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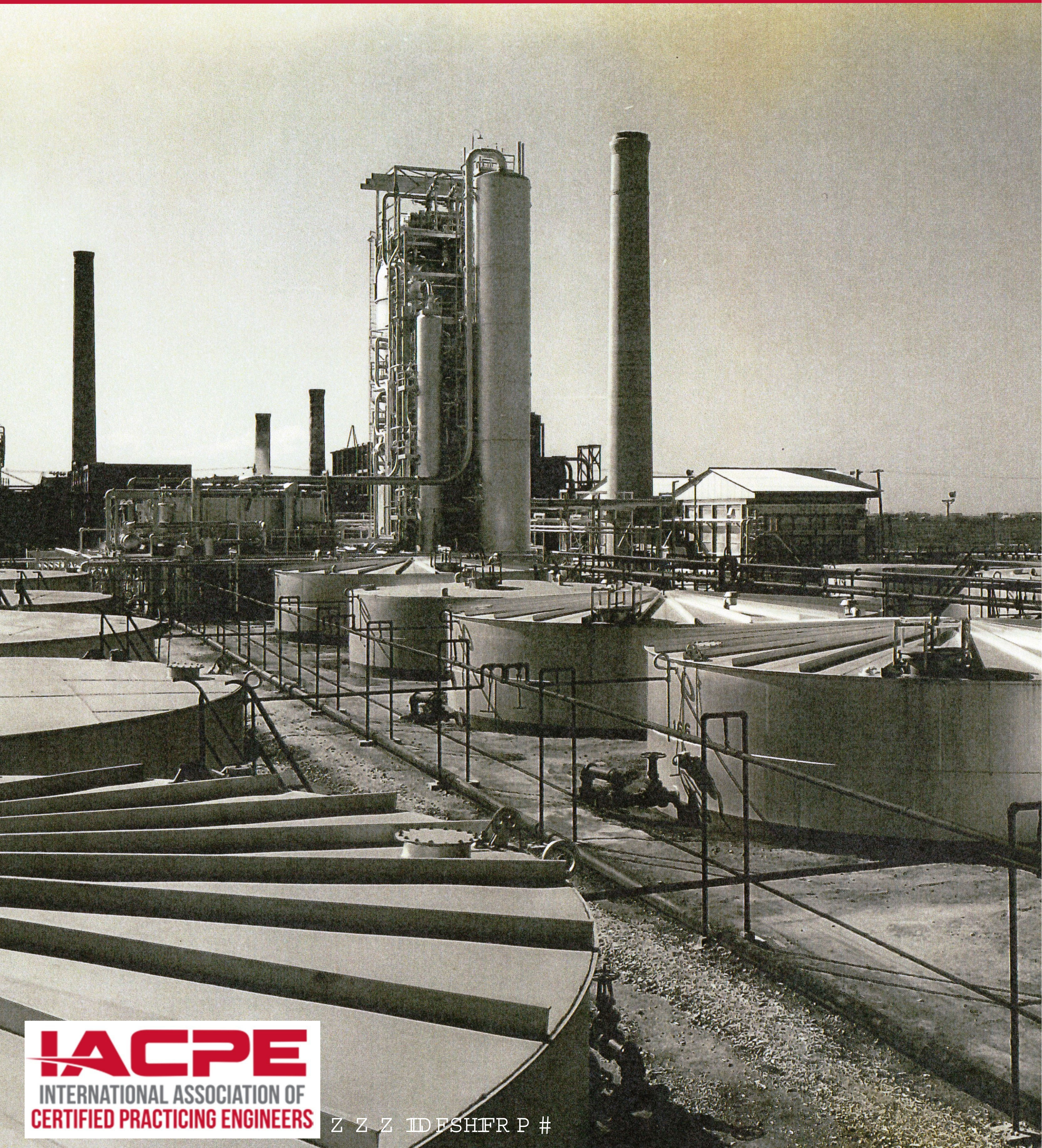

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In This Issue

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SPECIAL FEATURES

2021 EDITORIAL CALENDER

Month	March	May	July	September	November
Industry	Refining	LNG	Midstream & pipelines	Ethylene	Polymers
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Safety, Sustainability & Digital	Biorefining	Big data	Process Safety	Water treatment – Boilers and Cooling Towers	Environmentally Friendly Circular plastic

Rock Bottom View

Will Oil's Boom & Bust Price Cycles Soon Fade Into History?

Ronald J. Cormier, *Engineering Practice* Contributing Author

The hot weather is getting downright miserable from my porch in Central Texas, though hopefully some of you readers are also enjoying more temperate, enjoyable climes. Differences aside, the single global constant that we have all been challenged with over the last 18 months has been an extremely devastating one. The Covid-19 pandemic assured that no region on Earth be spared shocking, catastrophic collision with our lifestyles, health/hygiene, social contact, workplace locations, mobility habits, consumption patterns, and job losses. All of these unplanned sociological changes were frustrating, if not completely unprecedented, in modern times. At time of this article, these effects are comparatively insignificant compared to some 3MM+ souls who have perished, before vaccine development acted to slow the tide.

The rollout of national vaccination programs is also expected to unleash huge pent-up oil demand in key areas of the global economy, potentially boosting demand growth to the highest levels in oil's history. This surging demand will meet with a supply shortfall created by producers that cut capital expenditure (capex) sharply when prices fell in 2020. As a result of the COVID-19 crisis, conditions are ripe for a boom in oil prices during 2021-2022. These fundamentals lead us to suspect a possible new oil price super cycle during the period, but how long will it last?

A quick rise in oil price will put pressure on suppliers, expanding capex to meet rising demand. Consumers will leverage efficiency, as well as increasingly available new technologies, to slow—or even avoid altogether—the price of oil and its byproduct emissions. However, other than the pandemic-affected dent in the overall supply chain, fundamentals remain strong; significant correction will be required to return to normal in a relatively short period of time.

"We've never had anything like it—a collapse and then a boom-like pickup," said Allen Sinai, chief global economist and strategist at Decision Economics, Inc. "It is without historical parallel."

This would suggest a high probability that a price boom will occur, but also that it could be over quite quickly—within 18 months, or even less. Perhaps more important, this oil boom could possibly be near the world's last. The oil market system continues to become more flexible, with both supply and demand more elastic than in the past, making booms less likely to happen. And even if they do occur, peak prices are likely to be lower.

Energy transitions are also underway as government and companies work to curb emissions and tackle climate change, slowing the rate of growth in fossil fuels demand. At the same time, higher prices, even if they last for short periods of time, will spur further investment in alternative fuels and accelerate movement away from fossil fuels.

Intelligent oil/gas companies will grasp these opportunities created by rising prices to repair their balance sheets, refine their strategies, and—in some cases—greatly increase investment in lower-carbon businesses (some not necessarily related to their core competencies). Additionally, they will need to avoid overspending and jeopardizing future competitiveness. Heavy users of oil will have to take steps to mitigate the impact of higher fuel costs on their long-term financial health.

*Heads Up, Assuming These Two Givens**

**We share a similar common directional view of 1…Covid's continuing, now more predicable path…and 2…OPEC+'s behavior and wherewithal…..*

This "perfect storm" may just contain the exact factors which cause oil consumption to soar over the next 18 months. As with any commodity, keeping demand and supply in balance—or close to it—is essential for stable oil prices. Since their 2020 low point, when a pandemic-induced slowdown in the global economy caused demand to slump, prices have risen as economic activity has started to pick up. This trend should accelerate due to an emerging imbalance between demand and supply.

As vaccinated individuals resume many of the ordinary activities denied them over the past year, oil demand could experience one of its strongest-ever growth periods. Several emerging themes could drive oil demand sharply higher.

