Report of Cooperative Education

Fouling in a Distillation Column Used in Purification of Sugarcane Molasses Derived Ethanol

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Cooperative Title:	Fouling in a Distillation Column Used in Purification of Sugarcane Molasses Derived Ethanol
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Abstract

Clogging of the fouling on the trays leading to the failure of distillation column which used in purification of ethanol produced from fermentation of sugarcane molasses with yeast. At present, the clogging of the fouling occurs in short operating time, the fastest is 7 days, resulting in shutdown the production process to maintenance the distillation column about 1-2 days, energy consumption to start the boiler and warm the distillation column to run the process. The causes were analyzed base on study the operating data collected in the period of 2015-2017 in term of performance of process and quality of sugarcane molasses and process water. In this study, fouling is identified the compositions using Fourier Transform Infrared Spectroscopy (FTIR) and X-Ray fluorescence (XRF). The main compositions of fouling are sulfur and calcium, mainly from the sugarcane molasses. A little aluminium and silicon are mainly from the process water because the kaolin clay ($Al_2H_2O_9Si_2$) was found in the fouling while amino silicate was found in the sludge but not found in the molasses. However, the main cause of fouling formation is sedimentation of solid particle in the molasses therefore the increasing of the residence time for decanter can be able to remove more solid particle from the system, coating the surface of trays can reduce the scratches and controlling the LSI value of process water to be zero can avoid fouling from calcium carbonate from process water.

Keywords: Alcohol, Distillation, Ethanol, Fermentation, Fouling, Mash, Molasses, Sugarcane molasses, Yeast

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CHAPTER I

INTRODUCTION

1.1 Background

Thai Agro Energy Public Company Limited (TAE) manufactures and sells fuel ethanol (Ethyl alcohol) from fermentation of sugarcane molasses, cassava chips and rice for sale to oil companies as additive for gasohol production with 99.8% purity by volume. The plant operates two production lines including with the first production line using sugarcane molasses as feedstock, have production capacity 150,000 liters per day was established and obtained a license to produce and sell fuel ethanol from the Department of Industrial Works, Ministry of Industry in 2003 and the second production line using cassava chips, rice and sugarcane molasses as feedstock, have production capacity 200,000 liters per day was commenced construction in 2010.

The process of producing ethanol from sugarcane molasses by fermentation with yeast consists of molasses preparation for prepare suitable medium for the yeast growth and ethanol production by yeast, cultivation of yeast cells to growth in the exponential (Log) phase for used in the fermentation process, continuous fermentation of molasses with yeast for convert the glucose to ethanol and purification the products with two distillation columns are the first column is vacuum distillation and the second column is distillation column under pressure and increase the purity of ethanol to 99.8 %Vol with dehydration unit.

From the ethanol production process of Thai Agro Energy Public Company Limited (TAE). The company found problem of clogging of the fouling on the trays within the vacuum distillation in a short time since 2017, normally plant is shutdown to maintenance the system every four months. Moreover, at the present the plant is shutdown with a short period of time, the fastest is seven days, to clean the distillation trays due to clogging of the fouling on the trays.

1.2 Objectives

1.2.1 To study on the composition of fouling in vacuum distillation column of PC1

1.2.2 To provide an advice of fouling in vacuum distillation column of PC1 solution

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1.3 Scopes of Work

1.3.1 Study the theory of ethanol fermentation with yeast

1.3.2 Study the ethanol fermentation process of TAE

1.3.3 Study the retrospective operation data

1.3.4 Data analysis

1.3.5 Analysis the composition of fouling

1.3.6 Conclusion and discussion

1.4 Expected Output

1.4.1 Identify the composition and cause of fouling

1.4.2 Guidelines for study solution to achieve the fouling

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CHAPTER II

LITERATURE REVIEW

2.1 Ethanol

Ethanol or Ethyl alcohol (C_2H_5OH) is a flammable, colorless liquid with characteristic odor. Ethanol is prepared by chemical synthesis process and produced by fermentation of carbohydrates with yeasts and refined to a purity. Ethanol is widely used as a solvent, substrate in chemical production process, additive in gasoline to increase octane number and is the principle type of alcohol in alcoholic drinks. A mixture gasoline with at least 10% of ethanol is known as gasohol. The common gasohol variant is "E15", containing 15% ethanol and 85% gasoline. These gasohol concentrations are generally safe for automobile engines. Ethanol 1.5 volume can instead the energy of 1 volume of gasoline, so ethanol has Gasoline Gallon Equivalency (GGE) value of 1.5.

Ethanol blended fuel is widely used as a car fuel. The most cars in U.S. also run on blends of 10% ethanol and 90% gasoline

Octane number or Antiknock Rating is the value represented the ability of fuel to resist engine knocking when fuel be ignited with air of an internal combustion engine is determined by the percentage by volume of iso-octane in an iso-octane-heptane mixture.

Table 2.1. Properties of ethanol

Density	0.7893 g/cm^3 (at 20 °C)
Melting point	-114.14 ± 0.03 °C
Boiling point	78.24 ± 0.09 °C
Solubility in water	miscible

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2.2 Sugarcane Molasses [1]

Sugarcane molasses is a byproduct from the sugarcane production process. The cane is harvested when its content 12.3%-16% sucrose while glucose and fructose content at its lowest. The cane is burnt to remove leaves, trash and weed that might disturb the sugarcane production process. The harvested cane is chopped into small lengths before transport to the milling process. The sugarcane processing have two main stages including with extract as much sucrose as possible from stems by removal the juice from cane stalks and refinement to the sugar.

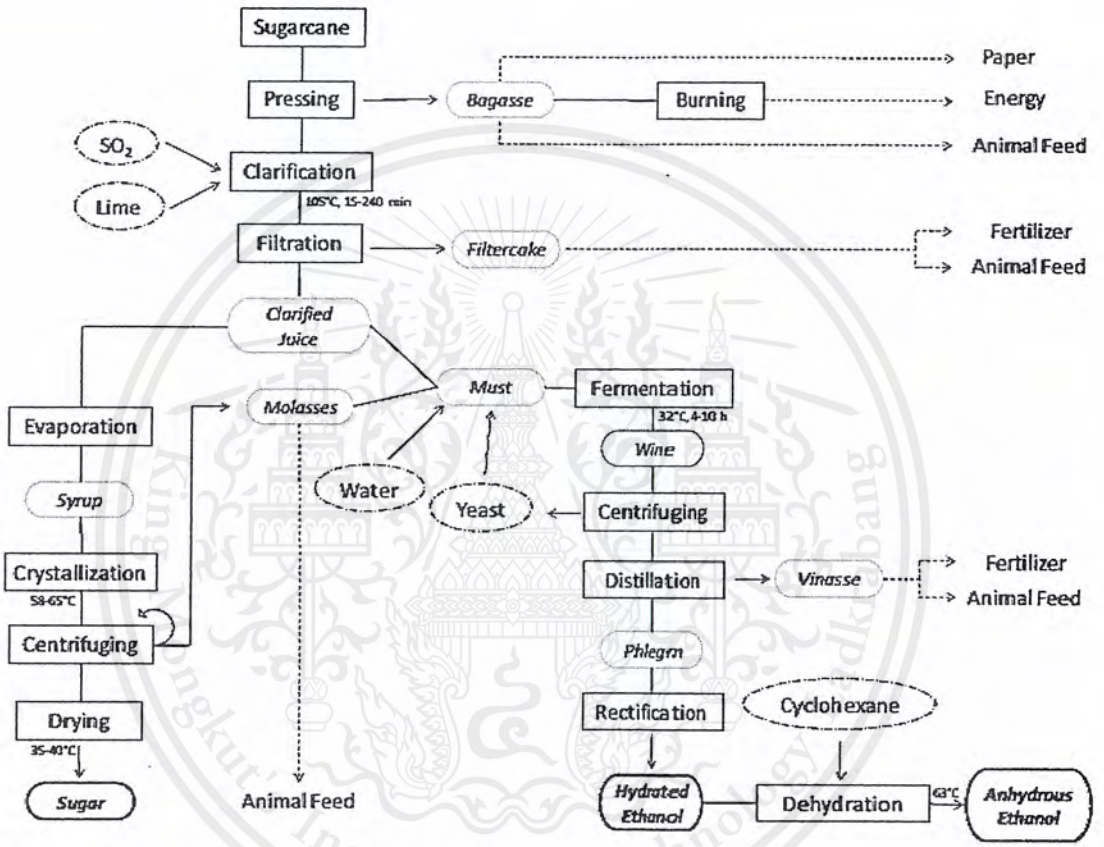

Figure 2.1. Sugarcane industrial processing [2]

Harvested sugarcane stems are chopped into small length, crushed using roller mills and using a diffuser to extract the juice. The stems had extracted is called bagasse which is used as fuel to generate power or is used for an animal feed or paper production. The contaminates are removed from the juice, clarified and adjust the pH by heat and lime. In some process, sulfur dioxide (SO_2) is added to coagulate the soluble solid and decrease the viscosity of juice. The juice is concentrated using evaporation to produce syrup, boiling until it become supersaturated and crystallization the sucrose from supersaturated syrup to be a sugar. The liquid residue from crystallization the supersaturated syrup is called molasses.

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The compositions of molasses are variable depending on the species of cane and sugar production methodologies but the quality of the molasses is defined by Thai Industrial Standard (394-2524) as following the molasses mush have brix solid more than 79 ° Brix, Total Sugar as Invert (TSAI) more than 50% and pH value between 5.0-6.0.

