ENGINEERING PRACTICE

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SPECIAL FEATURE

Design Guidelines for Chemical Treatments in Distillation Columns

IACPE
INTERNATIONAL ASSOCIATION OF CERTIFIED PRACTICING ENGINEERS

WWW.IACPE.COM

ENGINEERING PRACTICE

VOLUME 1
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ABOUT

International Association of Certified Practicing Engineers provides a standard of professional competence and ethics. Identifies and recognizes those individuals that have meet the standard. And requires our members to participate in continuing education programs for personal and professional development.

In additional to insuring a professional level of competency and ethics the IACPE focuses on three major areas of development for our members: Personal, Professional, and Networking.

HISTORY

The **International Association of Certified Practicing Engineers** concept was formulated by the many young professionals and students we meet during our careers working in the field, running training courses, and lecturing at universities.

During question and answer sessions we found the single most common question was: What else can I do to further my career?

We found, depending on the persons avail able time and finances, and very often dependent on the country in which the person was from, the options to further ones career were not equal.

Many times we found the options available to our students in developing countries were too costly and or provided too little of value in an expanding global business environment.

The reality is that most of our founders come from countries that require rigorous academic standards at four year universities in order to achieve an engineering degree. Then, after obtaining this degree, they complete even stricter government and state examinations to obtain their professional licenses in order to join professional organizations. They have been afforded the opportunity to continue their personal and professional development with many affordable schools, programs, and professional organizations. The IACPE did not see those same opportunities for everyone in every country.

So we set out to design and build an association dedicated to supporting those engineers in developing in emerging economies.

The IACPE took input from industry leaders, academic professors, and students from Indonesia, Malaysia, and the Philippines. The goal was to build an organization that would validate a candidates engineering fundamentals, prove their individuals skills, and enhance their networking ability. We wanted to do this in a way that was cost effective, time conscience, and utilized the latest technologies.

MISSION

Based on engineering first principles and practical real world applications our curriculum has been vetted by academic and industry professionals. Through rigorous study and examination, candidates are able to prove their knowledge and experience. This body of certified professionals

engineers will become a network of industry professionals leading continuous improvement and education with improved ethics.

VISION

To become a globally recognized association for certification of professional engineers.

IACPE
INTERNATIONAL ASSOCIATION OF CERTIFIED PRACTICING ENGINEERS

LETTER FROM THE PRESIDENT

KARL KOLMETZ

ARE YOU A BORN LOOSER?

Many people believe that they were born in a losing environment. Perhaps they were born to a disadvantaged family. Leading them to believe there is no reason to try to succeed because of these external, non-controllable circumstances and then the lack of effort becomes a self-fulfilling prophecy.

This year I will celebrate my 60th birthday and over the years I have seen numerous people handed great opportunities that resulted in failures, as well as countless people with almost no opportunities that became successful. We are not born losers. We are not born winners. We are born decision makers and our decisions will determine our success or failure.

One may decide to condemn themselves to being a "born loser" by choosing not to try and improve themselves due to the external, non-controllable circumstances. Or one can decide in spite of these circumstances to work hard and move their lives in a good moral direction resulting in amazing opportunities. Doors of opportunity begin to open for people who work hard and are moral.

People you already know, including some you are not even aware of, will open doors of opportunity for hard working and moral individuals. One individual who helped me, with no motive other than goodwill, was Dr. James T. Richardson at the University of Houston. I was working a fulltime job and going to night school two nights per week. He encouraged and helped me through the challenging effort of working fulltime and attending night school.

In my life I have strived to help people who are hardworking and honest. I am not alone - there are many people who help those who help themselves. Dr. Richardson has my utmost respect and thankfulness for his help, but I do not owe him anything in return. My job now is to pay forward the goodwill Dr. Richardson provided me onto another hardworking and moral individual.

We are all born decision makers. The decisions we make in 2015 will have a great effect on our lives in 2020. Deciding not to try in 2015 is the easy path; to work hard and be moral is the difficult path. No matter what environment we were born into, we can choose to work hard and be moral

Over the past 60 years there were times I found myself on the wrong path. I predict that when you turn 60, if you are truthful, you will admit the same thing. The great thing about life is that we can choose to change paths.

What path will you choose in 2015? There is an easy path and difficult path to choose between. We are not born losers. We are not born winners. We are born decision makers and our decisions will determine our success or failure.

All the Best in Your Career and Life,

Karl

INDUSTRY NEWS

Indonesia's major petrochemical producer **PT Chandra Asri Petrochemical** plans to begin construction of a Rp 5.6 trillion (US$435 million) synthetic-rubber plant in Cilegon, Banten, early next year to take advantage of growing tire demand both at home and in other Asian countries.

PTT Global Chemical, Thailand's largest chemical company, and **Marubeni Corp**., a Japanese trading and investment house, is considering building a world-scale petrochemical complex that would use natural gas liquids, particularly ethane, produced in the Marcellus and Utica shale plays, according to Ohio Gov. John Kasich's office. With a site selected, the partnership will take the next 12 to 16 months to complete engineering design and permitting for the site, according to the governor's office.

French oil major **Total S.A.** is selling a 50 percent stake in its sole U.S. refinery in Port Arthur, Texas, and has retained investment bank Lazard to advise on the deal. Total, which has been trying to reduce its downstream exposure for three years, intends to remain operator of the 225,000 barrels-per-day (bpd) plant, which it has owned for more than 40 years, the source said. The move reflects the company's efforts to shift more capital toward production.

Barito Pacific to spend USD 317 Million for power plant.

Diversified petrochemical company **PT Barito Pacific (BRPT)** plans to build a power plant with a generation capacity of 150 megawatts (MW) near its industrial compound in Cilegon, West Java, with an initial investment of around Rp 4 trillion (US$317 million).

KLM Technology Group has just completed the third in their equipment design software series. First was a units conversion program, followed by a hydraulic line sizing program and now a control valve sizing program.