- Consumer interest in travel is growing. Major travel/leisure researchers show US consumer interest in hotels and airline bookings rose sharply in 1Q21, which will help boost jet fuel demand, the one major fuel still well below pre-pandemic levels (it is not expected to fully recover until 2024). It should be noted that many countries and regions outside the US have yet to vaccinate significant portions of their citizenry. Conversely, in developed regions with significant vaccine coverage, the added confidence will also stimulate ground transportation and boost demand for gasoline and diesel, as consumers seek to reconnect with family members in distant places.
- Substantial personal savings were amassed by global consumers during lockdown. In the US, personal savings account for about 18% of disposable income—three times the amount during the 2008-2015 recession. According to Boston Consulting Group (BCG) calculations, if all the savings accumulated so far during lockdown were spent in one year, the US economy would grow by more than 8%, a rate not seen since the early 1950s.
- The global economy is improving. Given the underlying health of the global economy, combined with pent-up demand and significant discretionary funds available to meet that demand, global economic growth is set to boost oil consumption over the coming years. According to the International Monetary Fund (IMF), the global economy will grow by 6% this year and approximately 4% in 2022, helped by massive fiscal US stimulus packages plus those of many other countries.
- Jobless Benefits Phase-down..… notions in the US exist that it would be rational for some workers to choose jobless aid over a paycheck, if it amounted to more. But a recent study by the Federal Reserve Bank
- worker out of seven is likely to turn down a job offer because of the current $300 per week federal benefit, even considering a commute. Once these relief programs subside, the labor shortage, to the extent one exists, should end. Most impactful as a disincentive, is the US federal jobless benefit, which expires during the first week of September, and is not likely to be renewed. By 2024, most advanced economies will have returned close to their pre-pandemic growth path.
- Companies are reconfiguring supply chains; Supply may lag during the "hunting" phase…Companies that were working with lean inventory and just-in-time methods during the pandemic suffered the greatest negative impacts. The global supply chain is fragile—as the container ship Ever Given, recently stuck in the Suez Canal made clear—and it will be important to boost inventories above pre-pandemic levels. Transporting more products and components to fill negative inventories will require more oil as fuel to meet rising demand (and likely some whipsaw effect creating inventory excesses) in multi-modal transport.
- In addition, oil/gas companies reduced investment in upstream businesses by 35% in 2020, following the pandemic-induced demand decline. Investment levels are expected to remain low in 2021, as companies continue to control spending. This scenario, combined with a demand rebound, would force energy prices sharply higher.

But, The Oil Price Rise Will Be Over Sooner Versus Later….

Uncertainty around how these different forces play out makes it tough to predict when the boom will start or how high prices will go. But in terms of timing, an oil price boom based on a fundamental supply-demand imbalance could start as early as the third quarter of 2021 or be delayed until 2022. Are there good reasons to believe that it will not last for decades? Indeed, it could be over in 12 to 18 months.

Why? Because the oil industry and commodity markets have changed significantly during the past decade. The super cycle prior to 2008 had its origins in the 1980s, when lower prices caused a reduction in investment. These cuts allowed a semblance of market balance until the early 2000s, when oil producers faced a sharp rise in demand, particularly in Asia—a situation that was ended by the global financial crisis of 2007 to 2008 (and oil prices exceeding $150 per barrel). Since that time, the industry has become far more responsive to changing external conditions. Here's how:

- Oil production projects are both faster and smaller (think shale recovery in the West).
- E&P has reduced upstream costs significantly since 2014.
- OPEC+ is more nimble than its predecessor, OPEC.
- Changes in oil prices impact demand more quickly now than in the past.
- Communications technologies and reconnaissance research firms have improved the flow and rate of up-to-date information, making the industry far more transparent.

Without further treatment, increased oil consumption will cause higher environmental emissions. However, there are strong reasons why the oil price boom, if it happens, could possibly be the world's last—a development that would clearly help the effort to combat climate change.

In Closing…..

The last oil boom—really? By the time of the midterm elections in November 2022, conservatives' gripes about federal work disincentives are likely to be a distant memory. We're more likely to be talking about full employment. Also, alternative, non-internal combustion vehicles are gaining public acceptance by the minute.

As the world emerges from the COVID-19 crisis, an oil price boom is looking increasingly likely. The market conditions that create the boom will also squeeze its path—with surging demand coinciding with a shortage of supply. The price expansion will not last long. Despite the boom's relatively short duration, oil producers and consumers should plan ahead to tap opportunities, preparing for a post-pandemic, lower-carbon era and mitigate the risks of higher prices. Will this scenario play out?….let's all watch closely.

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Corrosion Monitoring in CDU Overheads

Shahzeb Hassan, CEng PEng MIChemE

It would not be wrong to say that in order to achieve the highest return on investment (ROI), a combination of crude blends, unit operations, corrosion control program & unit maintenance plays a significant role. With the declining trends of oil refinery margins & implementation of some new regulations like Marine residual fuel standard (IMO 2020). The refineries are moving ahead towards expansions of new processing units notably residue hydrotreaters and crackers. In this situation, the refineries may prefer to buy heavy crudes for higher residual yields. Therefore, a declining crude quality could be a major factor of increased salts and total sulfur in the crude feed. Consequently, monitoring of corrosion in Crude distillation columns overheads will be an important factor to consider in order to avoid units unwanted shutdowns and downtime losses. Corrosometer and corrosion monitoring through ER Probes by using checkmate Data Logger will only be covered in this writeup.

CDU OVERHEADS CHEMISTRY

One of the most common techniques for corrosion control is blending corrosive crudes with less-corrosive crudes, dependent upon refinery configuration and crude flexibility.

Most salts are diluted in the water phase that's why the crude oil's water content should be minimised, e.g. by draining crude oil storage tanks. A typical H_2O limit for desalted crude oil is max. 0.5 wt%. [1]

Varying amounts of chloride salts (i.e. $CaCl_2$, $MgCl_2$) that forms HCl due to hydrolysis during desalting, CDU secondary preheat train and associated fired heaters. Some amount of HCl is controlled through caustic addition at the downstream of desalter but remaining HCl is travelled in the form of vapors to the overhead system. HCl is non corrosive in vapor form but when an aqueous dewpoint occurs in overhead where the majority of the HCl readily enters in the first water phase that's where the most corrosive condition occurs. [4,5]

Other than HCL, the acid gases like H_2S, organic acids, sulfur compounds are also present in overheads that not only varies the consumption of neutralizer but also boostup the acid corrosion during low pH conditions. When neutralizing amine reacts with HCl it forms ammonium chloride which is hygroscopic in nature that

absorbs moisture and may cause of under deposit corrosion. The salt point temperature is therefore very important to note inorder to identify the possible locations of NH_4CL sublimation.[5]

PRIMARY CONTROLS [1,2,4,5]

The Key performance indicators for any CDU overhead systems are:

- Boot water pH should be maintained between 5.5 to 6.5.
- Iron appearance in boot water sample should be less that 1 ppm.

Firstly, water washing is an important tool to 1) dilute low pH water phases at dew point conditions and to 2) wash out salts from overhead piping and heat exchangers / air coolers.

Secondly, Iron sulfide protective layer of 10-50 microns thickness on overhead system also provides control against corrosion but at the same time it is pH dependant, any disturbance in pH breaks the layer and its outcome receive in boot water sample in the form of increased iron.

Thirdly, the filmer is also the part of corrosion control program which is normally hydrocarbon based and forms a protective layer and also act as dispersant.

SECONDARY CONTROL [1,2,4,5]

An additional control other than process stream analysis is corrosion monitoring system. Thus, the corrosion rate should be less than 5 mpy.

The data of electrical resistance (ER) probes, connected to an on line data acquisition system or monitoring through checkmate data logger could be compared with the chemical analysis of accumulated sour water after condensation in the overhead system.

There are methods other than ER probes like mass loss coupon measurement. In this method, a weighted sample (coupon) of the metal or alloy under consideration is introduced into the process and later removed after a reasonable time interval normally 3-6 months. The coupon is cleaned of all the corrosion products and is reweighed.The weight loss is coverted to a corrosion rate or a metal loss.

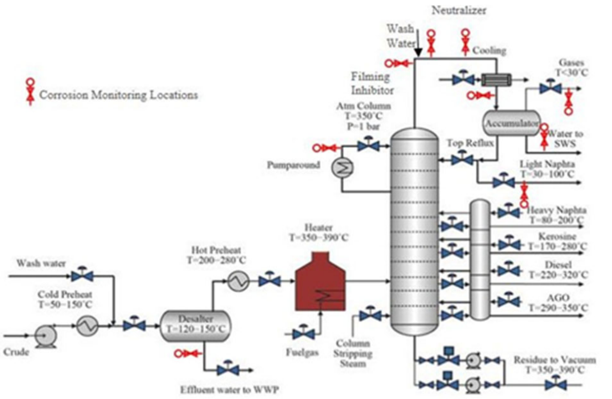

Figure 1. Typical Corrosion Monitoring Locations in Crude Distillation Tower Overhead System

ELECTRICAL RESISTANCE (ER) METHOD [6,7]

Retractable ER-probes of different models are being used since ages for measuring changes of electrical resistance of sensor made of carbon steel wire or cylinder.