Table 2.2. Composition of sugarcane molasses [1]

Constitutes	%
Moisture (%)	16.5-31.1
Crude Protein (%DM)	3.0-5.8
Ash (%DM)	8.1-18.4
Sucrose (%DM)	34.8-45.8
Total Sugar (%DM)	48-65.3
Calcium (%DM)	0.8-1.15
Phosphorous (%DM)	0.07-0.74
Magnesium (%DM)	0.35-0.61
Potassium (%DM)	2.4-5.19
Sodium (%DM)	0.1-0.22
Chloride (%DM)	2.98-3.10
Sulphur (%DM)	0.47-0.8
Copper (mg/kg DM)	10.7-79.0
Iron (mg/kg DM)	247-250.0
Manganese (mg/kg DM)	56.0-82
Zinc (mg/kg DM)	11.6-30.0
Cobalt (mg/kg DM)	1.21-2.7

Table 2.3. Mineral constituents in sugarcane molasses [3]

Constitutes	%DM
K_2O	2.3-6.5
Na_2O	0.03-0.06
SO_3	1.10-3.39
CaO	0.86-1.64
MgO	0.68-1.87
SiO_2	0.07-0.14
P_2O_4	0.07-0.74
Fe_2O_3	0.04-0.07

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2.3 Yeast [4]

Yeast is unicellular fungi is classification uses the characteristics of cell, is generally found on the plant leave, flowers, salt water, soil and also found in the intestinal tracts of an animal. One of the more well-known is *Saccharomyces Cerevisiae (S. cerevisiae)* have ability to ferment the carbohydrate for convert sugar to produce ethanol by metabolizes the sugar by splitting sugars into pyruvate two molecules, eliminate carbon dioxide out of pyruvate and hydrogen ions is added to create the molecule of ethanol. *Saccharomyces Cerevisiae (S. cerevisiae)* is commonly used as baker's yeast to produce the air in bakery which is carbon dioxide (CO_2) is trapped within bubbles and results in bakery expanding.

Table 2.4. Approximate composition (g/kg dry yeast) of industrially produced bakers and brewers yeasts. [5]

Composition in the cell	Brewer yeasts
Carbohydrate	390-600
Protien	370-420
Ash	73-81
Nucleic acid (DNA and RNA)	39-43
P	14-20
K	17
Na	0.7
Fe	1.3
Mg	0.1
Co	2.3
Cu	0.0002
Mn	0.033
Zn	0.0057
Pantothenate (Coenzyme A)	0.110-0.120
Choline (membranes)	3.80-4.55
Thiamine (Vit B_1)	0.092-0.150
Riboflavin (Vit B_2)	0.035-0.045
Nicotinic acid/niacin (NAD)	0.450
Pyridoxine (Vit B_6)	0.043-0.050
Biotin (biocytin)	0.001
p-aminobenzoate (folic)	0.005
Inositol (phospholipids)	3.9-5.0
Folic acid (1-C transfer)	0.010

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2.3.1 The Life Cycle of Yeast

Yeast procreate by budding with different rates. The time which yeast population is taken to double is called the "Generation time". When the yeast are placed into a suitable growth environment will have characteristic pattern to growth or increase the population with 4 stages showing on the figure 2.2.

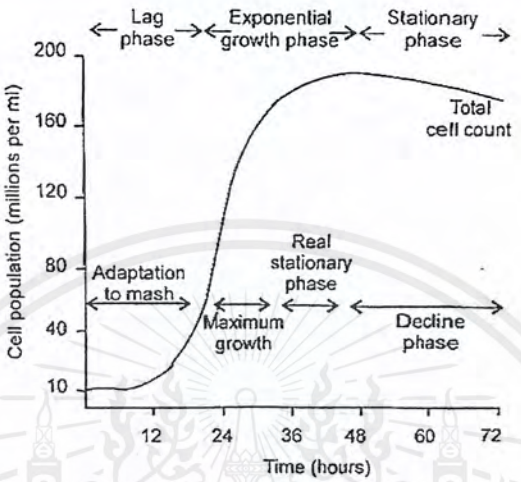

Figure 2.2. Typical yeast growth curve in distillery mash. [5]

1) Lag Phase After the yeast is placed into the fresh medium for inoculation, yeast attempt to adapt to the environment which is at this stage the yeast no apparent cell budding occurring. The number of populations remains as same as the initial but might grow in mass or volume, synthesizing enzymes and protein increased in metabolic activity. The length of this phase is dependent on verity factor, yeast species and environment conditions including with size of inoculum, time to recover from physical damage or shock in the transfer, time to synthesis enzymes or budding factor, time to synthesis new enzymes to metabolize the nutrients as sugar present in the medium.

2) Exponential (Log) Phase The yeast comes out of lag phase reach to exponential phase to start consume the sugar in the medium, glucose is consumed first, fructose and sucrose respectively. The number population of cells yeast increase rapidly with budding cells at the constant rate depending on consumption of medium and incubate condition, alcohol and flavor compounds will be produced. Carbon dioxide (CO_2) is produced which is trapped in bubble on the surface layer of foam on the alcohol. The rate of exponential of population number is generation time or doubling time.

3) Stationery Phase In this stage, the growth rate of yeast is decreased and reach to the stationary phase with limited by exhaustion of nutrients and accumulation of inhibitory metabolites. The most of flavor compound have been produced such as fusel oil, ester and sulfur compound. In this stage, there

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is not increase the population number because the yeast cell is not budding or the rate of budding cells is equal to the rate of dying cells.

4) Death Phase After reach to the stationary phase, a death phase follows, the yeast cells population is declined with exponentially due to there are not enough nutrients in the medium and percentage of alcohol is to risen.

2.3.2 Factors affecting yeast growth [5]

The alcohol fermentation need sources of nutrients in the media for yeast growth such as nitrogen, vitamins, minerals, oxygen (necessary for the initial stages of fermentation) and have suitable condition such as temperature, osmotic pressure, ethanol toxicity, metal ion, wild yeast and competitive bacteria to withstand stress cause. *Saccharomyces cerevisiae (S. cerevisiae)* growth well in temperature range between 35-43°C, moist, sugary (yeast cannot grow in very strong sugar – such as honey), pH between 4.5-6.5 and aerobic environments.

Yeasts are not necessary anaerobes, they are growing in the presence or absence of oxygen and sugar is used for energy production and to make the new yeast cells but if oxygen is sufficient, little ethanol is made by growing yeast due to the sugar s are utilized for energy production and to budding the new cells. When oxygen is reduced, the ethanol is made.

The fresh yeast is more than 90%, the water is needed for growth. Osmotic concentration increase in strong sugar media, the water potential of media reaches to lower than water potential of yeast cell, so water tends to move out of the yeast cell more than in.

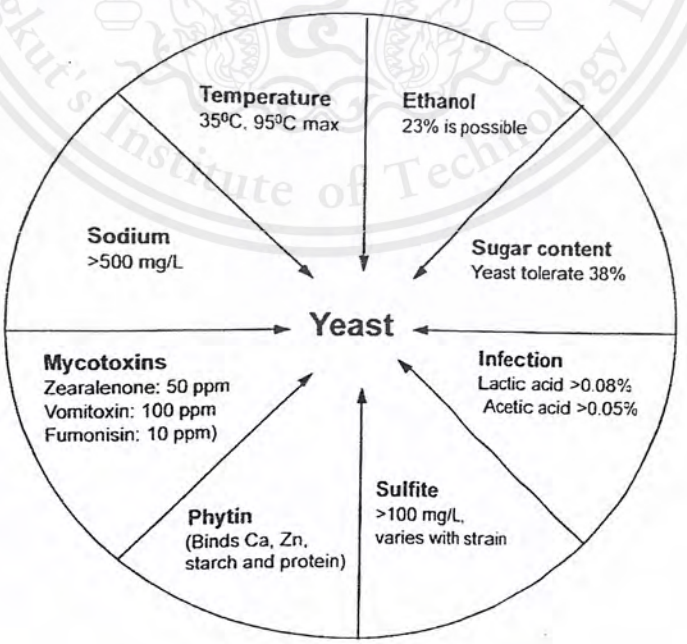

Figure 2.3. Stress factors affecting yeast activity [5]

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2.4 Ethanol Fermentation Production [6]

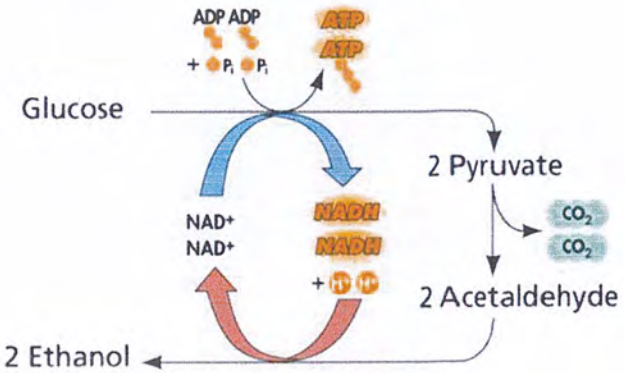

Figure 2.4. Alcoholic fermentation

Saccharomyces cerevisiae remains the most primary microorganism use for the ethanol production by fermentation. Fermentation is anaerobic pathway for breaking down six carbon atom of glucose with glycolysis as same as cellular respiration. After glucose has entered the yeast cell, enzyme under physiological condition catalyze the reaction changing the glucose molecules to two molecules of pyruvate and release two molecules of ATP and four molecules of hydrogen. The pyruvate is removed the carboxyl group by pyruvate decarboxylase enzyme to acetaldehyde and release two molecule of carbon dioxide and then NADH passes its electron to acetaldehyde to regenerate NAD+ and forming ethanol.

$$Glucose + 2ADP + 2P_i + 2NAD^+ \rightarrow 2\,Pyruvate + 2ATP + 2NADH + 2H^+$$

$$2\,Pyruvate + 2ADH^+ + 2H^+ \rightarrow 2\,Ethanol + 2CO_2 + 2NAD$$

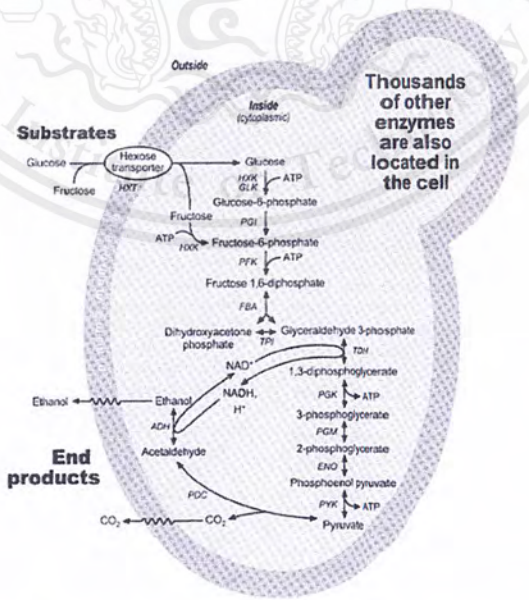

Figure 2.5. Glycolysis performed by yeasts in sugar-containing mashes [7]