KLM Technology Group with **Summit Technology Management** has completed a process basic design package of a coalescer and filter package for a Middle East Chemical Producer.

KLM Technology Group with **Summit Technology Management** has completed a process basic design package of a clay treater for a Middle East Chemical Producer.

PT. DTP awarded 2 years contract by PT Trihasco Utama, to perform "Remaining Life Assessment (RLA) of Pressure Vessels, Storage Tanks, Lifting Equipment and Drilling Rigs – Pertamina EP".

PT. DTP awarded contract by Konsosium Enerkon – Lemtek, to perform "RBUI (Risk Based Underwater Inspection) Assessment for 33 unit Offshore Platforms – PHE ONWJ".

Summit Technology Management is planning to conduct regional training conference in November 2015.

NEWS

CENTRAL JAVA, YOGYAKARTA AND EAST JAVA (INDONESIA) MARKETING ROAD TRIP

In June IACPE visited several colleges in Yogyakarta, Central Java and East Java Indonesia to introduce IACPE's program. The colleges visited boast engineering faculty specializing in Mechanical Engineering, Metallurgical Engineering, Chemical Engineering, Electrical Engineering, Civil Engineering, Industrial Engineering, Environmental Engineering and Mine Engineering.

The following universities were visited:

Janabadara University
Adisutjipto Technology Institute
Yogyakarta National Technology Institute
Atmajaya University
Widya Mataram University
Sanata Dharma University
Widya Dharma University
Darul Ulum Islamic Centre Sudirman Ungaran University
Tidar University
Muhammadiyah Surakarta University
Sutan Fatah Demak University
PGRI Semarang University
17 Agustus 1945 Semarang University
Santo Paulus Chemical Industry University
Petra Christian University
17 Agustus 1945 Surabaya University
Dipenogoro University

In those colleges IACPE met with the Dean, Vice Dean, head of the education programs, lecturer's, public relations and administration staff who all were receptive to the program IACPE offers.

IACPE is thankful for all of the colleges who welcomed our organization and gave our team the opportunity to let us introduce our program.










DESIGN GUIDELINES FOR CHEMICAL TREATMENT DISTILLATION COLUMNS

By:
Karl Kolmetz
KLM Technology Group, Johor Bahru, Malaysia

INTRODUCTION

Distillation is the application and removal of heat to separate hydrocarbons by their relative volatility or boiling points. This necessary addition of heat normally in the feed stream or at the tower bottoms via a re-boiler can also lead to unwanted consequences such as polymerization, corrosion and reverse solubility. The removal of heat can lead to sedimentation, solubility effects, corrosion and precipitation. The concentration of certain constituents by the distillation process can cause corrosion, polymerization, sediment fouling and flow phenomena effects.

A properly designed distillation column can reduce the effects of these consequences, but in certain applications the polymerization, corrosion and other effects are very prominent leading to reduced separation efficiency in the column. This reduced separation efficiency increases the need for column maintenance and unit down time. In these applications a review of tower internal design and process chemical treatments should be initiated. Previously a review of tower internal design was published (1), whereas this article will discuss the application of chemical treatments in distillation columns.

DISTILLATION ECONOMICS OF FOULING

Distillation is the most widely utilized separation technique and there are basically two main types of chemical treatments in distillation columns; one is for corrosion control and the second is fouling control.

Distillation can be utilized in very clean services such as ethylene fractionation which, might fractionate for greater than ten years with no loss in efficiency due to corrosion or fouling - to very highly corrosive and fouling services. In Butadiene distillation, which is a highly fouling application, some fractionation applications are measured in days.

There are a least four types of chemical treatments in the process industry distillation.

1. Antifoulants which include dispersants, inhibitors, metal deactivators, retardants, antscalants, and antipolymerants
2. Corrosion Inhibitors which include neutralizers, and both nitrogen and non-nitrogen-based filming corrosion inhibitors
3. Phase Separation Chemicals which include emulsion breakers, defoamers, antifoams, extraction aids, and solids-settling aids.
4. Scavengers which include agents to remove sulfides, oxygen, peroxide, and carbonyls.

Several general factors influence the corrosion or fouling potential of a distillation process. These include feedstock, temperatures, reboiler heat fluxes, and hydrocarbon residence time. The type of feedstock for a distillation column has a large influence on the fouling potential. Many crudes type have high higher fouling and corrosion potential than others. Feeds that have olefin or diene concentrations will have increased foaming and fouling potentials.

The general symptoms of tower corrosion or fouling are many but they may include;

1. Increasing or decreasing tower pressure drop
2. Inadequate separation leading to reduction in product capacity and purities
3. Tower temperature profile changes
4. Requirement to run the reflux rate higher or lower than design
5. Short re-boiler run lengths
   A. Increasing steam chest pressure
   B. Increasing condensate temperature
   C. Increasing steam flow
   D. Products not meeting specifications
6. Re-boiler fouling and plugging
7. Level control issues
8. Instrument issues such as the leads line to instrumentation plugging.

There are many benefits for utilizing chemical treatments, including increased capacity, reduced maintenance, and reduced environmental exposure leading to improved worker safety. By reducing the corrosion and fouling of a distillation column a tower may have higher separation efficiency. This increased separation efficiency can improved product quality while increasing capacity and production. Additionally increased separation efficiency can lead to lower energy consumption in re-boilers and refrigerated condensers.

Reducing the corrosion and fouling of a distillation column will reduce turnaround frequency. In one case at an ethylene plant the DeEthanizer reboiler cleanings averaged 21 days, and with proper chemical treatments went to 8 months. The increased run length will reduce maintenance costs with the added benefit of reducing personnel exposure to carcinogenic chemicals found in fouling deposits while cleaning the tower or reboiler. Some species like butadiene and benzene have been shown to be carcinogenic. The species can be released when cleaning the tower and reboilers leading to unnecessary exposure to personnel. This benefit extends beyond the typical return on investment.