For example, COSASCO Model 3500 Retractable Process Probes have a thin walled tubular sensing element made from the alloy of interest welded onto a body of the same material. Mild Steel bodies are Teflon coated. No other materials contact the corrosive process fluid. Materials of construction are carefully matched and welds are vacuum annealed during assembly to avoid preferential corrosion effects.

Figure 2. Model 3500

The ER probes is to be installed on the CDU Overhead lines on different locations where there is a possibility of corrosive environemnt and the corrosion rate can be measured directly through portable checkmate DL. The Checkmate Electrical Resistance Instrument provides high resolution and measurement accuracy of ER corrosion probes. The measurement cycle time for direct probe readings has been reduced to 30 seconds while still maintaining high accuracy. The checkmate with corrdata plus software option enables stored readings to be easily downloaded to a PC where graphing and analysis can be performed with corrdata plus software. The instrument is well suited for use in harsh field environments.

Figure 3. Checkmate ER Portable instrument

The portable ER measuring instrument can be connected or disconnected easily with the installed probes and feasible for a variety of different kind of probes with different shapes, sizes and materials. There are also flexibility of corrosion rates in different units like mils per year, mm per year and um per year.

PROCEDURE [3,6]

Electrical Resistance probes can be read using three different procedures: Quick, ID and New.The Quick reading allows the user to read a probe and view the result in approximately 30 seconds. The result of a Quick read can also be saved for future reference, calculation of corrosion rate and/or downloading to a PC. This screen will appear on the screen after processing of 30 sec.

The Div: reading is the cumulative metal loss (corrosion) of the probe element on a scale of 1,000 divisions. In the example above 214.7/1000 (two-hundred fourteen point seven one-thousandths of the element has been consumed by corrosion. In engineering units this metal loss would be expressed as 214.7/1000 or 0.2147 times the probe span

The Chk: reading is a measure of probe functionality or integrity. The initial value for ER probes is 800 ±50 divisions. It is recommended that a CHECK reading be taken and recorded immediately after unpacking a probe as it will be the value to which all subsequent CHECK readings will be compared. The general rule is that the CHECK reading should not vary by more than 1% (±10 divisions) from the initial value. If there is more than a 1% change, it is an indication of a loss in probe integrity and replacement is required.

The other method is through probe ID which is also written on the test tube given with the probe. Just dial the ID and wait for a 30 sec to pass for getting the result.

In order to check the rate through new method, go to the select probe type and select the installed probe and wait for 30 sec for processing towards results.

The final window that is shown on the instrument is displayed as follow. Repeatibility is recommended while performing this task to ensure that the final result is accurate. It would also be helpful if a proper past record is maintained.

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Corrosion monitoring and control in refinery process units by Alec groysman and Avihu hiram.

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TrayHeart
Tower Internals Design
TrayHeart is a professional software that performs hydraulic calculations for all types of tower trays, random and structured packings and liquid distributors. The development of TrayHeart started in 1998 and was continued jointly by universities, companies of the chemical industry and tower internals suppliers. TrayHeart ...
is based on multiple calculation models and large databases of packings, float valves, fixed valves, bubble caps, and liquid distributor templates
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Corrosion Control in Hydroprocessing Units | Keeping the Refining Hardware Safe, Reliable & Profitable

Dr. Marcio Wagner da Silva

INTRODUCTION

The highly competitive environment of the refining industry requires high availability and reliability of the refining hardware in the sense to maximize the operational lifecycle of the process units avoiding unnecessary shutdowns and production losses. One of the great threats to the availability and integrity of equipment in the refining industry is the corrosion phenomena that can lead to a reduction in the operation lifecycle of process equipment and, in extreme cases, severe accidents.

Some process units like FCC and hydroprocessing can suffer severe corrosion processes due to the process conditions that are subjected. The corrosion process in hydroprocessing units is receiving special attention in the last years due to the strong dependence of the downstream sector over these technologies considering that it's practically impossible to produce marketable derivatives without at least one hydroprocessing step, in this sense, maximize the operation lifecycle of these units can represent a great competitive advantage to refiners.

HYDROPROCESSING TECHNOLOGIES

Hydrotreatment technologies aim to remove contaminants from oil fractions, especially sulfur and nitrogen, in order to reduce SOx and NOx emissions by derivatives, as shown below.

$R\text{-}CH{=}CH_2 + H_2 \rightarrow R\text{-}CH_2\text{-}CH_3$ (Olefins Saturation)

$R\text{-}SH + H_2 \rightarrow R\text{-}H + H_2S$ (Hydrodesulfurization)

$R\text{-}NH_2 + H_2 \rightarrow R\text{-}H + NH_3$ (Hydrodenitrogenation)

$R\text{-}OH + H_2 \rightarrow R\text{-}H + H_2O$ (Hydrodeoxigenation)

Where R represents a hydrocarbon.

Figure 1 shows the typical arrangement for a hydrotreating unit with a single separating vessel, normally used for units of low severity.

The hydrotreating is applied in the finishing of the final products like gasoline, diesel or kerosene or like intermediate step in the refining scheme in refineries to prepare feed charges to other processes like Residues Fluid Catalytic Cracking (RFCC) or Hydrocracking (HCC) where the main objective is to protect the catalyst applied in these processes.

CORROSION PROCESSING IN HYDROTREATING UNITS

The corrosion phenomena in the hydroprocessing units can be divided into phenomena associated with high temperatures and associated with low temperatures. The corrosive processes associated with high temperatures are:

- Sulfide Corrosion
- Naphthenic Acid Corrosion

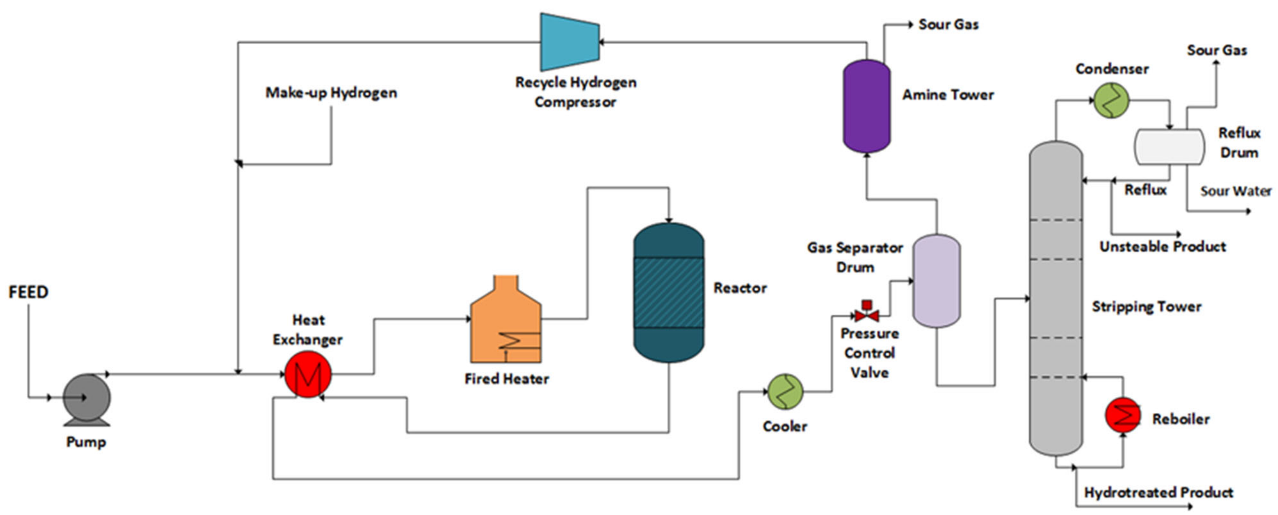

Figure 1 – Basic Process Flow Diagram for Low Severity Hydrotreating Process Units

- High Temperature Hydrogen Attack (HTHA)
- Hydrogen Embrittlement

The sulfide corrosion process is quite common in oil refineries and occurs due to the degradation of steel through the reaction of iron with sulfur compounds contained in the unit's feed streams, usually above 260 oC. In the case of regions of the unit without the presence of hydrogen, the application of steels containing 5 to 12% chromium is considered robust to ensure an adequate useful life for process equipment. According to Figure 2, the higher the chromium content in steel, the greater is the resistance to corrosion by sulfide. The addition of silicon to steels applied to hydrotreating units also contributes to reducing the rate of corrosion by sulfide.

