Report of Cooperative Education

Optimization of Catalyst and Adsorbent Replacement at a Waste Gas Treatment Unit

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A Report Submitted in Partial Fulfillment of the Requirements
for the Degree of Bachelor of Engineering (Petrochemical Engineering),
Department of Chemical Engineering, Faculty of Engineering,
King Mongkut's Institute of Technology Ladkrabang
Academic Year 2016

Cooperative Title: Optimization of Catalyst and Adsorbent Replacement at a Waste Gas Treatment Unit
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ABSTRACT

High pressure vent gas treatment unit (HPVGT) of the purified terephthalic acid (PTA) plant is used for discarding hydrocarbons in waste gases. The HPVGT unit consists of a catalytic oxidizer (CATOX), scrubber and adsorber. The hydrocarbons are converted to CO_2 and H_2O by $Cu/Mn/Al_2O_3$ catalysts packed in the CATOX. Carbon dioxide gas is removed from waste gases by the scrubber and the moisture is adsorbed by silica gel adsorbent packed in the adsorber.

Based on the recommendation by the vendors, 50-60 wt% of the $Cu/Mn/Al_2O_3$ catalysts are annually replaced while 60-70 wt% of silica gel adsorbent is annually replaced. In 2013, the second oxidation reactor and methyl acetate (MA) recovery unit were installed to decrease hydrocarbon byproducts in the waste gases. As a result, low hydrocarbons were found in the waste gases. For this reason, the temperature in the CATOX decreased from 110 to 75 °C resulting in lower catalyst deactivation rate. Low hydrocarbons in the waste gases also led to lower consumption rate of the adsorbent at the adsorber. As a matter of fact, the conversions of *p*-xylene and byproducts were still 100 % when the catalysts were replaced. It is therefore an opportunity loss to replace 50-60 wt% of the catalyst and 60-70 wt% of the silica gel adsorbent at too early stage. 50 wt% of fresh $Cu/Mn/Al_2O_3$ catalysts is equivalent to 9 MBaht, and 60 wt% of the silica gel adsorbent is equivalent to 0.8 MBaht. The objectives of this project are to optimize the replacement ratio of the $Cu/Mn/Al_2O_3$ catalysts and silica gel adsorbent. According to the optimum operating conditions at the CATOX and the adsorber, around 25 wt% of the catalyst and 13 wt% of silica gel adsorbent were replaced, respectively. The estimated saving cost is totally about 5.18 MBaht.

Keywords: Optimization, Catalytic Oxidizer, Catalyst, Adsorber, Adsorbent, Silica Gel

Acknowledgements

Foremost, I would like to acknowledge the Department of Chemical Engineering at King Mongkut's Institute of Technology Lardkrabang, provided me with the opportunity for internship life and my graduate experience benefitted greatly from the course I took. I express my deepest thanks to Siam Mitsui PTA Company Limited for opportunity to work here. And also to production department manager: Mr. Prajak Sophondirekrat, production assistant department manager: Mr. Suguru Ohta, and my mentor, production engineer: Mr. Nuthapong Sohsawangha for useful advices and guidance and all facilities during all the time.

In addition, I would like to express my sincere gratitude to my advisor, Assoc. Prof. Dr. Anchaleeporn Waritswat Lothongkum for the continuous support of my graduate project, for her patience, motivation and necessary knowledge. Without her assistance and dedicated involvement in every step throughout the process, this paper would have never been accomplished.

Finally, I wish to acknowledge my family for their unparalleled love, help and support. They gave me the opportunities and selflessly encouraged me throughout my years of study. I am forever thankful to my friends for their friendship, support and encouragement. This project would not have been possible without them.

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NOMENCLATURE

c_p	=	Heat Capacity (kJ/kg °C)
H_B	=	Length of Bed Used up to Break Point (m)
H_T	=	Total Bed Length (m)
H_{UNB}	=	Length of Used Bed (m)
K	=	1 + (0.0013 x amount of superheating(°C))
L	=	Heat of Vaporization (kJ/kg)
$\dot{m}$	=	Mass Flow Rate (kg/h)
$\dot{n}$	=	Molar Flow Rate (kmol/h)
n_{H_2O}	=	Mole of Water (mol)
n_{WG}	=	Mole of Waste Gases (mol)
P	=	Atmospheric Pressure (bar)
P_1	=	Upstream Absolute Pressure (kgf/cm^2 abs.)
P_2	=	Downstream Absolute Pressure (kgf/cm^2 abs.)
P_{H_2O}	=	Pressure of Steam (bar)
P_{WG}	=	Pressure of Waste Gases (bar)
R	=	Gas Constant (m^3·bar/K·mol)
r'_A	=	Rate of Reaction (molA/dm^3 s)
t_b	=	Break-point Time (°C)
t_t	=	Time Equivalent to Total Capacity (h)
t_u	=	Time Equivalent to Usable Capacity up to Break-point Time (h)
T	=	Temperature (°C)
T_{in}	=	Inlet Temperature (°C)
T_{out}	=	Outle Temperature (°C)
$\dot{V}$	=	Volumetric Relief Rate (km^3/h)
W	=	Maximum Flow Rate (kg/h)
w_i	=	Initial Weight (g)
w_t	=	Weight at Time (g)
ΔP	=	$P_1 - P_2$ (kgf/cm^2)

CHAPTER I
INTRODUCTION

1.1 Background

Siam Mitsui PTA Co., Ltd. (SMPC) is a joint venture between SCG Chemicals Co., Ltd. and Mitsui Chemicals Inc. The company produces purified terephthalic acid (PTA) to be used in producing polyester for the textile industry and polyethylene terephthalate (PET) resin manufacture of drinking water bottles.

The PTA plant consists of two major units, Crude terephthalic acid (CTA) unit and PTA unit. This project is the part of the CTA unit.

The CTA unit is used for the catalytic liquid phase air oxidation of para-xylene (PX). The catalysts include HBr and Co/Mn. Acetic acid is used to be solvent. Silicone oil is the anti-foaming agent to reduce foaming in the CTA reactor. The total air flow rate to reactor is adjusted to provide a vent gas oxygen concentration at the range of 3.0 - 4.0 vol%. The remaining waste gases consist of N_2, O_2, CO, CO_2 and hydrocarbons which are converted to CO_2 and H_2O by a high pressure vent gas treatment unit (HPVGT) which consists of catalytic oxidizer (CATOX), scrubber, and adsorber as shown in Figure 1.1. The CATOX has packed bed, Cu/Mn on alumina catalyst. The moisture will be adsorbed by packed bed, silica gel adsorbent in adsorber.

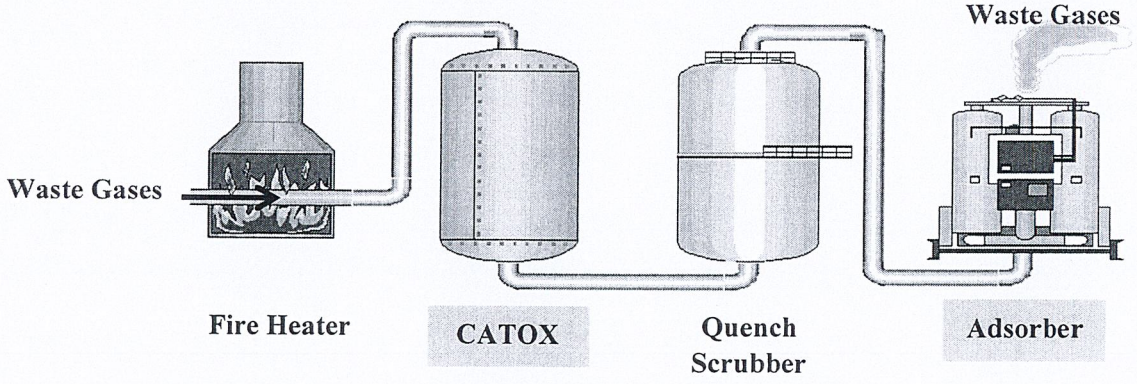


Figure 1.1 HPVGT Unit
[SMPC, 2016]

Currently, the Cu/Mn on alumina catalyst is annually replaced by fixed ratio at 50-60 wt%. And the silica gel adsorbent is annually replaced by fixed ratio at 50-60 wt%. The ratio of both replacement is fixed since the HPVGT unit is installed. In 2013, the second oxidation reactor and methyl acetate (MA) recovery unit are installed to decrease byproducts as hydrocarbons in the waste gases. The duty of the HPVGT unit decreases because of low hydrocarbons in the waste gases.

So this project would like to study to optimize the replacement ratio based on analysis data from spent catalyst and adsorbent, and estimated calculation method.

1.2 Objectives

1.2.1 To optimize percent replacement of Cu/Mn on alumina catalyst at the CATOX.

1.2.2 To optimize percent replacement of silica gel adsorbent at the adsorber.

1.3 Scopes of Work

1.3.1 To identify problems of catalyst and adsorbent replacement.

1.3.2 To provide the solution of the problems.

1.3.3 To optimize parameters for reducing amount of the catalyst and adsorbent replacement.

1.4 Expected Output

1.4.1 Reduce 10 wt% of used catalyst from 50 to 40 wt% (Expected saving cost is 2 MBaht/Year).

1.4.2 Reduce 10 wt% of used adsorbent from 60 or 70 to 50 wt% (Expected saving cost is 0.1 MBaht/Year)

CHAPTER II
LITERATURE REVIEW

This project is studying about the catalyst and adsorbent replacement at a waste gases treatment in CTA process. Many technologies are used to treat hydrocarbons in the waste gases. In each technology selection depends on waste gases conditions. The SMPC used the CATOX as packed-bed reactor. Catalyst is used in packed-bed reactor. In long time of operation, catalyst is deactivated. Operating conditions of CATOX affect to catalyst deactivated that is replaced every year. Adsorption is a unit for moisture reduction in the CTA unit. The adsorption unit is a pressure swing adsorption. Silica gel is used to adsorbed moisture in waste gases. Silica gel is replaced every year.

2.1 Process Description [SMPC, 2016]

The PX, acetic acid, catalysts solution and air are continuously fed to a single oxidation reactor at constant rate, and the PX is converted to CTA, which contributes to minimize decomposition of the acetic acid and the PX. The total air rate to oxidation reactor is adjusted to keep the vent gas oxygen concentration at 3.8 vol% on a volatile-free basis. The reactor effluent is discharged continuously to slurry drum. The bottom agitator of the reactor prevents the solid built-up on the internal wall of the oxidation reactor and maintains solids in suspension. The slurry from bottom of reactor is continuously to separation unit for separate solvent from solid. The solvent and catalyst are recovered to oxidation reactor. Then, the solid is continuously to dryer unit for prevention of lump. After that the CTA powder from the dryer unit is continuously fed to silo and then feeding to the PTA unit for purification as shown in Figure 2.1.

A distillation column, the vent line of oxidation reactor is connected to distillation column. The function of this distillation column is to remove water produced by the reaction by way of effectively utilizing the heat of reaction to maintain the acetic acid concentration in oxidation reactor constant. Heat generated by the exothermic oxidation reaction is removed by the vaporization of reaction solvent. The vapor stream was leaving the distillation column to 4 heat exchangers. The vent gas after heat exchange is continuously to condenser, a portion of distillate in condenser is discharged through Reversed Osmosis Membrane unit (RO unit) in order to recover the contained acetic acid. The uncondensed gases leaving condenser are continuous to waste gas scrubber column. In this section, acetic acid in the vapor is recovered by scrubbing the vapor with water, and sent to the acetic acid recovery unit. Then, the waste gases consist N_2, O_2, CO, CO_2, O_2, hydrocarbons and water, are continuous to the HPVGT unit as shown in Figure 2.2. The hydrocarbons as a volatile organic compounds (VOCs) and the CO are converted to CO_2 and H_2O for environmental protection.

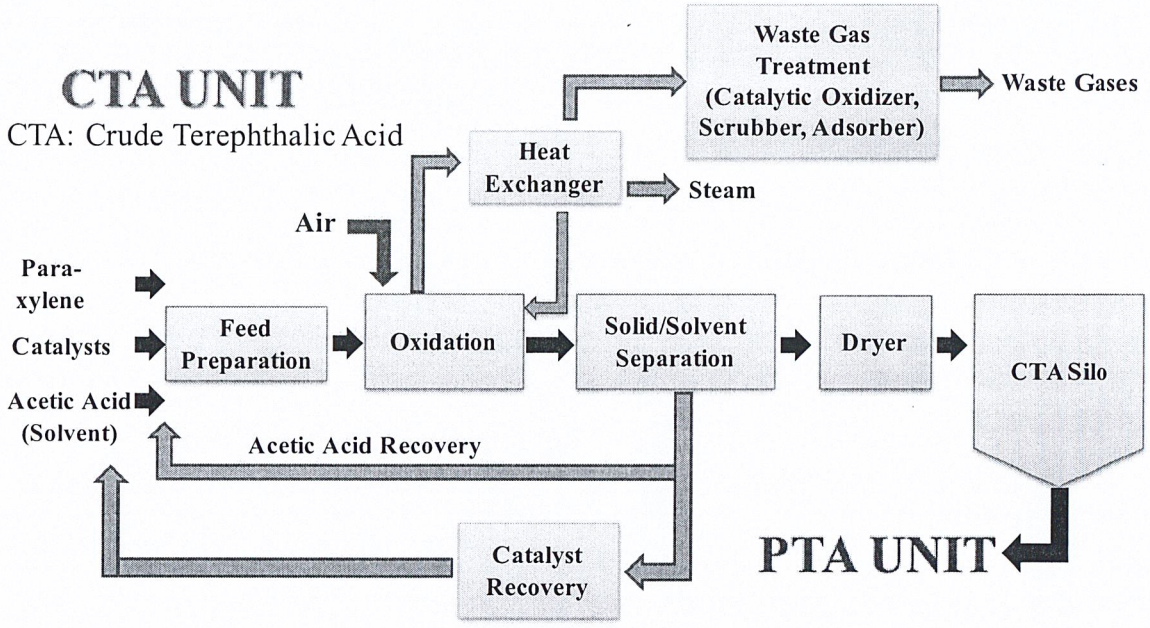


Figure 2.1 Process Flow Diagram of CTA Unit

[SMPC, 2016]

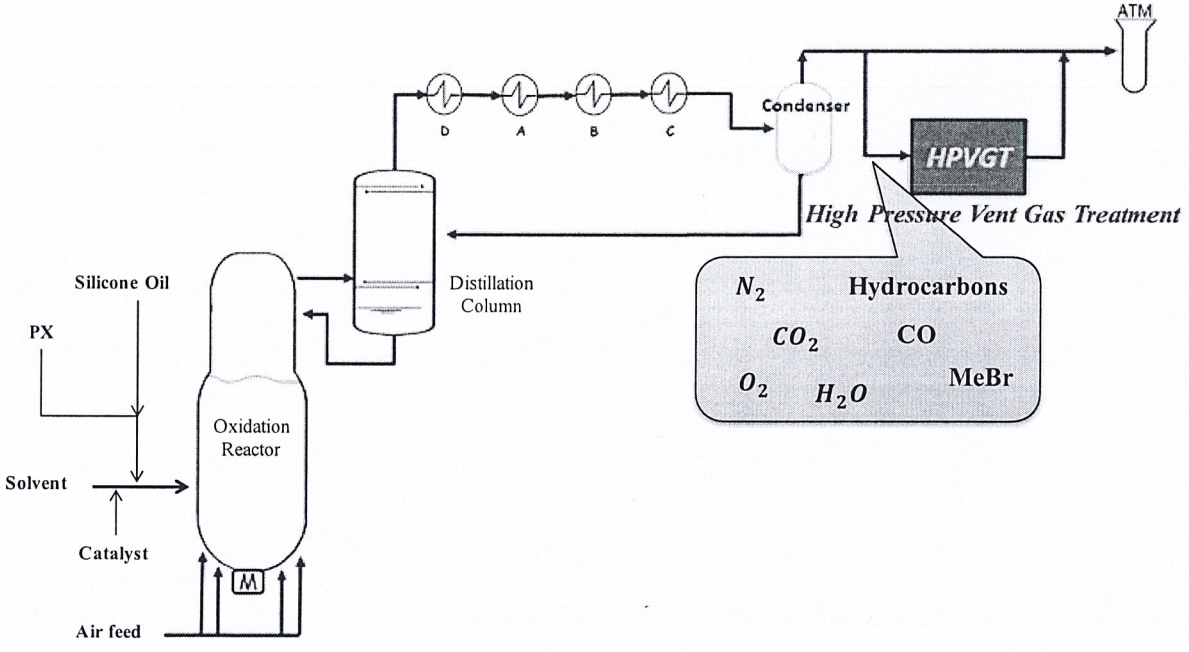


Figure 2.2 Components in Waste Gases

[SMPC, 2016]

2.2 Volatile Organic Compounds (VOCs) [Minnesota, 2016]

VOCs are carbon-based chemicals that easily evaporate to gas at room temperature. The VOCs are commonly referred to as solvents. The VOCs are found in everyday items such as paints, paint strippers, varnishes, lacquers, wood preservatives, craft kits, glues, fuel, aerosols, cleaners, pesticides, cigarette smoke, and dry-cleaned clothes. They act as carriers and can dissolve grease. Formaldehyde, benzene, toluene, and acetone are all considered the VOCs. The VOCs are released to the environment in a number of ways. Paint, furnishings, gasoline, smokes from fires, and even stored products such as closed paint canisters may release large amounts of the VOCs to the air. Renovation of building leads to an accumulation of the VOCs within enclosed spaces, thus accounting for higher levels of VOCs indoors compared to outdoors. Once VOCs are released to the environment in form of gases, they can react with sunlight to form ozone or smog. The primary route of exposure to the VOCs is by inhalation. Less commonly, children may be exposed through direct contact with skin. Inhaling the fumes from toluene and other VOCs, known as glue sniffing, is another source for exposure among teenagers.

Health effects from the VOCs are usually temporary and improve once the source of the exposure is identified and removed. These effects can include irritation of the eyes, nose, throat, and skin. Headache, nausea, and dizziness may occur, as well as fatigue and shortness of breath. Health effects vary depending on the chemicals involved and the duration of the exposure. Formaldehyde and pesticides are considered probable carcinogens. Research is examining potential health effects related to prenatal exposures to the VOCs. Exposure to benzene can result in headache, dizziness, accelerated heart rate, tremors, drowsiness, and confusion. Benzene can affect the bone marrow by decreasing production of red blood cells and platelets. High-level exposure to benzene of a long duration is known to cause leukemia and other cancers of the blood-forming organs in humans. The effects of benzene exposure during pregnancy are not known.

2.2.1 Mechanisms and kinetics of catalytic oxidation of VOCs [Muhammad Shahzad Kamal, Shaikh A. Razzak, and Mohammad M. Hossain, 2016]

The mechanisms proposed for the complete catalytic oxidation of VOCs generally fall into three main categories:

1. Marsevan Krevelen (MVK) model
2. Langmuir-Hinshelwood (L-H) model
3. Eley-Rideal (E-R) model.

The MVK model considers that the reaction occurs between the adsorbed the VOCs and the lattice oxygen of the catalyst rather than the oxygen in the gas phase. This model assumes that the oxidation of the VOCs takes place in two steps as shown in Figure 2.3. In the first step, the adsorbed VOCs react with oxygen in the catalyst, resulting in the reduction of the metal oxide. In the second step, the reduced metal oxide is re-oxidized by the gas phase oxygen present in the feed. As the catalyst is first reduced and then re-oxidized, this mechanism is also known as the redox mechanism. In the steady state, rates of the reduction and oxidation steps must be equal. This model has been widely used for kinetics modeling of oxidation reactions of hydrocarbons over metal oxide catalysts. According to the MVK mechanism, the rate of oxidation of the VOCs can be expressed by Equation 2.1.

$$-r_{VOC} = \frac{k_{O_2} k_{VOC} P_{VOC} P_{O_2}}{\gamma k_{VOC} P_{VOC} + k_{O_2} P_{O_2}} \tag{2.1}$$

where

$-r_{VOC}$: Reaction rate ($mol/m^3/s$)

P_{VOC} : Partial pressure of the VOCs

P_{O2} : Partial pressure of oxygen

k_{VOC} : Rate constant of VOCs oxidation

k_{O2} : Rate constant of catalyst re-oxidation

γ : The stoichiometry coefficient of O_2 in the oxidation

The L-H mechanism assumes that the reaction takes place between the adsorbed VOCs and the adsorbed oxygen. Therefore, it is essential for both the VOCs and oxygen molecule (species) to be adsorbed on the surface of the catalyst. The VOCs and oxygen may adsorb on similar type of active sites (single site L-H model) or two different types of active sites (duel site L-H model). Accordingly, the rate expressions for the single site L-H model and duel site L-H model are different as expressed by Equations 2.2 and 2.3, respectively.

$$-r_{VOC} = \frac{kK_{O_2}K_{VOC}P_{VOC}P_{O_2}}{(1+K_{VOC}P_{VOC}+K_{O_2}P_{O_2})^2} \quad (2.2)$$

$$-r_{VOC} = \frac{kK_{O_2}K_{VOC}P_{VOC}P_{O_2}}{(1+k_{VOC}P_{VOC})(1+k_{O_2}P_{O_2})} \quad (2.3)$$

where

K_{O_2} : The equilibrium constant for the adsorption of oxygen

K_{VOC} : The equilibrium constant for the adsorption of VOCs

The advantage of this model is that it not only includes the reaction rate but also takes into consideration of the adsorption of VOCs and oxygen.

The E-R mechanism, the reaction occurs between the adsorbed oxygen species and reactant molecules in the gas phase. The controlling step is the reaction between an adsorbed molecule and a molecule in the gas phase. The following equation represents the kinetic expression based on the E-R mechanism in Equation 2.4.

$$-r_{VOC} = \frac{kK_{VOC}P_{VOC}P_{O_2}}{(1+k_{VOC}P_{VOC})} \quad (2.4)$$

The validity of each mechanism strongly depends on the properties of the catalyst (active metal and the support) as well as on the nature of the VOCs. Generally, one of the above models provides a good fit for the experimental data for the oxidation of the VOCs over metal-oxide and noble-metal catalysts.

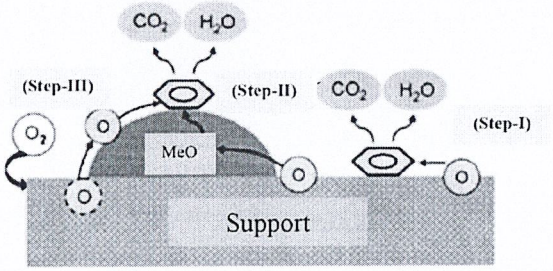


Figure 2.3 Schematic of Oxidation of VOCs (Benzene) on MnO

[Muhammad Shahzad Kamal, Shaikh A. Razzak, and Mohammad M. Hossain, 2016]

2.3 VOCs Reduction Technology [U.S. Environmental Protection Agency, 2006]

Currently available commercial technologies for off-gas treatment can be categorized into three main groups: Burning (thermal treatment), adsorption, and separation (Biofiltration) as shown in Figure 2.4. Thermal treatment is an oxidation process in which the temperature is increased to destroy contaminants in the vapor phase. Adsorption technologies involve the separation of contaminants by medium or matrix. Biofiltration treatment technologies take advantage of living organisms that consume or metabolize off-gas chemicals prior to off-gas discharge. Other emerging technologies include photolytic treatment and non-thermal plasma treatment, which destroy contaminants using ultraviolet (UV) light or electrical energy. These technologies are used for industrial applications.

2.3.1 Thermal Treatment

The thermal treatment of contaminants is a frequently used technology combusting or oxidizing the VOCs to carbon dioxide and water. Specific applications include direct-flame thermal oxidation, flameless thermal oxidation and catalytic oxidation. Thermal (non-catalytic) processes typically operate at temperatures exceeding 760 °C, with a typical minimum residence time over 0.5 seconds. Regenerative and recuperative system designs can be used to minimize operating costs by recovering a portion of the energy generated in the combustion process to preheat influent gases. The catalytic oxidation, the most commonly used thermal treatment off-gas technology, uses a catalyst and heat to oxidize contaminants in the vapor stream. The low VOCs concentrations typically seen in the HPVGT applications often require additional fuel or heat input to supported oxidation. Halogenated contaminants, however, also form halogen acids, which cannot be discharged directly into the atmosphere. The acids also tend to "poison" the catalyst. Traditionally, the gas stream must be passed through a scrubber to remove the acid. In addition, thermal treatment of chlorinated organic compounds has the potential to form various products of incomplete combustion.

2.3.2 Adsorption

The simplest process for off-gas treatment discussed in this document is adsorption of contaminants. The adsorption refers to the attraction and retention of organic contaminants to the surface of an adsorbent material. The key feature of the adsorbent material is that it is extremely porous and provides a large surface area for adsorption to take place. Although this

technology concentrates contaminants and can be used to treat reasonably large volumes of off-gas, ultimately the adsorbent must either be disposed of as a hazardous waste or regenerated, thus releasing the contaminants for further treatment. Activated carbon is the most widely used adsorbent material. Other adsorbent materials include alumino-silicate crystal structures known as "zeolites" and synthetic polymers. Selection of an appropriate adsorbent material is primarily a function of the contaminant to be adsorbed, although the adsorption capacity of certain materials may be adversely affected by the relative humidity of the off-gas stream.

2.3.3 Biofiltration

Biofiltration processes are used to biologically degrade VOCs present in remediation off-gas streams. The off-gas streams are passed through a bed or vessel of biologically active filter material. The VOCs in the vapor stream are adsorbed onto the filter media and subsequently degraded to inert compounds, usually carbon dioxide and water, by the microorganisms. Various biofiltration media (organic or synthetic) can be used for these systems.

2.3.4 Non-Thermal Plasma

Non-thermal plasma technologies are relatively new technologies and involve the destruction of vapor phase compounds by ionizing the compounds in the gas stream, thereby creating a plasma. This process typically occurs at temperature ranging from 32 to 121 °C (hence the term "non-thermal"). By adjusting conditions under which plasma formation occurs, the free radicals formed recombine into non-toxic simple compounds that can be released to the atmosphere. Specific plasma technologies include silent discharge plasma, gas-phase corona reactor, tunable hybrid plasma, and low pressure surface wave plasma. The techniques differ principally in the methods of applying electric fields to impart energy to the air stream and destroy the VOCs, and amount of energy required. Each technique uses a power source and a flow-through reactor vessel.

2.3.4 Photolytic and Photocatalytic Technologies

Photolytic technologies use UV light to ionize the VOC-laden vapor stream. The UV light furnishes energy to excite and break the molecular bond of the VOCs creating free radicals. The photocatalytic technologies are similar to photolytic technologies; however, UV light is used in the presence of a catalyst (usually titanium dioxide). The reaction resulting from

the contact between the UV light and the catalyst produces hydroxyl radicals that destroy the VOCs. The use of the catalyst allows VOCs destruction to occur at, or near, room temperature.