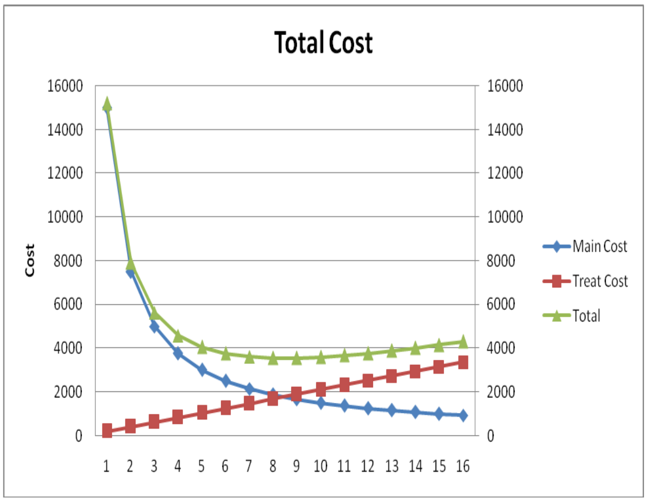
A typical return on investment for a chemical treatment programs should be 100%. If you extend your run length from one month to 8 months if can be as high as 1000%.

Each chemical treatment program needs to be evaluated correctly to calculate the return on investment. The total maintenance cost of cleaning a tower or reboiler needs to be calculated and plotted against the cost of the chemical. Each cost is inverse to each other.

As chemical treatment increases, the maintenance cost decreases, but the chemical cost increases. The sum of the two costs will form a minimum at the optimum treatment dosage and maintenance interval. Environment considerations may shift this minimum to reduce potential exposure.

For example, if it cost USD 15,000 to clean a heat exchanger the maintenance monthly cost will be 15,000 divided by the number on months on line. Do not forget to factor in the environmental decontamination cost. If chemical cost is USD $200.00 per month and increases 5% per month for each month of increased life, these two costs can easily be plotted to obtain the proper desired run length of the application. In this example energy cost was not considered.

The goal would be to achieve the calculated run length at the lowest possible cost. Treatment targets might be 10% residual chemical and 90% consumption of the chemical injected. It is a good practice to measure the residual chemical in the tower bottoms because of the reboiler circulation rate is much higher than most people envision. A typical reboiler will only have about 30% vaporization rate and can have 3 to 10 times the tower bottoms product flow rate.



A good rule of thumb is 25 ppm or less of chemical treatment based on the feed stream. This rule of thumb, like most rules of thumb depends on many factors such as the chemistry, concentration of the inhibitor and severity of the fouling potential.

CORROSION CONTROL

Corrosion is a major issue in distillation equipment even with proper designs. Multiple factors can interact and create corrosive attack. With the current run length of plants between maintenance outages approaching five years, corrosion control is a must to maintain distillation efficiency and recovery.

Areas of corrosion in distillation include; crude distillation, vacuum distillation, and solvent extraction. Proper metallurgy selection and then proper chemical treatment is essential to prevent corrosion in the distillation equipment for hydrocarbon and chemicals processing.

Corrosion treatment chemicals include neutralizers, filmers, and other corrosion inhibitors. These chemical can prevent or mitigate damage from galvanic bimetallic, aqueous acidic, and under-deposit corrosion, as well as pitting.

Crude Distillation

Corrosion in refinery crude distillation units is a common industry problem. Acids or salts present in the distillation column overhead system may cause corrosion when the right conditions exist. For this reason, it is common practice to inject corrosion inhibitors, neutralizer chemicals, or in some instances wash water to control corrosion in the column overhead system.

Crude Distillation Unit overhead corrosion diminishes unit reliability and operation in a number of ways. Some effects of overhead corrosion include equipment replacement and repair, lost throughput, reprocessing costs, offspec products, and downstream unit fouling. The two most common causes of overhead corrosion, acid corrosion and under salt corrosion stem from the presence of hydrochloric acid (HCl). Acid corrosion occurs when a condensed water phase is present and is most often characterized by a general metal thinning over a wide area of the equipment. The most problematic form of acid corrosion occurs when a pipe wall or other surface operates at a temperature just cool enough for water to form. HCl in the vapors forms an acidic azeotrope with water leading to potentially very low pH droplets of water.

Under-salt corrosion occurs when corrosive salts form before a water phase is present. The strong acid HCl reacts with ammonia (NH_3) and neutralizing amines—both weak bases—to form salts that deposit on process surfaces. These salts are acidic and also readily absorb water from the vapor stream. The water acts as the electrolyte to enable these acid salts to corrode the surface. Pitting typically occurs beneath these salts. (3)

The principal agent causing overhead corrosion is hydrochloric acid, although amine hydor-chlorides, hydrogen sulfide, organic acids, sulfur oxy-acids, and carbon dioxide can also contribute to overhead corrosion. Oxygen, introduced through poorly managed water wash systems can make corrosion worse.

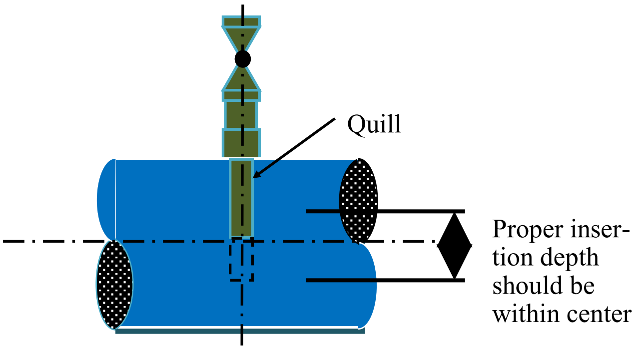
Hydrochloric acid induced overhead corrosion is primarily controlled by chloride management in the incoming crude oil and secondarily controlled by the use of supplemental injection of organic neutralizers and corrosion inhibitors in the overhead system. Chloride management consists of good crude tank handling, desalting, and then polishing/neutralizing with aqueous sodium hydroxide, which is commonly called caustic.