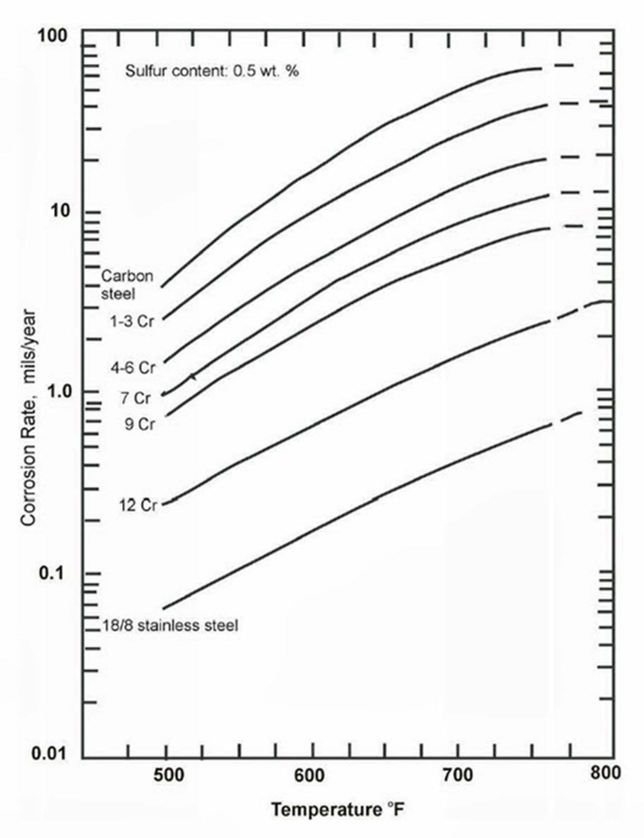

Figure 2 – Resistance of Steel to Sulfidation as a Function of Chromium Content

In the regions where hydrogen is present, the corrosive process is even more severe and follows a different mechanism from the one in the absence of this compound due to the reducing nature of the atmosphere (presence of H2S). In these cases, austenitic stainless steels are used, especially in severe process conditions such as deep hydrotreatment or hydrocracking units.

Naphthenic corrosion generally occurs in units subjected to the processing of currents with high acidity. The control parameter used is the number of total acidity (TAN) which is defined as the amount of KOH required to neutralize 1.0 gram of the intermediate, usually a number of total acidity above 0.30 mg KOH / g and higher temperatures at 240 oC can indicate the possibility of corrosion by naphthenic acids, in addition to these factors the turbulent flow regimes contribute to accelerating the corrosion rates in this case. The control of the total acidity of the crude oil can indicate the need for control measures regarding the naphthenic corrosion in hydroprocessing units, however, the combination of high acidity with reduced levels of sulfur in the crude oil and consequently of the intermediate currents can lead to greater severity of the corrosive process in this case, since the low sulfur content limits the formation of the protective layer of iron sulfide (FeS). Combating the mechanism of naphthenic corrosion usually involves the addition of molybdenum to steel, providing greater resistance to attack by naphthenic acids.

The attack by hydrogen at high temperature (HTNA) causes the reduction of the mechanical resistance of the steel due to the formation of flaws in the material structure caused by the reaction between hydrogen and carbon, according to the mechanism below.

$$8\,H + C + Fe_3C \leftrightarrow 2\,CH_4 + 3\,Fe \quad (1)$$

The presence of methane in the structure induces the formation of cracks in the steel structure and can lead to premature failures. In this case, preventive actions require the selection of adequate alloy steel (Cr, Mo, and V) and operation within the recommended pressure and temperature parameters, operating below the Nelson curve, as shown in Figure 3.

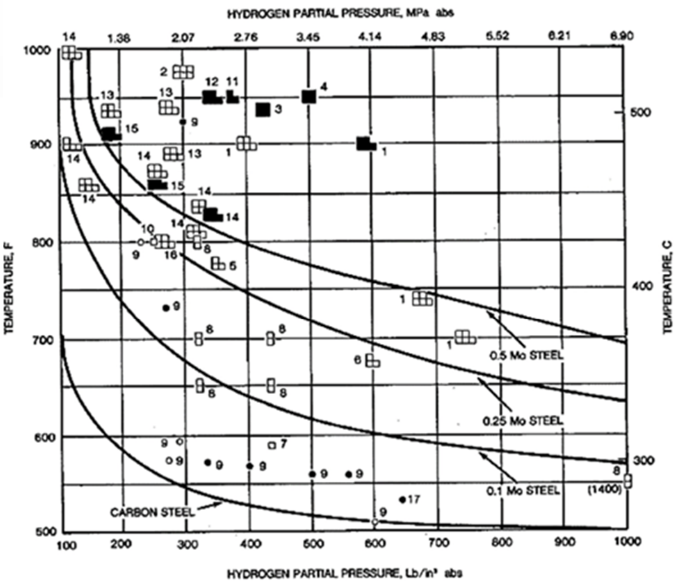

Figure 3 – Nelson Curve (Steel Operation Limits - Temperature x H2 Partial Pressure) - API 571/2011

The hydrogen embrittlement mechanism involves the contamination of steel by molecular hydrogen (H2) leading to the risk of failure, especially in periods of instability such as stopping and starting the process unit. The procedure for stopping and starting hydrotreating units is normally carried out at the lowest possible pressure as well as controlling the cooling or heating rate of the reaction system. Figure 4 shows the mechanism for the embrittlement of steel by hydrogen.

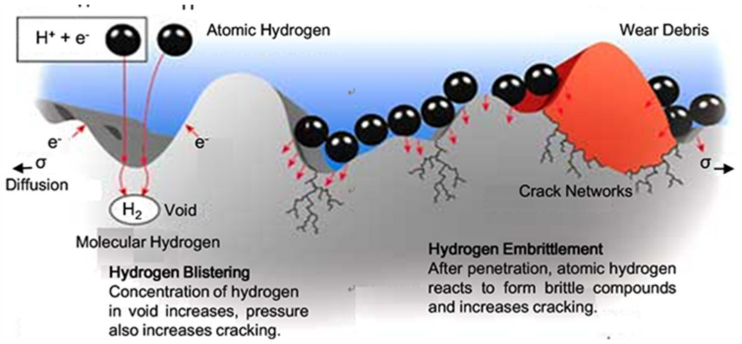

Figure 4 – Hydrogen Fragilization Mechanism (ZHANG, 2016)

Due to the need for high temperatures the above mechanisms are usually of concern in the load and reaction heating sections.

Corrosion processes associated with low temperature normally occur in the hydrogen separation and recycling sections of the hydrotreating units. The main mechanisms are:

- Salt Deposition
  1. NH4Cl, HCl
  2. NH4F, HF
  3. NH4HS
  4. H2S Fragilization
- Stress Corrosion During Shutdowns
  1. Attack by Polythionic Acids
  2. Chloride attack

The corrosion process resulting from the salts deposition is associated with the contaminants present in the charge currents of the hydroprocessing units. The processing of currents containing sulfur and nitrogen leads to the formation of H2S and NH3 in the unit's outlet currents as recycle gases, such gases can be combined to produce ammonium disulfide (NH4HS), according to reaction 2.

$$\mathbf{NH3_{(g)} + H2S_{(g)} \leftrightarrow NH4HS_{(s)}} \qquad \mathbf{(2)}$$

The concentration of salts formed depends on the content of contaminants in the unit's load, so units dedicated to the hydrotreating of bottom barrel streams tend to show more severe processes of corrosion by this mechanism.

Refiners typically use washing water injection to minimize the deposition of corrosive salts at key points on the unit such as the inlet pipes of the unit's separation section and replacement hydrogen. Figure 5 indicates the washing water injection point normally used in hydrotreating units.

The quality of the washing water is a relevant factor in the control of corrosion and salt deposition. Some refiners use boiler water or steam condensate for this service, however, due to the high cost of demineralized water, the application of rectified water from acid water rectification units is more common. In this case, the use of rectified waters from deep conversion units such as delayed coking and FCC should be avoided, which may contain cyanides that accelerate the corrosive process. Another relevant factor is the temperature of the wash water, the water needs to be injected in temperature below the salt deposition temperatures. The salt deposition temperatures vary with the severity of the hydrotreating units once the partial pressure of the salts is higher to high hydroprocessing pressures.