2.3.5 Membrane Separation

Membrane separation technologies remove the VOCs from the air or vapor mixture by passing the waste stream through a membrane designed to be more permeable to organic molecules than to air. These membrane separation systems can be configured as single-stage systems (typically used to treat concentrated industrial process streams) or as two-stage systems (commonly used to treat more dilute streams generated from site remediation).

2.3.6 Other Technologies

The Gas absorption technologies involve processes in which contaminant vapors are dissolved into a liquid solution. This process is referred to as scrubber. In some cases, the contaminant in the vapor stream chemically reacts with a component of the absorbent solution.

2.4 General Technology Selection [SMPC, 2016]

The technologies selection includes 5 main topics that is:

1. Components in the waste gases
2. Concentration in the waste gases
3. Flow rate of the waste gases
4. Decomposition of components
5. Inlet temperature.

From the HPVGT designed, the VOCs is component in the waste gases. The concentration of the VOCs is higher than 10 ppm. The flow rate is around 2,400 m^3/h. Higher than 80% decomposition is required. And fire is not required in this unit. Example, 200 ppm toluene is the component in the waste gases. Flow rate of the waste gases is 500 m^3/h. 95% decomposition and non-fire in the HPVGT unit is required as shown in Figure 2.5. So, the CATOX is the thermal treatment technologies which is used.

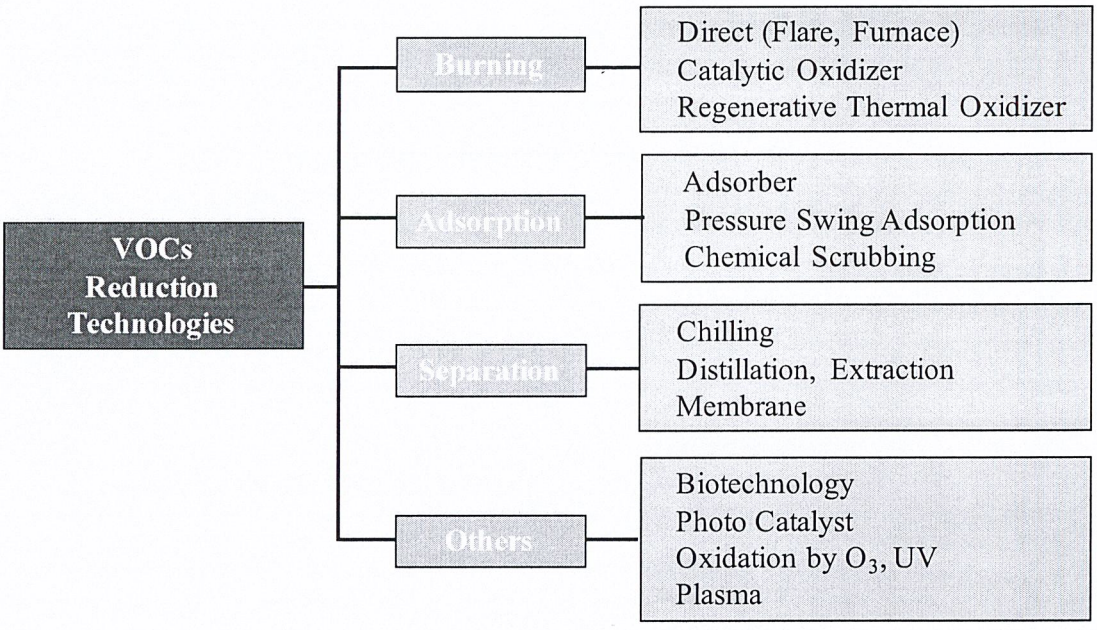


Figure 2.4 VOCs Reduction Technology

[SMPC, 2016]

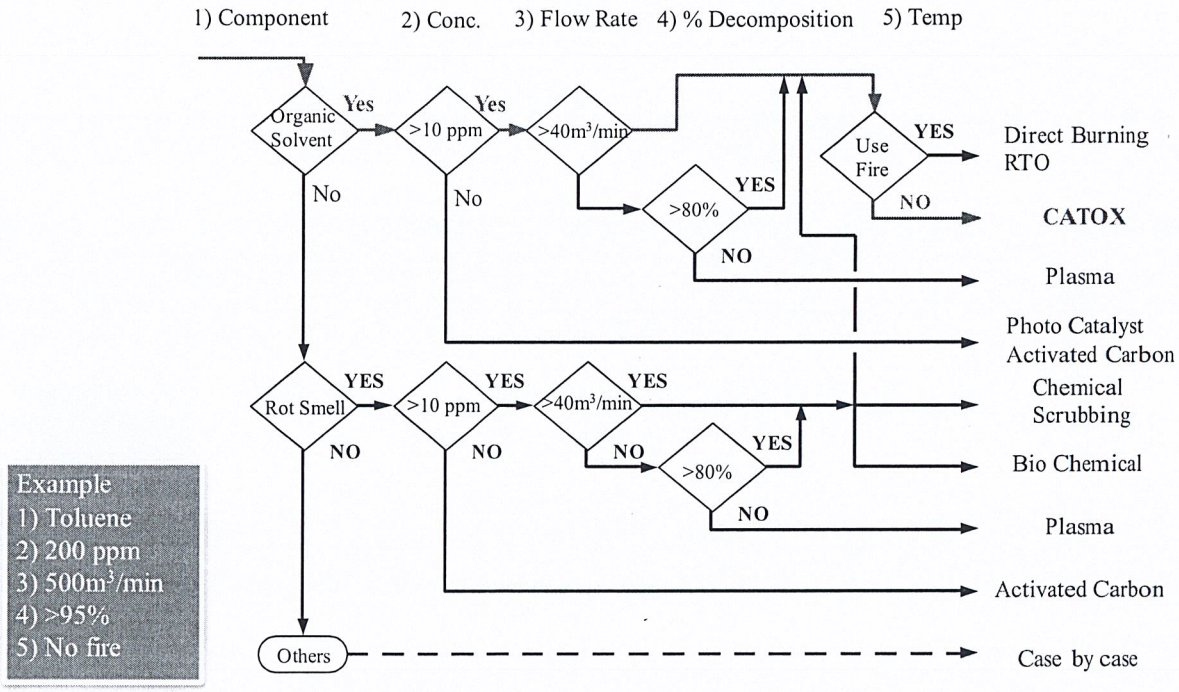


Figure 2.5 General Technology Selection Guideline

[SMPC, 2016]

2.5 The Thermal Treatment Technologies [U.S. Environmental Protection Agency, 2006]

The thermal treatment technologies destroy the hydrocarbons in a vapor stream at elevated temperatures (exceeding 315.55 °C) by combusting or oxidizing the hydrocarbons to carbon dioxide and water. The general chemical reaction for hydrocarbons oxidation is as follows:

$$C_xH_y + (x+y/4)O_2 + \text{Heat} \rightarrow xCO_2 + y/2H_2O + \text{Heat} \quad (2.5)$$

where

C_xH_x = Hydrocarbons

O_2 = Oxygen

CO_2 = Carbon dioxide

H_2O = Water

Heat is required to achieve the necessary temperature for this reaction to occur; the required temperature is a function of several factors, including the presence of a catalyst. The heat shown in the right side of the equation represents the heat released by the reaction. The hydrocarbons in off-gas and other environmental remediation systems are typically in the form of VOCs.

Thermal oxidation systems are commonly used to control the VOCs generated from petrochemical processing, chemical processing, painting, printing, and pharmaceutical industrial sources.

The thermal oxidation unit typically consists of a fan or blower to move VOC-laden air; a filter-mixer to mix the VOC-laden air; a fan to supply combustion air; a combustion unit (reaction chamber) consisting of a refractory-lined chamber and one or more burners; heat recovery equipment (heat exchanger); and a stack for atmospheric discharge of the treated exhaust. In some cases, post-oxidation treatment units are included. Figure 2.6 shows a generalized flow diagram for a typical thermal oxidation system.

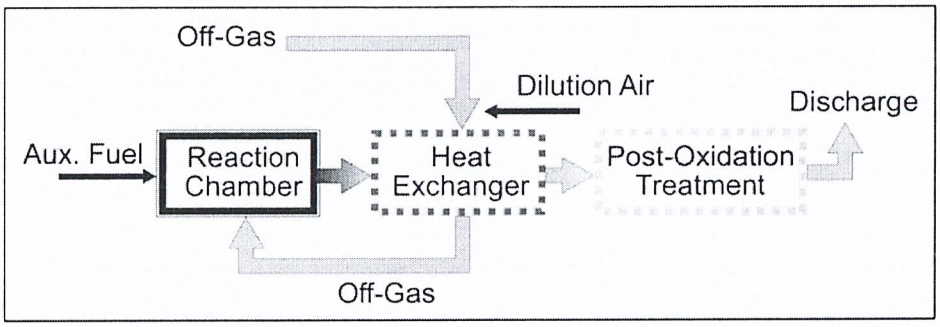


Figure 2.6 Generalized Flow Diagram of Typical Thermal Oxidation System [U.S. Environmental Protection Agency, 2006]

Three general types of thermal oxidation systems are available for controlling VOC emissions:

- Direct-flame thermal oxidizers (DFTO)
- Flameless thermal oxidizers (FTO)
- Catalytic oxidizers (CATOX)

Key variables within each type of thermal oxidation system include the following:

- Extent and type of heat recovery system
- Post-oxidation treatment requirements (such as scrubbing)
- Metallurgy requirements for equipment
- Utility energy cost and source (heat from electricity, propane, natural gas, or fuel oil)

Each type of system operates somewhat differently, but all types destroy contaminants by raising the temperature of the gas stream to a sufficient level to promote oxidation (or combustion) of contaminants to carbon dioxide and water as shown in Equation (2.5). The VOCs in the off-gas act as a fuel source for the oxidation reaction. If the VOC concentrations are relatively low, there may be insufficient fuel to promote oxidation, and auxiliary fuel must be added (such as natural gas or fuel oil). Sometimes the VOC concentrations are too high for the oxidation reaction to proceed safely, and the off-gas must be diluted with ambient air.

High VOC concentrations are typically treated using non-catalytic thermal oxidation systems, and lower VOC concentrations are often treated using the CATOX systems. The DFTO and FTO non-catalytic thermal oxidizers typically operate at 649 to 1,093 °C, and the

CATOX system typically operate at 260 to 482 °C. If the off-gas contains sufficient concentrations of VOCs to sustain the high operating temperature, a catalyst is not needed. Where the off-gas VOC concentrations are relatively low, a catalyst will lower the amount of auxiliary fuel that must be supplied to sustain the oxidation reaction, and operational expenses will be reduced compared to a non-catalytic system.

In a complete oxidation reaction, the VOCs are oxidized to carbon dioxide and water. If halogenated compounds are present in the off-gas (such as a brominated VOCs), the resulting combustion products can include acid gases (such as hydrobromic acid). The acid gases require further treatment with an acid scrubber (for example, caustic solution to neutralize the acid) prior to discharge. The efficiency of a thermal oxidation system is the 3 T functions: 1.) Temperature, 2.) Time (residence time in the combustion zone), and 3.) Turbulence (mixing of the VOCs and oxygen)

2.5.1 Direct-Flame Thermal Oxidizers

The simplest type of thermal oxidizer is a DFTO system without heat recovery (no heat exchanger following the combustion chamber). These systems are sometimes called "direct-fired thermal oxidizers" or "afterburners" and do not use a catalyst. In the DFTO system, contaminated vapor from off-gases enters a reaction chamber, where an open flame burns the vapors and additional fuel. The VOCs are oxidized as they are exposed to the necessary oxidation temperatures.

2.5.2 Flameless Thermal Oxidizers

Combustion in the FTO systems occurs within a chemically inert, porous ceramic bed heated to oxidation temperatures. In the FTO systems, the mixing zone is where the fuel is pre-mixed with off-gas at the inlet of the reactor before it passes through a pre-heated ceramic matrix, which heats the organic vapors. Once the vapors reach oxidation temperature, they auto-ignite in the system's reaction zone. The energy released by combustion heats the ceramic matrix of the mixing zone. If the waste stream has sufficient energy content, then the system is self-sustaining after it reaches its operating temperature. One vendor claims that VOC vapor streams with as little as 10 British thermal units per cubic foot (BTU/ft^3) can sustain the temperatures necessary for oxidation. Like the DFTO systems, this approach does not use a catalyst to aid combustion. Figure 2.7 presents a schematic diagram of the FTO system.

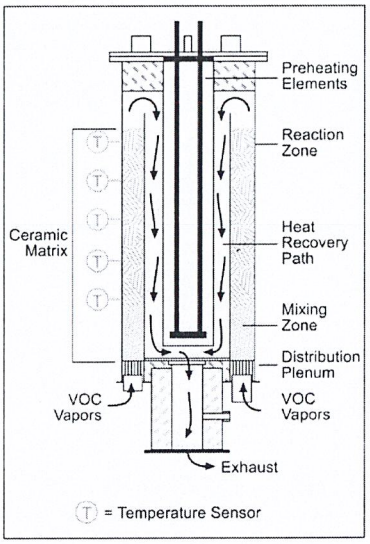


Figure 2.7 Flameless Thermal Oxidizer System
[U.S. Environmental Protection Agency, 2006]

2.5.3 Catalytic Oxidizers

The CATOX system uses a catalyst and heat to oxidize off-gas contaminants. The catalyst enables the oxidation reaction to occur at much lower temperatures than required by non-catalytic thermal oxidation systems. Most the CATOX systems operate at 260 to 482 °C depending on the compound being oxidized and the catalyst. The addition of a catalyst accelerates the rate of oxidation by adsorbing oxygen and the contaminant on the catalyst surface, where they react to form carbon dioxide and water. As with non-catalytic thermal oxidation systems, when brominated VOCs are present in the contaminant off-gas stream, acid gas is produced.

The most common catalysts for VOCs combustion are the noble metals platinum, palladium, and rubidium. The metal is deposited on an aluminum oxide-coated ceramic or stainless steel substrate to produce the monolith (or honeycomb) form of the catalyst. Other types of catalyst are base-metal catalysts, such as chromium- or manganese-oxides. Base-metal catalysts are usually supplied in pelletized form. Metal oxide catalysts are typically used to treat vapor streams containing brominated compounds.

In the CATOX system, the contaminated off-gas stream is preheated prior to its interaction with the catalyst. The off-gas stream then enters the catalytic chamber and is

evenly distributed over the catalytic beds. An exothermic combustion reaction takes place and the treated vapor (combustion products and byproducts) is then discharged.

The primary advantage of the CATOX systems compared to other thermal oxidation systems is the lower energy requirement resulting from lower oxidizing temperatures. Consequently, operating costs are lower. Also, less costly metallurgy can be used in the CATOX systems than in non-catalytic oxidizers because of the lower operating temperatures. In addition, the catalyst increases the rate of reaction, which lowers the residence time of the contaminants in the reaction chamber and allows use of a smaller reaction chamber than with non-catalytic systems to process the same flow rate.

The following sequence of steps is involved in the catalytic conversion of reactants to products:

1.Transfer of reactants to and products from the outer catalyst surface

2.Diffusion of reactants and products within the pores of the catalyst

3.Activated adsorption of reactants and the desorption of the products on the active centers of the catalyst

4. Reaction or reactions on active centers on the catalyst surface

At the same time, energy effects arising from chemical reaction can result in the following:

1. Heat transfer to or from active centers to the catalyst-particle surface
2. Heat transfer to and from reactants and products within the catalyst particle
3. Heat transfer to and from moving streams in the reactor
4. Heat transfer from one catalyst particle to another within the reactor
5. Heat transfer to or from the walls of the reactor

Some of the advantages of catalytic incinerators are:

1. Lower fuel requirements as compared with thermal incinerators
2. Lower operating temperatures
3. Minimum insulation requirements
4. Reduced fire hazards
5. Reduced flashback problems

The disadvantages include:

1. Higher initial cost than thermal incinerators
2. Catalyst poisoning
3. Necessity of first removing large particulates
4. Catalyst-regeneration problems
5. Catalyst disposal

2.5.4 Hybrid Thermal/Catalytic Oxidizer Systems

Because off-gas from process systems fluctuates in concentration over time, hybrid thermal/Cat-Ox systems (also called hybrid systems) are designed to allow the process system to be operated at a higher temperature without a catalyst (thermal mode) in the initial stages of an off-gas treatment when the extracted VOC contaminant concentrations are usually at their highest. When the VOC concentrations in the off-gas decrease, the hybrid system converts to operate as the CATOX system. Many vendors offer hybrid oxidizer systems. Figure 2.8 shows a typical hybrid system.

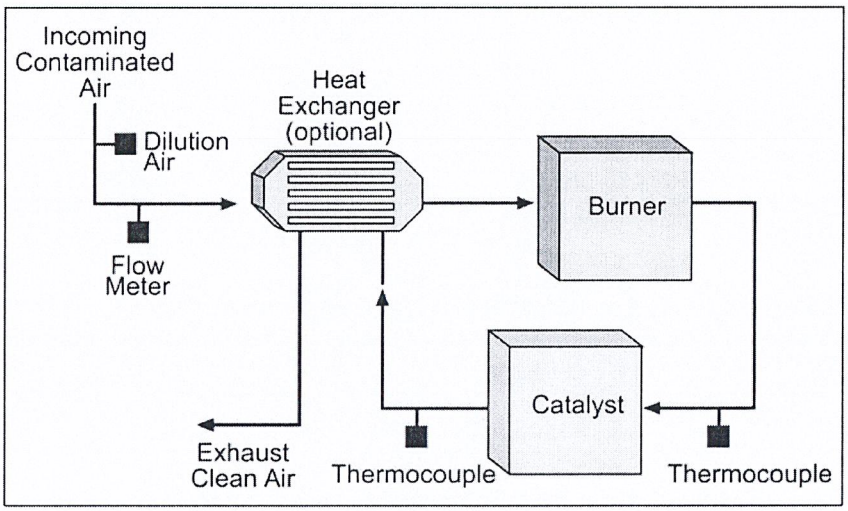


Figure 2.8 Hybrid Thermal/Catalytic Oxidizer System
[U.S. Environmental Protection Agency, 2006]

2.5.5 Recuperative Thermal Oxidizers

Figure 2.9 shows a recuperative thermal oxidizer. In these systems, combustion takes place, and then the hot, treated vapor from the reaction or catalytic chamber is directed to a heat exchanger shell. Incoming off-gas flows through the tubes of the shell-and-tube heat

exchanger, and heat is exchanged from the hot, treated vapor stream to the cool, incoming untreated vapor stream. The streams do not mix. Because the influent stream is preheated in the heat exchanger, less fuel is needed to bring the contaminated vapor up to oxidation temperature. Recuperative systems can recover up to 70 percent of the heat of the reaction chamber effluent; therefore, they require substantially less energy than non-recuperative systems. When chlorinated solvents are extracted, the design of recuperative heat exchangers generally limits flue gas cooling to avoid condensing acid gases onto heat exchanger surfaces and minimize corrosion.

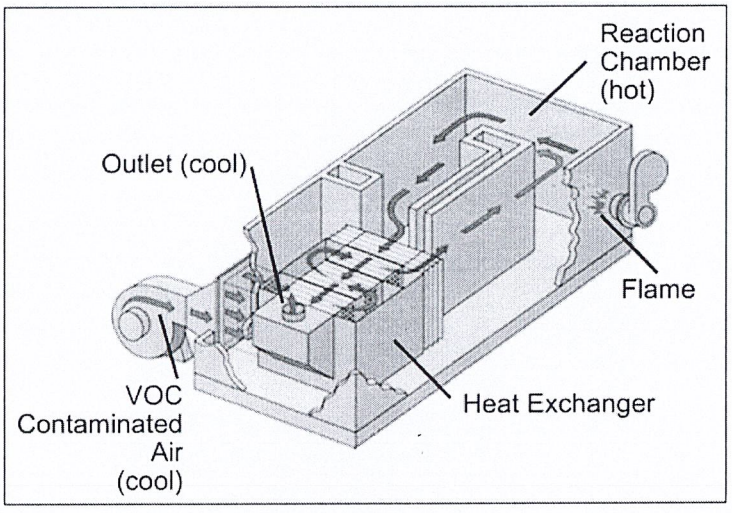


Figure 2.9 Recuperative Thermal Oxidizer
[U.S. Environmental Protection Agency, 2006]

2.5.6 Regenerative Thermal Oxidizer

Regenerative thermal oxidizers (RTO) use more complex and more efficient heat exchange systems than recuperative systems to heat incoming off-gas and promote the oxidation reaction. These units consist of a series of beds of heat-resistant media (such as ceramic) that absorb energy from the hot combustion product outlet gas. That energy is then used to preheat the incoming off-gas. Figure 2.10 shows a typical regenerative thermal oxidizer system. The inlet gas first passes through a hot bed of ceramic transfer blocks that heats the stream to its ignition temperature (and cools the bed). If the desired temperature is not attained, a small amount of auxiliary fuel is added in the combustion chamber. The hot gases then react, releasing energy in the combustion chamber and while passing through another bed of ceramic transfer blocks, thereby heating the second bed to the combustion chamber outlet temperature. The

process flows are then switched: now the inlet stream is fed to the hot bed. This cyclic process affords very high energy recovery (up to 95 percent) and may occur several times each hour. It should be noted that complex controls and large, high-temperature valves add to the capital cost of these types of systems. However, the lower expense for energy can off-set these higher capital costs in some cases.

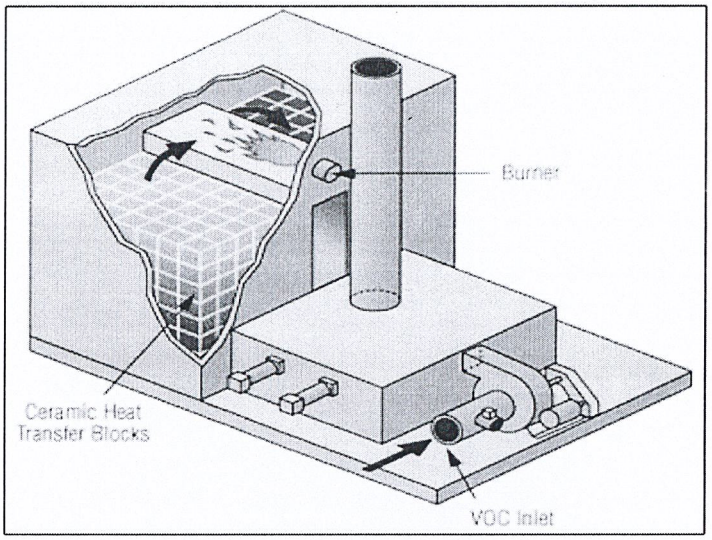


Figure 2.10 Regenerative Thermal Oxidizer
[U.S. Environmental Protection Agency, 2006]

2.6 Packed-bed Reactor (PBR) [H. Scott Fogler, 2014]

The principal difference between reactor design calculations involving homogeneous reactions and those involving fluid-solid heterogeneous reactions is that for the latter, the reaction takes place on the surface of the catalyst. Consequently, the reaction rate is based on mass of solid catalyst, W, rather than on reactor volume, V. For a fluid-solid heterogeneous system, the rate of reaction of a species A is defined as

$$-r_A' = mol\ A\ reacted/(time \times mass\ of\ catalyst) \tag{2.6}$$

The mass of solid catalyst is used because the amount of catalyst is what is important to the rate of product formation. The reactor volume that contains the catalyst is of secondary significance. Figure 2.11 shows a schematic of an industrial catalytic reactor with vertical tubes packed with solid catalyst.

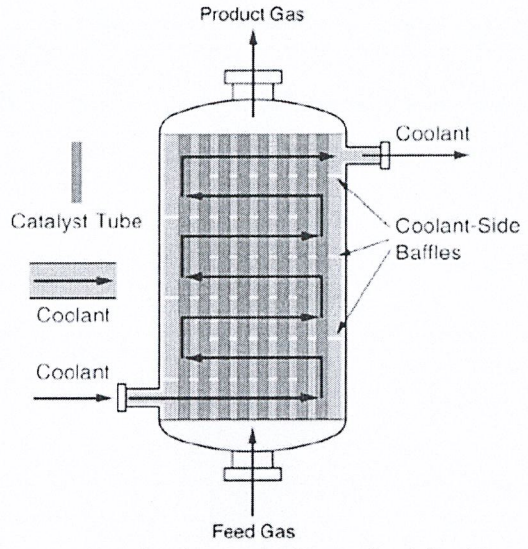


Figure 2.11 Longitudinal Catalytic Packed-bed Reactor

[H. Scott Fogler, 2014]

2.6.1 PBR Mole Balance

In the three idealized types of reactor just discussed (the perfectly mixed batch reactor, the plug-flow tubular reactor), and the perfectly mixed continuous-stirred tank reactor), the design equations were developed based on reactor volume. The derivation of the design equation for a PBR will be carried out in a manner analogous to the development of the tubular design equation. To accomplish this derivation, we simply replace the volume coordinate in Equation 2.7 with the catalyst mass coordinate W as shown in Figure 2.12.

$$\text{In} \quad - \quad \text{Out} \quad + \text{Generation} = \quad \text{Accumulation}$$

$$F_{A/V} - F_{A/(V+\Delta V)} + r_j \Delta w \qquad = \qquad 0 \tag{2.7}$$

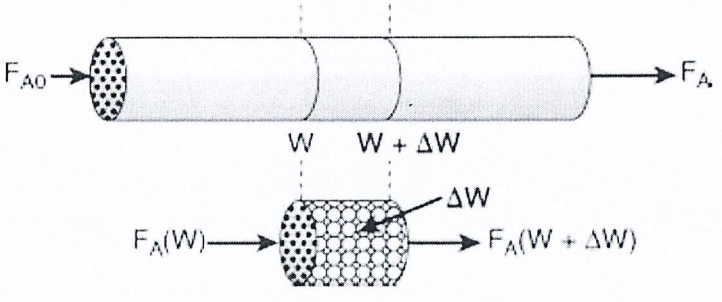


Figure 2.12 Packed-bed Reactor Schematic

[H. Scott Fogler, 2014]

The PBR is assumed to have no radial gradients is concentration, temperature, or reaction rate. The generalized mole balance on species A over catalyst weight ΔW results in Equation 2.8.

$$\text{In} - \text{Out} + \text{Generation} = \text{Accumulation}$$

$$F_{A/W} - F_{A/(W+\Delta W)} + r'_A \Delta W = 0 \tag{2.8}$$

The dimensions of the generation term in Equation 2.8 are

$$(r'_A)\Delta W = \frac{moles\ A}{(time)(mass\ of\ catalyst)}(mass\ of\ catalyst) = \frac{moles\ A}{time} \tag{2.9}$$

which are, as expected, the same dimensions of the molar flow rate F_A. After dividing by ΔW and taking the limit as $\Delta W \rightarrow 0$, we arrive at the differential form of the mole balance for a packed-bed reactor:

$$\frac{dF_A}{dW} = r'_A \tag{2.10}$$

When pressure drop though the reactor and catalyst decay are neglected, the integral form of the packed-catalyst-bed design equation can be used to calculate the catalyst weight.

$$W = \int_{F_{A0}}^{F_A} \frac{dF_A}{r'_A} = \int_{F_A}^{F_{A0}} \frac{dF_A}{-r'_A} \tag{2.11}$$

W is the catalyst weight necessary to reduce the entering molar flow rate of species A, F_{A0}, to a flow rate F_A.