Refinery crude feeds contain water and inorganic salts (sodium, magnesium, and calcium chloride). Hydrolysis of calcium and magnesium chlorides ($MgCl_2$ and $CaCl_2$) occurs when crude oil is heated in the pre-heat exchangers and fired heaters. (2)

Many refiners inject caustic into the crude feed to the crude unit distillation tower to control condensation of hydrochloric acid downstream of the distillation tower in the overhead line. Caustic injection is carefully balanced with chloride levels measured in the overhead receiver.

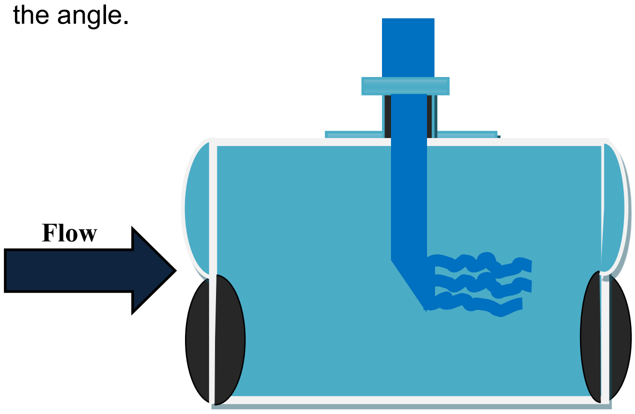
Typically, operators specify chloride levels to be between 10 and 30 ppm. The lower limit is set to avoid over-treatment with caustic. Over treatment with caustic can result in contamination of the heavy products from the crude distillation tower with sodium, which can affect downstream units such as cokers, visbreakers, and Fluid Catalytic Cracking (FCC) Units. One best practice limits sodium to 25 ppm in the visbreaker feed.

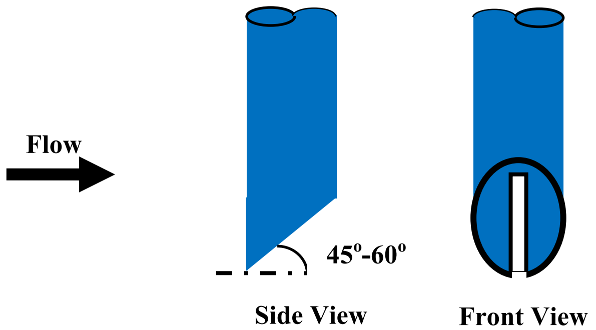
Caustic treatment has been ongoing for many years and the lessons learned from caustic treatment can be applied to other types of chemical treatments. How the chemical treatment is introduced to the process is very important to the success of the treatment. A typical injection quill might look like the following example.



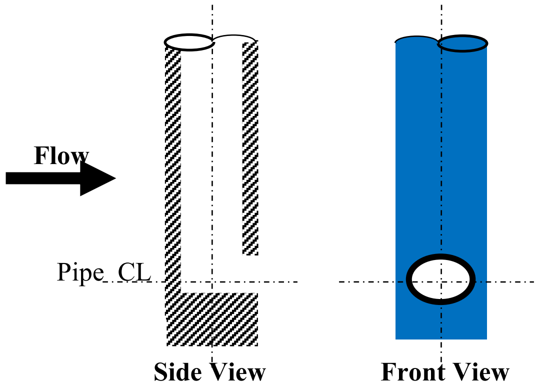
Generally, the most effective position for chemical injection is at the center of the pipe. The highest fluid velocity is normally at the center of the line, therefore, injection at this point is intended to prevent concentration of the chemical at the edge where the velocity is low due to friction and will ensure efficient distribution of the chemical treatment.

The design of a chemical injection quill uses an open end quill with a beveled tip that is slotted. The concept for this design is that the process stream pushes the treatment mixture through the slot in the quill which will create turbulence and mixing downstream. Moreover, this design restricts the treatment flow to the pipe centerline area promoting mixing and dilution prior to contacting the pipe wall. It also is used to minimize the vortexes that form on the back side of a non angled quill. The angle and the slot minimize the down stream vortexes that are formed. If non-slotted some recommendations are to reverse the angle.





The preferred design of a caustic injection quill is one that directs the caustic flow downstream, such as the side-hole quill, with the opening oriented downstream.



Naphthenic Acids in Crude and Vacuum Tower

Processing crude oils containing high levels of calcium naphthenates can present a number of operating challenges. Two processing technologies can help refiners successfully process these crudes. The first is a metals removal technology developed to remove calcium in the crude unit desalting operation and the second would be chemical treatments in the crude and vacuum columns. (3)

Several crude oils have come into production within the last few years that contain high levels of calcium naphthenates. Typically, these crudes are medium to heavy (specific gravity 0.89 – 0.95 kg/l), highly biodegraded oils, high in naphthenic acid content, and containing high concentrations of calcium ion in the formation water.

The calcium naphthenates found in many crude oils are largely insoluble in oil, water and solvents. Calcium naphthenates can cause fouling in separators, hydrocyclones, heat exchangers and other upstream production equipment. When blended into refinery crude oil feedstocks, these crudes can create a number of processing and product quality challenges in the tank farm, crude unit and downstream units.

These processing issues result from several observed attributes of crude oil blends containing calcium naphthenates :

- High calcium content of atmospheric and vacuum resids
- Higher levels of low molecular weight organic acids in crude unit distillation column overheads
- Increased high temperature naphthenic acid corrosion activity

Higher Levels of Organic Acids in Crude Unit Overhead Systems

Processing crudes high in calcium naphthenates, as with many high TAN (Total Acid Number) crude oils, can result in higher loadings of low molecular weight organic acids and CO_2 in the upper portions of the crude and vacuum columns and overhead condensing systems. The amount and distribution of lower molecular weight acids and CO_2 in these systems is a function of the distribution of organic acid molecular weights in the crude oil, plus heater outlet, side cut, and column overhead temperatures.