The embrittlement by wet H2S can lead to the embrittlement of carbon steel due to the

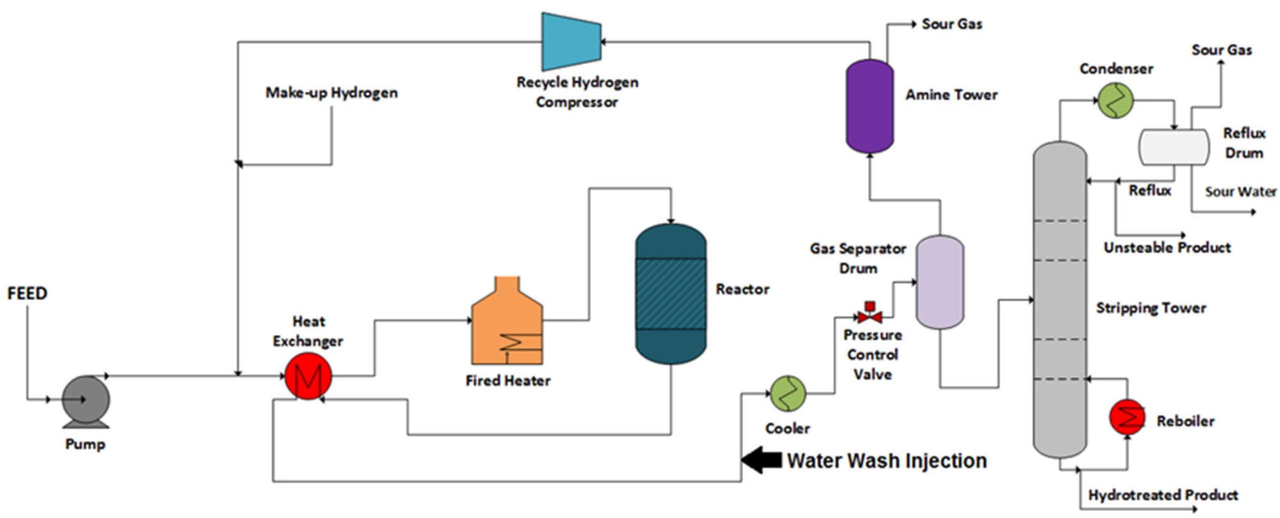

Figure 5 – Washing Water Injection Point in Hydrotreating Units

presence of H2S or NH4HS in the presence of water. In this case, the correct selection of materials and post-welding stress relief treatment can mitigate the risk of failure.

The embrittlement by polythionic acids is common in cargo heating and effluent cooling systems in the reaction systems. In this case, contamination with oxygen and water during maintenance stops leads to the formation of acids and risk of corrosion under stress, the appropriate selection of stainless steels (Stainless Steel 321 and 347) as well as the inertization of systems with hydrogen or nitrogen during maintenance stops can minimize the risks of corrosion by polythionic acids.

Chloride corrosion is a particular concern for hydrotreating units that consume hydrogen from catalytic reforming units. These units consume chlorine in the process of regenerating the acid function of the catalyst and, there may be contamination by chloride (HCl) in the hydrogen produced leading to contamination of the hydrotreatment unit. Austenitic stainless steels are very susceptible to failure due to chloride attack and their application should be avoided in regions susceptible to chloride contamination and under temperatures above 60 oC.

CONCLUSION

The availability of hydroprocessing units is a key issue for refiners as mentioned above and the control of the unit's corrosive process plays a key role in ensuring reliable and safe operations of the refining hardware, especially hydroprocessing units dedicated to the treatment of bottom barrel streams that operate under more severe process conditions and under a higher content of contaminants. In the current scenario, the relevance of these units to the profitability of refiners has become even more critical in view of the greater severity in the treatment of bottom barrel or intermediate streams in order to meet the new quality requirements for marine fuel oil (BUNKER) in compliance with IMO 2020.

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HEAT TRANSFER TECHNOLOGY

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Process Safety Principles Applied to Corrosion Control in Crude Units

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Corrosion Control continues to be a challenge for refineries, it has traditionally depended on various rules-of-thumb to determine the amount of neutralizing agent; wash water rates, overhead pH setpoint, etc. As shale oils and heavier feed processing increases, additional factors like Light Organic Acids, H2S and Organic Chlorides start to play a role in corrosion control, and the traditional approach (HCl corrosion) may not work; there is not a unique or simple solution for the corrosion control. This paper describes how using the principles of Process Safety Management: know, understand, learn, commit and manage the risk of corrosion it will be possible to establish a good Corrosion Management Plan. Knowing the contaminants, understand the reaction mechanisms and learn from previous experiences allow the reader to commit and improve plans for Corrosion Mitigation.

INTRODUCTION

Corrosion can result in serious accidents, even catastrophes. Refineries need to manage their plants safely and therefore a proper corrosion management strategy is required. Corrosion management strategy is comprised of many factors including knowing the risk, understanding the risk, learn from previous experiences, commitment (from all involved) and continuous improvement. The same pillars of Process Safety (Ref.1). In this paper the first three are covered: know the risk, understand it and learn from previous experiences…. The areas of commitment and continuous improvement are for the reader to work.

KNOWING THE RISK

The process conditions, crude characteristics, corrosion mechanisms, materials of construction, all are important to consider. Corrosion control continues to be a challenge as it has traditionally depended on various rules- of-thumb to determine the amount of neutralizing agent; wash water rates, overhead pH set-point, etc. As opportunity crude processing increases, additional factors like Light Organic Acids, H2S and Organic Chlorides start to play a role in corrosion control, and the traditional approach (HCl control; caustic and ammonia) may not work. It means the changes are forcing the refiner to keep adapting to new scenarios: knowing the risk is an ongoing process.

MANAGING THE RISK

Previous studies (Ref. 2) considered a very important "human error" component in the not -so-good management of corrosion, in the order of 65- 85%. They also consider that the causes of corrosion accidents are: lack of awareness, education, knowledge, training, incorrect design, insufficient control and supervision, lack of motivation, wrong operation, etc. These elements, in the Process Safety World means: not enough understanding the risk and poor management

LEARNING FROM PREVIOUS EXPERIENCES

As there is not a unique solution (one-fits-all), this paper first describes the corrosive elements in the crude overhead system (including crude quality) and some operating strategies that worked and may help the reader to - learning from previous experiences- conduct its own corrosion control assessment and define the Corrosion Management Strategy that works best for its particular case.

CORROSIVE AGENTS

HYDROCHLORIC ACID (HCL)

Overhead corrosion has been associated with hydrochloric acid formation and chloride salts formation and deposition. The overhead systems of Crude Columns, Pre-flash Drums and, to a much lesser degree, Vacuum Columns are susceptible to HCl corrosion mechanisms. All crudes contain some quantities of salts depending on location, characteristics of the field, age of the well, formation water, etc. Well known chloride salts such as sodium, calcium and magnesium hydrolysis are represented in the equations below:

$$MgCl2 + 2H2O \longrightarrow Mg(OH)2 + 2HCl \quad \text{(Eq. 1)}$$
$$CaCl2 + 2H2O \longrightarrow Ca(OH)2 + 2HCl \quad \text{(Eq. 2)}$$
$$NaCl + H2O \longrightarrow Na(OH) + HCl \quad \text{(Eq. 3)}$$

The composition of the salts varies with crude but typically the NaCl is considered to be 82% of the total salts, 15% for the MgCl2 and the rest for the

Calcium chloride. This numbers can be used as a "first approach" for the evaluation but each crude needs to be analyzed and evaluated to ensure an adequate program.

The hydrolysis of the salts is temperature dependant, being the magnesium chloride the first one to transform into HCl at temperatures as low as 150 C (300F). Calcium and Magnesium form HCl at normal crude unit furnace operating conditions: 345 – 360 C (approx.650- 680 F). There is also some Sodium hydrolysis at temperatures above 370 C (698 F) (Ref. 3).

Due to the fact that almost no sodium chloride hydrolyzes at atmospheric conditions, the addition of caustic to the crude was a common practice to reduce the amount of HCl formation in the overhead system. This may be beneficial but not always, as too much sodium will create and unfavorable scenarios in units downstream (DCU, FCC, etc.)

The HCl formed by hydrolysis is not corrosive unless there is water present. Above the dew point, it is relatively non-corrosive, however, as the overhead stream is cooled and acids or chloride salts (e.g., ammonium or amine chlorides) are formed, rapid corrosion can occur. In some units, these temperatures are reached in the overhead of the tower, and in some poorly designed or operated towers even in the top trays/packing section. These salts are corrosive primarily due to being hygroscopic, and the water they absorb immediately forms HCl in the local environment beneath the salt deposit. This high HCl content is responsible for the corrosion, fouling, shock condensation, etc. as will be presented in the next section.