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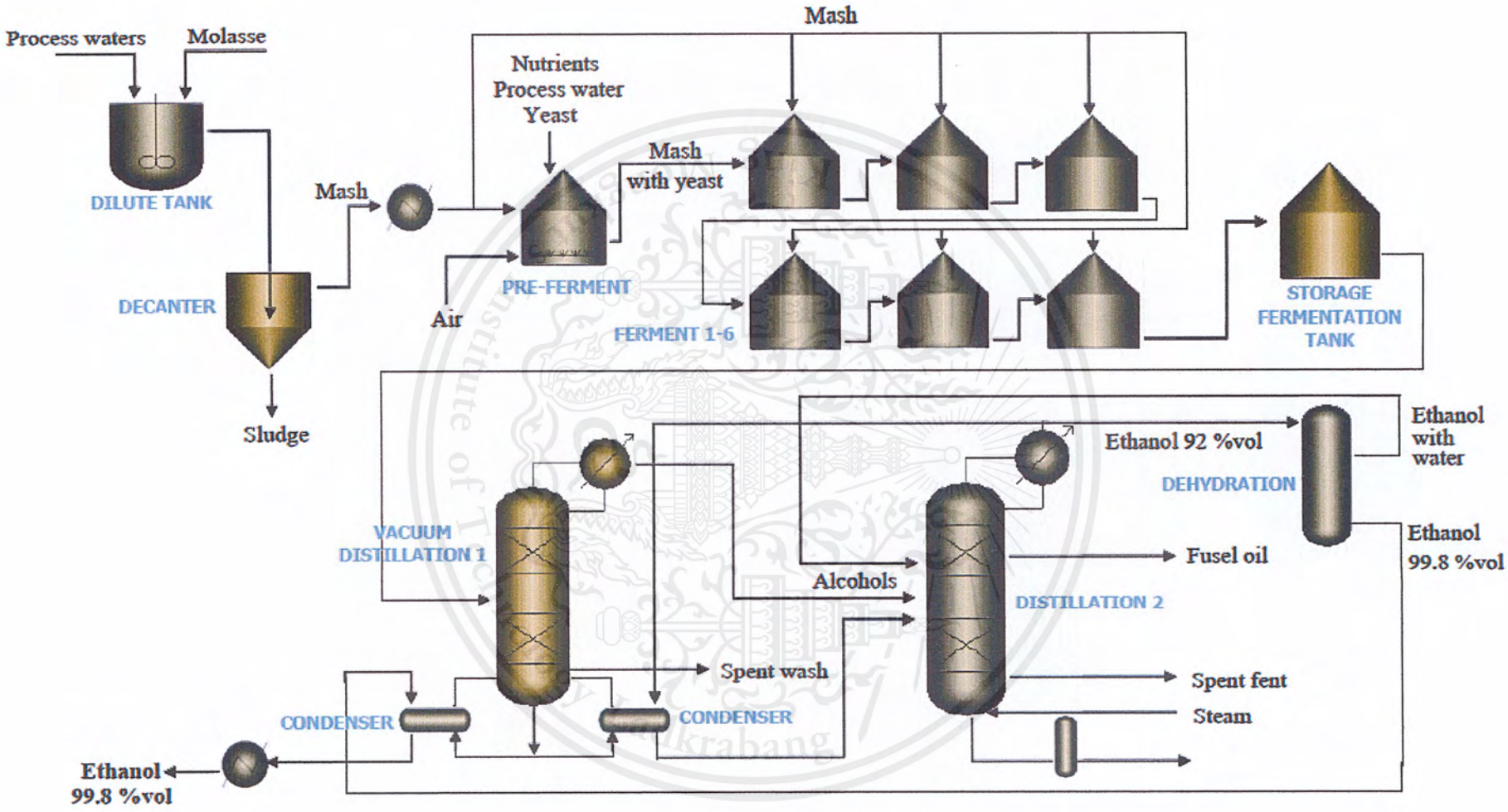

Figure 2.6. TAE ethanol production process

2.4.1 TAE ethanol production process

1) Mash Preparation The production process of ethanol fermentation of molasses with *Saccharomyces cerevisiae* yeast beginning with preparing the mash, is the diluted molasses with process water to the °Brix required value, to prepare the molasses to be qualified for the work of the yeast. Molasses is mixed with 80°C process water to be mash 30-35 °Brix and 22-25% Total Sugar as Invert in mash then the mash into the decanter, which is used to separate solid particles in mash. The solid particle to the bottom of the decanter by gravity is called sludge.

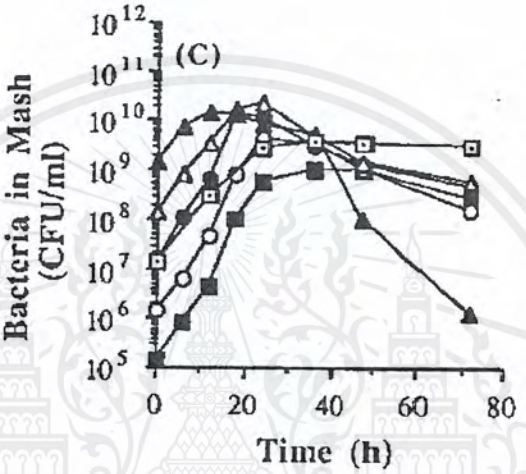

Figure 2.7. Growth of *Lactobacillus* inoculated at various levels into mash fermentation
at 30°C. The mash contained yeast cells at approximately 106 CFU/ml. [7]

Normally, sugarcane molasses are contaminated with bacteria and the growth rate of bacteria increase quickly. Therefore, the residence time in each stage of the ethanol fermentation by yeast is very important, if used for a long time to settle the solid particle, the bacteria will occur a lot in the process. Bacteria that occur during the fermentation of molasses which is significant to reduce %yield of ethanol due to the bacteria will consume sugar and leave lactic acid and acetic acid are toxic to the yeast at 1-4 %w/v and 0.05-0.09 %w/v respectively.

2) Pre-fermentation Mash from decanter is divided to two parts. The first part is diluted with process water again to prepare for yeast incubation because concentrate sugar in mash affect to inhibition the growth of yeast. Therefore in pre-fermentation stage, the mash is necessary to control in rang 16-30°Brix and 11-22% of Total Sugar as Invert to prevent osmosis pressure removes water molecules out of the yeast cells. Nutrients A and B, air, anti-

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bacterial and anti-foam are added to the pre-fermentation tank and incubate at 30-40°C for yeast growth to the logarithmic phase. The second part of mash will be going to the food for ethanol production with yeast in fermentation stage.

Table 2.5. Reactants of TAE ethanol production process

Constitutes	Composition
Molasses	Sucrose, Protein, Moisture, Ash
Yeast	Protein, Lipid, Ash, Mannan, Glycogen
Nutrient A	C, O, N, H
Nutrient B	N, H, P, O
Anti-foam	-
Anti-microbial	C, H, P, O
Process water	-
CIP	NaOH

3) Fermentation Mash with yeast from pre-fermentation and anti-bacterial are fed to the first continuous fermentation tanks, is quality controlled in weak acid, 6.5-9.5 °Brix and alcohol 6.5 %Vol. The second part mash is added into each continuous fermentation tanks which are controlled at 30-40 °C and net residence time is 36 hours. After completely fermentation, the quality of products mush are weak acid, 35 °Brix, 9.0 %Vol of alcohol and low %TSAI. The overall products are collected in fermentation storage tank before going to distillation column.

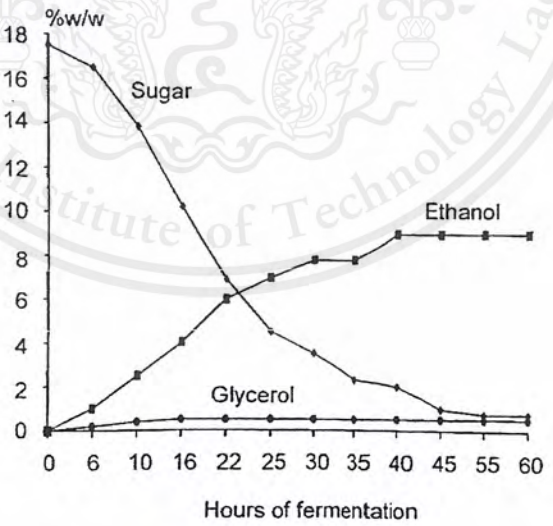

Figure 2.8. Progress of a typical fermentation [5]

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At the fermentation step, ethanol and carbon dioxide are produced and minor end products of metabolism lower ethanol yields are produced too. The glycerol and organic acids, pyruvic, lactic acid and acetic acid are two secondary end products are produced during alcoholic fermentation. The concentration over 0.8% of lactic acid and over 0.5% of acetic acid will affect the yeast growth, high level of bacteria can be reduce 3.8-7.6% of ethanol, 1% loss in a small plant producing about $12x10^6$ L of ethanol/year. The higher pH value of mash will increase osmotic stress and lower flux of pyruvate or addition of sulfite into fermentation can simulate the conversion of dihydroxyacetone phosphate to the glycerol. Higher alcohol (fusel oil) is the one of minor end products are n-propanol, amyl alcohol, isoamyl alcohol, isobutanol and phenethyl alcohol. However, they is not effect to inhibition the yeast or reduced the yield of ethanol.

Table 2.6. The influence of pH on production of glycerol and organic acids* [5]

Product[a]	pH 3.0	pH 4.0	pH 5.0	pH 6.0	pH 7.0
Ethanol	171	177	173	173	150
Carbon dioxide	181	190	188	188	161
Glycerol	6.2	6.6	7.8	7.8	22.2
Acetic acid	0.5	0.7	0.8	4.0	8.7
Lactic acid	0.8	0.4	0.5	1.6	1.9

*adapted from Neish and Blackwood, 1951 by permission.
[a]millimoled of product per millimole glucose fermented.

4) Distillation The products from fermentation process was sent to the distillation process to separate unwanted substances from ethanol. The distillation has three unit including with vacuum distillation, pressure distillation and dehydration unit. Products from the fermentation storage tank of the fermentation process is fed into a vacuum distillation which has been heated by the distillate from the top of pressure distillation and product from dehydration unit. The normal boiling point of a compound is an indicator of volatility of compound, the compound have low boiling will evaporate to the vapor come out at the top of vacuum distillation column and condensed to 45-55 %Vol liquid ethanol with condenser. The compound have high boiling point will come out at the bottom of vacuum distillation column which is a waste water is called spent wash. 45-55 %Vol liquid ethanol is fed to the pressure distillation and gain the product at the top of pressure distillation column is 92 %Vol ethanol. The bottom products of the pressure distillation column is spent fent which is recycled to used for dilute molasses at mash preparation unit and Pre-fermentation. 92 %Vol of ethanol was sent to the dehydration unit to remove the water, the top product is 99.8 %Vol of ethanol. Vacuum and pressure distillation column are fixed valve tray type.