The higher loadings of organic acids and CO_2 in crude unit distillation towers and overheads from processing high TAN crude oils may cause higher than desired corrosion activity in these areas.

In some cases, the current means of controlling aqueous overhead or tower corrosion may be inadequate under these new conditions. Refiners may need to re-assess the capabilities of their overhead wash water systems, or have to utilize different corrosion inhibitor chemistries that are more effective under the new system conditions.

An additional concern for chemical treatment in the crude unit overhead is the application of the filmer technology. This filmer, commonly known as the corrosion inhibitor, forms a thin film on the metallurgy and prevents corrosion. However most of the commercial filmers have a certain surfactancy and can cause a water emulsion to occur in the naphtha product stream. The water in the naphtha stream can caused downstream unit problems, mainly corrosion issues. Proper selection of corrosion inhibitors to minimize this effect should be taken into consideration when refiners consider different filmer technologies.

Increased High Temperature Naphthenic Acid Corrosion Activity

Processing crude oil blends high in TAN can increase the potential for naphthenic acid corrosion in crude oil distillation units. This phenomenon has been well documented in industry literature. If not controlled, high temperature naphthenic acid corrosion can result in higher equipment replacement costs, lower unit reliability and availability, and increased severity of downstream unit fouling due to elevated levels of iron naphthenates in crude unit distillates. Color stability may also be affected by the presence of iron naphthenates in crude unit distillates.

Naphthenic acid corrosion activity is dependent upon a number of key variables. The most important variables include:

- The naphthenic acid content of the hydrocarbon streams, typically measured by TAN (mg KOH/gram sample). Naphthenic Acid based corrosion is either reduced or augmented depending on:
  a. Wt. % sulfur
  b. Whether TAN is high or low
  c. Whether fluid phase is liquid or vapor
- The temperature of the metal surfaces being contacted by the corrosive hydrocarbons
  a. Naphthenic acids concentrate above 260 C boiling range
  b. Highest concentration in 316-427 C boiling range
  c. Lowest temperature where attack occurs ~200 C (400 F)
  d. Above 450 C (825 F) disintegrates into lower molecular weight acids
  e. Naphthenic acids corrosion activity is often high in location where acids condense out of the vapor phase.
- The shear stress of the hydrocarbon moving across the metal surface (a function of velocity and turbulence of the flowing stream)
  a. At low velocity, acid concentration caused by boiling and condensing causes attack. Small erosion effect on corrosion if velocity is between 1.2-6.5 ft/sec.

b. At high velocity, multiphase stream rapid corrosion can occur due to erosion-corrosion. Naphthenic acid corrosion is accelerated in furnaces and transfer lines where the velocity of the liquid/vapor phase is increased. High turbulence areas have severe corrosion.

c. Turbulence and cavitation in pumps may result in rapid attack

- The type of alloy in use where hydrocarbon TAN, surface temperature and shear stresses make the system susceptible to naphthenic acid corrosion attack

  a. Metallurgy - 316SS, 317SS and materials with higher alloys (more molybdenum) are more resistant to naphthenic acid corrosion.

Many areas of the crude distillation unit can be susceptible to high temperature naphthenic acid corrosion. These areas can most simply be identified as those which:

1. Are exposed to hydrocarbon fluids that contain corrosive levels of naphthenic acids

(Generally considered to be any stream with TAN > 0. 5 mg KOH/g, though lower thresholds apply in some cases).

2. Operate at temperatures of 220 – 400°C (425 – 750°F), and:

3. Are constructed with metallurgy not generally considered to be resistant to naphthenic acid corrosion attack. 316, 316L, 317 or 317 L stainless steels are generally considered to be resistant materials.

Areas of the crude unit that are susceptible to naphthenic acid corrosion according to the above parameters typically include:

- Hot crude preheat exchanger network
- Atmospheric heater tubes
- Atmospheric tower transfer line
- Lower section of atmospheric tower (lining, trays) and associated atmospheric gas oil (AGO) pump around/product draw system
- Atmospheric tower bottoms line and any bottoms heat exchangers (if not integrated with vacuum unit)
- Vacuum heater tubes
- Vacuum tower transfer line

- Vacuum tower (lining, trays, packing) and associated LVGO, and HVGO pump around/product draw systems
- Vacuum tower over flash draw and “pump back” lines and associated equipment
- Vacuum tower bottoms line and heat exchangers

Other areas of the unit may also be susceptible depending on crude blend properties, unit design, operating conditions and actual materials of construction.

One of the greatest concerns refiners face when processing high TAN crudes is the potential for high temperature naphthenic acid corrosion attack. However, years of experience in this area have yielded several strategies that can be implemented to identify susceptible areas of the unit, to successfully mitigate naphthenic acid corrosion, and to effectively monitor this type of corrosion activity.

The first phase of an engineered solution is to perform a comprehensive high TAN impact assessment of a crude unit processing a target high TAN blend under defined operating conditions. An important part of the any solution system is the design and implementation of a comprehensive corrosion monitoring program. Effective corrosion monitoring helps confirm which areas of the unit require a corrosion mitigation strategy, and provides essential feedback on the impact of any mitigation steps taken.

With a complete understanding of the unit operating conditions, crude oil and distillate properties, unit metallurgies and equipment performance history, a probability of failure analysis can be performed for those areas which would be susceptible to naphthenic acid corrosion. Each process circuit is assigned a relative failure probability rating based on the survey data and industry experience.

Corrosion inhibitors are often the most economical choice for mitigation of naphthenic acid corrosion. Effective inhibition programs can allow refiners to defer or avoid capital intensive alloy upgrades, especially where high TAN crudes are not processed on a full time basis.

The use of Best Practices for high temperature inhibitor applications ensures that the correct amount of inhibitor is delivered safely and effectively to all of the susceptible areas of the unit.

Crude blending is the most common solution to high TAN crude processing. Blending can be effective if proper care is taken to control crude oil and distillate acid numbers to proper threshold levels.