HYDROGEN SULPHIDE (H2S)

In the past, most of refiners where not really concerned in regards of the presence of H2S as at low concentrations, compared with HCl content, the buffering effect in pH was not substantial. Nowadays with the increased processing of shale oils and heavy oils, the equation changes, and in some cases, this may be as serious as the HCl driven corrosion. The H2S produces two main problems: a buffer effect which requires large quantities of neutralizer to adjust the pH, and the secondary, it reacts with the Iron chloride produced by the HCl attack over Iron; as shown in the equations below:

$$HCl + Fe \longrightarrow FeCl2 + H2 \qquad \text{(Eq. 4)}$$

$$H2S + Fe \longrightarrow FeS + H2 \qquad \text{(Eq. 5)}$$

$$H2S + FeCl2 \longrightarrow FeS + 2HCl \qquad \text{(Eq. 6)}$$

H2S potential formation is not normally found in the crude assays as there are many factors affecting the H2S generation from the sulphur compounds in the crude. The determining factor is not the amount of total sulphur but the compounds thermal decomposition potential (Ref. 4). Concerns with H2S are related to transportation and environmental considerations, but very little attention was given to H2S formation in the crude overhead systems. As a rule of thumb, concentrations of H2S in the overhead water greater than 25 ppm is a sign of upcoming trouble. As more H2S is in the system, more amine is needed to adjust the pH, a high accumulator pH will require excessive amounts of neutralizing amines (Ref. 5) that may cause corrosion problems due to excessive amine salts.

This is a particular concern when running opportunity crudes. In crudes with a high H2S concentration -or high H2S formation potential -, the classical HCl corrosion approach does not work. The use of amines or ammonia to control pH where the HCl is less corrosive, has the unpleasant side-effect of promoting H2S corrosion.

AMMONIA (NH3)

Ammonia itself is not normally found in crudes, but may occur in some crudes (ref 5, 13). If ammonia is present in the formation water, this ammonia can be transferred back to the crude in the desalter (section 3.3). If overhead drum pH is higher than 7.5, NH4SH may be formed and corrosion by H2S will occur:

$$NH3 + H2S \longrightarrow NH4SH \qquad \text{(Eq. 7)}$$

The NH4SH is more common in Hydrotreaters but an incorrect pH adjustment in the crude unit can create a problem. In the section 3.8 (overhead drum pH control), the presence of ammonia will be studied.

INTERACTION BETWEEN H2S & HCL

In the Ammonia itself is not normally found in crudes, but may occur in some crudes (Ref. 6,9). If ammonia is present in the formation water, this ammonia can be transferred back to the crude in the desalter (section 3.3). If overhead drum pH is higher than 7.5, NH4SH may be formed and corrosion by H2S will occur:

$$HCl + Fe \longrightarrow FeCl2 + H2 \qquad \text{(Eq. 8)}$$

$$H2S + FeCl2 \longrightarrow FeS + HCl \qquad \text{(Eq. 9)}$$

$NH_3 + HCl \longrightarrow NH_4Cl$ (Eq. 10)

$NH_3 + H_2S \longrightarrow NH_4HS$ (Eq 11)

Equation 8 shows the reaction in an acidic environment, and equation 9 in an alkaline environment, if using ammonia or its derivates to control pH we may favorite one or other reaction for corrosion.

The NH4SH is more common in Hydrotreaters but an incorrect pH adjustment in the crude unit can create a problem. In the section 3.8 (overhead drum pH control), this risk will be explained in further detail.

USE OF H2S SCAVENGERS (CRUDE TREATMENT)

Every day, use of H2S scavengers increases so the crude oil can be properly handled. This is of a particular importance for some opportunity crudes. Most of these crudes are treated, in the production facilities, with amine-based scavengers. These amines when entering the desalter may portioned to oil phase and will react with the HCl in the overhead system; freeing some H2S that will affect the pH of the system and, as previously described, excessive ammonia will create NH4HS corrosion.

ORGANIC CHLORIDES

In recent years it has being found the presence of organic chlorides in the crude (when heated at vacuum distillation conditions); these organic chlorides can not be removed in the desalter and are not seen in the crude distillation cuts, but will appear in the HVGO side cut and may impact the hydrotreaters operation.

Organic chlorides will not be covered extensively in this paper. It is mentioned here as a reference due to the fact that organic chlorides cannot be removed in the desalting process, and cannot be mitigated before it hits the hydrotreating section.

LOA (LIGHT ORGANIC ACIDS)

Typically, LOA are produced from cracking in the distillation furnace, this effect has not been found to be important when running crude furnaces below 350 C (660 F) or in traditional crudes. A Refiner experienced an increased amine consumption in the overhead system (to control the pH), that cannot be explained, when increasing furnace temperature to comply with production requirements:

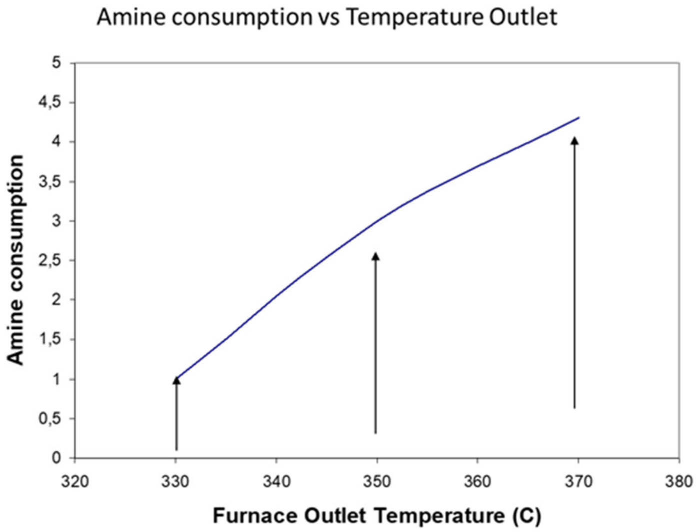

Fig. 1. Incremental Amine consumption for pH control

A study done in a lab facility in high Naphthenic, high sulphur crude revealed than the present of LOA in the overhead system is 10 bigger when heating the oil at 370 C vs 200 C (Ref. 11). The presence of LOA is another contributing factor that consumes neutralizer and makes a pH buffering effect, making the overhead neutralizer system very difficult to control.

NAPHTHENIC ACIDS

Normally, naphthenic corrosion does not attack in the crude unit overhead system, but it may create problems at Diesel section or below depending on TAN, Sulphur content, Temperature and flow characteristics (Ref. 15).

Naphthenic acids with low molecular weight are considered as Light organic acids, covered in section 2.6.

PARAFFINIC CRUDES

Paraffins, formally speaking do not affect the corrosion process, but affects the operation of the desalter, and then allow corrosive species (salts) to continue their path to the overhead system. This is one of the reasons why blending crudes based on API only is not a good practice. It is recommended to do bottle test and get support from your chemical vender before it is too late (Ref. 14). A more detail explanation of the effects on emulsion stabilizers in desalters is covered in section 3.1

OPERATIONAL ASPECTS OF CORROSION

In the previous sections the effects of main contaminants were described, in this section the approach is to provide refiner with examples and practical know-how to approach the corrosion potential problem keeping in mind one of the pillars of Process Safety: learning from previous experiences.

DESALTER OPERATION

A Desalter is a piece of equipment designed for removing the salts from the crude using proper mixing with water, electricity (electric field) and chemicals. Desalters are designed for a particular crude or for few of them with similar characteristics with a particular water quality. Desalter design is normally focussed on reducing the number of salts by 90-99% depending on the refiner needs.

A desalter removes much of the salts and water from crudes, which reduces the number of chlorides in the overhead. The desalter can be chemical or electrical, and some units have two desalters in series, or "Double Desalting". About 95% of the salts can generally be removed in a single stage desalter. The overhead chloride contents are dependent on the desalting efficiency, use of caustic injection (if any), and the crude salt levels.

If the number of salts in the crude is not very high, a desalter with 90% efficiency may be sufficient, if resultant chloride content in the overhead water is below 20 ppm. But the same desalter may not be able to remove 50% of the salts if the crude quality changes, and then the refiner will have a problem with very high chloride levels in the overhead water.

DESALTER WASH WATER QUALITY

The source and quality of the water used for desalting is one of the most important parameter for the desalter operation, especially when dealing with heavy or Naphthenic crudes.