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2.5 Distillation [8]

Distillation is separation process which separation components in a mixture by difference in relative volatility or boiling point in chemical or petrochemical industries. The distillation mostly used to be separation method for liquid mixtures. However, it sensitive in energy and operation cost is high about 50% of plant's operating energy cost. The alternatives to separation process for liquid mixture without the distillation are fraction distillation are membrane separation, adsorption, and solvent extraction but is not separation components by difference in relative volatility or boiling point as the distillation. The high boiling point of liquid mixture or mixture can decomposition when operate at high temperature, vacuum distillation is used. The vacuum distillation operate at low pressure because the vapor pressure of the liquid while boiling will be equal to or greater than the external pressure, which is the pressure of the atmosphere at that moment. The pressure affecting the boiling point of the liquid. Therefore, components that can evaporate and boil at low temperature. The distillation is typically two different types.

2.5.1 Tray distillation column

Within the column have the trays that has been make a hole on the tray for vapor upward through contact the liquid on the trays. The liquid is holed on the tray by weir. Liquid enter from the down-comer by flood the weir of the tray above. The vapor overcome this liquid to move up the column and vapor and liquid are contacted on the tray becomes bubble or froth which mass transfer take place. Tray column performs well in high loading of liquid and vapor, high corrosion resistance and higher pressure drop.

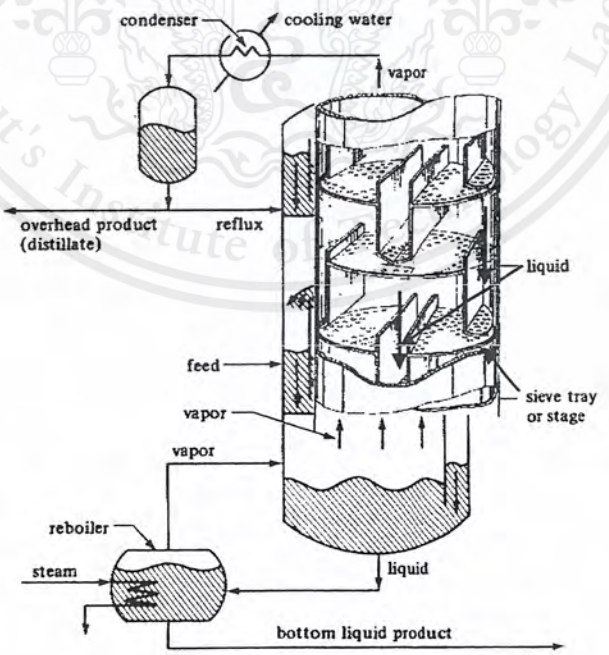

Figure 2.9. Distillation column [9]

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Bubble area follow as: [10]

1) Bubble regime, the mixture of vapor and liquid were mild. The vapor will slowly float through the liquid up through the hole on the tray. The conditions of this liquid rather station therefore mixing characteristics like this is not needed in practice.

2) Foam regime, a contact area between the vapor and liquid high due to the liquid like beer. Causing mass transfer even more but the potential for flooding.

3) Froth regime, the mixture of liquid and vapor thoroughly because the high flow rate of vapor result to a liquid layer on the tray was thrown violently. In a typical refinery mass transfer in liquid determines mass transfer limit, and that this condition is very high. The characteristics like this is need in practice.

4) Spray regime, the flow rate of steam is very high and is continuing to make a mixed thoroughly but this state will look into the liquid droplets. Mix poorly as a result, the state is effectively lowered due to the mass transfer is not good.

2.5.1.1 Tray types

1) Sieve tray is most popular because the structure is easy to building and cheap. It is a circle across the region is perorated plate with holes for vapor pass through above the tray, the vapor velocity prevent the liquid weeping or flowing down through the hole, flowing down only at the down comer. The design of number and hold size are depending on vapor flow.

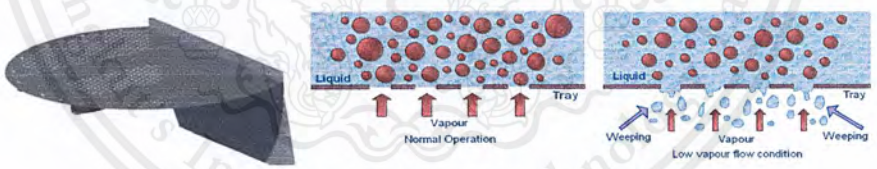

Figure 2.10. Sieve Tray [11]

2) Valve tray is a hole caps (flap) that can move up and down to cover the hole. The movement of the flap depends on the flow rate of vapor. If high flow rates of vapor, flap will move up and then the vapor flow through a gap to contact the liquid. If a low flow rate, flap moves down to prevent liquid flowing down pass the hole to the tray below.

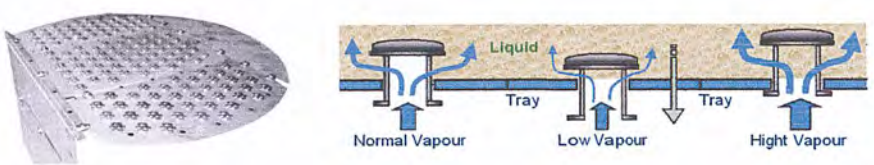

Figure 2.11. Valve Tray [11]

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3) Bubble cap tray is the best efficiency and expensive. The appearance is a tray with small tube popped up is covered with cap. Usually equipped with slots to allow the vapor pass through contact with the liquid forming bubble on the tray. Bubble cap tray can operate at low liquid and vapor rate.

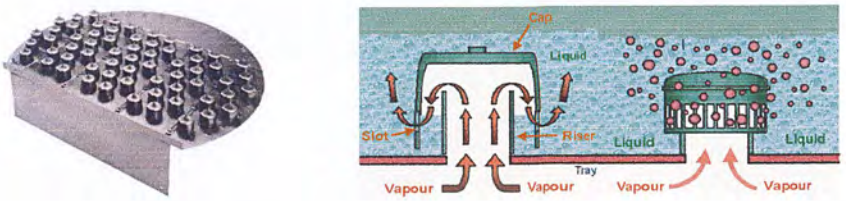

Figure 2.12. Bubble Cap Tray [11]

4) Dual flow tray is a sieve tray but without downcomer. The design to reduce the stagnate zone and promote back missing. The liquid and vapor contact at the hole, the vapor move up to the tray above and the liquid move down to the next tray in the same hole.

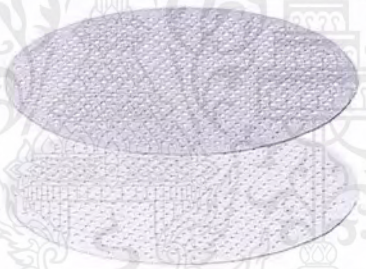

Figure 2.13. Dual Flow Tray [12]

5) Baffle tray is a tray that was used for a specific task, such as refining the need to reduce the pressure inside the distillation column or used for distillation with a high chance of fouling occurring due to this tray have lowest stagnate zone. Baffle tray has 3 types.

5.1) Shed decks trays is an iron beam at an angle across the column without stagnate zones and residence time is low. This tray has the chance of fouling is almost zero but there has so much open area to 50% and make very low efficiency.

5.2) Disk and donuts trays is steel with a slightly sloped. The liquid will flow from the inner circle ring and roll out to the outer circle ring. The fouling of this is low along with efficiency.

5.3) Side to side trays is steel beams were installed slope at the wall of the column and the follow the liquid to splash from side to side. The fouling potential is low along with efficiency.

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(A) (B) (C)

Figure 2.14. (A) Shed Decks Trays, (B) Disk and Donut Trays, (C) Side to Side Trays [13]

Table 2.7. Comparison between common conventional trays [14]

Factors	Sieve	Valve	Bubble-Cap	Dual-Flow
Capacity	High	High	Moderate high	Very high
Efficiency	High	High	Moderate high	Least
Turndown ratio	~50%	~25-30%	10%	Least
Entrainment	Moderate	Moderate	High	Low-moderate
Pressure Drop	Moderate	Moderate	High	Low-moderate
Cost	Low	~1.2 of sieve	~2.3 of sieve	Least
Maintenance	Low	Low-moderate	Relative high	Low
Fouling Tendency	Low	Low-moderate	High	Extremely low
Effects of Corrosion	Low	Low-moderate	High	Very low
Main Application	Often used when turndown is not critical	Where high turndown is required	Extremely low liquid flow & where leakage must be minimized	Capacity revamps, highly fouling and corrosion services

Turndown ration refers to the width of operation range of a distillation column on ratio of maximum capacity to minimum capacity.

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2.5.2 Packed distillation column [8]

Packed column is a distillation column are filled or packed with material bed are allow the vapor flow pass through to contact the liquid, performs well at low pressure. Packed column suitable for low liquid and vapor loading, at high flow parameters or heavy fouling and corrosion the capacity and efficiency can reduce.

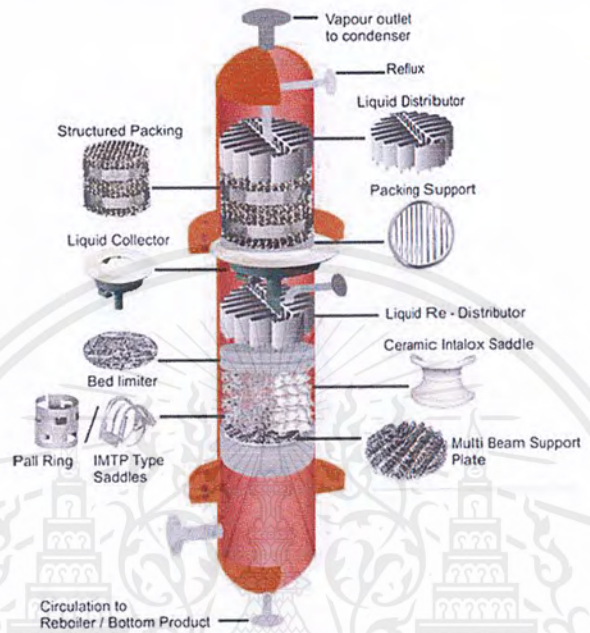

Figure 2.15. Packed distillation column [15]

1) Random packed column is specific geometrical shapes of packing bed are packed randomly in the column.