2.6.2 Definition of Conversion

In defining conversion, we choose one of the reactants as the basis of calculation and then relate the other species involved in the reaction to this basis. In virtually all instances it is best to choose the limiting reactant as the basis of calculation. We develop the stoichiometric relationships and design equations by considering the general reaction

$$aA + bB \rightarrow cC + dD \tag{2.12}$$

The uppercase letters represent chemical species and the lowercase letters represent

stoichiometric coefficients. Taking species A as our basis of calculation, we divide the reaction expression through by the stoichiometric coefficient of species A, in order to arrange the reaction expression in the form

$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D \tag{2.13}$$

to put every quantity on a per mole of A basis, our limiting reactant.

The conversion X_A is the number of moles of A that have reacted per mole of A fed to the system:

$$X_A = \frac{Moles\ of\ A\ reacted}{Moles\ of\ A\ fed} \tag{2.14}$$

Because we are defining conversion with respect to our basis of calculation, we eliminate the subscript A for the sake of brevity and let $X=X_A$. For irreversible reactions, the maximum conversion is 1. For reversible reactions, the maximum conversion is the equilibrium conversion X_e.

2.7 Catalysts [H. Scott Fogler, 2014]

Catalysts have been used by humankind for over 2,000 years. The first observed uses of catalysts were in the making of wine, cheese, and bread. It was found that it was always necessary to add small amounts of the previous batch to make the current batch. However, it wasn't until 1835 that Berzelius began to tie together observations of earlier chemists by suggesting that small amounts of a foreign substance could greatly affect the course of chemical reactions. This mysterious force attributed to the substance was called catalytic. In 1894, Ostwald expanded Berzelius' explanation by stating that catalysts were substances that accelerate the rate of chemical reactions without being consumed. During the 175 years since Berzelius' work, catalysts have come to play a major economic role in the world market. In the United States alone, sales of process catalysts in 2007 were over $3.5 billion, the major uses being in petroleum refining and in chemical production.

2.7.1 Definitions

A catalyst is a substance that affects the rate of a reaction but emerges from the process unchanged. A catalyst usually changes a reaction rate by promoting a different

molecular path ("mechanism") for the reaction. For example, gaseous hydrogen and oxygen are virtually inert at room temperature, but react rapidly when exposed to platinum. The reaction coordinate shown in Figure 2.13 is a measure of the progress along the reaction path as H_2 and O_2 approach each other and pass over the activation energy barrier to form H_2O. Catalysis is the occurrence, study, and use of catalysts and catalytic processes. Commercial chemical catalysts are immensely important. Approximately one third of the material gross national product of the United States involves a catalytic process somewhere between raw material and finished product. The development and use of catalysts is a major part of the constant search for new ways of increasing product yield and selectivity from chemical reactions. Because a catalyst makes it possible to obtain an end product by a different pathway with a lower energy barrier, it can affect both the yield and the selectivity.

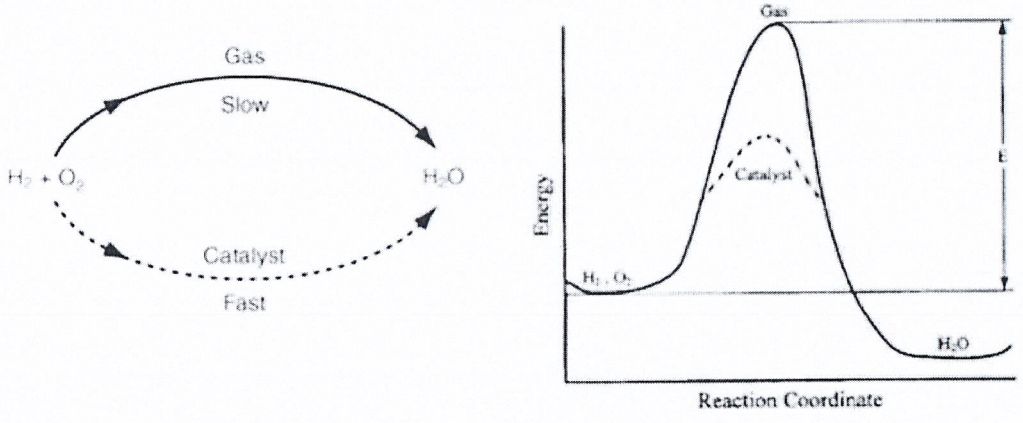


Figure 2.13 Reaction Coordinator

[H. Scott Fogler, 2014]

A heterogeneous catalytic reaction occurs at or very near the fluid–solid interface. The principles that govern heterogeneous catalytic reactions can be applied to both catalytic and non-catalytic fluid–solid reactions. The two other types of heterogeneous reactions involve gas–liquid and gas–liquid–solid systems. Reactions between gases and liquids are usually mass-transfer limited.

2.7.2 Catalyst Properties

Ten grams of this catalyst possess more surface area than a U.S. football field

Catalyst types:

- Porous
- Molecular sieves
- Monolithic
- Supported
- Unsupported

2.7.3 Catalytic Gas-Solid Interactions

For the moment, let us focus our attention on gas-phase reactions catalyzed by solid surfaces. For a catalytic reaction to occur, at least one and frequently all of the reactants must become attached to the surface. This attachment is known as adsorption and takes place by two different processes: physical adsorption and chemisorption. Physical adsorption is similar to condensation. The process is exothermic, and the heat of adsorption is relatively small, being on the order of 1 to 15 kcal/mol. The forces of attraction between the gas molecules and the solid surface are weak. These van der Waals forces consist of interaction between permanent dipoles, between a permanent dipole and an induced dipole, and/or between neutral atoms and molecules. The amount of gas physically adsorbed decreases rapidly with increasing temperature, and above its critical temperature only very small amounts of a substance are physically adsorbed. The type of adsorption that affects the rate of a chemical reaction is chemisorption. Here, the adsorbed atoms or molecules are held to the surface by valence forces of the same type as those that occur between bonded atoms in molecules. As a result, the electronic structure of the chemisorbed molecule is perturbed significantly, causing it to be extremely reactive. Interaction with the catalyst causes bonds of the adsorbed reactant to be stretched, making them easier to break.

2.7.4 Steps in a Catalytic Reaction

A photograph of different types and sizes of catalyst is shown in Figure 2.14. A schematic diagram of a tubular reactor packed with catalytic pellets is shown in Figure 2.15. The overall process by which heterogeneous catalytic reactions proceed can be broken down into the sequence of individual steps shown in Figure 2.16 for an isomerization reaction.

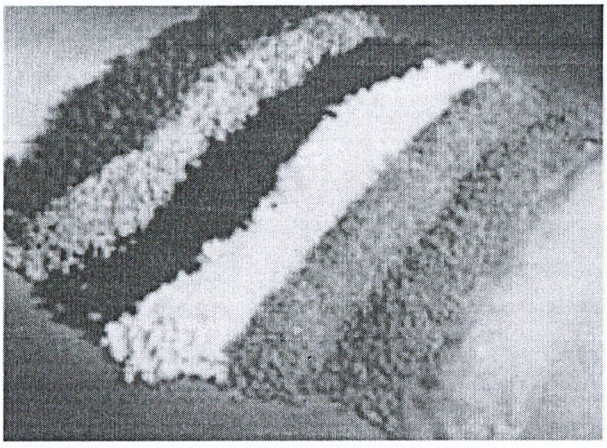


Figure 2.14 Different shapes and Sizes of Catalyst

[H. Scott Fogler, 2014]

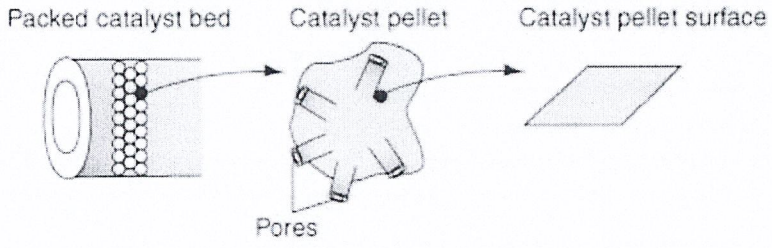


Figure 2.15 Catalytic Packed-bed Reactor—Schematic

[H. Scott Fogler, 2014]

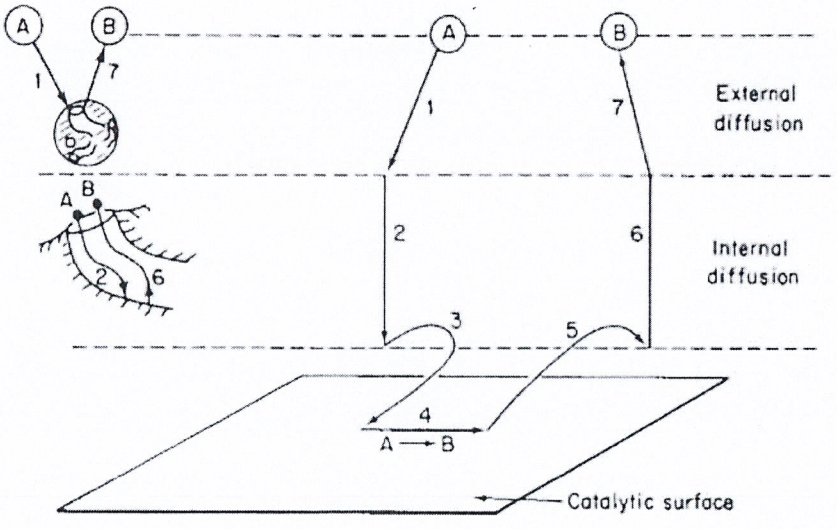


Figure 2.16 Steps in a Heterogeneous Catalytic Reaction

[H. Scott Fogler, 2014]

Each step is shown schematically in Figure 2.16.

1. Mass transfer (diffusion) of the reactant(s) (e.g., species A) from the bulk fluid to the external surface of the catalyst pellet
2. Diffusion of the reactant from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalytic surface
3. Adsorption of reactant A onto the catalyst surface
4. Reaction on the surface of the catalyst (e.g., A → B)
5. Desorption of the products (e.g., B) from the surface
6. Diffusion of the products from the interior of the pellet to the pore mouth at the external surface
7. Mass transfer of the products from the external pellet surface to the bulk fluid

The overall rate of reaction is limited by the rate of the slowest step in the mechanism. When the diffusion steps (1, 2, 6, and 7) are very fast compared with the reaction steps (3, 4, and 5), the concentrations in the immediate vicinity of the active sites are indistinguishable from those in the bulk fluid. In this situation, the transport or diffusion steps do not affect the overall rate of the reaction. ln other situations, if the reaction steps are very fast compared with the diffusion steps, mass transport does affect the reaction rate. In systems where diffusion from the bulk gas or liquid to the catalyst surface or to the mouths of catalyst pores affects the rate, changing the flow conditions past the catalyst should change the overall reaction rate. In porous catalysts, on the other hand, diffusion within the catalyst pores may limit the rate of reaction and, as a result, the overall rate will be unaffected by external flow conditions even though diffusion affects the overall reaction rate.

2.8 Types of Catalyst Deactivation [H. Scott Fogler, 2014]

There are three categories into which the loss of catalytic activity can traditionally be divided: sintering or aging, fouling or coking, and poisoning.

2.8.1 Deactivation by Sintering (Aging).

Sintering, also referred to as aging, is the loss of catalytic activity due to a loss of active surface area resulting rom the prolonged exposure to high gas-phase temperatures. The active surface area may be lost either by crystal agglomeration and growth of the metals deposited on the support or by narrowing or closing of the pores inside the catalyst pellet. A

change in the surface structure may also result from either surface recrystallization or the formation or elimination of surface defects (active sites). The reforming of heptane over platinum on alumina is an example of catalyst deactivation as a result of sintering.

Figure 2.17 shows the loss of surface area resulting from the flow of the solid porous catalyst support at high temperatures to cause pore closure. Figure 2.18 shows the loss of surface area by atomic migration and agglomeration of small metal sites deposited on the surface into a larger site where the interior atoms are not accessible to the reaction. Sintering is usually negligible at temperatures below 40% of the melting temperature of the solid.

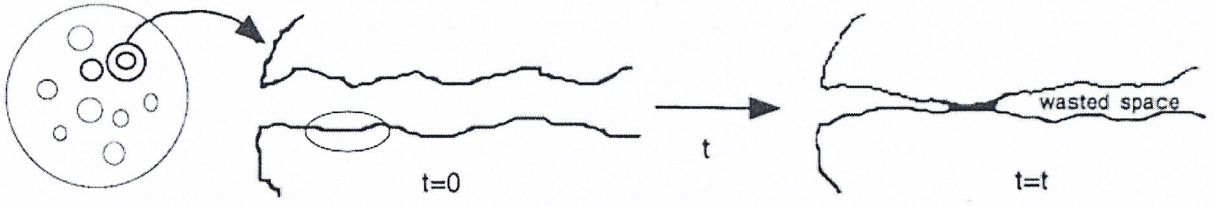


Figure 2.17 Decay by Sintering: Pore Closure
[H. Scott Fogler, 2014]

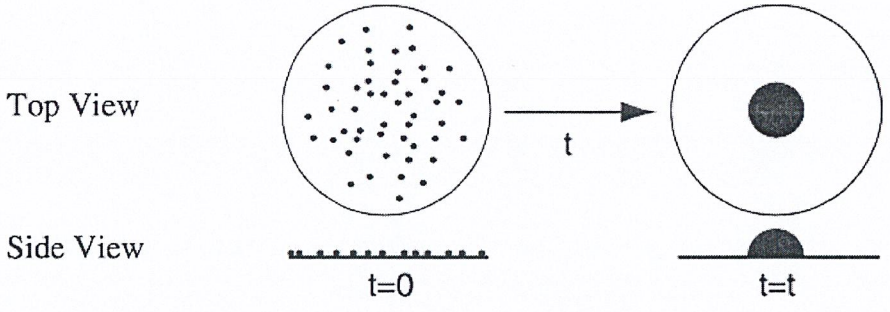


Figure 2.18 Decay by Sintering: Agglomeration of Deposited
[H. Scott Fogler, 2014]

2.8.2 Deactivation by Coking or Fouling

This mechanism of decay (see Figures 2.19 and 2.20) is common to reactions involving hydrocarbons. It results from a carbonaceous (coke) material being deposited on the surface of a catalyst. The amount of coke on the surface after a time t has been found to obey the following empirical relationship:

$$C_C = At^n \qquad (2.15)$$

Where C_C is the concentration of carbon on the surface (g/m^2) and n and A are fouling parameters, which can be functions of the feed rate. When possible, coking can be reduced by running at elevated pressures and hydrogen-rich streams. Catalysts deactivated by coking can usually be regenerated by burning off the carbon.

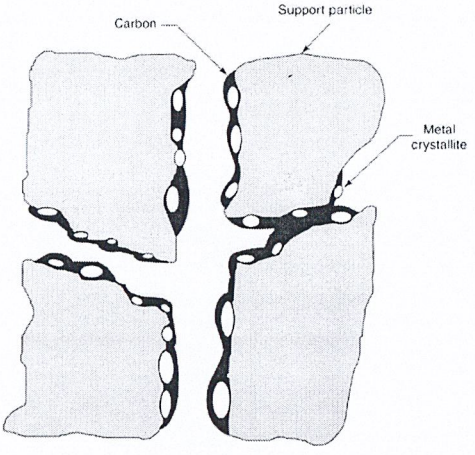
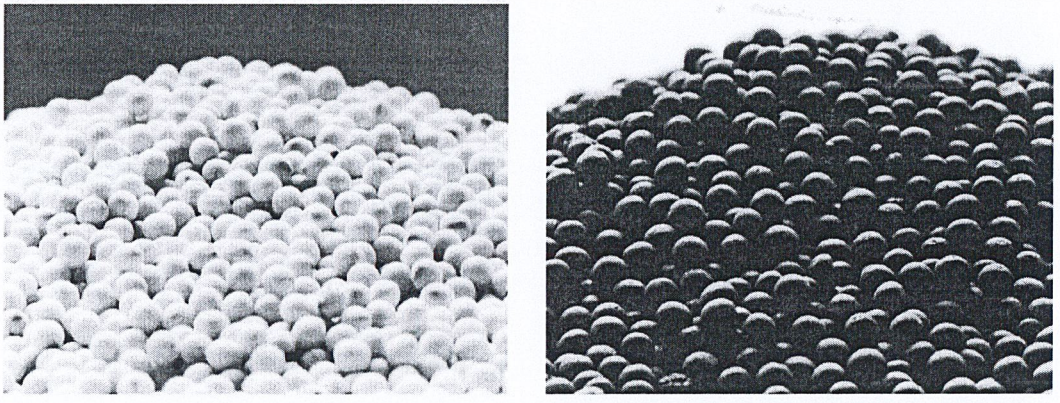


Figure 2.19 Schematic of Decay by Coking

[H. Scott Fogler, 2014]



(a) Fresh catalyst (b) Spent catalyst

Figure 2.20 Decay by Coking

[H. Scott Fogler, 2014]

2.8.3 Deactivation by Poisoning

Deactivation by this mechanism occurs when the poisoning molecules become irreversibly chemisorbed to active sites, thereby reducing the number of sites available for the

main reaction. The poisoning molecule, P, may be a reactant and/or a product in the main reaction, or it may be an impurity in the feed stream.

Poison in the feed. Many petroleum feed stocks contain trace impurities such as sulfur, lead, and other components which are too costly to remove, yet poison the catalyst slowly over time. For the case of an impurity, P, in the feed stream, such as sulfur. The surface sites would change with time as shown in Figure 2.21.

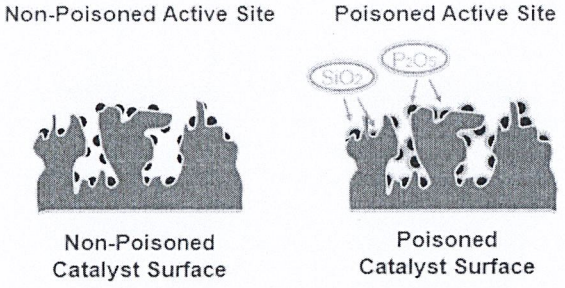


Figure 2.21 Decay by Poisoning
[Nikki Universal Co., Ltd., 2015]

2.9 Catalytic Oxidizer [SMPC, 2016]

Waste gas (WG) stream enters CATOX, most of the organic compounds in WG are converted to carbon dioxide and water in the catalyst bed. The catalyst is Cu and Mn based on alumina. The carbon monoxide in WG is converted to carbon dioxide. The oxidation of methyl bromide also produces elemental bromine, Br_2. The heat release from the catalytic oxidation of WG raises the temperature of WG stream about 100 °C to an exit temperature near 390 °C. The HPVGT performance is regulated by adjusting bypass flow of heat exchanger to control the inlet temperature to CATOX. Control of both CATOX inlet and outlet temperatures is necessary for proper temperature control. The differential across the catalyst bed is a good indicator of changes in vent stream combustible's content. A rise in the temperature differential could be an indication of a rise in the vent stream combustible's content. If temperature control cannot be achieved by adjusting bypass flow of heat exchanger, then the HPVGT system should be bypassed and purged. The stream exiting CATOX passes through on the tube side of heat exchanger. It is cooled by the exit gas from heat exchanger to 195 °C before entering the bottom quench section of vent scrubber. The primary purpose for the quench section in heat exchanger is to cool WG below a maximum scrubber exit temperature of 40°C. This exit temperature must

be maintained whenever the vent from heat exchanger is used in adsorber in order to maintain the required performance of the desiccant. Then, dry gas is recovered or released to environment as shown in Figure 1.1.

2.9.1 Catalyst Replacement

From design of the CATOX, used and fresh catalyst positions as shown in Figure 2.22. Overall layers can be separated into 2 layers (Top and Bottom) which fix in 50 wt%. Top is the address of the used catalyst and bottom for fresh catalyst. In each replacement of the catalyst, used catalyst (Red Zone) is wasted and fresh catalyst (Green Zone) is reused. 50 wt% of fresh catalyst (Yellow Zone) is replaced for located at the bottom of column as shown in Figure 2.22.

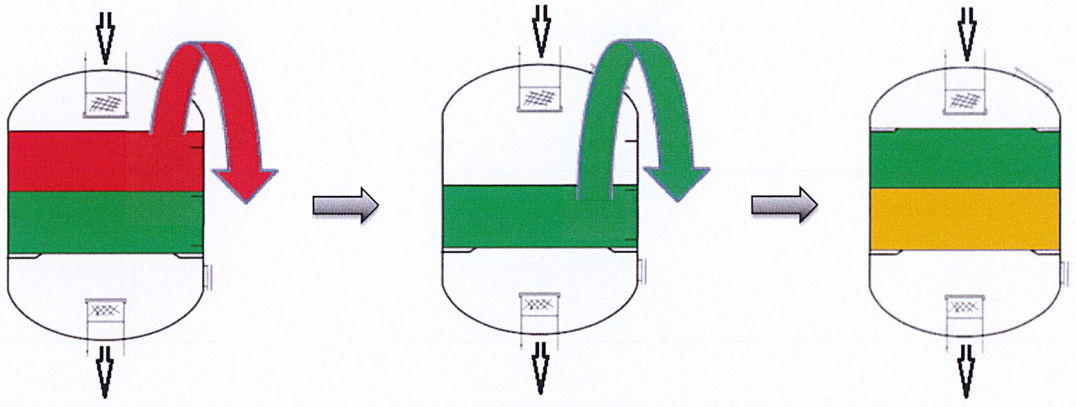


Figure 2.22 Steps of Catalyst Replacement
[SMPC Plant Number 3, 2016]

2.9.2 Reaction in the CATOX

The oxidation reaction destroys the hydrocarbons in a vapor stream at elevated temperatures by oxidizing the hydrocarbons to carbon dioxide and water. The chemical reaction for oxidation is as follows:

$$C_xH_y + (x+y/4)O_2 + \text{Heat} \rightarrow xCO_2 + y/2H_2O + \text{Heat} \quad (2.5)$$

$$4CH_3Br + 7O_2 \rightarrow 2Br_2 + 4CO_2 + 6H_2O + \text{Heat} \quad (2.16)$$

$$2CO + O_2 \rightarrow 2CO_2 + \text{Heat} \quad (2.17)$$

From the reaction, the catalyst deactivated is estimated by use heat transfer of reaction. Oxidation reaction is exothermic reaction, and reaction will be occurring when operation at high temperature or operation at low temperature by catalyst. The inlet temperature (around 300 °C) is not high enough for reaction by itself. Therefore, when the catalyst deactivates, the reaction will not occur. Then, the temperature does not increase.

2.10 Adsorption [W. L. McCable, J. C. Smith, and P. Harriott, 2015]

Normally, fluid is passed through the packed bed at the constant flow rate. At the inlet to the bed, the solid is assumed to contain no solute at the start of the process. As the fluid first comes in contact with the inlet of the bed, most of the mass transfer and adsorption takes place here. As the fluid passes through the bed, the concentration in this fluid drops very rapidly with distance in the bed and reaches zero well before the end of the bed is reached. The concentration profile at the start at time t_1 is shown in Figure 2.23, where the concentration ratio c/c_0 is plotted versus bed height. The fluid concentration c_0 is the feed concentration and c is the fluid concentration at a point in the bed.

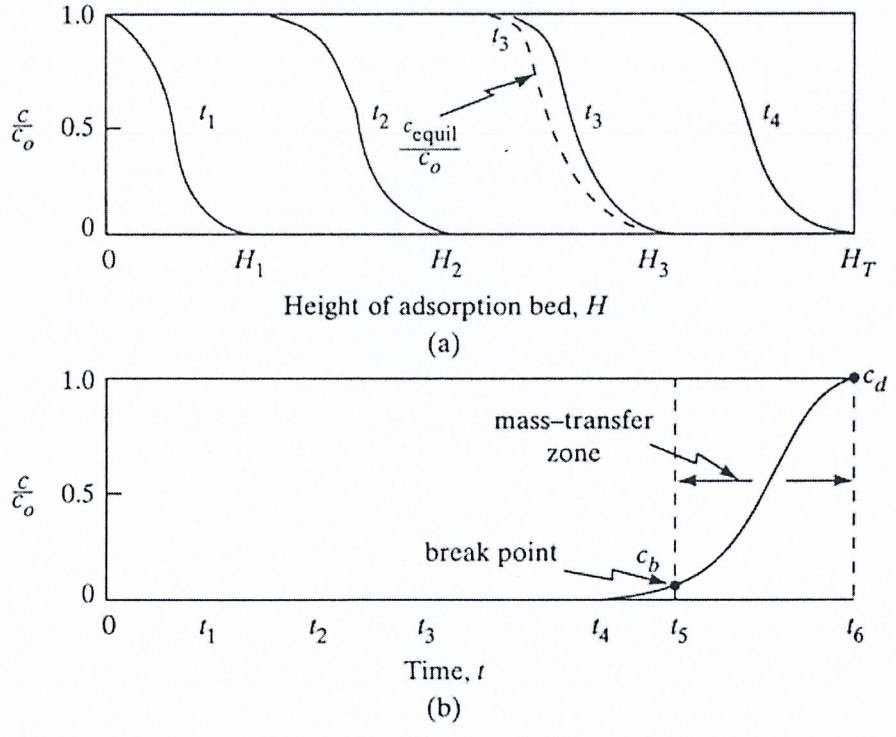


Figure 2.23 (a) Profiles at Various Positions and Times in the Bed, (b) Breakthrough Concentration Profile in the Fluid at Outlet of Bed
[W. L. McCable, J. C. Smith, and P. Harriott, 2015]

After a short time, the solid near the entrance to the tower is almost saturated, and most of the mass transfer and adsorption now takes place at a point slightly farther from the inlet. At a later time t_2, the profile or mass-transfer zone where most of the concentration change takes place has moved farther down the bed. The concentration profiles shown are for the fluid phase. Concentration profiles for the concentration of adsorbates on the solid would be similar. The solid at the entrance would be nearly saturated, and this concentration would remain almost constant down to the mass-transfer zone, where it would drop off rapidly to almost zero. The dashed line for time t_3 shows the concentration in the fluid phase in equilibrium with the solid. The difference in concentrations is the driving force for mass transfer.

