, volume 6)*

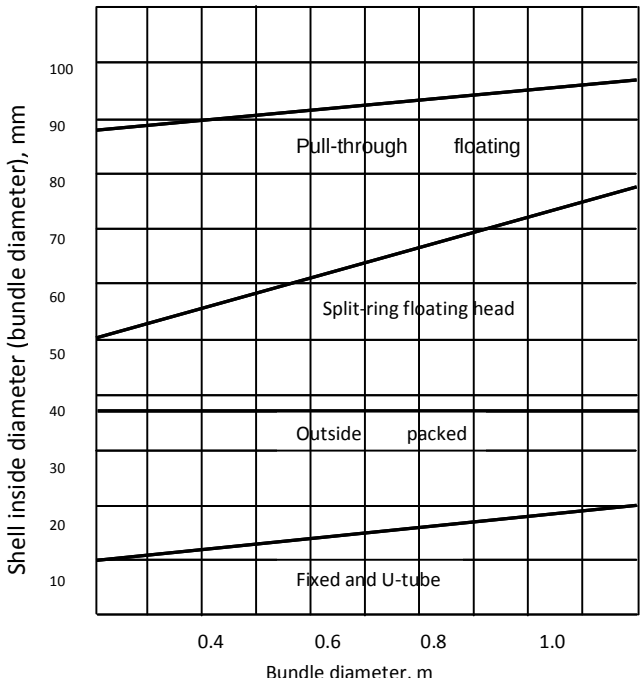


Figure 9.2: - *Shell bundle clearance (**Source: -** Coulson and Richardson's, volume 6)*

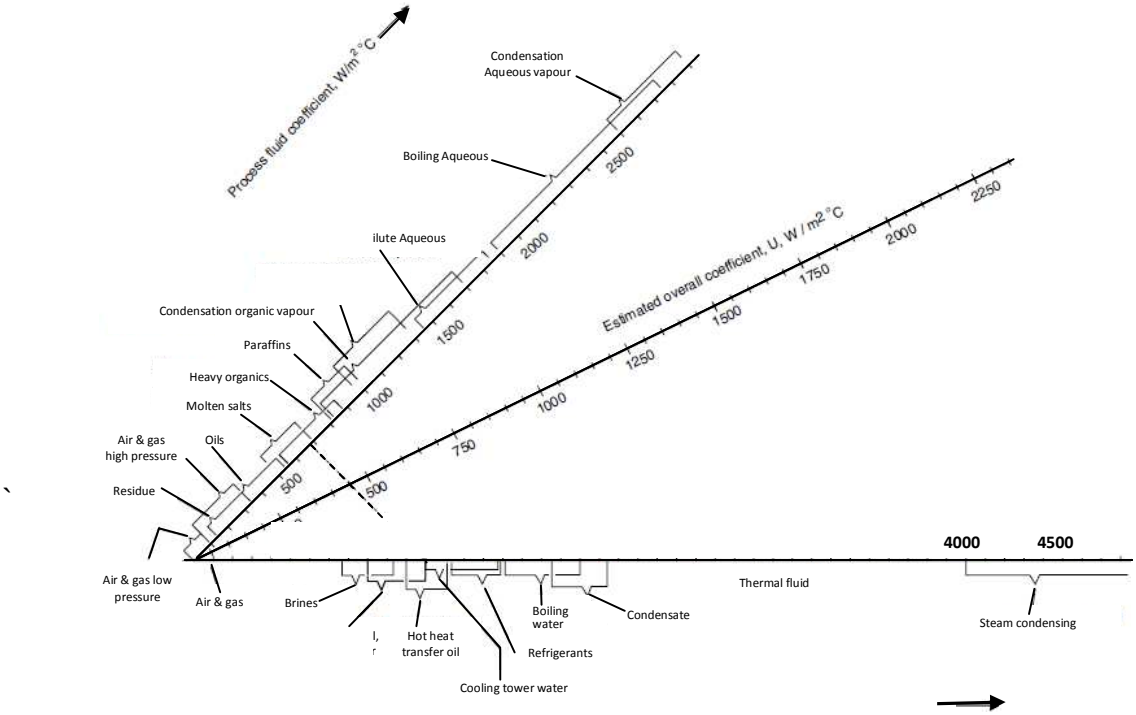


Figure 9.3: - *Overall coefficients (**Source: -** Coulson and Richardson's, volume 6)*

(Join process side to service side and read U from center scale)

Estimation of Heat Exchanger Bundle diameter

An estimate of the bundle diameter Db can be obtained from equation:

$$D_b = d_o \left(\frac{N_t}{K_1}\right)^{\frac{1}{n_1}}$$

$$N_t = K_1 \left(\frac{D_b}{d_o}\right)^{n_1}$$

Which is an empirical equation based on standard tube layouts. The constants for use in this equation, for triangular and square patterns, are given in the table below.

Table 9.2: - *Constants for use in empirical equation to estimate bundle diameter*

Triangular pitch, $p_t = 1.25d_o$					
No. of passes	1	2	4	6	8
K1	0.319	0.249	0.175	0.0743	0.0365
n1	2.142	2.207	2.285	2.499	2.675
Square pitch, pt = 1.25d_o					
No. of passes	1	2	4	6	8
K1	0.215	0.156	0.158	0.0402	0.0331
n1	2.207	2.291	2.263	2.617	2.643

*(**Source: -** Coulson and Richardson's, volume 6)*

Table9.3: - Classification of water hardness

Hardness Range (mg $CaCO_3$/ml)	**Description of Hardness**
0-50	Soft
50-100	Modestly soft
100-150	Slightly hard
150-200	Modestly hard
200-300	Hard
>300	Very hard

*(**Source: -** South African Water Quality Guidelines, Volume 1)*