2) Structures packed column is corrugated or crimped sheets are stacked in the column.

3) Grid packed column is open-lattice structure are arranged packing in the column, have high open area resulting in high capacity, high tolerance to fouling and low pressure drop.

(a) (b) (c)

Figure 2.16. Types of packed distillation column (a) random packed column, (b) grid packed column and (c) structure packed column [8]

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Table 2.8. The rules of thumb for selecting trays or packing distillation column [8]

Tray distillation column	Packed distillation column
1. Compounds contain solids or foulants	1. Compounds are sensitive in temperature
2. There are many internal transitions	2. Pressure drop is important
3. Loads of liquid are high	3. Loads of liquid are low
4. Lack of experience in the service	4. The tower diameter are small
5. vessel wall needs periodic inspection	5. Highly corrosive service
6. There are multiple liquid phases	6. The system is foaming
	7. The ration of tower diameter to random packing is greater than 10

2.6 Fouling [16]

Fouling is defined as the accumulation and formation of the unwanted materials compound on the surfaces of equipment result to retrograde the capacity of the surface to transfer heat under difference if temperature conditions and plugging the equipment to obstruct the fluid flow. Fouling has been recognized as a problem in design and operation which affects to the operation of the equipment in two categories: Firstly, the fouling will increase the resistance transfer of heat and reduces the effectiveness of heat exchanger. Secondly, the pressure drop across the equipment is increased by reason of the cross sectional area of the equipment is reduced by fouling deposition occur.

2.6.1 Types of fouling

The fouling has been recognized base on the different physical and chemical processes involved to fouling main type as:

1) Particulate fouling is the deposition of suspended solid particles in the fluid is settled due to gravity and accumulate on the surface of equipment. The particulate fouling involves deposition of material dispersed in the fluids, clay, mineral particles in the natural water, deposition of salt in desalination, additive in feedstock. The particulate fouling is influenced by temperature of the equipment surface, concentration of suspended solid particles in fluid, and fluid flow velocity, if the fluid velocity is low, the chance that solid particles will precipitate high rate.

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2) Crystallization or precipitation fouling is the crystallization of dissolve substance in the fluid. Crystallization fouling generally occurs with aqueous solutions, is common when untreated water. The mechanism controlling of crystallization fouling is nucleation.

3) Chemical reaction fouling is the deposition cause of chemical reactions between reactants contained in the fluid, is not a reactant form on the surface equipment or participant on the surface. This fouling can occur in a wide range of temperature and may react as a corrosion to the equipment surface.

4) Corrosion fouling is chemical in the fluid or electrochemical reaction between the equipment surfaces and fluid.

5) Biological fouling or biofouling is generally problems in water stream. The microorganism such as yeast, bacteria, molds and fungi accumulate on the equipment surface and generate the slime is called biofilm to cover itself to create suitable condition for growth and prevent destroyed, the slime is sticky film so, it difficult to remove.

6) Solidification or freezing fouling is the freezing of higher melting of substance onto the surface. This fouling is affected by mass flow rate of fluid, temperature, concentration of the solid precursor in the fluid feed and crystallization conditions.

2.6.2 Fouling process

The fouling process is considered into two stage are fouling deposition and fouling removal as:

1) Formation of foulant in bulk fluid.

2) Transport of foulant to the deposit site on the equipment surface.

3) Formation fouling at the deposit site.

4) Removal of fouling out of the deposit site.

5) Transport of fouling to the fluid.

The overall of fouling process is indicated by fouling resistance (R_f), is measured by test or evaluated from operating equipment. The represent between fouling occur and time is showed in fouling curve.

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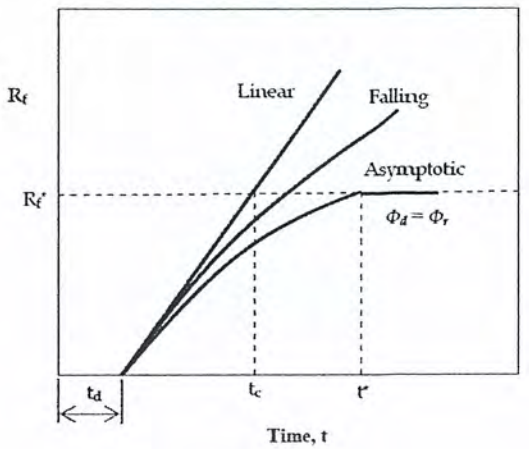

Figure 2.17. Fouling curve [16]

The delay time (t_d) indicates an initial period of time where no fouling occurs on the surface, the delay time is not predictable but the trend of increase or decrease the delay time period depending on the surface roughness. The new surface have longer delay time period, if the surface are used or cleaned, the delay time period is shorted due to the surface is disturbed to scratch.

Linear fouling curve is constant of deposition rate and removal rate or different between deposition rate equal to removal rate of the fouling

Falling rate fouling curve is decreasing deposition rate and constant or increasing removal rate

Asymptotic fouling curve is constant deposition rate and removal rate directly proportion to the deposit thickness until that rates are the same at the asymptote.

2.6.3 Parameters affecting fouling

1) Fluid flow velocity has directly strong effect on the fouling rate both deposition and removal rate. The high fluid flow velocity result to fluid eddies and shear stress at the equipment surface and then the fouling rate is decreased because the suspended solid particle in fluid will deposit in low fluid flow velocity. If the process is operated at high fluid flow velocity will reduce the sedimentation and accumulation form on the surface of deposit.

2) Surface roughness is effect to form of the nucleation site which is the first step of forming the fouling. The roughness surface is good chance for deposit attach and sticking on the surface. The smooth surface can prevent fouling formation.

3) Fluid properties such as the viscosity and density effect to the sheer stress, is key element in removal process.

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4) Impurity and suspended solid can initiate or substantially increase fouling. The suspended solid can cause to particulate fouling by sedimentation or settling of particle under gravity or pressure in the equipment. The high velocity can prevent effect from suspended solid.

5) Design considerations of equipment as tray distillation column if have stagnate zone or sharp transitions, it good position for fouling forming easily.

2.7 Langelier Saturation Index (LSI) [17]

Fouling cause from water such as in the kettle is caused by minerals and salts are contained in the water from natural water source are separated from water and deposition on the surface. The minerals can be a fouling such as calcium carbonate, calcium sulfate, calcium phosphate, silica, hydroxide and sulfite of iron and magnesium. Solubility of salt in water can determined by multiplication of solubility as Ca^{2+} and SO_4^{2-}. When calcium sulfate ($CaSO_4$) have multiplication of solubility more than solubility product constant (k_{sp}) that is supersaturated solution so, $CaSO_4$ will beginning to crystallize result to fouling forming.

The Langelier Saturation Index (LSI) is a calculation method for measure of a solution's ability to deposit or dissolve of calcium carbonate contain in the water, is used as indicator of the corrosivity and fouling formation of water. The LSI is related to the deposition of calcium carbonate to fouling formation.

The Langelier Saturated Index is defined as different between pH is an actual pH of water is determined by measurement and pH_s is pH calculation

$$LSI = pH_{actual} - pH_s$$

pH = Measurement
pH_s = A + B – C - D
A = Water Temperature Factor
B = Total Dissolved Solid Constant Factor
D = Calcium Hardness Factor

Table 2.9. Prediction of fouling/corrosion with the Langelier Saturation Index. [17]

LSI	Corrosive Characteristics	Corrosive Characteristics
+2.0	Nonaggressive	Highly aggressive
+1.0	Nonaggressive	Moderately aggressive
0	Nonaggressive	Nonaggressive
-1.0	Moderately aggressive	Nonaggressive
-2.0	Highly aggressive	Nonaggressive

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2.8 Fourier Transform Infrared Spectroscopy (FTIR) [18]

FTIR is a method used to obtain an infrared spectrum of absorption or transmitted of a solid, liquid and gas to determine chemical structure. When IR radiation is passed through a material, some radiation is absorbed by the sample and some passes through (is transmitted). The resulting signal is a spectrum representing a molecular 'fingerprint' of the sample, different molecules structure produce different spectral fingerprints.

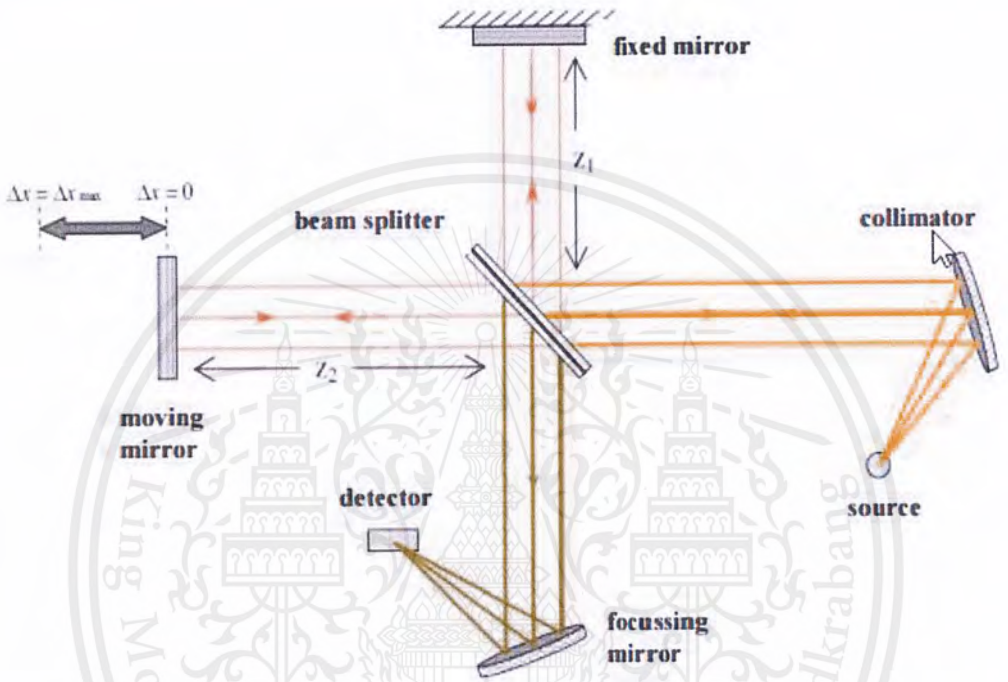

Figure 2.18. FTIR spectroscopy [19]

2.9 X-Ray fluorescence (XRF) [20]

X-Ray fluorescence is analytical method to determine the composition of materials both solid, liquid and gas. The method is accurate, fast and require minimum of sample preparation. XRF spectrometer system can be divided into two group are energy dispersive system (EDXRF) and wavelength dispersive systems (WDXRF). The element can be analyzed by EDXRF are elemental range from sodium to uranium (Na to U) and the element can be analyzed by WDXRF are elemental rang from beryllium to uranium (Be to U). The concentration range goes from ppm to 100%.