2.2.10.1 Breakthrough concentration curve

As seen in Figure 2.23a, the major part of the adsorption at any time takes place in a relatively narrow adsorption or mass-transfer zone. As the solution continues to flow, this mass-transfer zone, which is S-shaped, moves down the column. At a given time t_3 in Figure 2.23a, when almost half of the bed is saturated with solute, the outlet concentration is still approximately zero, as shown in Figure 2.23b. This outlet concentration remains near zero until the mass-transfer zone starts to reach the tower outlet at time t_4. Then the outlet concentration starts to rise, and at t_5 the outlet concentration has risen to c_b, which is called the break point.

After the break-point the concentration is rapidly rise to the point c_4 which is the end of the breakthrough curve. The break-point concentration represents the maximum that can be discarded and is often taken as 0.01 to 0.05 for c_b/c_0.

2.10.2 Capacity of column and scale-up design method

Typically, adsorption process is designed by using results from experiments in laboratory scale. It is more accurate than predicted results from diffusion and mass transfer. The total shaded area represents the total or stoichiometric capacity of the bed as shown in Figure 2.24. It is calculated by

$$t_t = \int_0^{\infty} (1 - \frac{c}{c_0}) dt \tag{2.18}$$

The usable capacity of the bed up to the break-point time t_b is the crosshatched area as shown in Figure 2.24. It is calculated by

$$t_u = \int_0^{t_b} (1 - \frac{c}{c_0}) dt \tag{2.19}$$

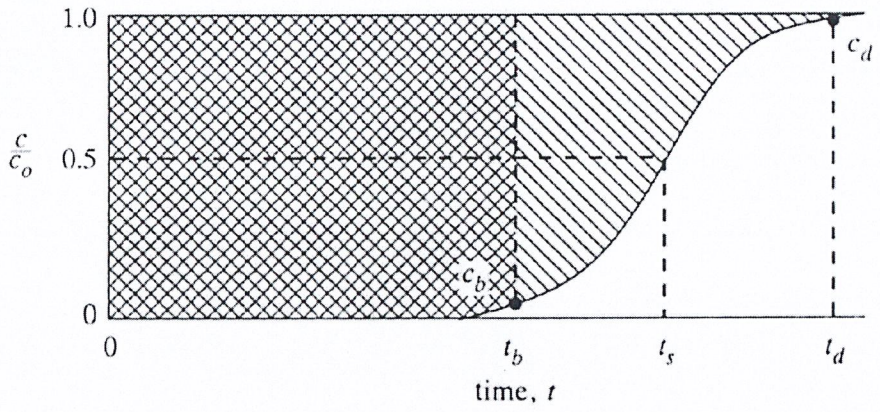


Figure 2.24 Determination of Capacity of Column from Breakthrough Curve [W. L. McCable, J. C. Smith, and P. Harriott, 2015]

The ratio of t_u/t_t is the fraction of the total bed capacity or length utilized up to the break point. Hence, for a total bed length of H_T, H_B is the length of bed used up to the break point.

$$H_B = \frac{t_u}{t_t} H_T \tag{2.20}$$

The length of unused bed H_{UNB} is then the unused fraction times the total length

$$H_{UNB} = (1 - \frac{t_u}{t_t}) H_T \tag{2.21}$$

The H_{UNB} represents the mass transfer section which is depend on the fluid velocity. However, it is independent of total length of the column. Therefore, H_{UNB} is measured by using laboratory scale which is used small diameter laboratory column packed with designed adsorbent as same as in this project which find breakthrough curve from literature. It is shown later. Then the full-scale adsorber bed can be designed simply by first calculating the length of bed needed to achieve the required usable capacity, H_B, at the break point. The value of H_B is directly proportional to t_b. Then the length H_{UNB} of the mass-transfer section is simply added to the length H_B needed to obtain the total length, H_T

$$H_T = H_{UNB} + H_B \tag{2.22}$$

This is widely used for design method. It depends on the conditions in the laboratory column being similar to those for the full-scale unit. In the scale-up, not only may it be necessary to change the column height, but also the actual throughput of fluid might be different from that used in the experimental laboratory unit. Since the mass velocity in the bed must remain constant for scale-up, the diameter of the bed should be adjusted to keep it constant. However, it should be used spare are around 50% of used bed for design.

2.11 Pressure Swing Adsorption (PSA) [The Linde Group, 2016]

Pressure swing adsorption is the one of adsorption process type which is used for removing one or more components of a moisture or liquid stream. It is removed by adsorb unwanted components (adsorbate) on the surface of the solid (adsorbent). In commercial processes, the adsorbent is usually in the form of small particles in a fixed bed. The stream line is passed through the bed and the solid particles adsorb unwanted components from the steam line. When the bed is almost saturated, the flow is changed to the other beds to adsorb unwanted. For the old bed, it is regenerated by using the pure product. However, it is normally regenerated by using thermal so that desorption occurs.

2.2.11.1 Physical Properties of adsorbents [Zhe Xu, 2013]

Many adsorbents have been developed for several years for a wide range of separations. Typically, the adsorbents are in the form of small pellets or beads. The ad sorption often occurs as a monolayer on the surface of the fine pores, although several layers sometimes occur. Physical adsorption, or van der Waals adsorption, usually occurs between the adsorbed molecules and the solid internal pore surface.

For the adsorption process, it has several steps which is in series as shown in Figure 2.25.

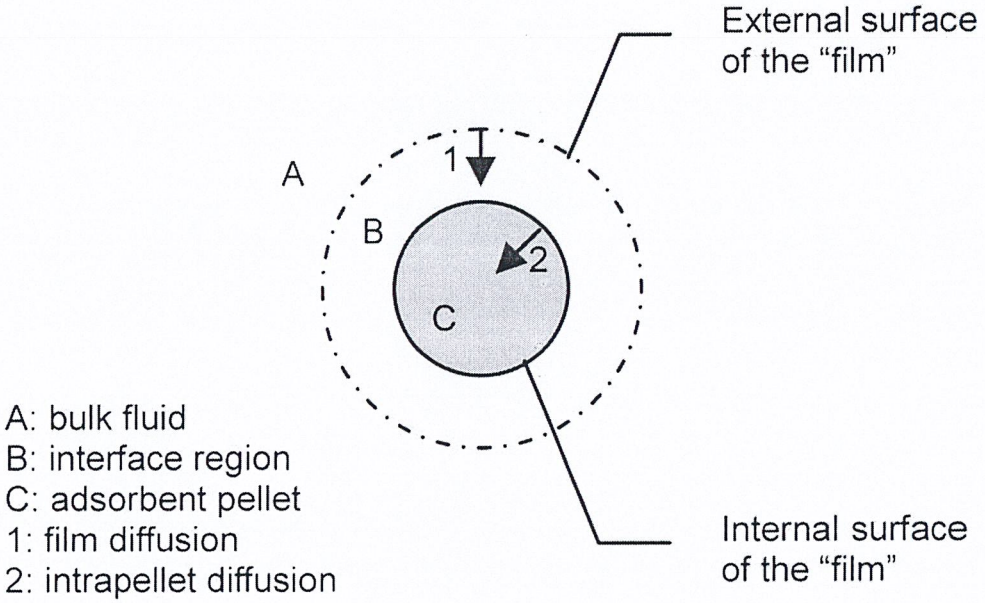


Figure 2.25 Adsorption Process

[Zhe Xu, 2013]

When the fluid is flowing past the particle in a fixed bed, the solute first diffuses from the bulk fluid to the gross exterior surface of the particle. Then the solute diffuses inside the pore to the surface of the pore. Finally, the solute is adsorbed on the surface.

2.2.11.2 The nature of adsorbents

For the good adsorbents, it should have the highest surface area and lowest pressure drop for flow through the bed. To be attractive commercially, an adsorbent should embody these features.

1. It should have a large internal surface area.
2. The area should be accessible through pores big enough to admit the molecules to be adsorbed. It is a bonus if the pores are also small enough to exclude molecules which it is desired not to adsorb.
3. The adsorbent should be capable of being easily regenerated.
4. The adsorbent should not age rapidly, that is lose its adsorptive capacity through continual recycling.
5. The adsorbent should be mechanically strong enough to withstand the bulk handling and vibration that are a feature of any industrial unit.

2.2.11.3 Commercial adsorbents

There are several commercial adsorbents which is chosen from several applications. If engineer choose wrong adsorbent for any application, adsorption process for separation will have the failure or cannot separate adsorbate from stream. So, the commercial adsorbents are described below.

1. Activated Carbon. It is made by thermal decomposition of wood, vegetable shells, coal and others. It has surface areas of 300 to 1200 m^2/g with average pore diameter of 10 to 60 Angstrom. Activated carbon may be used as a powder which mixed with the liquid to be treated and then removed by filtration. It may also be used in granular form. When the use of carbon is low, it is normally economic to regenerate it.
2. Silica gel. This is made by acid treatment of sodium silicate solution and then drying. Unlike the activate carbons, the surface of silica gel is hydrophilic and it is commonly used for drying gases and also finds applications where there is requirement to remove unsaturated hydrocarbons.

3. Activated alumina. It is used when required high resistant to attrition. It is high capacity more than silica gel at higher temperatures. It is made by controlled heating of hydrated alumina. Activated alumina has a high affinity for water in particular and for hydroxyl groups in general. It cannot compete in terms of capacity or selectivity with molecular sieves although its superior mechanical strength is important in moving-bed applications.
4. Molecular sieve (zeolites). These zeolites are porous crystalline aluminosilicates that form an open crystal lattice congaing precisely uniform pores, which makes it different from other types of adsorbents. It has a rage of pore sizes. Zeolite are used for drying, separation of hydrocarbons, mixtures, and many other applications.
5. Synthetic polymers (resins). These are made by polymerizing two major types of monomers. Those made from aromatics such as styrene and divinylbenzene are used to adsorb nonpolar organics from aqueous solutions. Those made from acrylic esters are usable with more-polar solutes in aqueous solutions.

2.2.11.4 PSA in SMPC

Pressure swing adsorption is a widely used technology for the purification of gases. This regeneration process is accomplished by reducing the pressure. At the moderate pressures found in compressed air systems, such as 100 pounds per square inch, an adsorbent can support a certain amount of moisture. When that pressure is dropped to ambient air pressure, the adsorbent can only support a smaller amount of moisture. By swinging the pressure from high to low, it is possible to adsorb large quantities of moisture at the higher pressure, and then release that moisture at the low pressure. This technique is called pressure swing adsorption. By alternating between two adsorbent filled vessels, one vessel being on line and removing moisture at high pressure, and the other off line releasing the trapped moisture at low pressure, it is possible to thoroughly dry a gas.

Adsorption of impurities is carried out at high pressure being determined by the pressure of the feed gas. The feed gas flows through the adsorber vessels in an upward direction. Impurities such as water, heavy hydrocarbons, light hydrocarbons, CO_2, CO and nitrogen are selectively adsorbed on the surface of the adsorbent material.

The pressure swing adsorption process has four basic process steps:

- Adsorption
- Depressurization
- Regeneration
- Repressurization

For Regeneration, the regeneration phase consists of basically five consecutive steps:

- Pressure equalization

Depressurization starts in the co-current direction from bottom to top. The hydrogen still stored in the void space of the adsorbent material is used to pressurize another adsorber having just terminated its regeneration. Depending on the total of adsorbers and the process conditions, one to four of these so-called pressure equalization steps are performed. Each additional pressure equalization step minimizes hydrogen losses and increases the hydrogen recovery rate.

- Provide purge

This is the final depressurization step in co-current direction providing pure hydrogen to purge or regenerate another adsorber.

- Dump

At a certain point of time, the remaining pressure must be released in counter-current direction to prevent break-through of impurities at the top of the adsorber. This is the first step of the regeneration phase when desorbed impurities leave the adsorber at the bottom and flow to the tail gas system of the PSA plant.

- Purging (regeneration)

Final desorption and regeneration is performed at the lowest pressure of the PSA sequence.

- Repressurization

Before restarting adsorption, the regenerated adsorber must be pressurized again. This is accomplished in the pressure equalization step by using pure hydrogen from adsorbers presently under depressurization. Since final adsorption pressure cannot be reached with pressure equalization steps, repressurezation to adsorption pressure is carried out with a split

stream from the hydrogen product line. Having reached the required pressure level again, this regenerated adsorber takes over the task of adsorption from another vessel having just terminated its adsorption.

PSA uses a number of adsorption columns in a cycle. The columns are packed with an adsorbent. There are different adsorbents to choose from, depending on the impurities in the feed stream as shown in Table 2.1.

Table 2.1: The different adsorbents in the PSA

Type	**Main Adsorption Duty**
Aluminum oxides	Water
Silica gel	Water, CO_2, C_{4+}
Activated carbon	CO_2, CH_4, C_{2+} ,N_2
Molecular sieve (zeolite)	CH_4, CO, N_2
Carbon molecular sieve	O_2

The separation process using PSA is based on adsorption and is used for purification of gases like hydrogen in refineries. Depending on the process, adsorbents like molecular sieve, activated carbon, and silica gel are used in PSA beds. For adsorb from off-gas steam, activated carbon and silica gel are used most of the time as used in PTA process.

2.12 Adsorbent Replacement [SMPC, 2016]

The adsorbent in adsorber is sucked out, and it is screened by size selection. The adsorbent was screened (size diameter bigger than 3 mm.), it is reloaded again in bottom of column (fix 40-50 % of column). Then, the new adsorbent is loaded in upper around 50-60% of column as shown in Figure 2.26.

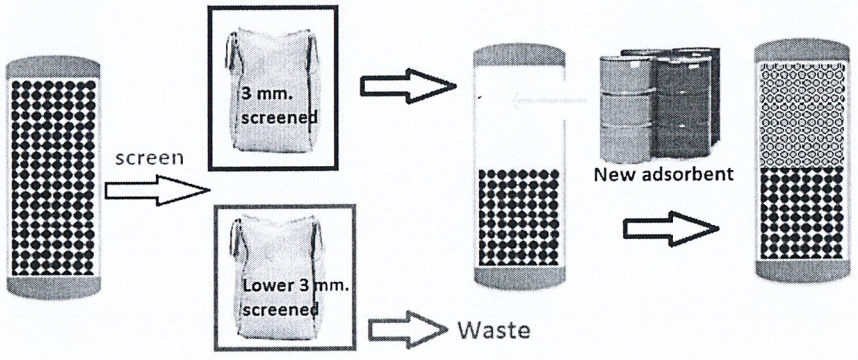


Figure 2.26 Step of Adsorbent Replacement
[SMPC, 2016]

CHAPTER III
RESEARCH METHODOLOGY

The research methodology has 2 parts that are catalyst replacement and adsorbent replacement. Root cause of catalyst and adsorbent replacement is identified by analysis. Catalyst replacement ratio is estimated by reaction temperature of the CATOX. Conversion calculation is used to check the reaction in the CATOX. Estimated data is used to calculate optimize and cost saving of catalyst replacement. Adsorbent replacement is estimated by monitoring used silica gel. Adsorbed efficiency is analyzed for reusable used adsorbent. Amount of reusable used adsorbent is used to calculate optimize and cost saving of adsorbent replacement.

3.1 Catalyst Replacement

3.1.1 Study the catalyst replacement and find root cause of the catalyst replacement

3.1.1.1 Study operation and reaction in the CATOX

3.1.1.2 Study procedure of catalyst replacement in each times

3.1.1.3 Analyze inlet stream components of the CATOX

3.1.1.4 Take sampling of used catalyst to component test

3.1.2 Set new layer in column for estimation

Divide the layer of the CATOX from 2 layers to 3 layers by based on installed temperature indicators as shown in Figure 3.1.

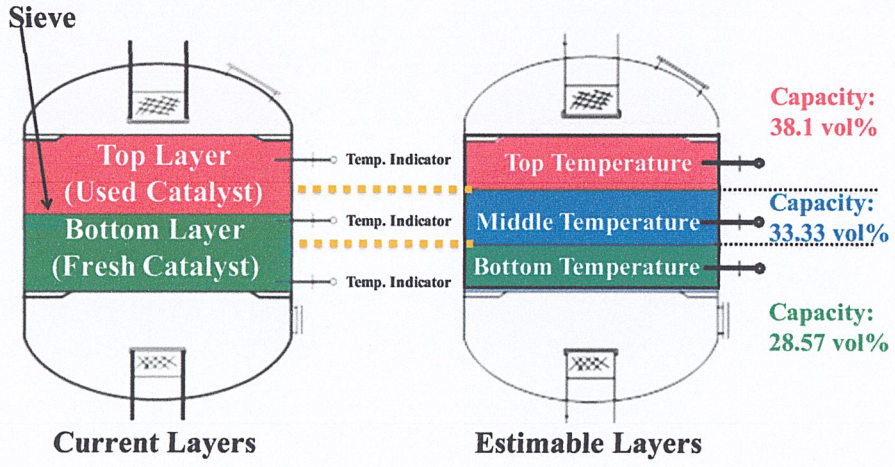


Figure 3.1 Estimable Layers
[SMPC Plant Number 3, 2016]

3.1.3 Estimate life time of catalyst and new ratio of catalyst replacement

3.1.3.1 Find the temperature in each layer

3.1.3.2 Estimate range of time at the decrease in temperature reaction

3.1.3.3 Estimate the decrease in temperature reaction for 1-year operation

3.1.3.4 Optimize new ratio of the catalyst replacement

3.1.3.5 Calculate cost saving

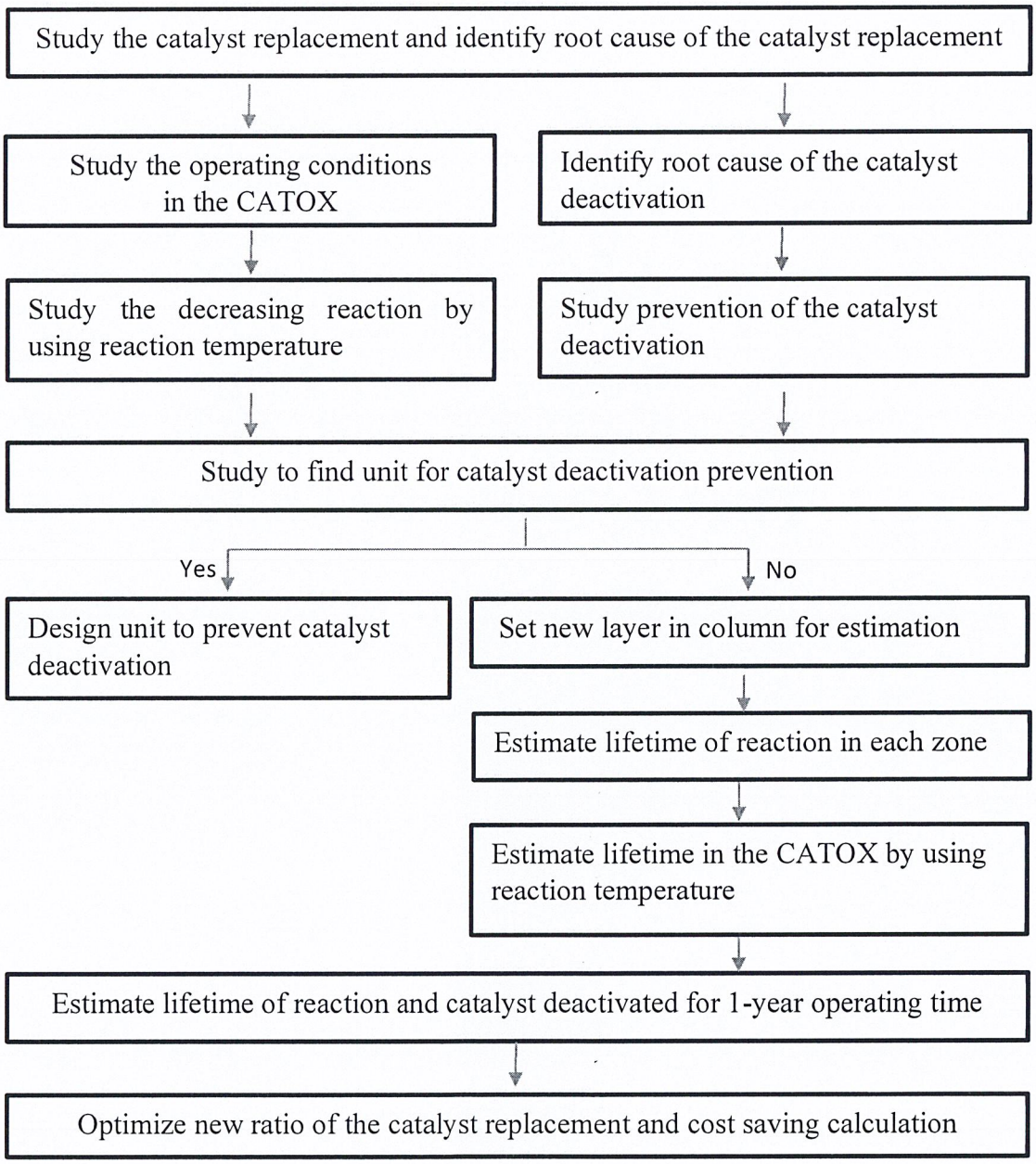


Figure 3.2 Flow Chart of Analytical Catalyst Replacement
[SMPC Plant Number 3, 2016]

3.2 Adsorbent Replacement

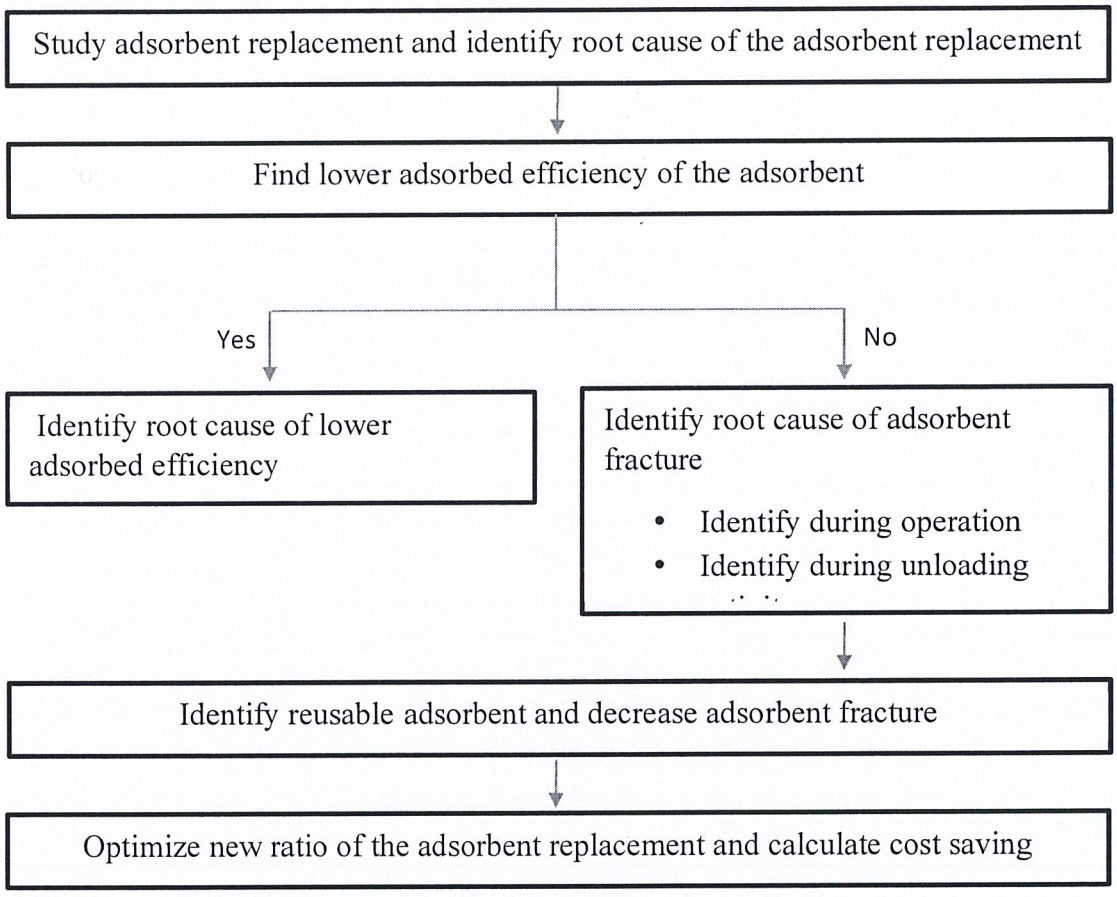


Figure 3.3 Flow Chart of Analytical Adsorbent Replacement [SMPC Plant Number 3, 2016]

3.2.1 Study and identify root cause of the adsorbent replacement

3.2.1.1 Study operation of the adsorber

3.2.1.2 Study procedure of adsorbent replacement every year

3.2.1.3 Analyze inlet stream components of the adsorber

3.2.2 Find lower adsorbed efficiency of the adsorbent

3.2.2.1 Find dew point in outlet stream of the adsorber

3.2.2.2 Analyze adsorbing ability of used adsorbent

3.2.3 Identify root cause of adsorbent fracture

3.2.3.1 Find pressure drop of the adsorber

3.2.3.2 Calculate flow rate of adsorber inlet stream

3.2.3.3 Identify adsorbent fracture during unloading activity

3.2.4 Optimize new ratio of the adsorbent

CHAPTER IV
RESULTS AND DISCUSSION

4.1 Optimization of Catalyst Replacement

4.1.1 The Reaction in the CATOX

Since the second oxidation reactor and MA recovery unit had been installed in 2013. It is decreasing the byproduct (hydrocarbons) occurrence rate. For this reason, the temperature in a reactor is also fell by 110 to 75 °C as shown in Figure 4.1. Moreover, the use rate of CATOX has been decreasing as a result of low hydrocarbons in the waste gases. As was previously stated, it indicated that the deactivation of catalyst might be decreased.