Fouling Control

Several general factors influence the distillation fouling potential of a process. These include feed stock, chemistry, temperatures, reboiler heat fluxes, and hydrocarbon residence time. The type of feedstock for a distillation column has a large influence on the fouling potential. Feeds that have olefin or diene concentration will have increase foaming and fouling potentials.

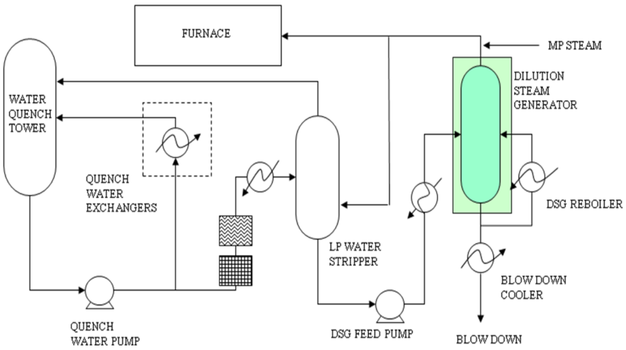
The column operating temperature affects fouling rates. In a refinery the crude unit and hydrotreater units might have towers that run under a vacuum to reduce the bottoms operating temperature to reduce fouling and product degradation. In an ethylene unit a DePropanizer tower might have the overhead cooling be refrigeration to reduce the tower bottom temperature. The goal would be to operate the column below the fouling initiation temperature of the contained fouling species.

For highly fouling services restrict the reboiler heat flux. A typical reboiler might have as much as 30% vaporization and high heat fluxes. Reducing the percent vaporization and using a lower heating medium will reduce fouling potential. The hydrocarbon residence time will affect the fouling rate. Design columns to have lower residence times in fouling services. At lower charge rates residence time is increased, minimize low charge rates when possible.

Olefin and Diene Polymerization in Ethylene Units

The pyrolysis cracking in olefin furnaces will produce olefin and diene compounds. The first cracking furnace was designed to produce crude butadiene for synthetic rubber applications, and the ethylene and propylene were flared as an unwanted co-product.

The styrene and the butadiene produced in the pyrolysis reactions can create issues in the downstream distillation columns. If the styrene is allowed to from an organics and hydrocarbons emulsion in the quench water tower, the styrene can travel with the normal water streams and when heated polymerize as in the following example. It is important to keep an emulsion from forming in the bottom of the quench water tower for this reason. The proper pH control in the tower will reduce the chance of emulsions.



Olefin Unit Distillation

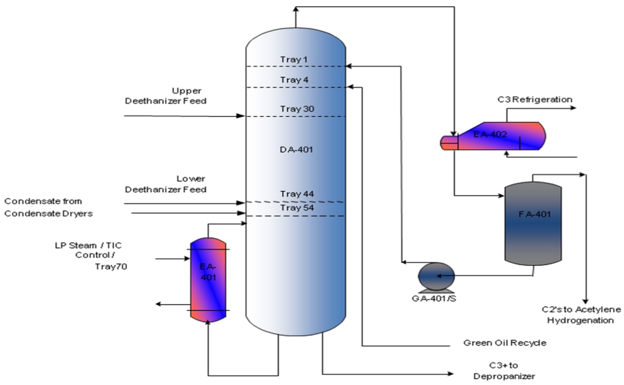
Olefin unit distillation is a series of tower separating the species. Each olefin vendor has their preferred flow sequence. Some will have the DeMethanizer first and some will have the DePropanizer first.

DeMethanizers

Each flow sequence will have similar issues with the olefins and di-olefins. Typically the DeMethanizer has only minor fouling potential. This is because the operating temperatures are below the polymer initiation temperature and the concentrations of the reactive monomers are low at this point in the process.

DeEthanizers

DeEthanizers can have very high fouling potentials depending on their operating conditions. One of the author's first assignments when he joined an ethylene gas cracker in 1995 was to trouble shoot a DeEthanizer polymerization issue. The margins were excellent and the unit was run at high capacity and severity – producing many olefins and di-olefins. The reboiler run lengths were about 20 days. The chemical vendors were given multiple opportunities to experiment. One vendor decided to try a dispersant and inhibitor at same time. The run lengths were successfully extended to 8 months. Later plant modifications were made to extend the run lengths.



DePropanizers

DePropanizers are one of the most challenging fouling potentials in an olefins unit due to the tower bottoms temperature being close to the polymerization initiation temperatures and the high concentration of the monomers (butadiene, styrene and isoprene). Some designs utilize a dual DePropanizer design with a low and high pressure towers to reduce the polymerization potential. Some designs utilize a single DePropanizer that has refrigeration in the overhead to reduce the polymerization potential.

Even with the dual towers and refrigeration fouling does occur because the butadiene species is re-boiled. In one application the producer decided to reduce the chemical treatment to save cost. The reboiler fouled to the extent that the bundle could not be pulled. The shell and tubes were sent to an external vendor for cleaning.

It is important to monitor the heat transfer coefficient, the tower pressure drop and consider the amount of residual chemical in the DePropanizer. A cross check of the monitoring of the heat transfer coefficient is the steam chest pressure.

A key point for chemical treatments is to remember the liquid flows and compositions inside the column. We tend to measure the external flows and compositions – feed, reflux and tower bottoms.

For example the following DePropanizer the stream flows and compositions may be reviewed. In the reflux there is an added recycle stream so the mass balance has to take this into account.