X-Rays produced by a source expose the sample, the element in the sample will emit fluorescent X-ray radiation with discrete energies which are characteristic of each element. A different energy of the radiation emitted by the sample represent in the different of colors determine the element are present in the sample. The intensities of energies determine how much of each element in the sample. The result show in a graph in term of energy, the position of peak determine the element in sample and the height of peaks determine the concentrations.

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Chapter III

Experimental

From study on the theory of ethanol production and cause analysis of the fouling layer on the tray within the vacuum distillation column have steps to perform the research as follows:

3.1 Theory study

Study the theory of ethanol production process of sugarcane molasses fermentation with yeast, fouling formation, reactants used in the production process, machinery equipment and the theory and research related to the characteristic of fouling.

3.2 Data analysis

3.2.1 Performance of process with different number of decanter.

3.2.2 Molasses quality (%TSAI) effect to the occurrence of the fouling in vacuum distillation.

3.2.3 Calculation of the Langelier Saturation Index (LSI) to prediction of fouling from process water.

1) Measuring the pH of process water with Digital pH-ORP meter (Cyberscan pH510)
2) Measuring the temperature of process water with thermometer
3) Measuring the total dissolved solid of process water with Mettle Toledo conductivity meter (EevenEsay)
4) Measuring the calcium hardness of process water with HANNA hardness test kit (HI3812)
5) Measuring the alkalinity of process water

3.3 Composition of sample analysis

3.3.1 Functional group analysis of molasses

1) Evaporate the water out of the molasses at 105 °C
2) Analyze the functional group of molasses with Fourier Transform Infrared Spectroscopy (FTIR)

3.3.2 Functional group analysis of fouling

1) Analyze the functional group of fouling with Fourier Transform Infrared Spectroscopy (FTIR)

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3.3.4 Composition analysis of sludge

1) Burning the fouling at 925 °C to determine percentage of organic and inorganic composition of sludge

2) Analyze the composition of sludge with X–Ray Fluorescence spectrometer (SRS3400)

3.3.5 Composition analysis of fouling

1) Burning the fouling at 925 °C to determine percentage of organic and inorganic composition of fouling

2) Analyze the composition of fouling with X–Ray Fluorescence spectrometer (SRS3400)

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Chapter IV

Results and Discussion

From the fouling problem on the trays within the vacuum distillation column of the first production lines (PC1). The fouling looks solid black, looks like frozen chocolate, coating the surface of distillation tray at the feed entered stage and 3-4 nearby trays.

Figure 4.1. Fouling on the trays within the vacuum distillation column of first production lines (PC1)

Evaporation the sludge from decanter to eliminate water off, result to the sludge have characteristic similar to the fouling.

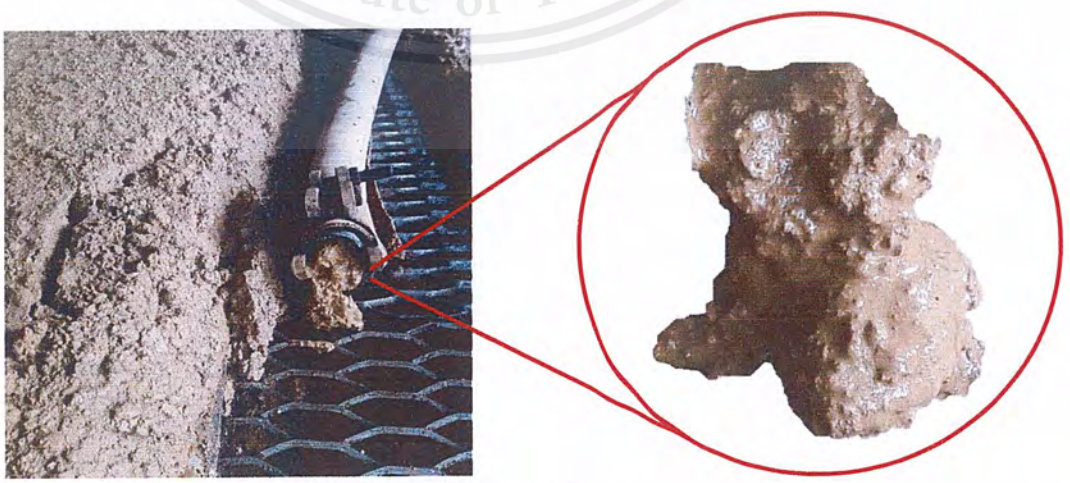

Figure 4.2. Sludge

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Figure 4.3. Fouling

Figure 4.4. Evaporate sludge

The fouling occur is may not a chemical reaction fouling or it is, only a little amount because the main reactants is used in a lot quality are only molasses which the composition is mostly sugar and moisture and process water, while yeast, anti-microbial, anti-foam, nutrient A, nutrient B and air are used as a very small quantity when compared with molasses and process water

Table 4.1. Feedstocks are used for production line PC1 per day

Feedstock	Mass fraction
Sugarcane molasses	0.39
Process water	0.59
Yeast	2.66×10^{-5}
Anti-microbial	3.33×10^{-6}
Nutrient A	2.99×10^{-4}
Nutrient B	9.99×10^{-5}

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4.1 Performance of process with different number of decanter

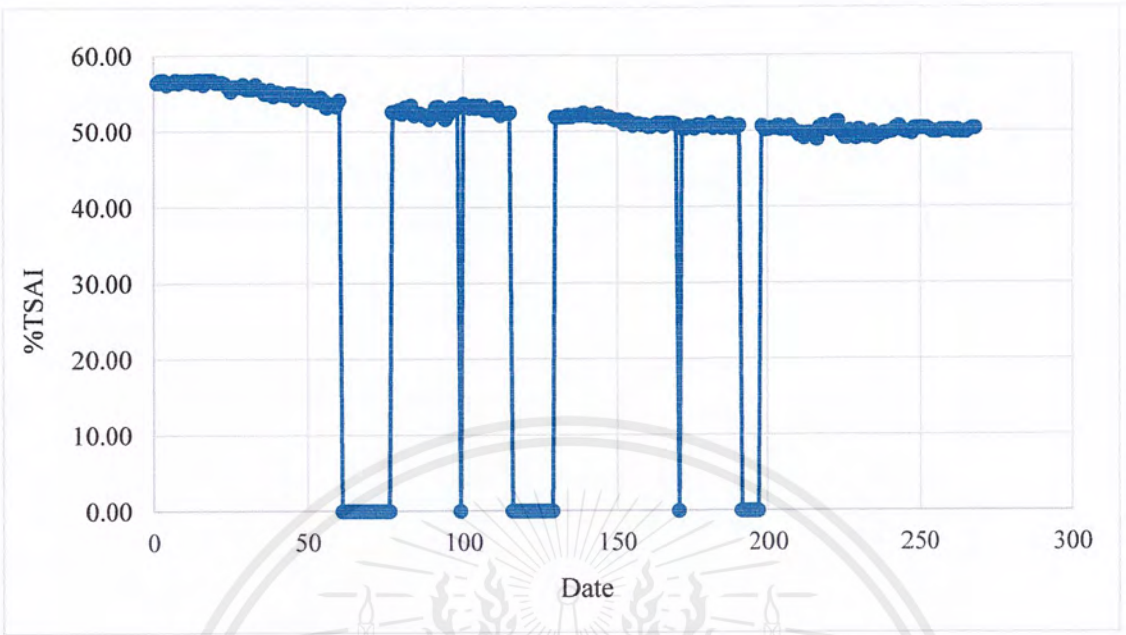

Figure 4.5. Graph show relationship between %TSAI of molasses are used in the ethanol production process of TAE PC1, run with 2 decanters, in 2015 (%TSAI = 0 is not operate the process, cleaning the vacuum distillation trays)

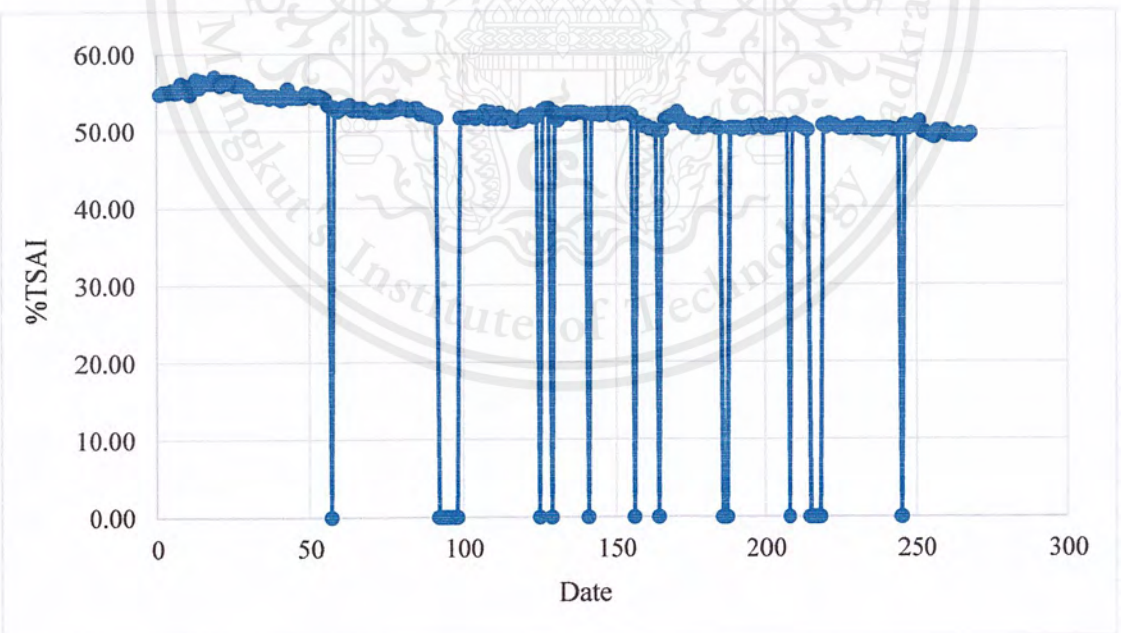

Figure 4.6. Graph show relationship between %TSAI of molasses are used in the ethanol production process of TAE PC1, run with 1 decanter, in 2017 (%TSAI = 0 is not operate the process, cleaning the vacuum distillation trays)

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The result from data analysis of performance of process with different number of decanter. At the present, the sugarcane molasses is high contained of bacteria and the bacteria growth rate is very high so, the residence time at the mash preparation step must is reduced. The figure 4.5 and 4.6 show the relationship between %TSAI of sugarcane molasses are used as a feedstock in 2015 which is the process run with 2 decanters and 2017 which is the process run with 1 decanter. %TSAI or total sugar as invert of molasses show the quality of molasses are used in each day. The result show that, if used 2 decanters, the process can operate with longer time without clogging of the fouling more than use only 1 decanter.