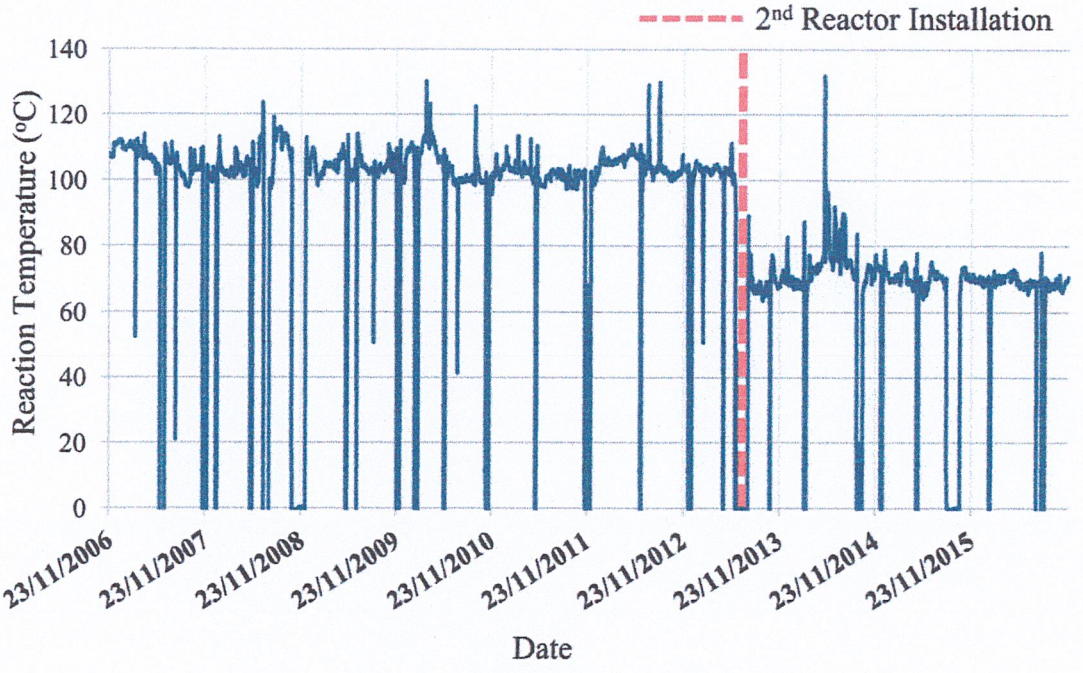


Figure 4.1 The Reaction Temperature since 2006
[SMPC Plant Number 3, 2016]

4.1.2 Components in the Waste Gases

Components in the waste gases were identified by analytical laboratory and gases detector in inlet stream of the CATOX. The components in waste gases consist of nitrogen (N_2), oxygen (O_2), carbon dioxide (CO2), steam (H_2O), carbon monoxide (CO), methyl acetate (MA), para-xylene (PX), methanol (MeOH), methyl bromide (MeBr), benzene, and toluene as shown in Table 4.1. To point out nitrogen gas considered to be the

major part of the waste gasses. On the other hand, hydrocarbons are the minor part of the waste gases.

Table 4.1 Components in the Waste Gases [SMPC Plant Number 3, 2016]

Components	Plant Number 3
WG Flow Rate (kmol/h)	6,670.04
Nitrogen (kg/h)	174,861.43
Oxygen (kg/h)	9,374.19
Carbon dioxide (kg/h)	3,224.22
Steam (kg/h)	698.01
Carbon monoxide (kg/h)	517.49
Methyl Acetate (kg/h)	286.63
p-Xylene (kg/h)	37.58
Methanol (kg/h)	21.93
Methyl Bromide (kg/h)	2.88
Benzene (kg/h)	2.77
Toluene (kg/h)	1.85

4.1.3 Cause of Catalyst Replacement

4.1.3.1 Deactivation by Sintering (Aging)

The CATOX is operated at low temperature when compare with melting point of Cu/Mn calatyst. Sintering is loss of surface area due to high operating temperature. So, sintering does not occur in the catalyst.

4.1.3.2 Deactivation by Coking or Fouling

Coking is physical blockage of surface by carbon or dust. The reaction in the CATOX is exothermic reaction as shown in Equation 4.1, 4.2, and 4.3.

$$C_xH_y + x+(y/4)O_2 \rightarrow xCO_2 + y/2H_2O + Heat \quad (4.1)$$

$$4CH_3Br + 7O_2 \rightarrow 2Br_2 + 4CO_2 + 6H_2O + Heat \quad (4.2)$$

$$2CO + O_2 \rightarrow 2CO_2 + Heat \quad (4.3)$$

The hydrocarbons are burned in the CATOX and the decrease in reaction temperature depends on operating time after catalyst replacement as shown in Figure 4.2. It is shown that the catalyst is deactivated by coking. The sampling used of the catalyst is correlated with the fresh catalyst as shown in Figure 4.3. The active site of catalyst will be coated by coking of hydrocarbons as a brown catalyst.

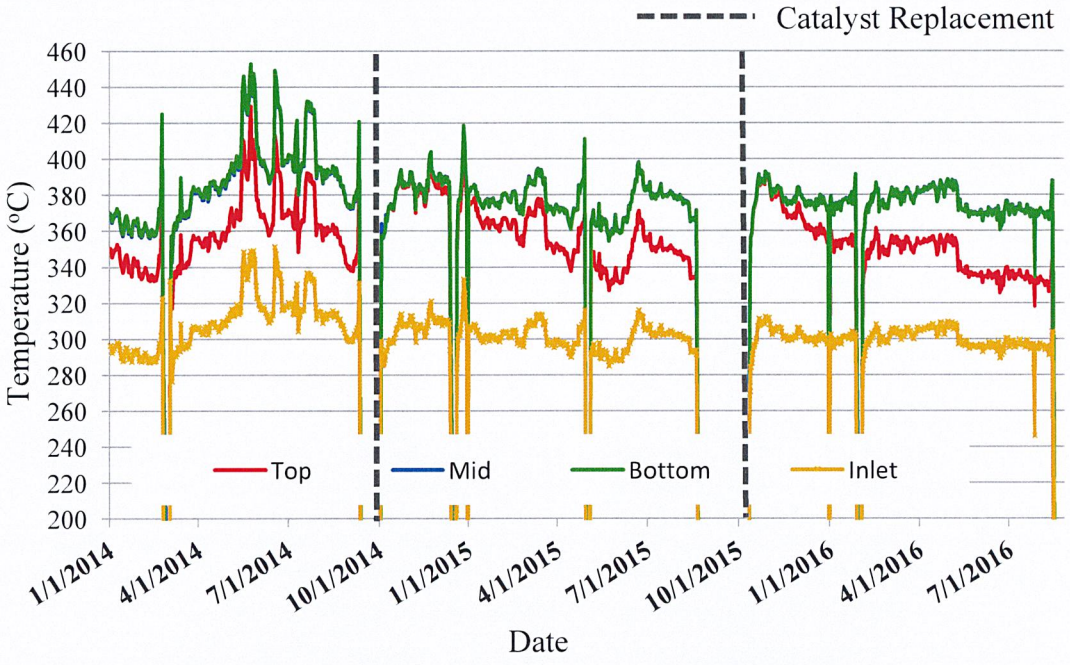
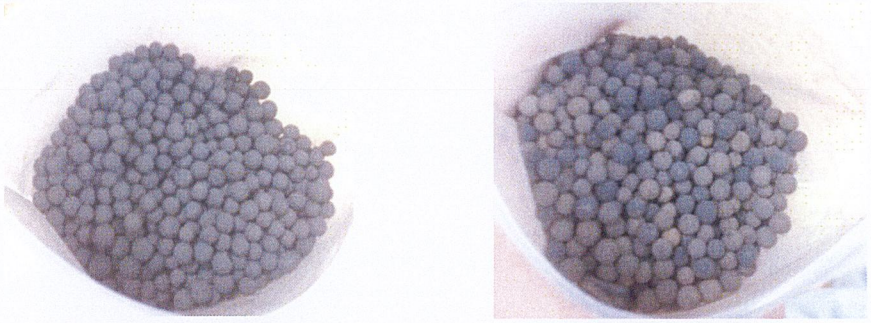


Figure 4.2 Operating Temperature of the CATOX since 2014
[SMPC Plant Number 3, 2016]



Fresh Catalyst **Used Catalyst**

Figure 4.3 Sampling of Used Catalyst
[SMPC Plant Number 3, 2016]

4.1.3.3 Deactivation by Poisoning

The silicon is poison substance. The Cu/Mn on alumina is designed by Haldor Topsoe as vender for process which uses silicone oil as a solvent. So, poisoning does not occur in the catalyst.

4.1.4 Conversion of Hydrocarbons in Waste Gases

4.1.4.1 MA Conversion

The MA or Methyl Acetate is a hydrocarbon. The reaction completed as 100 percent conversion in the CATOX. Before the catalyst is replaced, the conversion is still high as shown in Figure 4.4.

4.1.4.2 PX Conversion

The PX or p-Xylene is a hydrocarbon. The reaction completed as 100 percent conversion in the CATOX. The conversion of PX is low in sometimes because of failure in operation or analytical laboratory in that time. Before the catalyst is replaced, the conversion is still high as shown in Figure 4.5.

4.1.4.3 MeOH Conversion

The MeOH or Methanol is a hydrocarbon. The reaction completed as 100 percent conversion in the CATOX. The conversion of MeOH is not stable but before the catalyst is replaced, the conversion is still high as shown in Figure 4.6.

4.1.4.4 MeBr Conversion

The MeBr or Methyl Bromide is a hydrocarbon. The reaction completed as 100 percent conversion in the CATOX. Before the catalyst is replaced, the conversion is still high as shown in Figure 4.7.

4.1.4.5 Benzene Conversion

The benzene is a hydrocarbon. The reaction completed as 100 percent conversion in the CATOX. The conversion of benzene is low in sometimes because of failure in operation or analytical laboratory in that time. Before the catalyst is replaced, the conversion is still high as shown in Figure 4.8.

4.1.4.6 Toluene Conversion

The toluene is a hydrocarbon. The reaction completed as 100 percent conversion in the CATOX. The conversion of toluene is low in sometimes because of failure in operation or analytical laboratory in that time. Before the catalyst is replaced, the conversion is still high as shown in Figure 4.9.

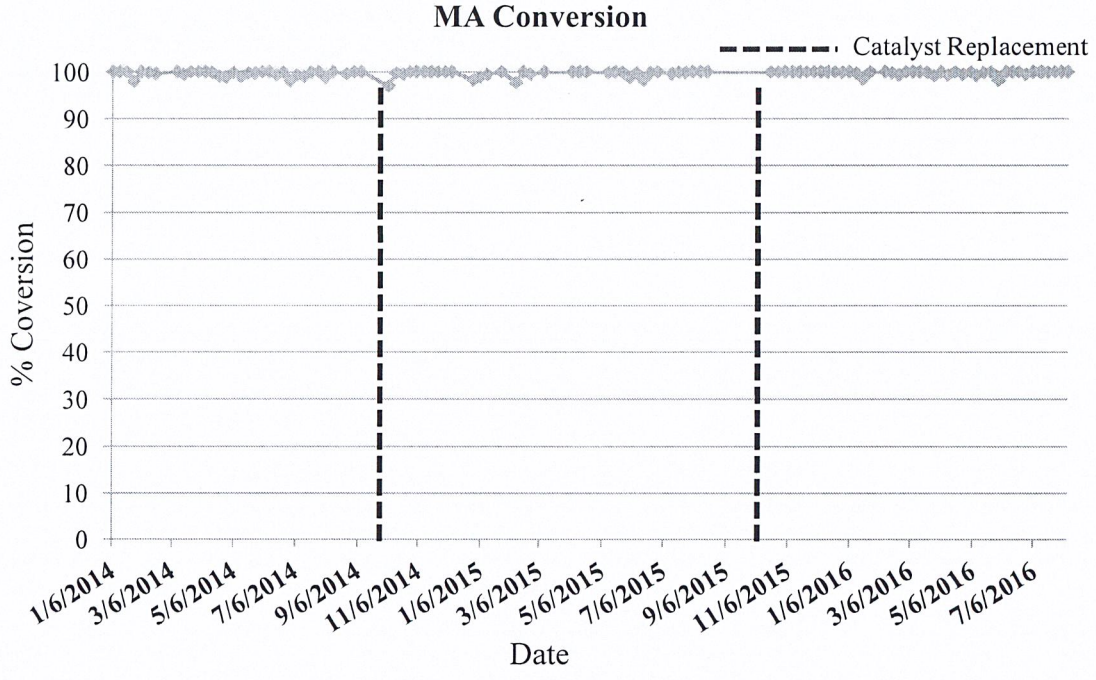


Figure 4.4 Conversion of MA
[SMPC Plant Number 3, 2016]

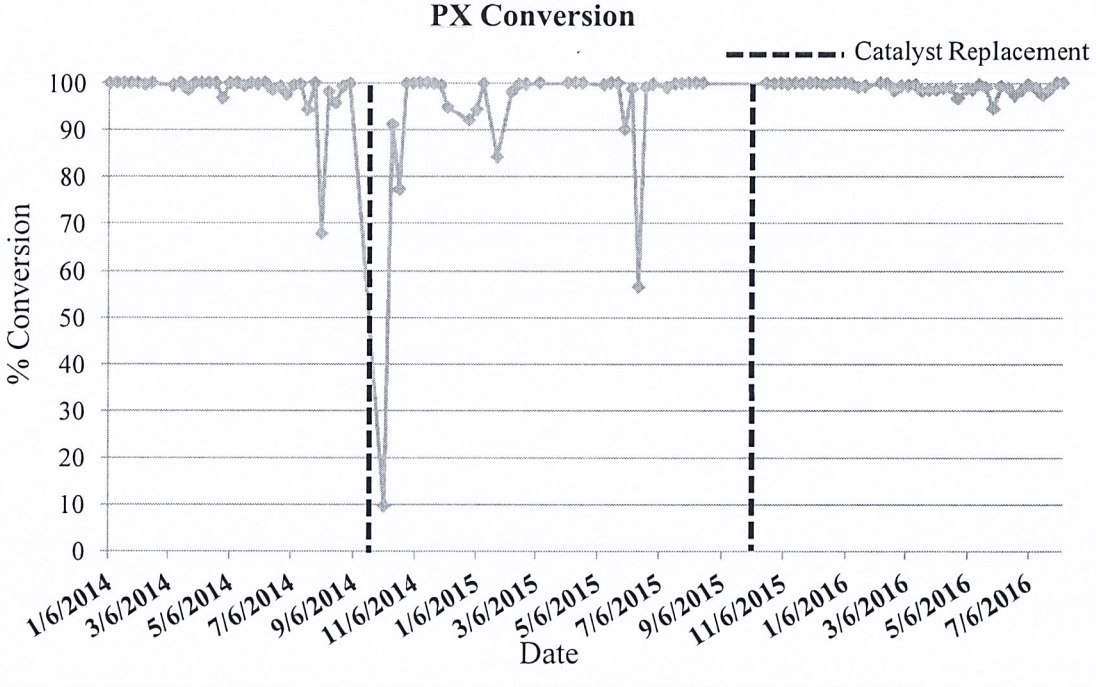


Figure 4.5 Conversion of PX
[SMPC Plant Number 3, 2016]

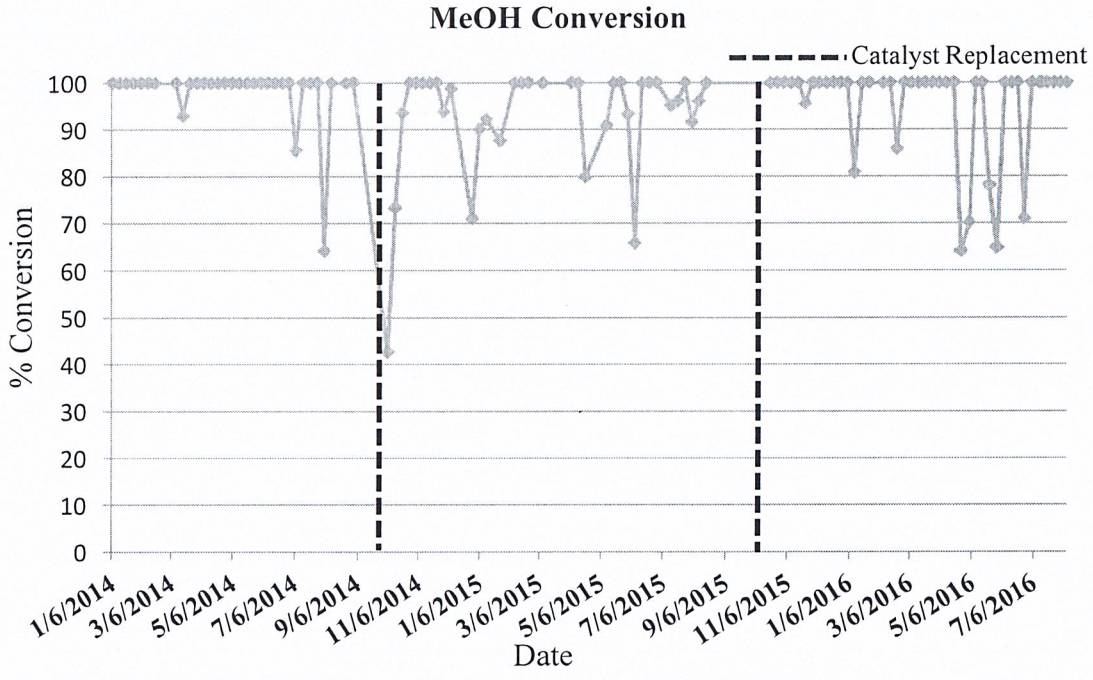


Figure 4.6 Conversion of MeOH
[SMPC Plant Number 3, 2016]

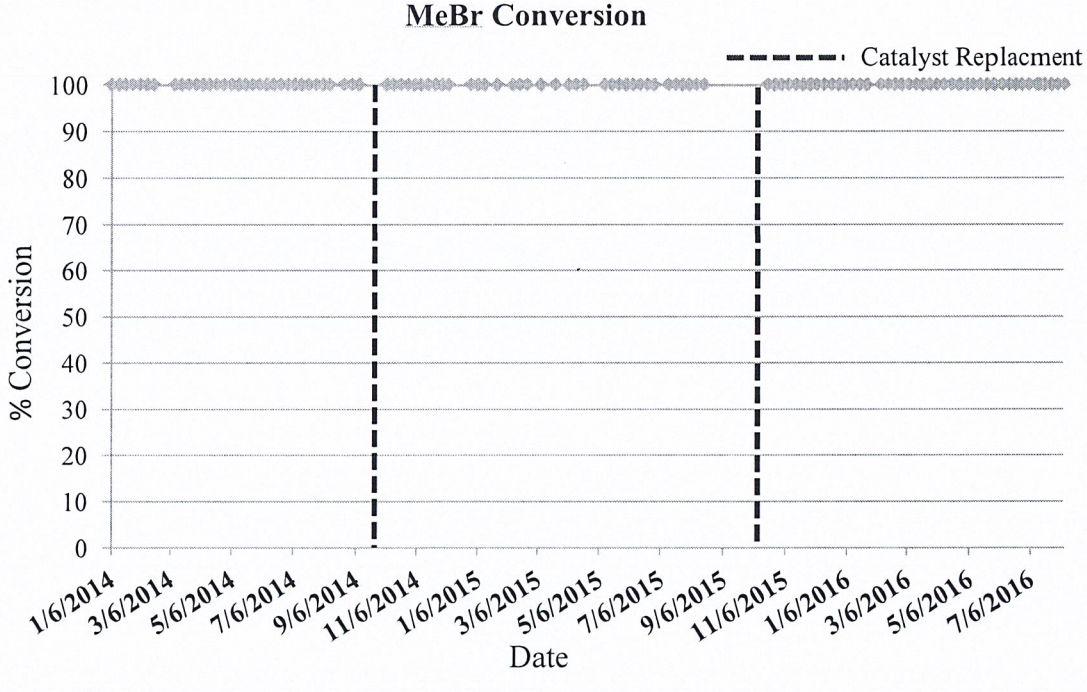


Figure 4.7 Conversion of MeBr
[SMPC Plant Number 3, 2016]

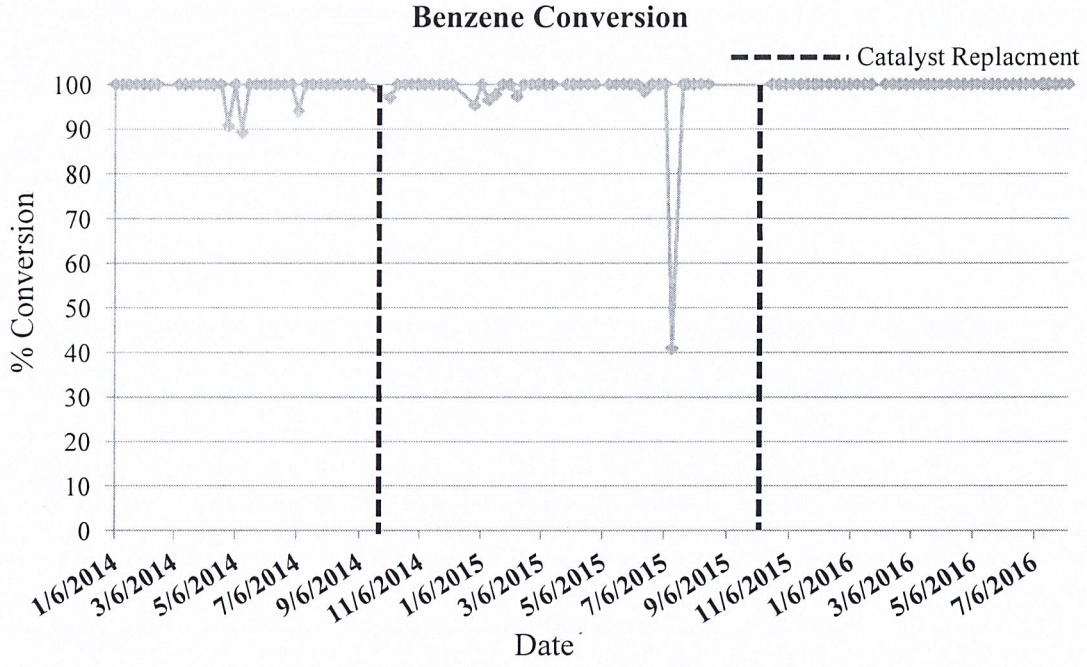


Figure 4.8 Conversion of Benzene
[SMPC Plant Number 3, 2016]

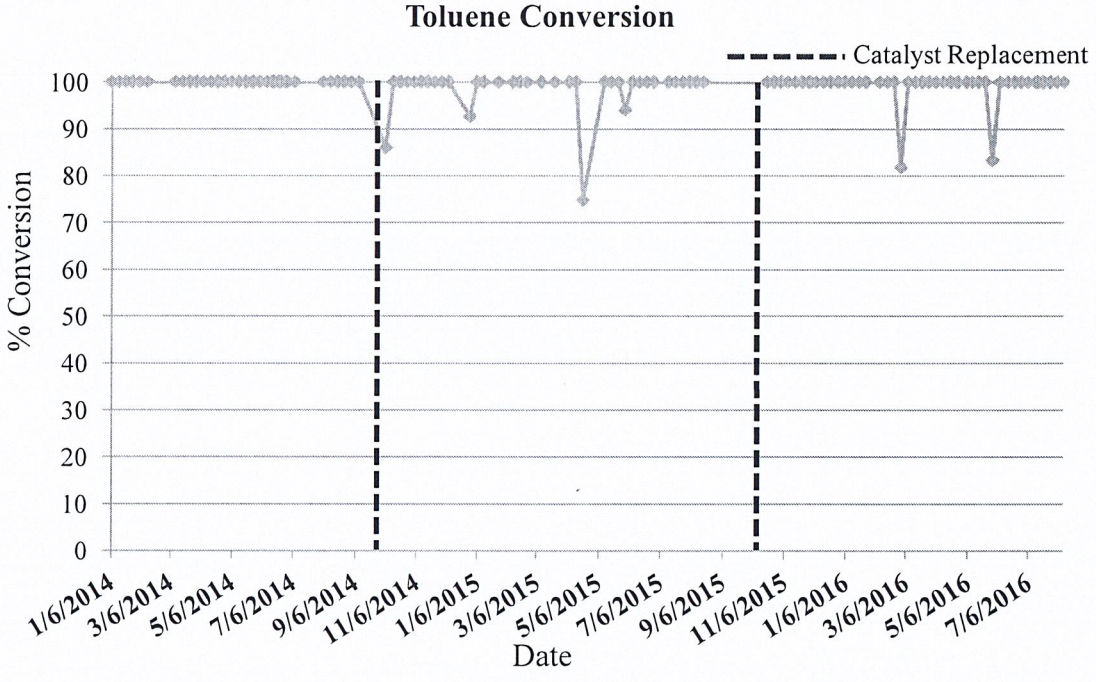


Figure 4.9 Conversion of Toluene
[SMPC Plant Number 3, 2016]

4.1.5 Conversion of CO in Waste Gases

4.1.5.1 CO Conversion

The reaction completed as 100 percent conversion in the CATOX. The conversion of CO is low in sometime because of failure in operation or analytical laboratory in that time. Before the catalyst is replaced, the conversion is still high as shown in Figure 4.10.

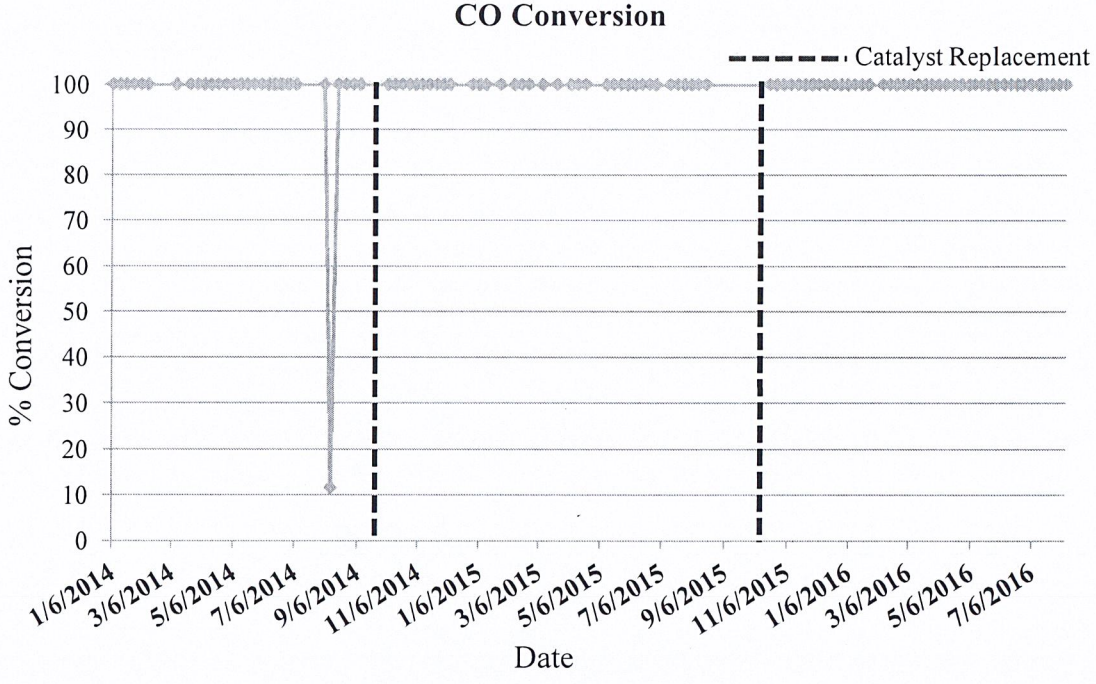


Figure 4.10 Conversion of CO
[SMPC Plant Number 3, 2016]

4.1.6 Operating Temperature

4.1.6.1 Operating Temperature from 2013 to 2014

The operating temperature is detected from 25 July 2013 to 10 September 2014 by temperature indicators as shown in Figure 4.11. The operating temperature consists of inlet temperature, top temperature, middle temperature, and bottom temperature. 350 °C is operating temperature at 100 percent conversion. The temperatures are higher than 350 °C because the peaks of temperature depend on the inlet temperature. The inlet temperature depends on operating condition of the CTA process at that time. The top, middle, bottom temperature equal since start up. The top temperature is decreasing since the twenty-second of operating time. On the other hand, the middle and bottom

temperature is still the same. The reaction is decreasing only top zone, that indicate the catalyst is deactivated in this zone.