Stream	Flow	Composition	Temperature
Feed	45 t/hr	Butadiene 14%	56 C
Reflux + Recycle	56 t/hr	Butadiene 1%	43 C
Distillate	67 t/hr	Butadiene 1%	43 C
Internal Flow above the feed	57 t/h		
Internal flow below the feed	102 t/hr		
Reboiler Circulation	172 t/hr	Butadiene 23%	85 C
Tower Bottoms	34 t/hr	Butadiene 23%	85 C

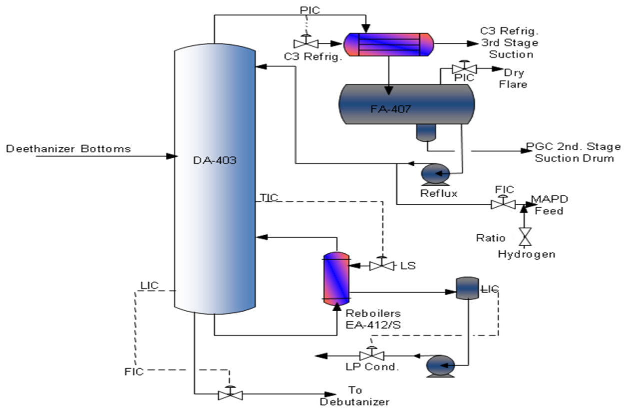
Here is an example of butadiene fouling in the bottoms of a DePropanizer column.

DeButanizers

In theory Debutanizers in Olefin Plants should be a controllable application, but they seem to have many challenges. Most of the butadiene fouling species should enter with the feed and be distilled overhead. The styrene and isoprene would normally be in the py gas from the quench system, but small concentrations will be in the DeButanizer. From the feed point to the overhead condenser will need some inhibitor as the di-olefins will be concentrated in the distillate. Some plants only add inhibitor to the overhead condenser.

The reboiler, even though it has high temperatures, should have low fouling potential. If the tower is not controlled properly and the fouling species, the di-olefins, are allowed to be present in the reboiler, fouling will occur. This can happen by under loading the tower and reducing tray efficiency.

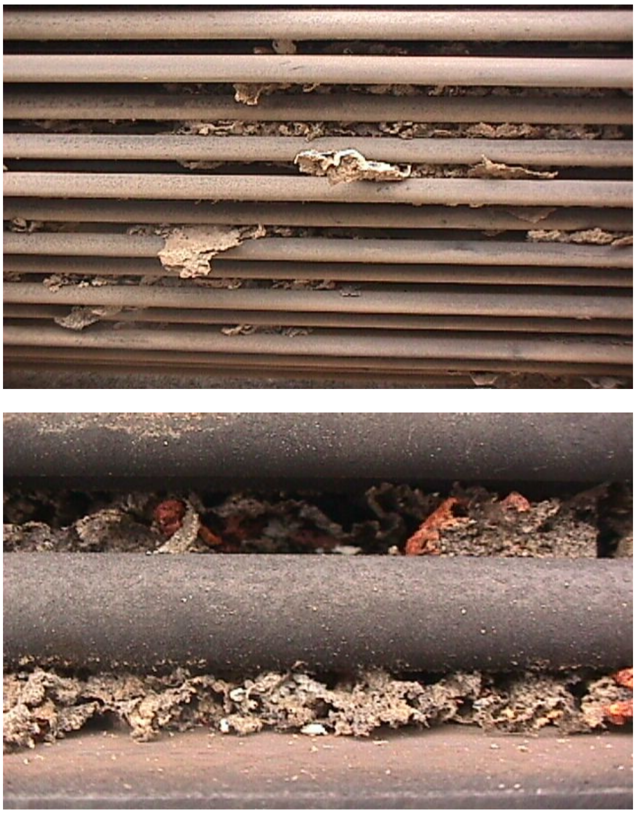
For a tray operation to be efficient there needs to be 70% of the design vapor and liquid loading. What often happens on the Debutanizer is that feed rate might be 60% of the design rate. The operations personnel tend to match the reflux rate to the feed rate, not understating that a low feed rate needs increased reflux needs to meet this 70% efficiency requirement.



As the tray efficiency decreases the fouling species travels down the column and fouls the trays and reboiler. The tray efficiency guideline is important to review during start up and low feed rate scenarios.

Monitor the tower bottoms chemical treatment during start up and other non routine scenarios to insure the higher temperature of the tower bottoms is protected from fouling during these events.

Butadiene fouling in an overhead condenser



Styrene Applications

Styrene monomer is the fourth largest chemical produced on an industrial scale and most ethylbenzene is utilized in styrene monomer production. The largest chemical produced on an industrial scale is ammonia for fertilizer production, followed by crude oil refining, and then ethylene by furnace pyrolysis. Styrene monomer has been manufactured commercially for more than fifty years with advances in the key unit operation areas of reactor design and distillation.

Styrene monomer (SM) is an important petrochemical used in the production of polystyrene and other styrenic resins such as acrylonitrile butadiene styrene (ABS) and styrene acrylonitrile (SAN). Ethylbenzene (EB) is produced primarily by alkylation of benzene with ethylene. EB is then converted to SM by dehydrogenation.

Radial Bed Reactor Overview

The feedstock, ethylbenzene, is catalytically dehydrogenated to styrene in the presence of steam in a fixed bed, radial flow reactor system. The dehydrogenation reaction is favored by low pressures and is generally conducted under deep vacuum. Toluene, benzene, and some light compounds are formed as by-products. The overall reaction is endothermic with heat supplied by steam in the adiabatic reactors. Reactor effluent waste heat is recovered through heat exchange with combined feed and by generating steam which is utilized in the process. The off gas stream is compressed, processed through the off gas recovery section, and used as fuel in the steam super heater. The condensates from the condenser and off gas recovery section flow into the separator where hydrocarbon and water phases separate. The dehydrogenated mixture is fractionated to recover the styrene monomer product and recycle ethylbenzene, as well as benzene and toluene by-products. Inhibitors are added to prevent styrene polymerization in the process equipment.