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4.2 Sugarcane molasses quality (%TSAI) effect to the occurrence of the fouling in vacuum distillation

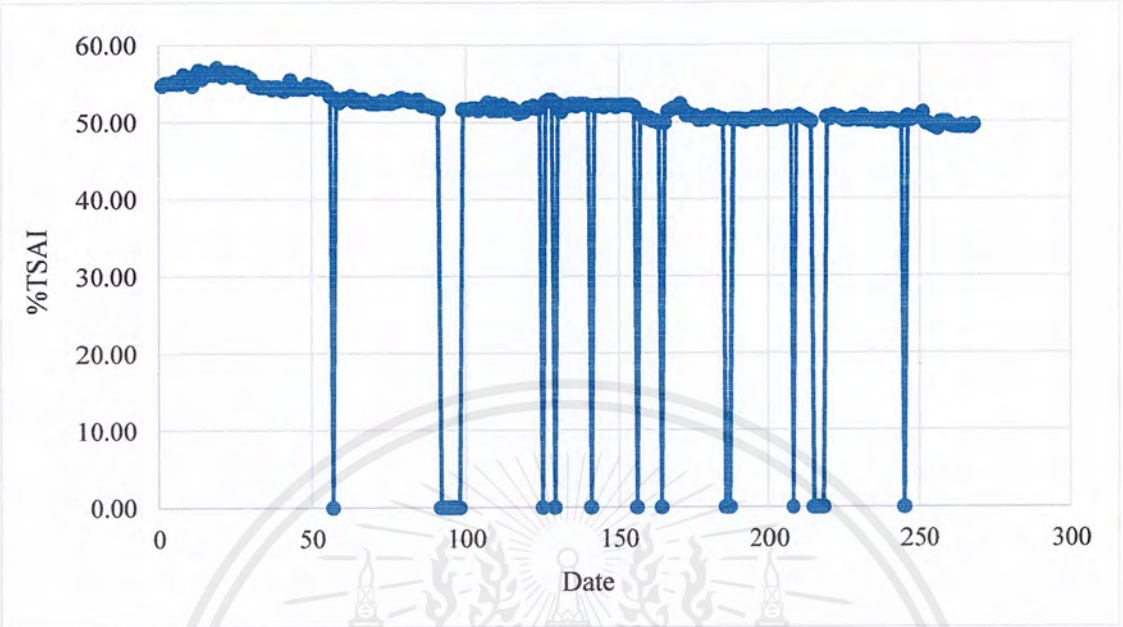

Figure 4.7. Graph show relationship between %TSAI of molasses are used in the ethanol production process of TAE PC1 in 2017 (%TSAI = 0 is not operate the process, cleaning the vacuum distillation trays)

The result from sugarcane molasses quality (%TSAI) effect to the occurrence of the fouling in vacuum distillation. The high value of %TSAI of molasses which is low contaminate contain. The process can operate with long time without clogging of the fouling. In the other hand, if the low value of % TSAI, the process can operate with short time because the clogging of the fouling. The results showed that the quality of molasses may be one of the factors on the fouling formation because if the molasses have low quality (more contaminates), the impurities can enter into the system a lot as well due to the production process is not sediment removal system good enough.

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4.3 Calculation of the Langelier Saturation Index (LSI) to predict of fouling from process water

Table 4.2. Measurement the parameters of process water

Parameter*	**Value**	**Factor**
pH	8.2	-
Water Temperature	24 °C	2.02
Total Dissolved Solid	135.87 mg/L	9.79
Calcium Hardness	103.5 mg/L	2.01
Alkalinity	25 mg/L	1.39
Volatile Fatty Acid	50 mg/L	-
LSI = 8.2 - (2.02 + 9.79 - 2.01 – 1.39) = **0.21**		

*average parameter

The Process Water calculated index Langelier (LSI) to observe the ability in the fouling of water, was found that the process water has value LSI = 0.21 which is considered to be the appropriate value for the water that does not cause the fouling.

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4.4 The Functional group of molasses and fouling using FTIR

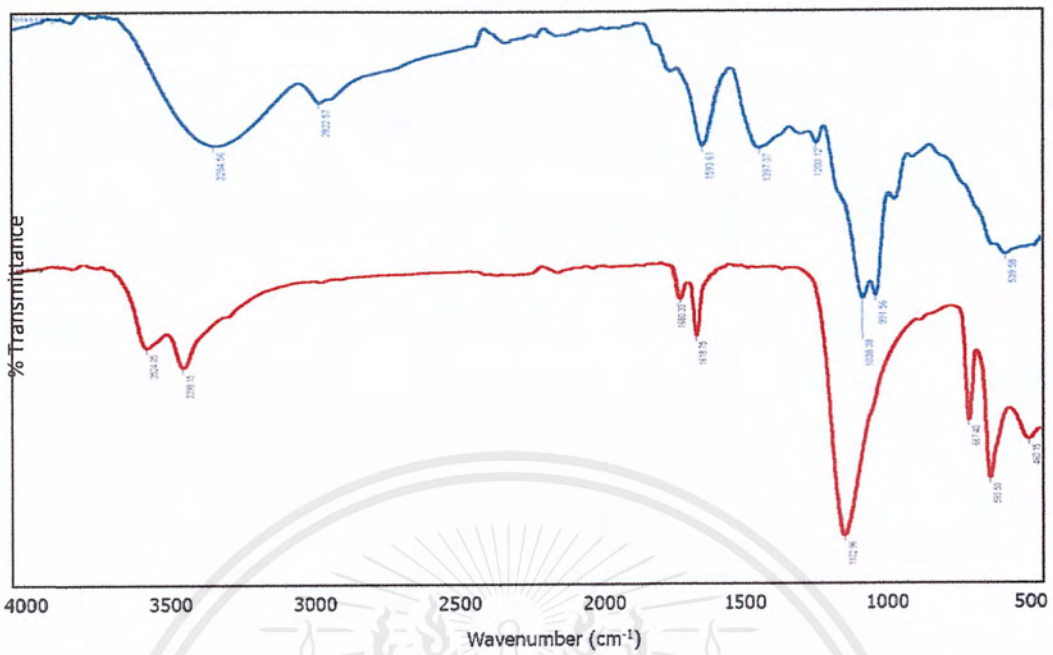

Figure 4.8. FTIR spectra of molasses (-) and fouling (-)

From analysis of the samples to determine the functional groups of molasses and fouling using FTIR. The result show the functional group of evaporation molasses consist of inorganic phosphates, aliphatic amino acid salts, alkynes monosubstituted, aliphatic hydrocarbons and primary aliphatic alcohols. The functional group of fouling consist of alumino silicates and primary aliphatic alcohols.

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4.5 The composition of sludge and fouling using XRF

Table 4.3. Analysis the composition of sludge and molasses using XRF

Composition (%)	Sludge	Fouling
O	44.600	48.200
Mg	0.277	-
Al	0.472	0.123
Si	6.400	0.808
P	0.322	0.310
S	16.600	24.200
K	5.220	0.271
Ca	26.000	26.100

Table 4.4. Analysis the composition of sludge and molasses using XRF

Composition (%)	Sludge	Fouling
MgO	0.460	-
Al_2O_3	0.893	0.232
SiO_2	13.700	1.730
P_2O_5	0.738	0.709
SO_3	41.400	60.500
K_2O	6.290	0.326
CaO	36.400	36.500

The results of analysis of the elemental composition of sludge and fouling showed that the main composition of the sludge are 16.600 % are sulfur and 26.000 % of calcium. The main composition of the fouling are 24.200 % of sulfur which is from the molasses and anti-microbial and 26.100 % of calcium which is from the molasses because the lime is added to the sugar production. Aluinium, Silicon and Phosphorous are from the process water in form of kaolin clay.

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Chapter V

Conclusions

5.1 Conclusions

This project is to fine out the cause analysis of fouling formation on the tray within the vacuum distillation column of ethanol production. Can be summarized as follows:

5.1.1 The fouling forms in short operating time at low % TSAI of sugarcane molasses.

5.1.2 Main compositions in the fouling are 24.200 % of sulfur and 26.100 % of calcium which are mainly from the sugarcane molasses.

5.1.3 Process water is slightly affect to the fouling.

5.2 Recommendations

5.2.1 At the mash preparation step, the anti-microbial can used as the inhibition of bacteria growth in sugarcane molasses in order to increase the residence time for decanter to be able to remove more solid particle from the system.

5.2.2 The filter should be installed in order to remove solid particles in molasses before enter the distillation column.