Some general rules for desalter water are (Ref 3):

a. Low oxygen water, below 100 ppb

b. Low ammonia water (below 150 ppm). If coming with high ammonia from the overhead the ammonia may be transferred back to the crude. This case is very common with heavy crudes.

c. Good quality stripped water. This is a very difficult task to achieve. Normally the stripped water quality varies a lot. Some refiners have reported variation in the stripper water quality as high as 50 to 1000 ppm ammonia in the same units running the same crudes. Ideally the ammonia level in the desalter wash water should be kept below 150 ppm.

d. Avoid hard water as the hardness will cause solids to form at desalter conditions. These solids can stabilize the rag layer in the desalter and/or form fouling deposits; maximum recommended hardness is 150 ppm $CaCO_3$.

e. High pH water (above 8.0) promotes the formation of emulsions in the desalter when the basic compounds react with naphthenic acids to form naphthenate salts e.g., sodium or ammonium naphthenate, which are essentially soap molecules. To control the water pH caustic or sulphuric acid have been used. Caustic is really a bad idea if heavy Naphthenic crude is been treated due to stable emulsion formation. Some problems have been reported in NPRA Q&A (Ref. 7) with the use of H_2SO_4 that evolves to SO_3= and creates corrosion problems in the overhead.

f. If crude processed is Naphthenic the best way to control the pH of the water is combining the water from atmospheric, vacuum distillation and sour water strippers. Use of caustic is strongly not recommended.

EMULSION'S STABILITY

Desalter is very sensitive to crude variations, especially if emulsion stabilizer like paraffin is present in the crudes (shale-oil, etc.). A refinery designed a desalter for 17 API crude with 30 ptb salts and with the use of chemicals were able to reduce the salts by 95% which was good enough. The same desalter produced a big rag layer and poor salt removal when operated on another crude slate of 15 API diluted with 30 API crude (to match the 17 API design). Crude API is not the "rule" for running desalters. Each crude has to be studied in details with the help of the chemical vendor. Temperature, wash water quality, electric field, chemical dosage and detail follow up of crude performance in the desalter are needed to establish the right "operating window"

Previous described case (Ref. 6) indicated that presence of paraffinic molecules in the 15 API crude was the source of the problem that created a “almost impossible” to break emulsion in the desalter. To solve the problem, a series of adjustment in the desalter operation including using different chemicals were performed.

The changes in the desalter chemical, brings another topic for review: using the right chemical. In some cases, the wrong chemical will not demulsify but emulsify the interface water-oil (Ref. 6). It is strongly recommended to perform several “bottle test” with the chemicals to

find the best option. It may be the case that some crudes cannot be fed to desalter unless a big slate is processed to give the refinery enough time to absorb the upsets and ensure a good desalting process.

METALLURGICAL SOLUTIONS

Use of alloys alone is seldom an economic method of corrosion control in the crude overhead systems, as extremely expensive alloys would be needed for all the exchangers, vessels, piping and other components. Especially in existing units which require extensive revamp with consequential loss of operating time. The use of alloy is sometimes recommended to solve severe problems, especially in exchangers or air cooler tubing. Titanium and Monel Alloy 400 are typical upgrades for the tubing. Others units are successfully using Admiralty Brass or 70-30 Cu-Ni.

As mentioned in section 2, there are many corrosive elements that can trigger corrosion and all must be studied carefully before moving into a “metallurgical solution”

A metallurgical solution like Monel is a very good strategy if HCl corrosion is the only problem. In contrary, it may be a very bad strategy if there is risk of NH_4SH attack at high water pHs. This is likely if using the SWS water as desalter water. Ammonia in the SWS water will travel to the overhead system and increase the pH of water creating an environment where Monel is susceptible to corrosion.

To confirm the transfer of ammonia from the SWS in desalter, a test was done using SWS water for the desalter when running opportunity crudes: Amine neutralizer, caustic and filmic injection were stopped; the result was that only with SWS water in the desalter the pH in the overhead system reached 8-9. (Ref. 12).

But it is also true that running medium/lights crudes with SWS water in the desalter, has shown no issues with pH control, and Monel has been a good option.

It is strongly recommended that before going to a metallurgical solution, all the aspects of the corrosion problem must be evaluated including crude quality, SWS water quality, and potential interaction of chemicals or crude slates in desalter.

FURNACE TEMPERATURE

Traditionally Furnace Temperature if fixed due to design conditions; but when running atmospheric columns as Naphtha Recovery Units, this temperature may be adjusted to comply with the yields expected for a specific crude. Changing the Furnace Temperature can be one of the options to evaluate the presence of

LOA. A test done to identify the presence of LOA shown a drastic increase in neutralizer consumption to reach pH of 7-7.5 when changing the temperature between 330 and 370 C (Ref. 11). The amount of neutralizer increased 33% when furnace temperature increased from 330 to 350 C; and 67% when increasing from 350 to 370 C; after a detailed investigation of the crude and overhead water, it was found the presence of LOA in the overhead system. (See FIG. 1)

Even if the unit is designed to work at a fix temperature in the heater, the test of changing the furnace Outlet temperature for few hours may help to identified the LOA bad actors.

OVERHEAD TEMPERATURE

Another very important topic when designing is the selection of the tower overhead temperature. Design normally considers a temperature 5 to 10 C above the dewpoint, to avoid water condensation inside the tower. In addition,, there is another parameter that should be considered when designing or running the crude column. That is the Salt Point Temperature.

SALT TEMPERATURE (SALT FORMATION TEMPERATURE)

The salt point temperature is the temperature for NH_4Cl formation, from $NH_3(g)$ and $HCl(g)$ independent of water condensation temperature.

This point is strongly dependent on “buffer acids”, amount of water injected as stripping steam and ammonia content in the feed in the overhead treating program. It is not dependant on wash-water rate unless salt point temperature is close to Condenser temperature.

Calculation of salt point is a theoretical exercise based on the amount of ammonia and chlorides present in the overhead system under particular conditions of temperature and pressure. This calculation does not consider the presence of H_2S. There is literature available where both curves NH_4Cl and NH_4SH curves are described. (Ref. 13)

Main formula to calculate the Salt point is based on the equation: Kp

$$Kp(NH_4Cl) = ppNH_3 \times ppHCl \qquad \text{(Eq. 12)}$$

Where:

Kp =Dissociation constant for NH_4Cl $ppNH_3$ = Partial pressure of NH_3 $ppHCl$ = Partial pressure of HCl

For NH_4Cl, Kp can be expressed as:

$$\ln(Kp) = -21183.4/T + 34.17 \qquad \text{(Eq. 13)}$$

Where:

T is the salt point temperature expressed in K (Ref. 17)

Knowing the specific system, a salt point calculation can be done, to ensure the overhead system is running above the salt point temperature. Due to some inaccuracies in the calculation, it is recommended to set the top temperature between 5 to 10 C above the calculate Salt Point temperature.

In order to avoid under-deposit corrosion, the overhead system should be designed in order to make sure that "salt point temperature" is lower than condensers temperature or install a wash-water system in a point upstream of the salt point formation. In this case wash water will "wash" the salts formed, and have diluted them in the overhead accumulator.

The operating temperature, as mentioned before, should consider the "salt point" formation temperature, dew point temperature & possible shock condensation before selecting the correct overhead temperature and metallurgy. Presence of contaminants as describe in section 1, is also very important.

If H_2S is present, it is worth to also evaluate the salt point for ammonia bisulfide deposition. It is true that in most of the cases this will not happen in a Distillation unit, but with more and more opportunity crudes processing, this is factor that cannot be ignored.

SHOCK CONDENSATION

In most crude columns, the reflux enters the tower subcooled, so the top trays, or packing see several places where water condenses. Local water condensation is very likely to occur whenever the vapour contacts subcooled reflux or internals/piping carrying subcooled liquid. This locally condensed water picks up hydrogen chloride and sulfides and can cause severe corrosion (Ref. 8), this phenomenon is called: shock condensation.

WASH WATER

Water injection into the overhead line is sometimes used to saturate the system and wet the system before the formation of the initial condensation point and dilute the corrosion effect and/or to wash corrosion deposits away. If the purpose

is solely to wash deposits away, an intermittent wash (e.g., one hour per week) may be used.

The water sources can be re-circulated sour water from the reflux drum, fresh water, condensate or other. It is not always needed, but if needed, the water quality should be the best possible: less than 100 ppm H_2S, < 100 ppm NH_3, < 20 ppb Oxygen and pH in the range from 7-9.