The energy needed for the reaction is supplied by superheated steam (at about 720 ^{0}C) that is injected into a vertically mounted fixed bed catalytic reactor with vaporized ethylbenzene. The catalyst is iron oxide based and contains Cr_2O_3 and a potassium compound (KOH or K_2CO_3) which act as reaction promoters. Typically, 2.5-3 kg steam is required for each kilogram of ethylbenzene to ensure sufficiently high temperatures throughout the reactor. The superheated steam supplies the necessary reaction temperature of 550-620 ^{0}C throughout the reactor. The ethylbenzene conversion is typically 60-65%. Styrene selectivity is greater than 90%. The three significant byproducts are toluene, benzene, and hydrogen.

Styrene Distillation Overview

After the reaction, the products are cooled rapidly (perhaps even quenched) to prevent polymerization. The product stream (containing styrene, toluene, benzene, and un-reacted ethylbenzene) is fractionally condensed after the hydrogen is flashed from the stream. The hydrogen from the reaction is used as fuel to heat the steam (boiler fuel).

After adding a polymerization inhibitor, the styrene is vacuum distilled in a series of four or five columns (often times packed columns) to reach the required 99.8% purity. The separation is difficult due to the similar boiling points of styrene and ethylbenzene. Typical capacity per plant ranges from 70,000 to 100,000 metric tones per year in each reactor and most plants contain multiple reactors or units.

EB / SM Splitter Column

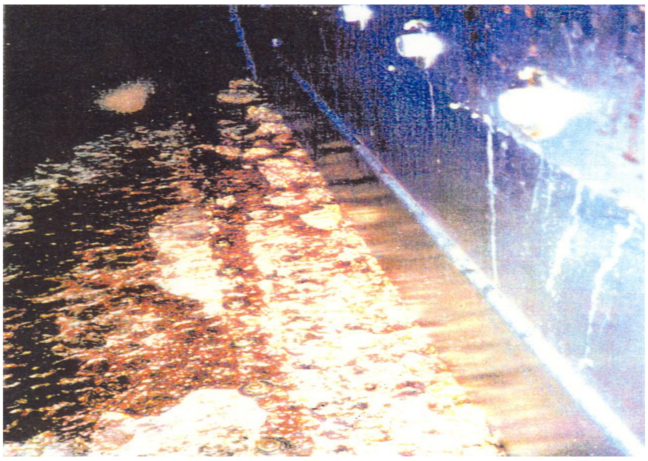
The purpose of an ethyl benzene (EB) / styrene splitter is to separate ethyl benzene from styrene. The distillate EB is recycled to Styrene reactors and the bottom product Styrene Monomer (SM) is sent to the Styrene Finishing column for heavy key removal. The EB impurity in the SM should be in the range of 100 ~ 500 ppm.

EB/SM Splitters are operated under vacuum due to the polymerization potential of styrene at elevated temperature. Polymers are undesirable in the monomer distillation column and can lead to plugging of distributors or packing and unit outages.

The rate of polymerization is directly proportional to time and increases exponentially with temperature. Both residence time and temperate must be minimized to reduce polymerization deposits. Current guideline is to keep the tower bottoms temperature below 120°C.

Generally steam ejector systems are used to maintain vacuum at the top of the tower. The typical column top pressure is 100 to 400 mbar and the internals are carefully designed to reduce the tower overall pressure drop, minimize liquid hold up, reduce the bottom temperature and residence time. Some producers are increasing the tower pressure due to improvements in inhibitor formulations. This can increase capacity and improve heat recovery.

Many trayed towers have been upgraded to structured packing due to the polymer formation. Here is an example of polymer formation in a trayed styrene tower.



For Styrene Monomer (SM) distillation there are at least three types of chemical treatments that are utilized normally together with synergy.

The first is a commodity chemical which is base loaded into the distillation towers and can be recycled to reduce cost. Along with the commodity chemical are specialty chemicals which are anti-polymers and retarders. The three components will need to be balanced to attain synergy, maximum styrene production while maintaining the lowest treatment cost.

The challenge of commodity chemical is the environmental and safety concerns. One of the first and still widely utilized low temperature commodity chemical inhibitors is TBC (tertiary-butyl catechol). TBC may cause permanent tissue damage. It is a low temperature inhibitor hat is added to the overhead of the column, in styrene storage tanks and during shipment.

Several high temperature commodity chemicals exist and function as retarders such as dinitrophenols, phenylenediamine, and hydroxylamines. They include DNP (Di-Nitrophenolic), DNBP (2-Sec-butyl-4,6-dinnitrophenol), DNPC, and dinitrocresol (DNC) compounds, which again has environmental and safety concerns, but they are less than TBC. A challenge of the nitrogen based inhibitors is that the tar residual is sometimes burned as fuel. These nitrogen based inhibitors can produce Nox as they are combusted.

DNBP may be one of the preferred commodity chemicals. In one application with DNPC the pH in the overhead of the column was lowered and some polymer was found cross linked in the tower bottoms.

The retarder acts as a safety net for an extended tower outage. Retarders have slower reaction rates to inhibit the polymerization. They react at 10^3 to 10^5 ranges providing extended protection during power failures. The retarder can be recycled for extended usage. A normal retarder dosage might be to maintain 400 to 600 ppm in the recycle stream.

True inhibitors have very fast reaction rates to inhibit the polymerization rates. An example would be nitroxyl stable free radical. A true inhibitor tends to react in the 10^7 to 10^8 ranges and typically only provides a few hours of protection.

The polymer concentrations are monitored in each of the last three fouling towers. The EB Recycle Column might be targeted to be at 1500 ppm polymer, while the SM Column might be targeted at 2.5% polymer, and the Finishing Column might be targeted at 10% polymer.

CONCLUSIONS

Proper chemical treatment in distillation systems involves understanding distillation principles such as residence time, internal vapor and liquid flows, reboiler design and the chemistry of the process.

Economics of chemical treatments and other engineering projects are very important and should be calculated for each application and project. Sometime the actual calculation will surprise you by being not what you expect.

A successful application of chemical treatment must include how the chemical is added to the process and potentially removed. Chemical treatments need to be reviewed on several levels including corrosion or fouling abatement within economic and environmental constraints.

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