5.2.3 Coating the surface of trays for reduce the scratches.

5.2.4 Control the LSI value of process water to be zero to avoid fouling from calcium carbonate from process water.

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APPENDIX

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APPENDIX A

Langelier Saturation Index [17]

A = Water Temperature Factor
B = Total Dissolved Solid Constant Factor
D = Calcium Hardness Factor

Table A.1. Water Temperature Factor

Water Temperature, °C	A
0	2.60
4	2.50
8	2.40
12	2.30
16	2.20
20	2.10
25	2.00
30	1.90
40	1.70
50	1.55
60	1.40
70	1.25
80	1.15

Table A.2. Total Dissolved Solid Constant Factor

TDS, mg/L	B
0	9.70
100	9.77
200	9.83
400	9.86
600	9.89
1000	9.90

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Table A.3. Calcium Hardness Factor

Calcium Hardness or Total Alkalinity in mg/L $CaCO_3$	C^* or D^*
10	1.00
20	1.30
30	1.48
40	1.60
50	1.70
60	1.78
70	1.84
80	1.90
100	2.00
200	2.30
300	2.48
400	2.60
500	2.70
600	2.78
700	2.84
800	2.90
900	2.95
1000	3.00

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APPENDIX B

Figure B.1. FTIR spectra of molasses

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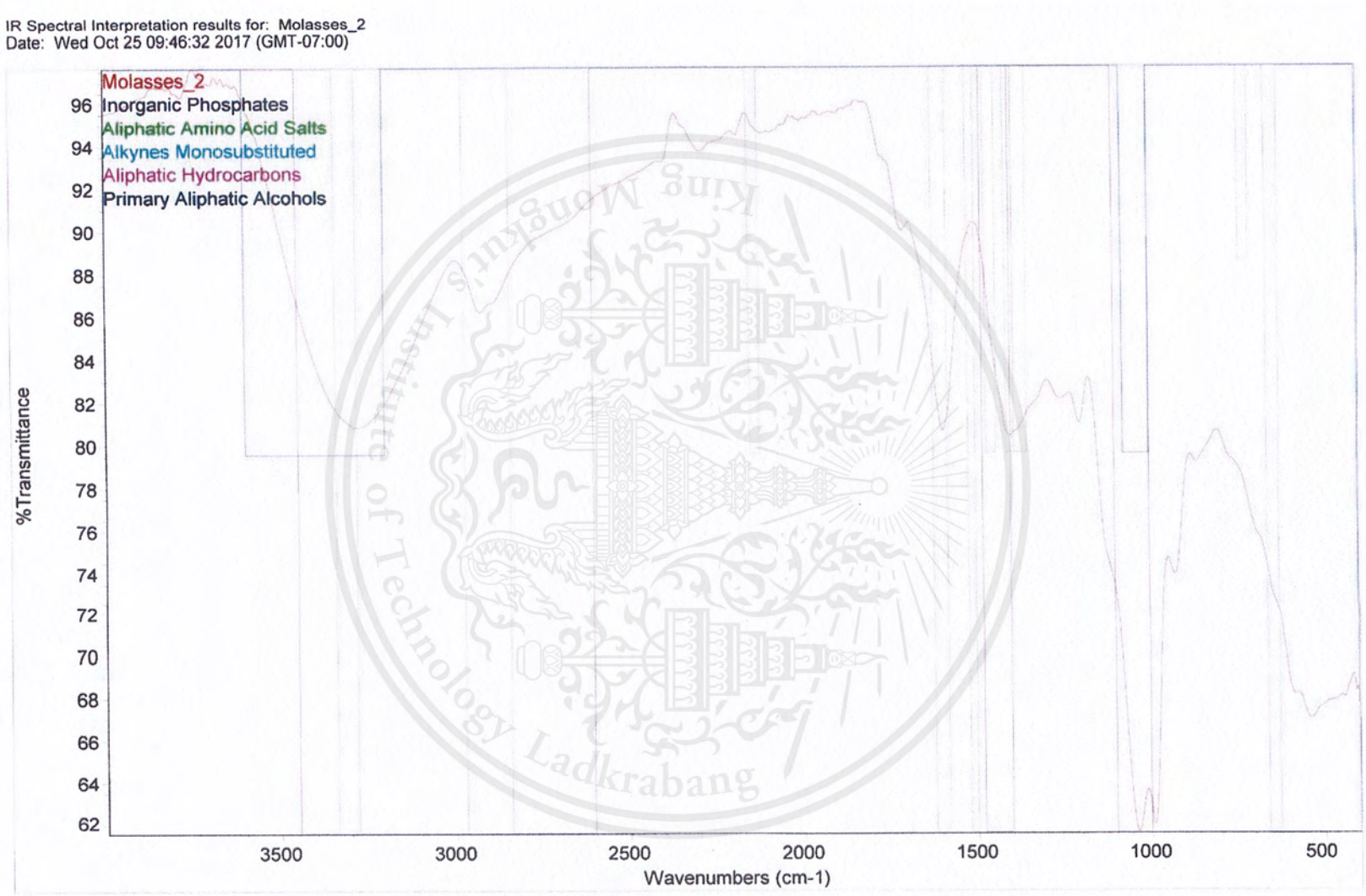

Figure B.2. Identify functional group of molasses with FTIR spectroscopy

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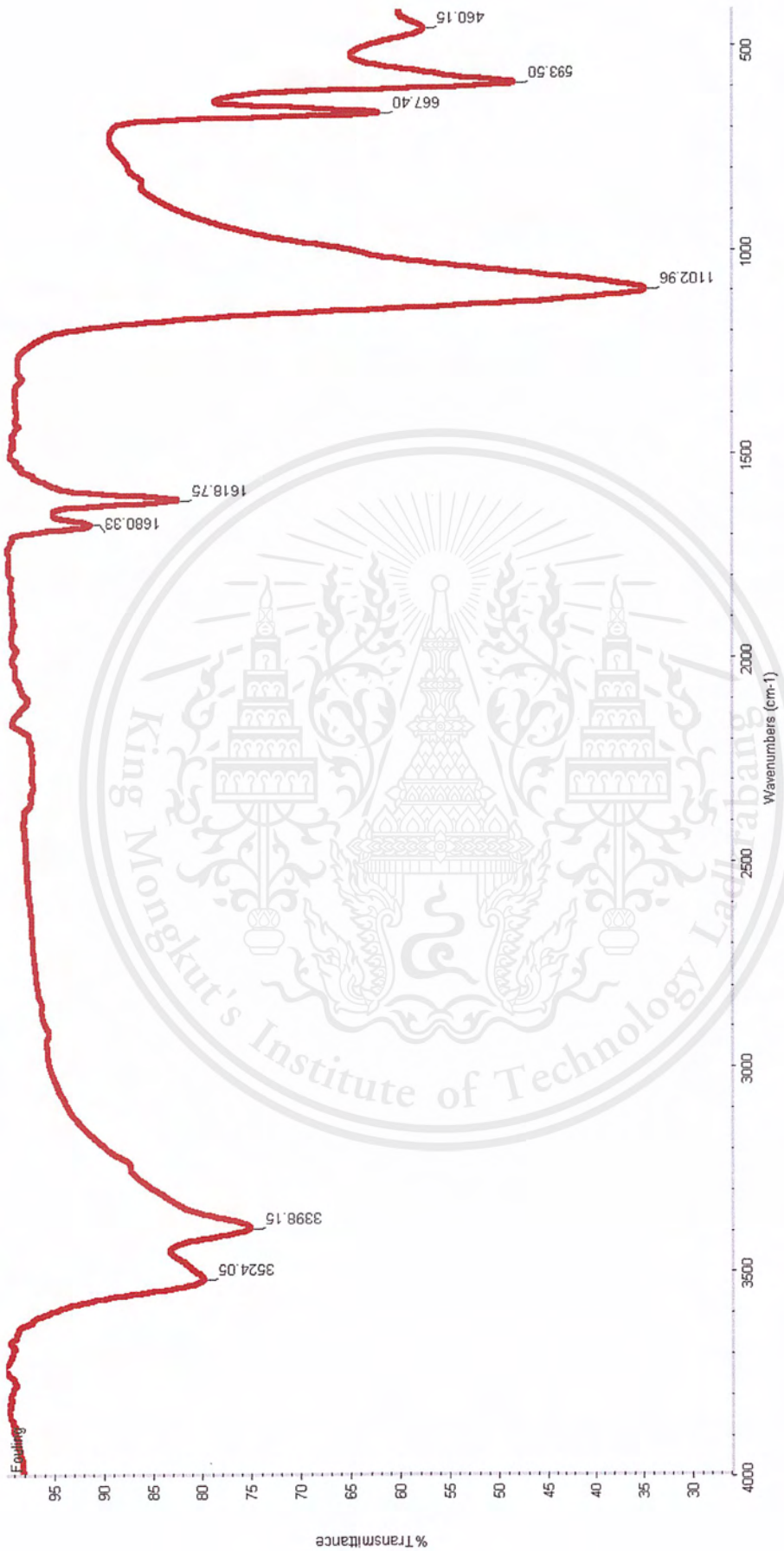

Figure B.3. FTIR spectra of fouling

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Figure B.4. Identify functional group of fouling with FTIR spectroscopy

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APPENDIX C

Table C.1. XRF sludge analysis

O	Mg	Al	Si	P	S	K	Ca	Compton	Rayleigh	Norm
	0.3 KCps	0.3 KCps	6.1 KCps	0.4 KCps	34.5 KCps	29.5 KCps	146.9 KCps			
44.6 %	0.277 %	0.472 %	6.04 %	0.322 %	16.6 %	5.22 %	26.0 %	0.96	1.02	100.00 %

Printed by Eval on 16-Nov-2017 09:40:52
Sample :XF61_002_02_sample 2_Sludge
Sample measured on 15-Nov-2017 18:03:36

Table C.2. XRF sludge analysis

MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	Compton	Rayleigh	Norm
0.3 KCps	0.3 KCps	6.1 KCps	0.4 KCps	34.5 KCps	29.5 KCps	146.9 KCps			
0.460 %	0.893 %	13.7 %	0.738 %	41.4 %	6.29 %	36.4 %	0.96	1.02	100.00 %

Printed by Eval on 15-Nov-2017 18:49:19
Sample :XF61_002_02_sample 2_Sludge
Sample measured on 15-Nov-2017 18:03:36

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Table C.3. XRF fouling analysis

O	Al	Si	P	S	K	Ca	Compton	Rayleigh	Norm
	0.1 KCps	0.7 KCps	0.4 KCps	43.0 KCps	1.3 KCps	127.6 KCps			
48.2 %	0.123 %	0.808 %	0.310 %	24.2 %	0.271 %	26.1 %	0.98	1.03	100.00 %

Printed by Eval on 16-Nov-2017 09:40:10
Sample :XF61_002_01_sample 1_Fouling
Sample measured on 15-Nov-2017 17:46:51

Table C.4. XRF fouling analysis

Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	Compton	Rayleigh	Norm
0.3 KCps	6.1 KCps	0.4 KCps	34.5 KCps	29.5 KCps	146.9 KCps			
0.232 %	1.73 %	0.709 %	60.05 %	0.326 %	36.5 %	0.98	1.03	100.00 %

Printed by Eval on 15-Nov-2017 18:49:19
Sample :XF61_002_01_sample 1_Fouling
Sample measured on 15-Nov-2017 17:46:51

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