4.1.6.2 Operating Temperature from 2014 to 2015

The operating temperature is detected from 3 October 2014 to 19 August 2015 by temperature indicators as shown in Figure 4.12. The operating temperature consists of inlet temperature, top temperature, middle temperature, and bottom temperature. 350 °C is operating temperature at 100 percent conversion. The temperatures are higher than 350 °C because the peaks of temperature depend on the inlet temperature. The inlet temperature depends on operating condition of the CTA process at that time. The top, middle, bottom temperature equal since start up. The top temperature is decreasing since the thirteenth of operating time. On the other hand, the middle and bottom temperature is still the same. The reaction is decreasing only top zone, that indicate the catalyst is deactivated in this zone.

4.1.6.3 Operating Temperature from 2015 to 2016

The operating temperature is detected from 12 October 2015 to 13 August 2016 by temperature indicators as shown in Figure 4.13. The operating temperature consists of inlet temperature, top temperature, middle temperature, and bottom temperature. 350 °C is operating temperature at 100 percent conversion. The temperatures are higher than 350 °C because the peaks of temperature depend on the inlet temperature. The inlet temperature depends on operating condition of the CTA process at that time. The top, middle, bottom temperature equal since start up. The top temperature is decreasing since the thirteenth of operating time. On the other hand, the middle and bottom temperature is still the same. The reaction is decreasing only top zone, that indicate the catalyst is deactivated in this zone.

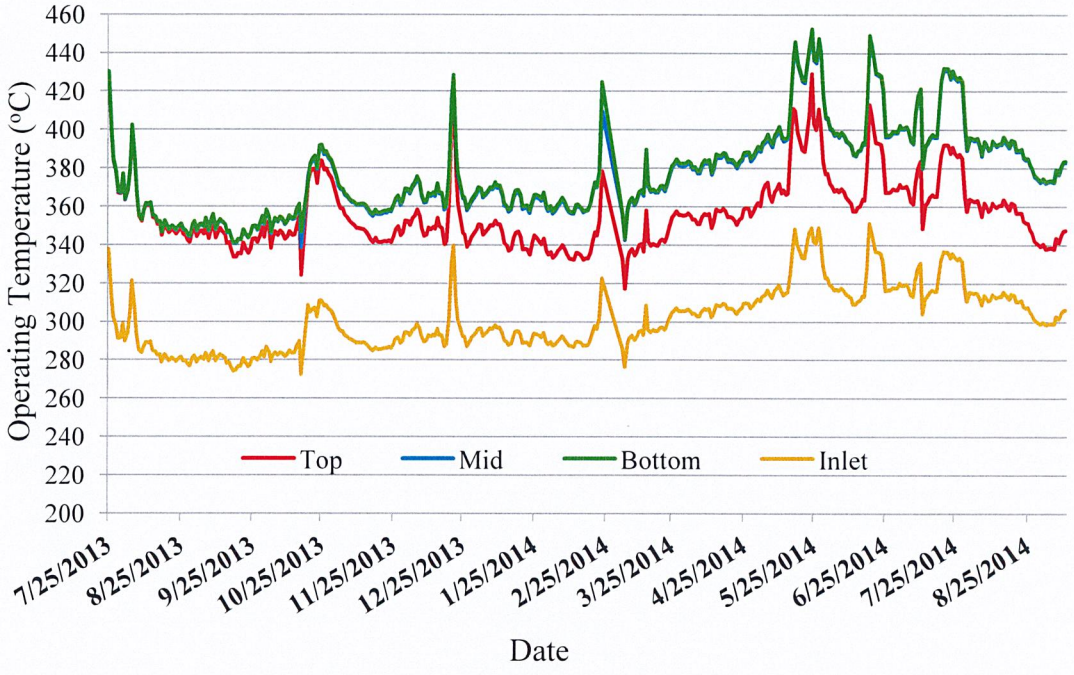


Figure 4.11 Operating Temperature from 2013 to 2014
[SMPC Plant Number 3, 2016]

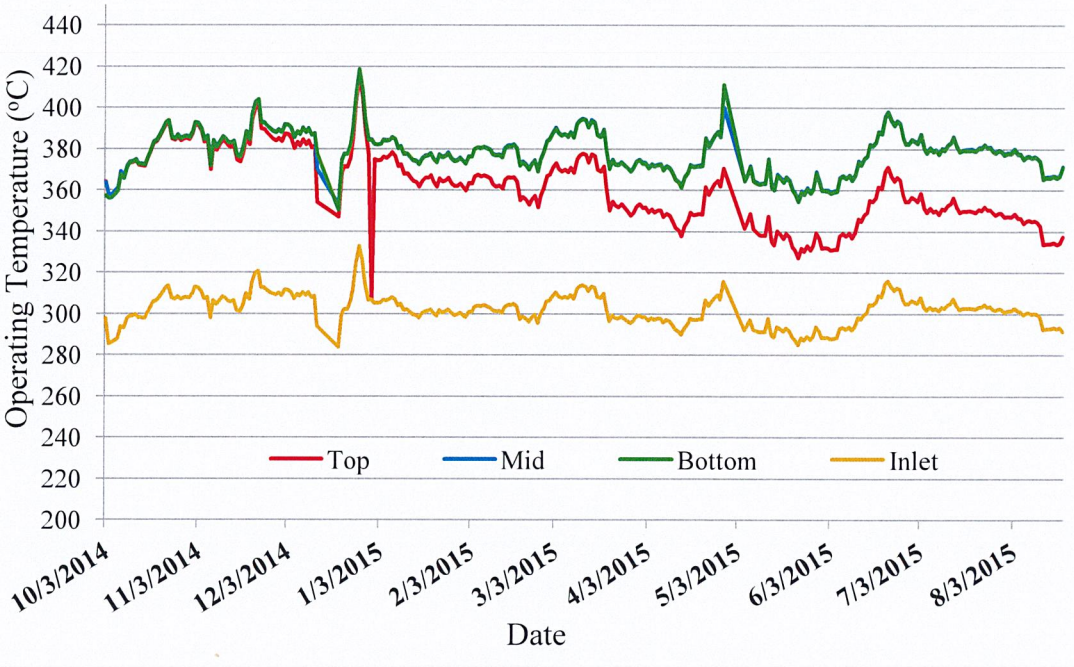


Figure 4.12 Operating Temperature from 2014 to 2015
[SMPC Plant Number 3, 2016]

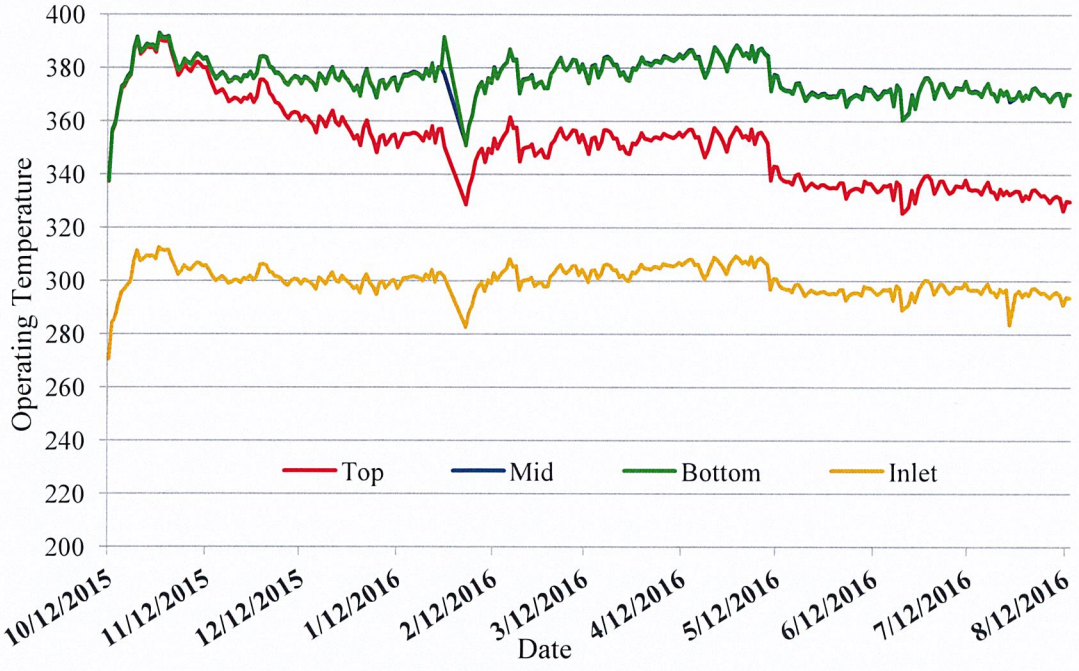


Figure 4.13 Operating Temperature from 2015 to 2016
[SMPC Plant Number 3, 2016]

4.1.7 Reaction Temperature from 2013 to 2016

From the operating temperature, the reaction temperature is identified in each zone. The reaction temperature is detected by calculation of different between the temperature in each zone with the inlet temperature. Figure 4.14, Figure 4.15, and Figure 4.16 are shown the temperature in each zone. The reaction temperature is decreased in top zone. So, the new ratio of the catalyst replacement is determined by estimable reaction temperature data. The top temperature is estimated by data in the range from catalyst replacement (2013) to catalyst replacement in next year (2014) until replacement in 2016.

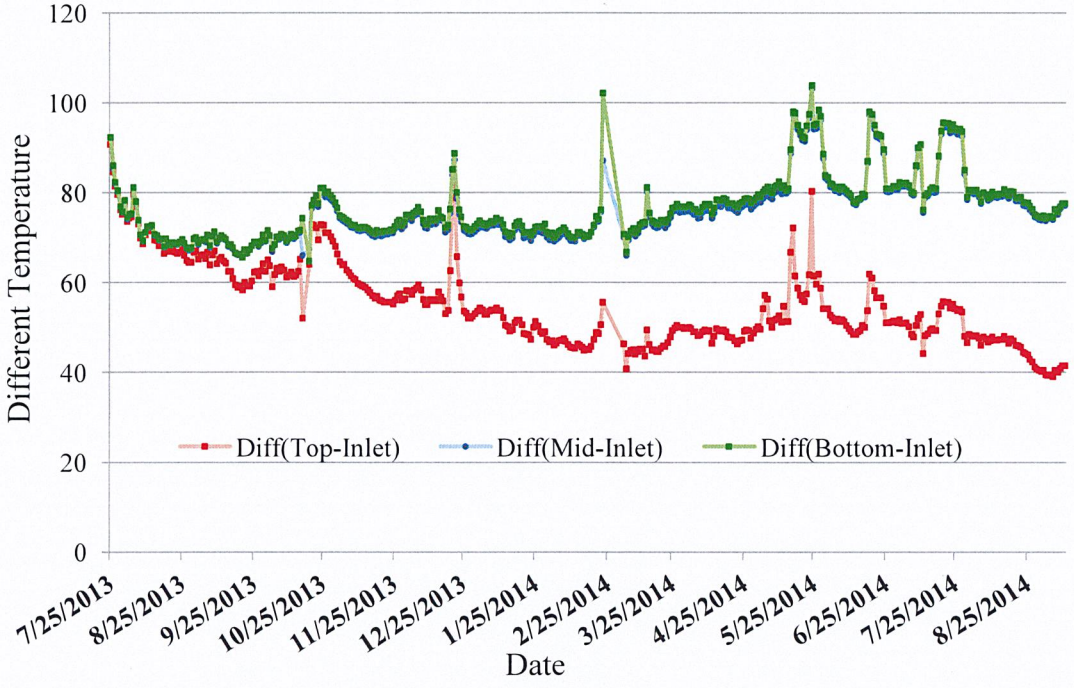


Figure 4.14 Reaction Temperature from 2013 to 2014
[SMPC Plant Number 3, 2016]

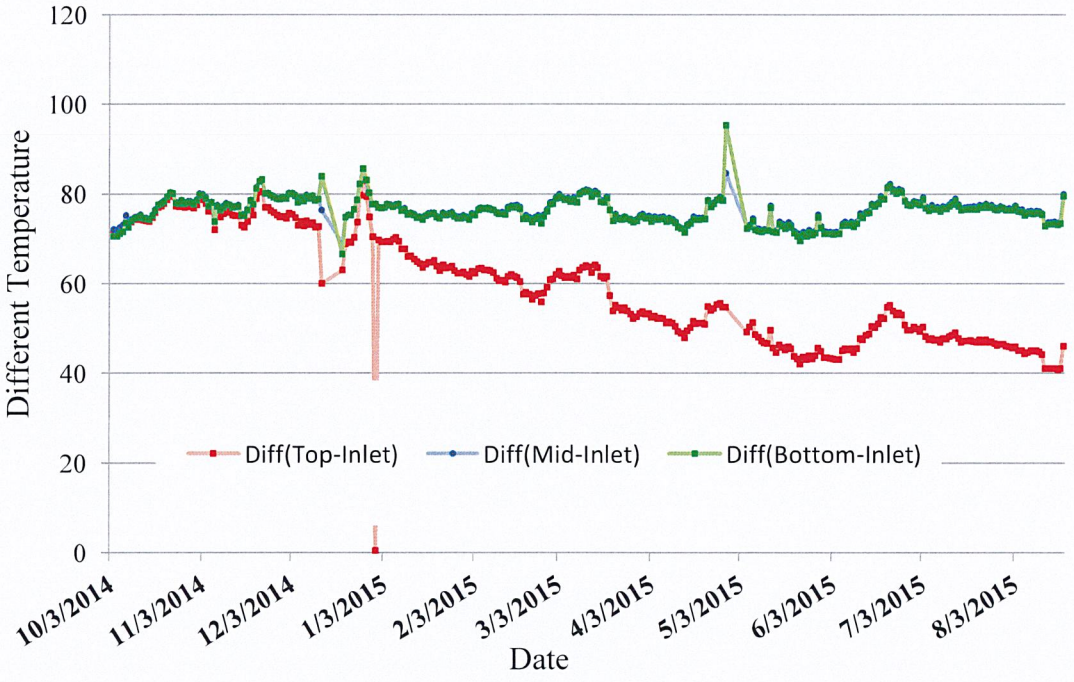


Figure 4.15 Reaction Temperature from 2014 to 2015
[SMPC Plant Number 3, 2016]

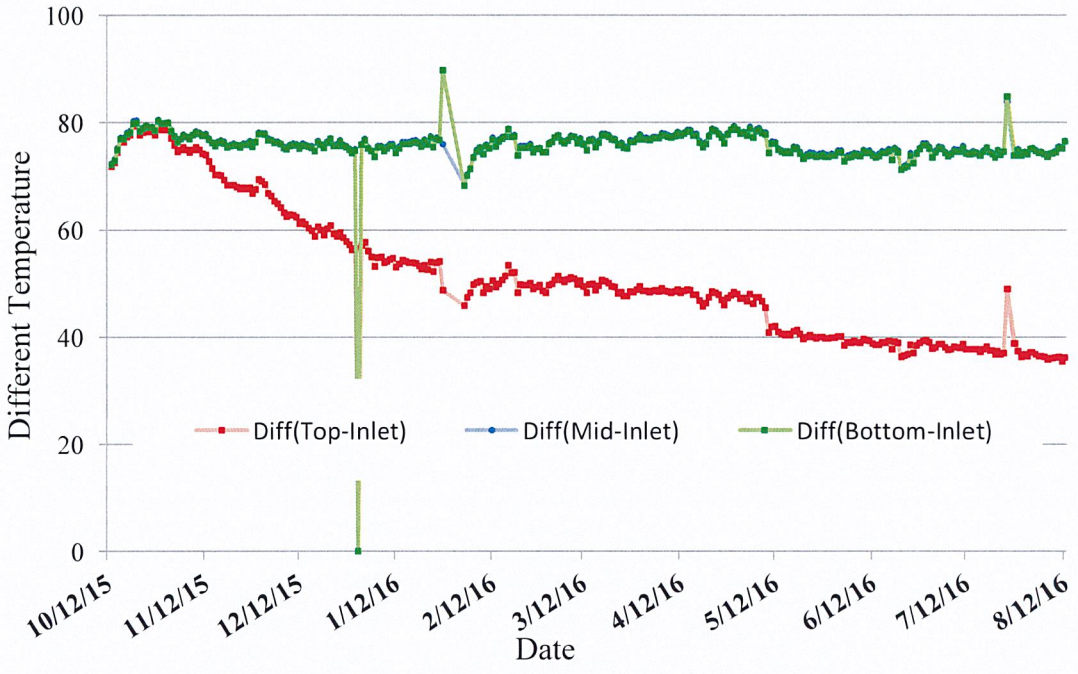


Figure 4.16 Reaction Temperature from 2015 to 2016
[SMPC Plant Number 3, 2016]

4.1.8 New Ratio

The estimable data from 2013 to 2014, 22 wt% is new ratio of replacement and 5.05 MBaht is cost saving as shown in Table 4.2. The estimable data from 2014 to 2015, 19 wt% is new ratio of replacement and 5.53 MBaht is cost saving as shown in Table 4.3. The estimable data from 2015 to 2016, 20 wt% is new ratio of replacement and 5.36 MBaht is cost saving as shown in Table 4.4. 0.8 is the safety factor of this project. So, ratio of catalyst replacement is 25 wt% in next time.

Table 4.2 Estimable Results of Reaction Temperature from 2013 to 2014 [SMPC Plant Number 3, 2016]

Ratio of Replacement	22/100
Amount of Catalyst (Drum)	49
Saving Cost (MBaht)	5.05

Table 4.3 Estimable Results of Reaction Temperature from 2014 to 2015 [SMPC Plant Number 3, 2016]

Ratio of Replacement	19/100
Amount of Catalyst (Drum)	43
Saving Cost (MBaht)	5.53

Table 4.4 Estimable Results of Reaction Temperature from 2015 to 2016 [SMPC Plant Number 3, 2016]

Ratio of Replacement	20/100
Amount of Catalyst (Drum)	45
Saving Cost (MBaht)	5.36

4.2 Optimization of Adsorbent Replacement

4.2.1 Dew Point in Outlet Stream of Adsorber

Dew point detector is located at the outlet stream of the adsorber. The dew point is used to check the moisture in dry gasses and check the adsorbing efficiency. The 12 October 2015 is the first day of operation after adsorbent replacement. –55 °C is low limit value for SMPC. If dew point has the value higher than -55 °C, it indicated that it has the moisture content. The dew point is decreased since the first day of operation as shown in Figure 4.17, that indicate adsorbed efficiency of adsorbent is still high. The highest of dew point is stopped operation at that time. So, lower adsorbed efficiency is not the root cause of adsorbent replacement.

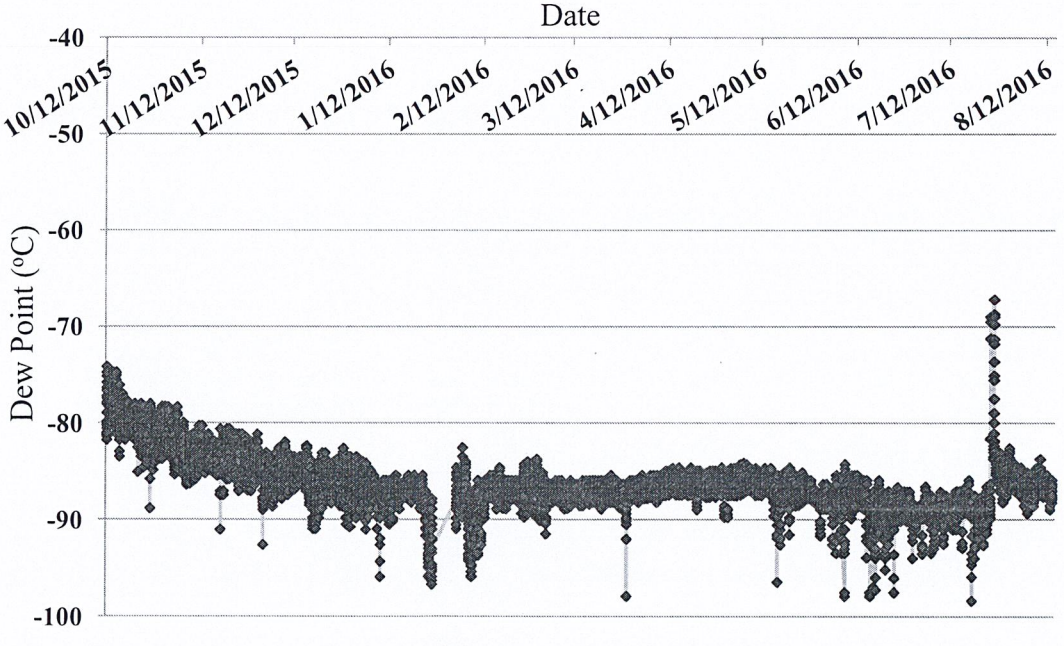


Figure 4.17 Dew Point of Waste Gases [SMPC Plant Number 3, 2016]

4.2.2 Report of Replacement

After screened, the data as shown in Figure 4.18. 30 wt% of used adsorbent is reused. The diameter of reused adsorbent is higher than 3 mm. 57 wt% of used adsorbent is waste, or is posted to vendor. The diameter of wasted adsorbent is higher than 3 mm. as be the same with reused adsorbent. 13 wt% of used adsorbent is dust or waste. The diameter of dust is lower than 3 mm. If the dust is reused, it may affect to the pressure drop in the adsorber. The consequence from pressure drop is it may impact to the pressure for pneumatic transfer powder of the PTA process. The waste should be reuse because of unbroken adsorbent. So, the waste is determined for reuse.

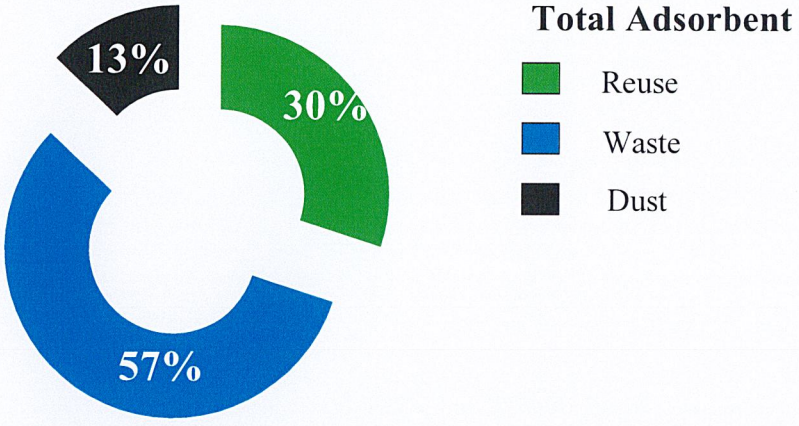


Figure 4.18 Report of Replacement (23 August 2016)
[SMPC Plant Number 3, 2016]

4.2.3 Adsorbing Ability

The adsorbing ability of used and fresh silica gel is compared as shown in Table 4.5. Used silica gel can adsorb moisture around 38.24 wt%. Fresh silica gel can adsorb moisture around 42.93 wt%. 20 ton of silica is used for 1 column. The capacity in adsorption is 7.7-ton water for used silica gel. The capacity in adsorption is 8.7-ton water for fresh silica gel. From calculation, the amount of moisture in the waste gasses is 2.05-ton water per batch. So, the used silica gel can be reuse.

Table 4.5 Adsorbing Ability of Used and Fresh Silica Gel [SMPC Plant Number 3, 2016]

Relative Humidity (%)	**Adsorbing Ability (Used Silica Gel)**	**Adsorbing Ability (Fresh Silica Gel)**
	wt% Silica Gel	wt% Silica Gel
90	38.24	42.93

4.2.4 Pressure Drop of Adsorber

The broken adsorbent has an effect to increased pressure drop. If the pressure drop and flow rate are constant, it indicates the adsorbent is not breaking while operation. The adsorbent might be broken while replacement because the vacuum pump is used for unloading of adsorbent.

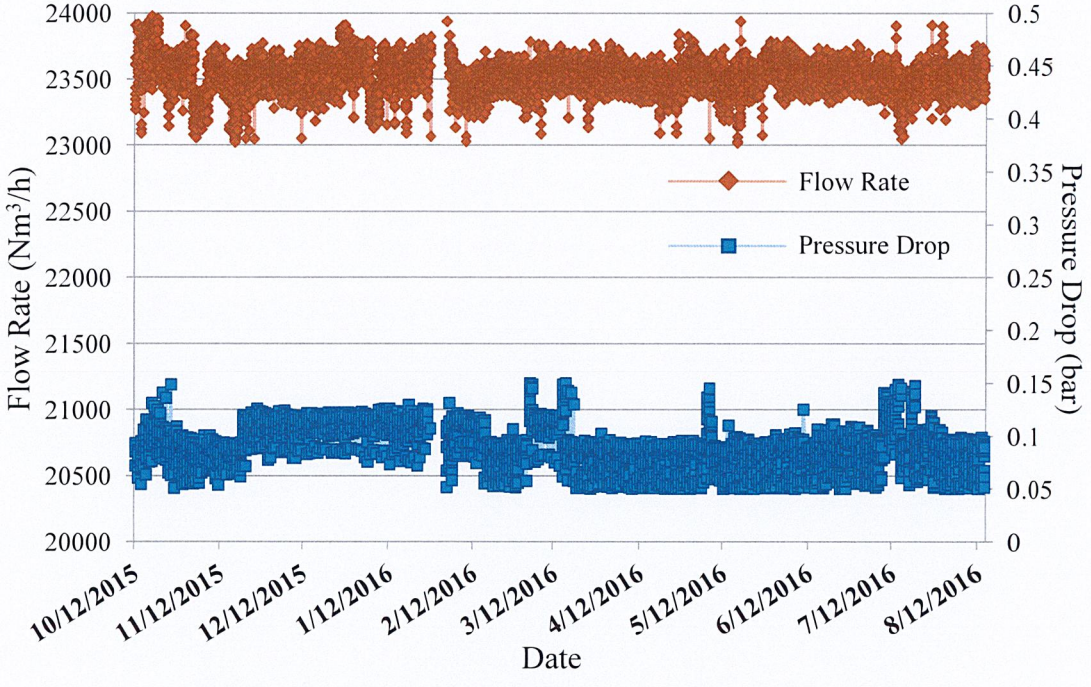


Figure 4.19 Flow Rate and Pressure Drop of Adsorber
[SMPC Plant Number 3, 2016]

4.2.5 New Ratio

The used adsorbent is higher than 3 mm. diameter, which will be reused. 13 wt% adsorbent is 5.3 ton, that is fresh adsorbent. Table 4.6 is shown the ratio of replacement is changed from 60 wt% to 13 wt%. Cost Saving is 0.65 MBaht.

Table 4.6 Properties of Replacement Data [SMPC Plant Number 3, 2016]

Used Adsorbent (wt%)	87
Fresh Adosrbent (wt%)	13
Fresh Adsorbent (ton)	5.3
Saving Cost (MBaht)	0.65

CHAPTER V
CONCLUSION

5.1 Conclusion

5.1.1 Catalyst Replacement

Catalyst is deactivated by coking mainly. According to the optimum temperatures at the CATOX, around 25 wt% of the catalyst was replaced instead of 50 wt%. Estimated saving cost is 4.53 about MBaht.

5.1.2 Adsorbent Replacement

Based on the optimum operating conditions at the adsorber (pressure drop and dew point), about 13 wt% of silica gel adsorbent instead of 70 wt% was replaced . Estimated saving cost is 0.65 MBaht.

5.2 Project Suggestions

5.2.1 Catalyst Replacement

The impact of project failure in percent catalyst replacement affects incomplete combustion in the CATOX. Incomplete combustion can cause the residual hydrocarbons in waste gases which will release to environment and cause fouling in gas expander turbine. Countermeasures are to increase inlet temperature of the CATOX and to setup contingency plans as shown in Table 5.1.

Table 5.1 Risks and Concerning Points [SMPC Plant Number 3, 2016]

<table>
<tr><th>Category</th><th colspan="2">Impact</th><th>Countermeasures</th></tr>
<tr><td rowspan="2">Process</td><td rowspan="2">Yes</td><td>Incomplete combustion in the CATOX</td><td rowspan="4">1. Increase inlet temperature of the CATOX
2. Setup contingency plans:
• Replace the $Cu/Mn/Al_2O_3$ catalysts during cleaning shutdown
• Temporary bypass the CATOX for $Cu/Mn/Al_2O_3$ catalysts replacement</td></tr>
<tr><td>The residual hydrocarbons contaminate in waste gases</td></tr>
<tr><td>Environmental Impact</td><td>Yes</td><td>The residual hydrocarbons in waste gases that release to environment</td></tr>
<tr><td>Machine</td><td>Yes</td><td>Fouling in Gas Expander Turbine</td></tr>
<tr><td>Safety</td><td>-</td><td colspan="2">-</td></tr>
<tr><td>Product Quality</td><td>-</td><td colspan="2">-</td></tr>
</table>

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APPENDIX

APPENDIX A
RAW DATA

1. Components in Waste Gases

Components in waste gases are identified. Components consist of nitrogen, oxygen, carbon dioxide, carbon monoxide, and hydrocarbons as shown in Table A.1. Oxygen, carbon dioxide, and carbon monoxide are detected by gas detector. Hydrocarbons are detected by analysis laboratory as shown in Table A.2. Table A.3 is shown components in outlet stream of the CATOX.

Table A.1 Components in Waste Gases [SMPC Plant Number 3, 2016]

Components	Plant Number 3
WG Flow Rate (kNm^3/h)	149.41
Oxygen (%)	4.3919
Carbon dioxide (%)	1.0986
Carbon monoxide (%)	0.28
Methyl Acetate (ppm)	1,516.30
p-Xylene (ppm)	198.79
Methanol (ppm)	116.01
Methyl Bromide (ppm)	15.23
Benzene (ppm)	14.68
Toluene (ppm)	9.81
Temperature (^oC)	34.9801
Pressure (barg)	8.6790

Table A.2 Inlet Concentration of each Component [SMPC Plant Number 3, 2016]

Date	CO (%)	Concentration (ppm)					
		MA	PX	MeOH	MeBr	Benzene	Toluene
1/6/2014	0.3703	1390	220	120	19	11	9.2
1/13/2014	0.3563	1380	160	120	18	9.7	7.2
1/20/2014	0.3575	1270	150	86	15	9.2	8.4
1/27/2014	0.3388	1330	180	110	17	10	8.7
2/3/2014	0.3347	1230	240	120	13	8.9	7.9
2/10/2014	0.3261	1340	210	130	13.9	9.2	8.6
2/17/2014	0.3250	1320	180	120	14	9.4	8.2
3/10/2014	0.2976	1930	140	130	13	11	8.3
3/17/2014	0.3298	1680	120	140	14	11	7.8
3/24/2014	0.3589	1100	150	110	11	9.9	12
3/31/2014	0.3559	1400	310	110	13	12	9.8
4/7/2014	0.3655	1580	210	120	13	11	9.8

4/14/2014	0.3554	1660	190	110	13	12	9.7
4/21/2014	0.3570	1620	200	100	14	12	4.9
4/28/2014	0.3920	814	110	37	7	6.4	10
5/5/2014	0.3896	2070	150	130	15	13	10
5/12/2014	0.3897	1410	270	99	14	12	10
5/19/2014	0.3678	2420	170	130	18	15	8.06
5/26/2014	0.3696	2600	108.02	98.69	18.12	13.84	10
6/2/2014	0.3808	1660	250	140	15	13	8.7
6/9/2014	0.3949	1180	176	95	10	12	9.3
6/16/2014	0.4115	1710	200	160	25	13	11
6/23/2014	0.4057	2560	230	140	22	17	12
6/30/2014	0.3837	1370	240	110	14	12	10
7/7/2014	0.4016	1650	190	110	20	15	9.4
7/14/2014	0.3962	1530	170	78	18	24	8.3
7/21/2014	0.3903	2240	170	110	16	14	12
7/28/2014	0.3843	2550	300	130	17	17	5.7
8/4/2014	0.3799	883	96	53	7.7	10	12
8/11/2014	0.3749	1590	320	87	13	25	12
8/25/2014	0.3710	1200	320	91	11	15	7.3
9/1/2014	0.3632	1540	140	110	13	11	12
9/8/2014	0.3742	124	310	47	66	13	0.3
10/6/2014	0.3228	1400	210	97	13	4.6	10
10/13/2014	0.3511	1500	180	99	11	22	9.4
10/20/2014	0.3647	1480	320	110	14	13	13
10/27/2014	0.3741	1480	270	85	13	19	12
11/3/2014	0.3446	1340	280	100	12	16	12
11/10/2014	0.3393	1440	260	100	11	15	12
11/17/2014	0.3944	1600	210	89	12	17	10
11/24/2014	0.3741	927	82	97	9.6	12	4.7
12/1/2014	0.3703	1610	170	440	13	9.1	9.8
12/8/2014	0.4203	137	31	100	12	14	4.3
12/29/2014	0.3837	1730	200	110	13	8.6	9.5
1/5/2015	0.3838	1590	210	140	12	10	11
1/12/2015	0.3669	1980	280	120	14	22	13
1/26/2015	0.3813	1710	220	110	13	25	11
2/9/2015	0.3832	1390	170	87	12	21	8.8
2/16/2015	0.3692	1720	170	90	14	14	10
2/23/2015	0.3747	1590	140	58.2	14	13	8.5
3/9/2015	0.3343	1390	137	192	13.4	11	9.01
4/6/2015	0.3211	2270	142	109.21	73.5	17	1.11
4/13/2015	0.3226	1690	180.49	81.4	14.3	16	9.28
4/20/2015	0.3330	720	135	117	11.51	6.79	8.49
5/11/2015	0.3642	1350	131	112	22.8	11	7.67
5/18/2015	0.3102	1320	152	121	10.7	13.8	7.2
5/25/2015	0.3009	1640	132	110	8.86	21.9	6.59

6/1/2015	0.3210	1260	170	76	11.3	14.3	9.49
6/8/2015	0.3281	1500	100	85	13	11.16	10
6/15/2015	0.3317	1410	200	62	13	10.3	8.4
6/22/2015	0.3662	1050	160	81	11	20.6	11
6/29/2015	0.3764	1370	220	93	12	13.3	9.8
7/13/2015	0.3485	1820	200	130	14	10.7	10
7/20/2015	0.3366	1520	320	120	14	19	10
7/27/2015	0.3320	1290	320	99	17	13	12
8/3/2015	0.3425	1430	290	83	13	12	12
8/10/2015	0.3375	1360	250	100	16	15	10
8/17/2015	0.3429	1590	210	110	14	9.4	9.9
10/19/2015	0.3318	2040	210	140	12	13	10
10/26/2015	0.3009	1950	260	130	14	12	13
11/2/2015	0.3107	1760	320	140	15	13	14
11/9/2015	0.3141	1860	220	96	13	12	20
11/16/2015	0.3050	2050	160	140	13	11	10
11/23/2015	0.3051	2140	190	110	12	16	8.2
11/30/2015	0.2771	1840	260	130	13	21	9.7
12/1/2015	0.2925	1700	290	121.95	13	21	12
12/7/2015	0.3099	1988.02	247.04	164.47	15	21	11
12/14/2015	0.2913	2035.13	260.14	209.17	14.07	18	10.69
12/21/2015	0.2898	2486	233.15	100	12.06	12	10.59
12/28/2015	0.3028	1770	300	145.42	15.51	20	11.23
1/4/2016	0.2964	1782.39	240.05	140	16	19	11
1/11/2016	0.2988	2180	260	141.82	12.06	16	9.51
1/18/2016	0.2987	1496.09	240.99	130.18	17	25	12
1/25/2016	0.2890	2037.84	296.39	346.5	13.14	17	9.52
2/8/2016	0.3562	2092.57	208.83	235.87	16.63	15.85	24.7
2/15/2016	0.3228	2815.61	213.37	190	10.63	27.31	11.82
2/22/2016	0.2948	2540	250	144.4	16.27	17.29	13.23
2/29/2016	0.2956	2125	341.67	198.41	16	14	15
3/7/2016	0.3019	2045.62	164.72	110	15.33	13.64	12.19
3/14/2016	0.3099	1330	340	132.42	16.16	22	13.74
3/21/2016	0.3143	1285.09	266.73	130	12	13.54	16
3/28/2016	0.3126	1620	240	103.93	12.19	27.25	11.32
4/4/2016	0.3361	1284.61	300.52	110	14	11.07	11
4/11/2016	0.3270	1270	290	100.97	11.6	18.44	14.89
4/18/2016	0.3266	966	239.55	84.96	13	21	14
4/25/2016	0.3220	1039.63	254.28	79.4	10.9	15.25	10.24
5/3/2016	0.3211	1226.55	178.26	123.22	20.11	14.7	9.36
5/9/2016	0.3240	1397.95	239.06	101.81	10.36	19	8.12
5/16/2016	0.3112	1446.92	157.83	122.39	16.18	19.08	12.44
5/23/2016	0.2960	1157.53	134.69	81.88	15.47	25	9.4
5/30/2016	0.2894	1110.02	172.15	92	17.55	13.5	7.66
6/6/2016	0.2870	1530	130	91.6	11.18	14	9.47

6/13/2016	0.2917	1465.32	167.33	77	15	12.7	8
6/20/2016	0.2862	1500	110	110	11.72	20.5	8.86
6/27/2016	0.3014	1750	150	85	14	15.77	9.4
7/4/2016	0.3067	1450	140	130	24	16.7	9.3
7/11/2016	0.3075	1650	140	130	14	16.93	7.7
7/12/2016	0.3055	1528.04	151.78	61	15	13.72	9.1
7/13/2016	0.2998	1300	140	131.78	13	13.45	10
7/18/2016	0.3003	1544.34	140.46	130	13	13	6.7
7/25/2016	0.2972	1760	130	106.81	14.42	9.69	7.51
8/1/2016	0.3016	1668.68	220	82	14	16	8
8/8/2016	0.3686	1280	160	120	14.06	15	7.31

Table A.3 Outlet Concentration of each Component [SMPC Plant Number 3, 2016]

Date	CO (%)	Concentration (ppm)					
		MA	PX	MeOH	MeBr	Benzene	Toluene
1/6/2014	0	0	0	0	0	0	0
1/13/2014	0	0	0	0	0	0	0
1/20/2014	0	0	0	0	0	0	0
1/27/2014	0	27.9	0	0	0	0	0
2/3/2014	0	0	0	0	0	0	0
2/10/2014	0	2.3	0.91	0	0	0	0
2/17/2014	0	4.95	0	0	0	0	0
3/10/2014	0	0	0.8	0	0	0	0
3/17/2014	0	8.32	0	9.9	0	0	0
3/24/2014	0	0	2.3	0	0	0	0
3/31/2014	0	0	0	0	0	0	0
4/7/2014	0	0	0	0	0	0	0
4/14/2014	0	2.59	0	0	0	0	0
4/21/2014	0	15.1	0	0	0	0	0
4/28/2014	0	8.52	3.7	0	0	0.6	0
5/5/2014	0	3.95	0	0	0	0	0
5/12/2014	0	14.3	0	0	0	1.3	0
5/19/2014	0	8.4	1.3	0	0	0	0
5/26/2014	0	6.08	0	0	0	0	0
6/2/2014	0	0	0.6	0	0	0	0
6/9/2014	0	0	0	0	0	0	0
6/16/2014	0	11.7	2.95	0	0	0	0
6/23/2014	0	3.74	1.8	0	0	0	0
6/30/2014	0	26	6	0	0	0	0
7/7/2014	0	12	1.2	16	0	0.9	0
7/14/2014	0	15	0.61	0	0	0	0
7/21/2014	0	2.57	9.9	0	0	0	0
7/28/2014	0.34	0	0	0	0	0	0
8/4/2014	0	10.6	31	19	0	0	0

8/11/2014	0	0	6	0	0	0	0
8/25/2014	0	5.2	14	0	0	0	0
9/1/2014	0	0	1.1	0	0	0	0
9/8/2014	0	0	0.57	27	0	0	0
10/6/2014	0	41.3	190	26	0	0	1.4
10/13/2014	0	3.73	16	6.4	0	0.67	0
10/20/2014	0	8.3	73	0	0	0	0
10/27/2014	0	0	0.36	0	0	0	0
11/3/2014	0	0	0.64	0	0	0	0
11/10/2014	0	0	0	0	0	0	0
11/17/2014	0	0	0	0	0	0	0
11/24/2014	0	0.243	0.09	6	0	0	0
12/1/2014	0	0	0.87	5.8	0	0	0
12/8/2014	0	0	1.6	29	0	0	0
12/29/2014	0	31	16	11	0	0	0.69
1/5/2015	0	16.6	12	11	0	0.47	0
1/12/2015	0	10.6	0.5	15	0	0	0
1/26/2015	0	0	35	0	0	0.9	0
2/9/2015	0	32	3.3	0	0	0.5	0
2/16/2015	0	1.06	0.53	0	0	0	0
2/23/2015	0	8.47	0.47	0	0	0	0
3/9/2015	0	0	0	0	0	0.3	0
4/6/2015	0	0	0	0	0	0	0
4/13/2015	0	0	0	16.4	0	0	0
4/20/2015	0	0	0	10.8	0	0	0
5/11/2015	0	1.91	0.65	0	0	0	1.93
5/18/2015	0	0	0	0	0	0	0
5/25/2015	0	0	0	7.4	0	0	0
6/1/2015	0	15.8	17	26	0	0	0
6/8/2015	0	2.19	1.2	0	0	0	0.59
6/15/2015	0	24.8	87	0	0	0	0
6/22/2015	0	0.83	1.5	0	0	0	0
6/29/2015	0	0	0.75	4.6	0	0	0
7/13/2015	0	7.66	2	5.1	0	0	0
7/20/2015	0	2.7	0.45	0	0	0	0
7/27/2015	0	1.02	0.6	8.4	0	0	0
8/3/2015	0	0	0	3.3	0	0	0
8/10/2015	0	0	0	0	0	0.25	0
8/17/2015	0	0	0	0	0	0	0
10/19/2015	0	0	0	0	0	0	0
10/26/2015	0	0	0.54	0	0	0	0
11/2/2015	0	0	0	0	0	7.7	0
11/9/2015	0	0	0.41	0	0	0	0
11/16/2015	0	0	0	6.4	0	0	0
11/23/2015	0	0	0.31	0	0	0	0

11/30/2015	0	0	0	0	0	0	0
12/1/2015	0	0	0	0	0	0	0
12/7/2015	0	0	0	0	0	0	0
12/14/2015	0	0	0.93	0	0	0	0
12/21/2015	0	0	0	0	0	0	0
12/28/2015	0	2.19	0	0	0	0	0
1/4/2016	0	0	0	27	0	0	0
1/11/2016	0	6.5	0.47	0	0	0	0
1/18/2016	0	22.18	2.49	0	0	0	0
1/25/2016	0	0	1.97	0	0	0	0
2/8/2016	0	0	0	0	0	0	0
2/15/2016	0	8.39	0.46	27	0	0	0
2/22/2016	0	18.1	4.2	0	0	0	0
2/29/2016	0	0	2.62	0	0	0	0
3/7/2016	0	0	0.93	0	0	0	2.22
3/14/2016	0	0	1.38	0	0	0	0
3/21/2016	0	2.36	4.76	0	0	0	0
3/28/2016	0	13.97	3.67	0	0	0	0
4/4/2016	0	0	4.69	0	0	0	0
4/11/2016	0	9.54	3.3	0	0	0	0
4/18/2016	0	0	2.1	30.49	0	0	0
4/25/2016	0	5.8	8.5	23.7	0	0	0
5/3/2016	0	0	2.33	0	0	0	0
5/9/2016	0	11.52	3.41	0	0	0	0
5/16/2016	0	1.82	0.58	26.87	0	0	0
5/23/2016	0	0	1.35	28.78	0	0	0
5/30/2016	0	19.48	9.53	0	0	0	0
6/6/2016	0	0	1	0	0	0	1.58
6/13/2016	0	0	1.96	0	0	0	0
6/20/2016	0	0	3	32	0	0	0
6/27/2016	0	8.57	2.4	0	0	0	0
7/4/2016	0	0	0.6	0	0	0	0
7/11/2016	0	0	1.5	0	0	0	0
7/12/2016	0	0	3.89	0	0	0	0
7/13/2016	0	0	1.7	0	0	0	0
7/18/2016	0	2.69	0	0	0	0	0
7/25/2016	0	0	0	0	0	0	0
8/1/2016	0	0	0	0	0	0	0
8/8/2016	0	0	0	0	0	0	0

2. Data of Catalyst

Capacity and cost of catalyst in the CATOX are used to calculate cost saving of this project. Table A.4 is shown catalyst weight in the CATOX and cost of catalyst per fiber drum.

Table A.4 Data of Catalyst [SMPC Plant Number 3, 2016]

Total Catalyst Weight in CATOX (kg)	32946.60
Catalyst Unit Weight Per Fiberdrum (kg)	150.00
Cost of Catalyst Per Fiberdrum (Baht)	82,194

3. Report of Adsorbent Screening

Amount of big bag is used to calculate percent of adsorbent. Adsorbent is separated in 2 types, consist of upper diameter 3 mm. and lower diameter 3 mm. The upper diameter 3 mm. is reused as shown in Table A.5.

Table A.5 Report of Adsorbent Replacement [SMPC Plant Number 3, 2016]

Total Adsorbent (Big Bag)	47
Upper Diameter 3 mm. (Big Bag)	41
Lower Diameter 3 mm. (Big Bag)	6
Reused Adsorbent (Big Bag)	14

4. Report Laboratory

Used adsorbent is identified to reused. The performance of adsorb is determined. The results of laboratory are used to calculate capacity of adsorbed moisture. Table A.7 is shown adsorbent weight in a adsorber and cost of adsorbent per kilogram.

Table A.6 Report Laboratory of Used and Fresh Adsorbent [Power Dry Co., Ltd., 2016]

Date	Time	%RH	Temperature (°C)	Used Silica Gel Weight (g)	Fresh Silica Gel Weight (g)
9/8/2016	2.20 pm.	90.7	30	43.75	42.51
9/9/2016	2.30 pm.	90	30	60.4	60.64
9/10/2016	11.30 am.	90	30	60.41	60.69
9/13/2016	11.00 am.	91	30	60.46	60.75

9/14/2016	11.30 am.	90.8	30	60.47	60.76
9/15/2016	11.00 am.	91	30	60.48	60.76
9/16/2016	11.30 am.	90.6	30	60.45	60.74
9/17/2016	10.00 am.	90.2	30	60.55	60.73
9/19/2016	11.00 am.	90	30	60.41	60.7

Table A.7 Data of Adsorbent [SMPC Plant Number 3, 2016]

Total Adsorbent Weight in a Adsorber (kg)	20,290.96
Adsorbent Unit Weight Per Bag (kg)	25
Cost of Adsorbent Per Kilogram (Baht)	33

5. Steam Table

Steam Table is used to calculate amount of moisture in the waste gases. The pressure of steam depends on waste gases temperature as shown in Table A.8. Figure A.1 is shown relation between temperature and pressure in Table A.8 for Equation A.1.

$$P = (7\times10^{-7}T^3) - (4\times10^{-6}T^2) + (7\times10^{-4}T) + 0.0055 \qquad (A.1)$$

where

P = Pressure (bar)

T = Temperature (^{o}C)

Table A.8 Saturated Steam, SI Units [J. M. Smith, H. C. Van Ness, and M. M. Abbott., 2005]

Temperature (^{o}C)	Pressure (kPa)	Pressure (bar)
1	0.657	0.00657
2	0.705	0.00705
3	0.757	0.00757
4	0.813	0.00813
5	0.872	0.00872
6	0.935	0.00935
7	1.001	0.01001
8	1.072	0.01072
9	1.147	0.01147
10	1.227	0.01227
11	1.312	0.01312
12	1.401	0.01401
13	1.497	0.01497
14	1.597	0.01597
15	1.704	0.01704
16	1.817	0.01817

17	1.936	0.01936
18	2.062	0.02062
19	2.196	0.02196
20	2.337	0.02337
21	2.485	0.02485
22	2.642	0.02642
23	2.808	0.02808
24	2.982	0.02982
25	3.166	0.03166
26	3.36	0.0336
27	3.564	0.03564
28	3.778	0.03778
29	4.004	0.04004
30	4.241	0.04241
31	4.491	0.04491
32	4.753	0.04753
33	5.029	0.05029
34	5.318	0.05318
35	5.622	0.05622
36	5.94	0.0594
37	6.274	0.06274
38	6.624	0.06624
39	6.991	0.06991
40	7.375	0.07375
41	7.777	0.07777
42	8.198	0.08198
43	8.639	0.08639
44	9.1	0.091
45	9.582	0.09582
46	10.09	0.1009
47	10.61	0.1061
48	11.16	0.1116
49	11.74	0.1174
50	12.34	0.1234

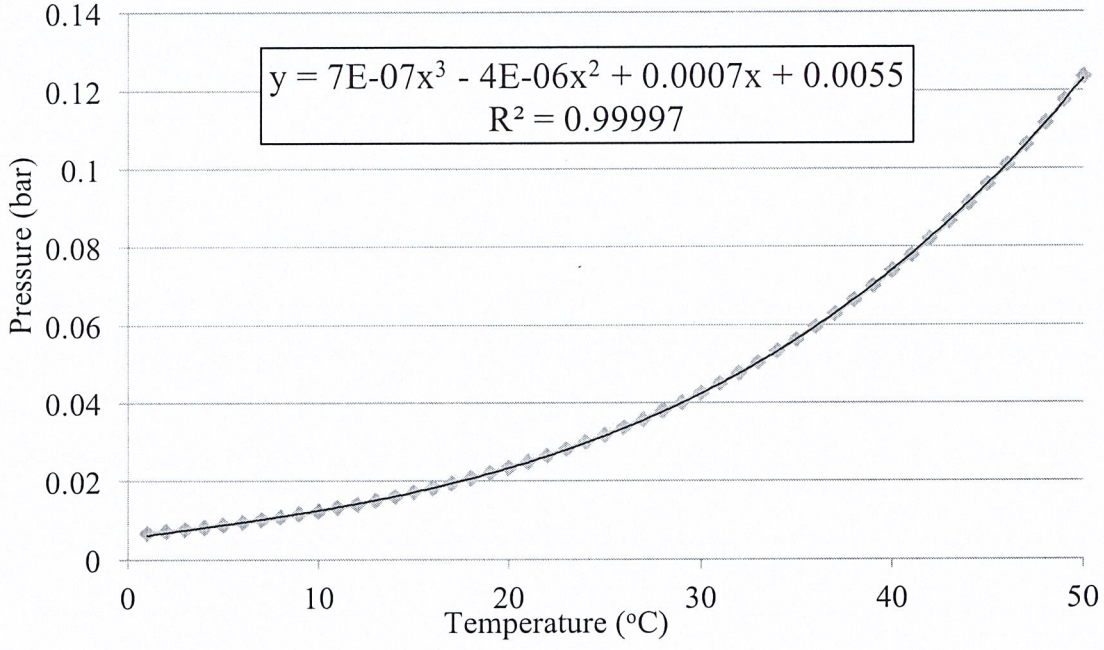

Figure A.1 Relation between Temperature and Pressure

[J. M. Smith, H. C. Van Ness, and M. M. Abbott., 2005]

6. Control Valve

The Cv value is used to calculate flow rate. The flow rate depends on traveling valve as MV% as shown in Figure A.2.

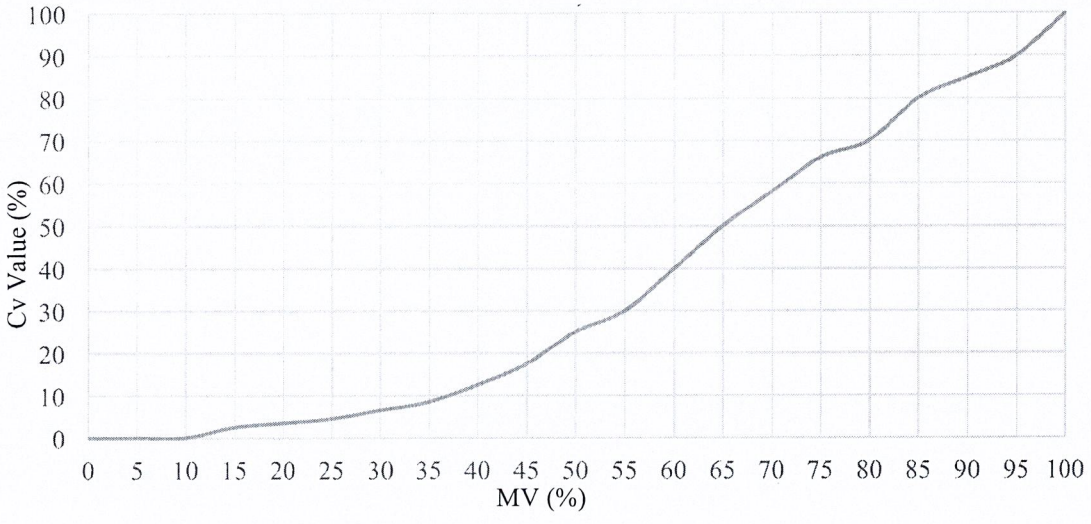

Figure A.2 Equal Percentage Characteristics

[Yamatake-Honeywell Keiki Co., Ltd., 2016]

APPENDIX B
MOLAR AND MASS FLOW RATE CALCULATION

Example of Calculation

1. Covert volumetric flow rate of waste gases to molar flow rate that used to calculate mass flow rate of hydrocarbons.

149.41 kNm^3/h = 149.41 km^3/h at 1 bar, 273 K

$$P\dot{V} = \dot{n}RT \tag{B.1}$$

$$1\ bar \times 149.41 \frac{km^3}{h} = \dot{n} \frac{kmol}{h} \times 8.31 \times 10^{-5} \frac{m^3\ bar}{mol\ K} \times 273K$$

$$\dot{n} = 6670.04\ \frac{kmol}{h}$$

2. Convert wt% of O_2 to mass flow rate of O_2.

$$\frac{4.3919}{100} \times 6670.04 \frac{kmol}{h} \times \frac{32\ kg}{kmol} = 9{,}374.19 \frac{kg}{h}$$

3. Convert ppm of MA to mass flow rate of MA.

$$\frac{1{,}516.30}{10^6} \times 6670.04 \frac{kmol}{h} \times \frac{28.34\ kg}{kmol} = 286.63 \frac{kg}{h}$$

4. Convert temperature of waste gases to vapor pressure that used to calculate mass flow rate of steam.

$$P = (7 \times 10^{-7} T^3) - (4 \times 10^{-6} T^2) + (7 \times 10^{-4} T) + 0.0055 \tag{A.1}$$

$$P = (7 \times 10^{-7} \times 34.9801^3) - (4 \times 10^{-6} \times 34.9801^2) + (7 \times 10^{-4} \times 34.9801) + 0.0055$$

$$P = 0.0550\ bar$$

5. Convert unit pressure of waste gases (kg/cm^2) to pressure (bar) that used to calculate mass flow rate of steam.

$$\left(3.6790\,\frac{kg}{cm^2}\times\frac{1}{1.01972}\,\frac{barg}{\frac{kg}{cm^2}}\right)+1.0133=9.5244\,bar$$

6. Calculate ratio of steam and waste gases that used to calculate mass flow rate of steam.

$$\frac{P_1}{n_1}=\frac{P_2}{n_2} \tag{B.2}$$

$$\frac{P_{H_2O}}{n_{H_2O}}=\frac{P_{WG}}{n_{WG}}$$

$$\frac{0.0550\,bar}{18\,\frac{g_{H_2O}}{mol}}=\frac{9.5244-0.0550\,bar}{28.34\,\frac{g_{WG}}{mol}}$$

$$\frac{g_{H_2O}}{kg_{WG}}=3.3936$$

7. Calculate mass flow rate of steam.

$$6670.04\,\frac{kmol_{WG}}{h}\times\frac{28.34\,kg_{WG}}{kmol_{WG}}\times3.3936\,\frac{g_{H_2O}}{kg_{WG}}\times\frac{1\,kg}{1000\,g}=698.01\,\frac{kg}{h}$$

Table B.1 Mass Flow Rate Calculation [SMPC Plant Number 3, 2016]

Components	Plant Number 3
WG Flow Rate (kmol/h)	6,670.04
Nitrogen (kg/h)	174,861.43
Oxygen (kg/h)	9,374.19
Carbon dioxide (kg/h)	3,224.22
Steam (kg/h)	698.01
Carbon monoxide (kg/h)	517.49
Methyl Acetate (kg/h)	286.63
p-Xylene (kg/h)	37.58
Methanol (kg/h)	21.93
Methyl Bromide (kg/h)	2.88
Benzene (kg/h)	2.77
Toluene (kg/h)	1.85

APPENDIX C
CONVERSION CALCULATION

Example of Calculation

1. Calculate conversion of MA. The data in Table A.2 and Table A.3 is used.

$$X_{MA} = \frac{\dot{n}_{MA,in} - \dot{n}_{MA,out}}{\dot{n}_{MA,in}} x100\% \qquad \text{(C.1)}$$

$$= \frac{1390 - 0\ ppm}{1390\ ppm} x100\%$$

$$= 100\ \%$$

Table C.1 Calculations of each Component [SMPC Plant Number 3, 2016]

Date	Conversions (%)						
	CO	MA	PX	MeOH	MeBr	Benzene	Toluene
1/6/2014	100	100	100	100	100	100	100
1/13/2014	100	100	100	100	100	100	100
1/20/2014	100	100	100	100	100	100	100
1/27/2014	100	97.90	100	100	100	100	100
2/3/2014	100	100	100	100	100	100	100
2/10/2014	100	99.83	99.67	100	100	100	100
2/17/2014	100	99.62	100	100	100	100	100
3/10/2014	100	100	99.43	100	100	100	100
3/17/2014	100	99.50	100	92.93	100	100	100
3/24/2014	100	100	98.47	100	100	100	100
3/31/2014	100	100	100	100	100	100	100
4/7/2014	100	100	100	100	100	100	100
4/14/2014	100	99.84	100	100	100	100	100
4/21/2014	100	99.08	100	100	100	100	100
4/28/2014	100	98.95	96.64	100	100	90.62	100
5/5/2014	100	99.81	100	100	100	100	100
5/12/2014	100	98.98	100	100	100	89.17	100
5/19/2014	100	99.65	99.24	100	100	100	100
5/26/2014	100	99.77	100	100	100	100	100
6/2/2014	100	100	99.76	100	100	100	100
6/9/2014	100	100	100	100	100	100	100
6/16/2014	100	99.32	98.52	100	100	100	100
6/23/2014	100	99.85	99.22	100	100	100	100
6/30/2014	100	98.10	97.50	100	100	100	100
7/7/2014	100	99.27	99.37	85.45	100	94.00	100
7/14/2014	100	99.02	99.64	100	100	100	100
7/21/2014	100	99.88	94.18	100	100	100	100

7/28/2014	11.54	100	100	100	100	100	100
8/4/2014	100	98.79	67.71	64.15	100	100	100
8/11/2014	100	100	98.12	100	100	100	100
8/25/2014	100	99.57	95.62	100	100	100	100
9/1/2014	100	100	99.21	100	100	100	100
9/8/2014	100	100	99.82	42.55	100	100	100
10/6/2014	100	97.05	9.52	73.19	100	100	86.00
10/13/2014	100	99.75	91.11	93.53	100	96.95	100
10/20/2014	100	99.44	77.19	100	100	100	100
10/27/2014	100	100	99.87	100	100	100	100
11/3/2014	100	100	99.77	100	100	100	100
11/10/2014	100	100	100	100	100	100	100
11/17/2014	100	100	100	100	100	100	100
11/24/2014	100	99.97	99.89	93.81	100	100	100
12/1/2014	100	100	99.49	98.68	100	100	100
12/8/2014	100	100	94.84	71.00	100	100	100
12/29/2014	100	98.21	92.00	90.00	100	100	92.74
1/5/2015	100	98.96	94.28	92.14	100	95.30	100
1/12/2015	100	99.46	99.82	87.50	100	100	100
1/26/2015	100	100	84.09	100	100	96.40	100
2/9/2015	100	97.69	98.06	100	100	97.62	100
2/16/2015	100	99.94	99.69	100	100	100	100
2/23/2015	100	99.47	99.66	100	100	100	100
3/9/2015	100	100	100	100	100	97.27	100
4/6/2015	100	100	100	100	100	100	100
4/13/2015	100	100	100	79.85	100	100	100
4/20/2015	100	100	100	90.77	100	100	100
5/11/2015	100	99.86	99.50	100	100	100	74.84
5/18/2015	100	100	100	100	100	100	100
5/25/2015	100	100	100	93.27	100	100	100
6/1/2015	100	98.75	90.00	65.79	100	100	100
6/8/2015	100	99.85	98.80	100	100	100	94.10
6/15/2015	100	98.24	56.50	100	100	100	100
6/22/2015	100	99.92	99.06	100	100	100	100
6/29/2015	100	100	99.66	95.05	100	100	100
7/13/2015	100	99.58	99.00	96.08	100	100	100
7/20/2015	100	99.82	99.86	100	100	100	100
7/27/2015	100	99.92	99.81	91.52	100	100	100
8/3/2015	100	100	100	96.02	100	100	100
8/10/2015	100	100	100	100	100	98.33	100
8/17/2015	100	100	100	100	100	100	100
10/19/2015	100	100	100	100	100	100	100
10/26/2015	100	100	99.79	100	100	100	100
11/2/2015	100	100	100	100	100	40.77	100
11/9/2015	100	100	99.81	100	100	100	100
11/16/2015	100	100	100	95.43	100	100	100

11/23/2015	100	100	99.84	100	100	100	100
11/30/2015	100	100	100	100	100	100	100
12/1/2015	100	100	100	100	100	100	100
12/7/2015	100	100	100	100	100	100	100
12/14/2015	100	100	99.64	100	100	100	100
12/21/2015	100	100	100	100	100	100	100
12/28/2015	100	99.88	100	100	100	100	100
1/4/2016	100	100	100	80.71	100	100	100
1/11/2016	100	99.70	99.82	100	100	100	100
1/18/2016	100	98.52	98.97	100	100	100	100
1/25/2016	100	100	99.33	100	100	100	100
2/8/2016	100	100	100	100	100	100	100
2/15/2016	100	99.70	99.78	85.79	100	100	100
2/22/2016	100	99.29	98.32	100	100	100	100
2/29/2016	100	100	99.23	100	100	100	100
3/7/2016	100	100	99.44	100	100	100	81.79
3/14/2016	100	100	99.59	100	100	100	100
3/21/2016	100	99.82	98.22	100	100	100	100
3/28/2016	100	99.14	98.47	100	100	100	100
4/4/2016	100	100	98.44	100	100	100	100
4/11/2016	100	99.25	98.86	100	100	100	100
4/18/2016	100	100	99.12	64.11	100	100	100
4/25/2016	100	99.44	96.66	70.15	100	100	100
5/3/2016	100	100	98.69	100	100	100	100
5/9/2016	100	99.18	98.57	100	100	100	100
5/16/2016	100	99.87	99.63	78.04	100	100	100
5/23/2016	100	100	98.99	64.85	100	100	100
5/30/2016	100	98.24	94.46	100	100	100	100
6/6/2016	100	100	99.23	100	100	100	83.32
6/13/2016	100	100	98.83	100	100	100	100
6/20/2016	100	100	97.27	70.91	100	100	100
6/27/2016	100	99.51	98.40	100	100	100	100
7/4/2016	100	100	99.57	100	100	100	100
7/11/2016	100	100	98.93	100	100	100	100
7/12/2016	100	100	97.44	100	100	100	100
7/13/2016	100	100	98.78	100	100	100	100
7/18/2016	100	99.82	100	100	100	100	100
7/25/2016	100	100	100	100	100	100	100
8/1/2016	100	100	100	100	100	100	100
8/8/2016	100	100	100	100	100	100	100

APPENDIX D
PECENT REPLACEMENT AND COST SAVING OF CATALYST CALCULATION

Example of Calculation

1. Estimate operating time at top zone of the CATOX. The slope of different temperature of top zone is estimated by logarithm function.

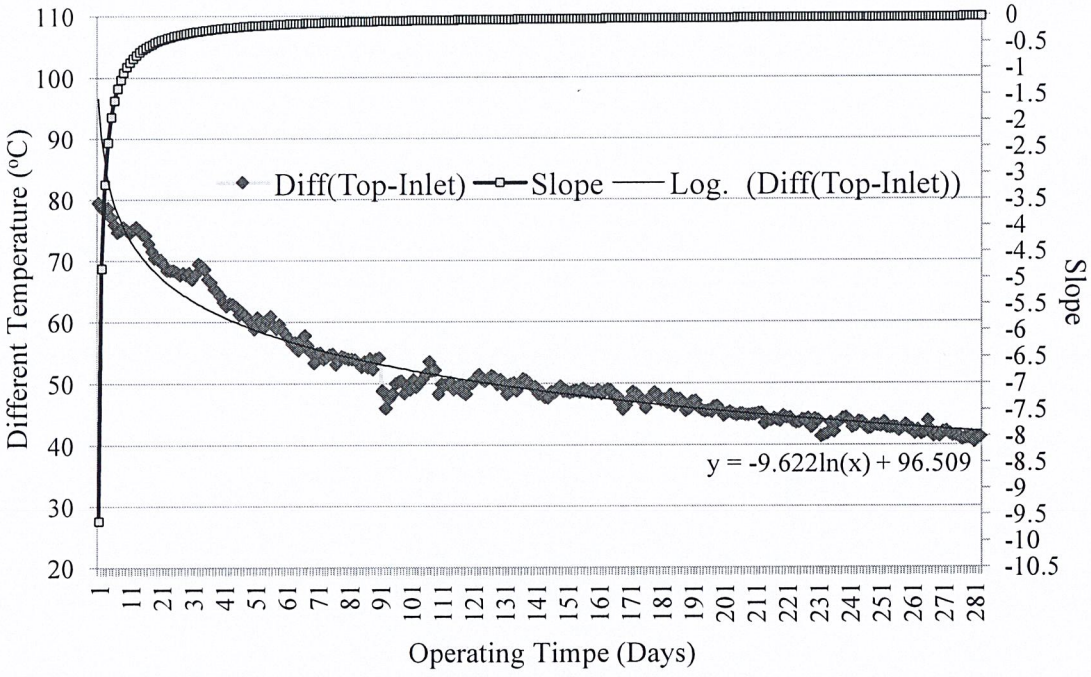

Figure D.1 Slope of Different Temperature
[SMPC Plant Number 3, 2016]

$$y = -9.622\ln(x) + 96.509 \tag{D.1}$$

$$\frac{dy}{dx} = \frac{d}{dx}(-9.622\ln(x)) \tag{D.2}$$

$$\frac{dy}{dx} = -9.622\frac{1}{x} \tag{D.3}$$

2. Estimate operating time at top zone of the CATOX. There are not exothermic reactions when the slope of different temperature of top zone is equal to zero.

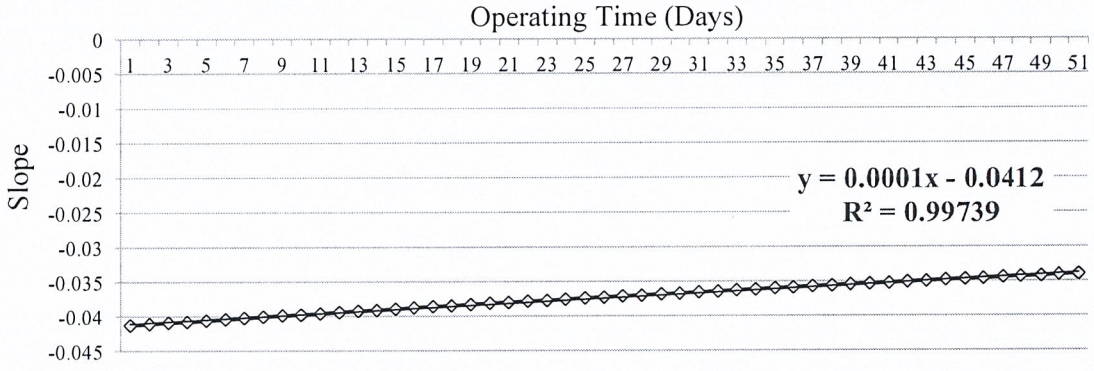

Figure D.2 Slope of Different Temperature in last 50 days [SMPC Plant Number 3, 2016]

From equation of linear in slope

$$y = 0.0001x + 0.0412 \quad \text{(D.4)}$$

At x-intercept

$$0 = 0.0001x + 0.0412$$

$$x = 412$$

So, the estimation of operating time at top zone is 412 days. Total operating time is shown in Table D.1.

Table D.1 Total Operating Time at Top Zone [SMPC Plant Number 3, 2016]

Operating Time before Estimation (Day)	Operating Time of Estimation (Day)	Total Operating Time and Shutdown Time (Day)
248	412	682

3. Convert the total operating time that is used to calculate wt% of catalyst deactivated in top zone.

$$682\ day \times \frac{1\ year}{365\ day} = 1.87\ years$$

$$\frac{100\ wt\%\ deactivated}{1.87\ year} = \frac{54\ wt\%\ deactivated}{1\ year}$$

So, 54 wt% of catalyst is deactivated in 1-year operation.

4. Convert 54 wt% deactivated in top zone to wt% of catalyst deactivated in the CATOX.

From capacity of top zone (38.1 wt%)

$$\frac{54\ wt\%\ deactivated}{38.1\ wt\%} = \frac{20.42\ wt\%\ deactivated}{100\ wt\%}$$

So, 20.42 wt% of catalyst is deactivated in 1-year operation.

5. Calculate amount of fresh catalyst for used catalyst replacement.

From capacity of catalyst in the CATOX (220 Drums)

$$\frac{220\ Drums}{100\ wt\%} = \frac{45\ Drums}{20.42\ wt\%}$$

So, 45 drums of fresh catalyst are used to replace.

6. Calculate cost of current ratio of replacement.

From 50 wt% catalyst replacement are 110 drums of fresh catalyst.

$$110\ drums \times \frac{140\ L}{1\ Drums} \times \frac{587.1\ Baht}{1\ L} = 9.04\ MBaht$$

So, replacement cost is 9.04 MBaht.

7. Calculate cost saving of proposed ratio of replacement.

$$45\ drums \times \frac{140\ L}{1\ Drums} \times \frac{587.1\ Baht}{1\ L} = 3.69\ MBaht$$

Cost Saving = 9.04 – 3.69 = 5.36 MBaht

So, cost saving is 5.36 MBaht.

Table D.2 Calculation of Cost Saving Reaction Temperature from 2015 to 2016 [SMPC Plant Number 3, 2016]

Total Operating Time (Year)	1.87
Catalyst Deactivated in 1-year operation at Top Zone (wt%)	53.60
Proposed percent weight of Replacement (wt%)	20.42
Amount of Fresh Catalyst for Replacement (Drum)	45
Cost Saving (MBaht)	5.36

APPENDIX E
ADSORBING ABILITY CALCULATION

1. Equipment
   1.1 Humidity
   1.2 Controller
   1.3 Oven
   1.4 Weight

2. Chemicals
   2.1 Fresh Silica Gel (43.75 g)
   2.2 Used Silica Gel (42.51 g)

3. Experiments
   3.1 Get fresh and used silica gel in close system.
   3.2 Control humid at 90 %RH in the system.
   3.3 Control temperature at 30 °C in the system.
   3.4 Record weight of fresh and used silica gel everyday until constant weight.

4. Adsorbing Ability Calculation

$$Adsorbing\ Ability = \frac{w_t - w_i}{100} wt\% \quad \text{(E.1)}$$

$$Adsorbing\ Ability = \frac{60.4 - 42.51}{100} wt\%$$

$$Adsorbing\ Ability = 38.05\ wt\%$$

So, adsorbing ability is 38.05 wt% for adsorption in 24 hours as shown in Table E.1.

Table E.1 Adsorbing Ability Calculation [Power Dry Co., Ltd., 2016]

Date	Used Silica Gel			Fresh Silica Gel		
	Weight (g)	Gain Weight (g)	Adsorbing Ability (wt%)	Weight (g)	Gain Weight (g)	Adsorbing Ability (wt%)
9/8/2016	43.75	-	-	42.51	-	-
9/9/2016	60.4	16.65	38.05	60.64	18.13	42.64

9/10/2016	60.41	16.66	38.08	60.69	18.18	42.76
9/13/2016	60.46	16.71	38.19	60.75	18.24	42.9
9/14/2016	60.47	16.72	38.21	60.76	18.26	42.93
9/15/2016	60.48	16.73	38.24	60.76	18.26	42.93
9/16/2016	60.45	-	-	60.74	-	-
9/17/2016	60.55	-	-	60.73	-	-
9/19/2016	60.41	-	-	60.7	-	-

APPENDIX F
COST SAVING OF ADSORBENT CALCULATION

Example of Calculation

1. Calculate cost of current ratio of replacement.

From 60 wt% adsorbent are 12,174.57 kg of silica gel.

$$12{,}174.57\ kg \times \frac{33\ Baht}{1\ kg} = 0.40\ MBaht$$

So, replacement cost is 0.40 MBaht.

2. Calculate cost saving of proposed ratio of replacement.

$$2{,}637.82\ kg \times \frac{33\ Baht}{1\ kg} = 0.08\ MBaht$$

Cost Saving (2 Vessels) = (0.40 – 0.08) x 2 = 0.65 MBaht

So, cost saving is 0.65 MBaht.

Table F.1 Calculation of Cost Saving [SMPC Plant Number 3, 2016]

Broken Adsorbent (wt%)	13
Proposed percent weight of Replacement (wt%)	13
Amount of Fresh adsorbent for Replacement (kg)	2,637.82
Cost Saving (MBaht)	0.65

APPENDIX G
FLOW RATE AND OUTLET TEMPERATURE CALCULATION

Countermeasure

Increase the reaction temperature by heating up inlet temperature of CATOX. The high inlet temperature is used to increase oxidation of the hydrocarbons. The heat exchanger A is heated by steam (5 bar) as shown in Figure G.1. Currently, valve of inlet steam is opened 38 %MV. So, the waste gases are increased temperature by the increase %MV of steam valve.

Example of Calculation

1. Calculate Cv value from MV% and CV%.

From maximum Cv value = 420

At 50 CV%: Cv Value = 0.5 x 420 = 210

The results of Cv value in each MV% are shown in Table G.1.

2. Calculate maximum mass flow rate of inlet steam that used to calculate maximum outlet temperature of the waste gases.

From Cv calculation formulas for water vapor (steam) in case $\Delta P \geq \frac{P_1}{2}$.

$$Cv = \frac{WK}{11.9P_1} \tag{G.1}$$

$$W = \frac{Cv \times 11.9P_1}{K}$$

$$W = \frac{420 \times 11.9 \times 5}{1 + (0.0013 + 0)}$$

$$W = 24{,}990$$

So, the maximum mass flow rate is 24,990 kg/h. And the mass flow rate in vary MV% is shown in Table G.2.

3. Calculate waste gases temperature in outlet stream of heat exchanger A.

$$Q_{steam} = Q_{WG} \tag{G.2}$$

$$\dot{m}L = \dot{m}c_p\Delta T \tag{G.3}$$

$$24{,}990\frac{kg}{h}\times 2095.9\frac{kJ}{kg} = 181{,}145\frac{kg}{h}\times 0.889\frac{kJ}{kg°C}\times(T_{out}-93)$$

$$T_{out} = 409.48\,°C$$

So, the maximum outlet temperature of waste gases is 409.48 °C. And the outlet temperature of waste gases in vary MV% is shown in Table G.3.

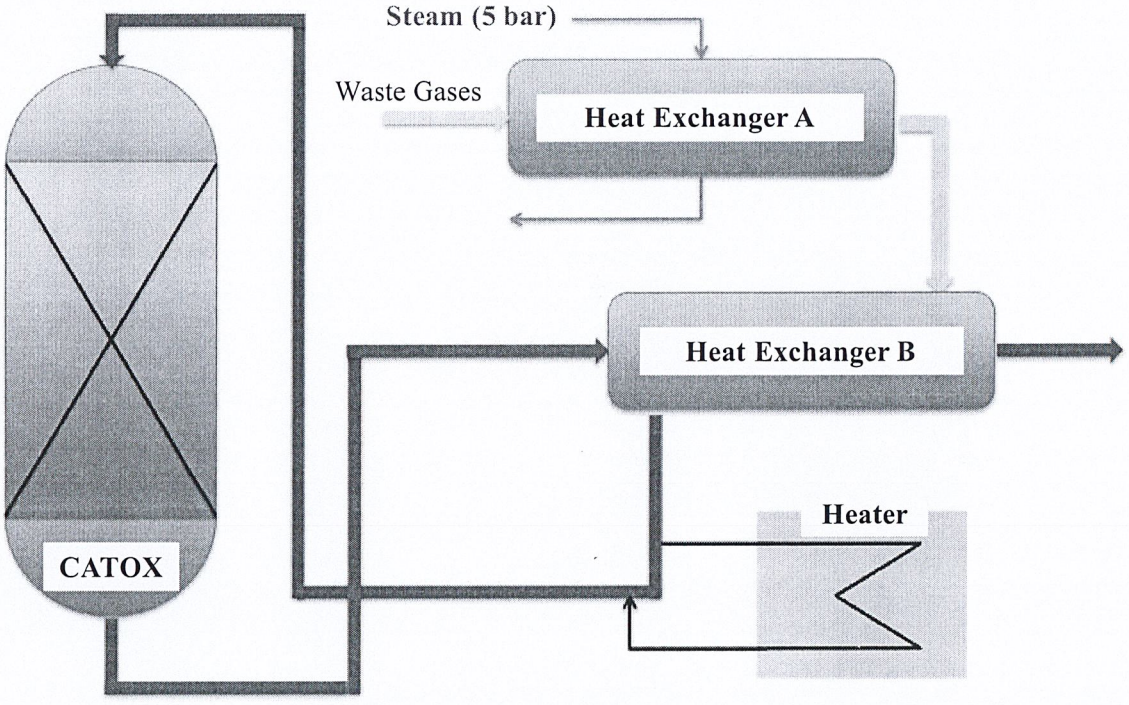

Figure G.1 Block Flow Diagram of the CATOX
[SMPC Plant Number 3, 2016]

Table G.1 CV Value Calculation [SMPC Plant Number 3, 2016]

MV%	CV%	Cv Value
0	0	0
5	0	0
10	0	0
15	2.5	10.5
20	3.5	14.7
25	4.5	18.9
30	6.5	27.3
35	8.5	35.7
40	12.5	52.5

45	17.5	73.5
50	25	105
55	30	126
60	40	168
65	50	210
70	58	243.6
75	66	277.2
80	70	294
85	80	336
90	85	357
95	90	378
100	100	420

Table G.2 Flow Rate Calculation [SMPC Plant Number 3, 2016]

MV%	Flow Rate (kg/h)
0	0
5	0
10	0
15	625
20	875
25	1,124
30	1,624
35	2,124
40	3,124
45	4,373
50	6,248
55	7,497
60	9,996
65	12,495
70	14,494
75	16,493
80	17,493
85	19,992
90	21,242
95	22,491
100	24,990

Table G.3 Outlet Waste gases Temperature Calculation [SMPC Plant Number 3, 2016]

MV%	Flow Rate (kg/h)
0	93
5	93

10	93
15	100.91
20	104.08
25	107.24
30	113.57
35	119.90
40	132.56
45	148.38
50	172.12
55	187.94
60	219.59
65	251.24
70	276.56
75	301.88
80	314.54
85	346.19
90	362.01
95	377.83
100	409.48

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