If the salt formation is happening upstream of the wash water injection point and it is not possible to relocate, then the operating temperature of the column must be increased to guarantee salt formation downstream of the wash water injection points. If this is not possible wash water injection is completely useless.

Before starting the wash water system, a detail evaluation of pros and cons should be undertaken by the process engineer with the assistance of the chemical vendor. Sometimes, the use of intermittent wash water creates a higher risk: if the chloride salt formation is elevated, the wash water will "wet" the salts increasing corrosion.

If the refiner suspects an important ammonia chloride formation downstream of the water injection point or even in the exchangers, the use of the wash water may break the tubes when removing the chlorides due to severe "under-deposit" corrosion.

When starting the wash water, the process engineer should monitor the chloride content in the overhead water. It is considered that the wash water is effective when the chloride content does not change after an earlier increase as shown in the graph below; if this peak is not seen, there are no chlorides in the system or the wash water is not effective (Ref. 9).

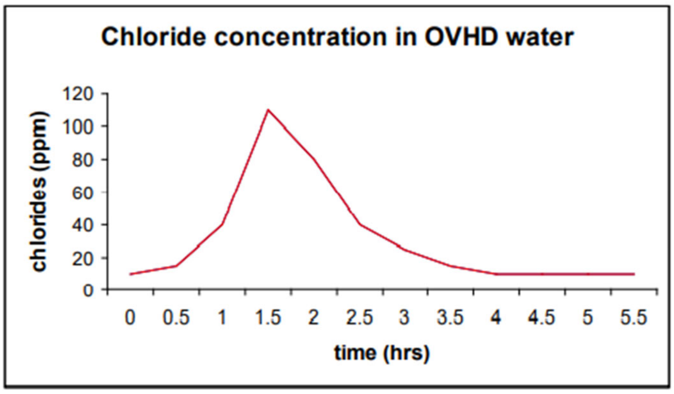

FIG. 2 Chloride content in overhead water during wash water

A well design water wash systems require:

Good spray nozzle design with a reasonable DP to assure good distribution. Good wash water distribution: Installing only one distributor in the main overhead line is a very bad idea. It will save cost at the beginning but the wash water system will not work.

The best location of the wash water system (if salt formation is not happening outside the exchangers) is at the inlet of each exchanger.

If the exchangers are fin-fan coolers add an injection distributor in each inlet line. For horizontal exchangers, a good designed spray nozzle system is needed with enough water, the overhead drum needs to be checked for water handling capacity before installing or revamping the wash water system.

If the wash water is not well distributed, localized water condensation, may lead to shock condensation and severe corrosion will occur.

CAUSTIC INJECTION

Caustic injection in the feed is being commonly used to convert the calcium and magnesium chloride to sodium chloride. This reduces the number of salts which hydrolyze and hence, the number of chlorides in the overhead. Most of the chlorides are already removed with the desalter effluent. As a rule of thumb, a single stage desalter should give a performance of >90% salt efficiency or <10 ppm chloride salts after desalting.

Caustic injection is the least expensive method to reduce the corrosion; the sodium chloride does not hydrolyze at normal furnace temperatures (below 360C) and will not produce chlorides in the overhead system. This is not a recipe for all crudes, as some crudes may form HCl at different temperatures as mentioned in section 1. Caustic must not be used upstream of desalter if the nature of the crude is to form emulsions (i.e., paraffinic crudes) as NaOH will act as a soap and it will make a very stable emulsion.

A note to remember: Caustic Injection is completely ineffective for Organic Chlorides removal.

USE OF SPENT CAUSTIC

In the past, spent caustic was commonly used when no restrictions were associated with the amount of Na in the residual fuel or the crude salts or contaminants were mainly inorganic chlorides.

The sodium hydroxide has been utilized in the Merox unit by reacting with mercaptan sulphurs and hydrogen sulphide; these contaminants

will increase the risk of corrosion in the overhead system due to presence of phenolic compounds.

Corrosion prevention in Crude Unit overhead systems is difficult enough without adding this bad actor. So, it is not recommended to use spent caustic if crudes are medium to heavy or shale oil type. Spent caustic is an inexpensive way to get ride of the caustic but will create more problems than solutions.

EXCESSIVE CAUSTIC INJECTION

It is “general knowledge” that as sodium level increases in the feed to Delayed Cokers or Visbreakers, the furnace fouling rate increases exponentially. It is also generally accepted that a maximum of 20 ppm Na in the feed to these units should be used for design and operations.

A study done in the late 80s in a refinery showed that the furnace fouling rate of a Visbreakers was exponential when the sodium in the feed to the unit exceeds the 25-ppm limit as shown in the graph below (Ref. 10).

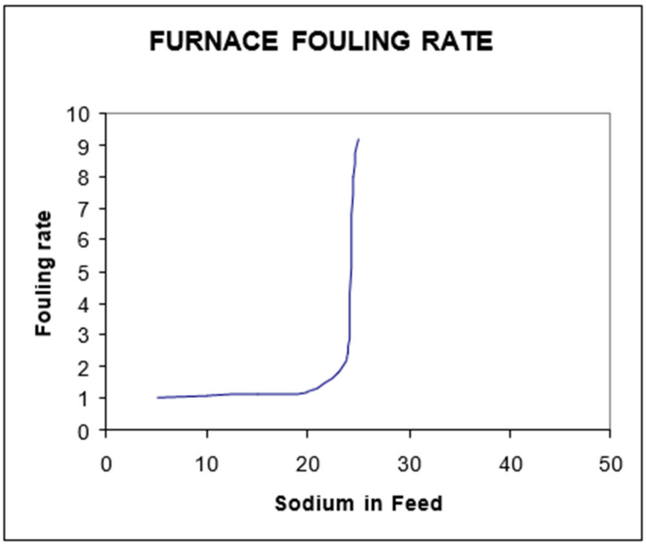

FIG. 3 Furnace Fouling Rate for a Visbreaker unit as a function of Na in the feed

Increase in the furnace fouling rate, affect the run length of the unit. When the fouling rate is elevated the Visbreakers needs to be taken out of service for more than a week to clean the furnace. Sometimes the decoking may burst the tubes and the solution becomes worst that the problem.

If the crude slates to the refinery changes, the use of caustic may create a big problem in the downstream units. One refinery decided, due to economical reasons, to install one desalter for one crude unit and run the other two with caustic injection. The idea was to run only medium-heavy crudes in the unit with desalter and the light crude in the other two units. This system worked very well for a period of time, but after changing the crude slates, the units without desalter where limited in the amount of caustic added and the refiner has a problem to decide what system was more critical: the overhead system of the crude units or the accelerated fouling rate in the downstream heaters (DCU, VBU).

OVERHEAD PH CONTROL

For many years this topic has been discussed and there is not a unique rule to follow. Many chemical vendors, designer and operation engineers believe the traditional rule of controlling the corrosion at pH between 6 and 7 because some studies indicated that at this pH range the corrosion is low. Others indicated that pH should be controlled above 7 and even others indicated ranges as high as from 7 to 8.

The reason for recommending a pH in the range between 6 and 7 can be found in the following curve (Ref 9,11,12):

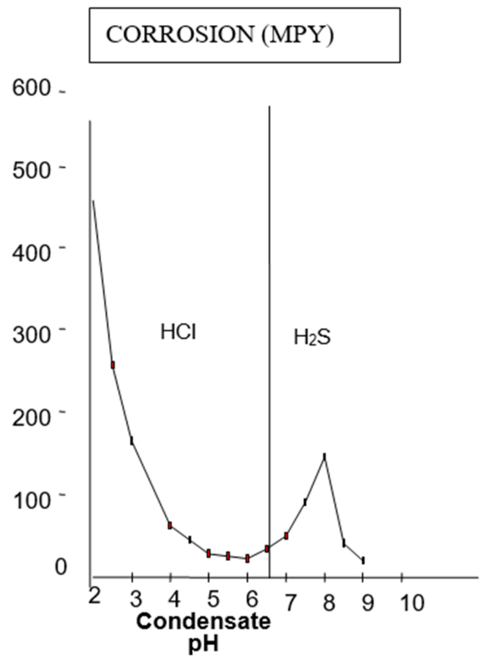

FIG. 4 Estimated Corrosion rates as function of Condensate pH

In this graph there is a clear indication that to avoid HCl corrosion the refiner should move to ranges above 6, but little mention was given to the risk of H2S corrosion at pHs of 7.5-8.5

A study done in 1993 (Ref. 13) recommended to adjust the pH as a function of the H2S and not as a function of the Chlorides. This is very important when the H2S in the water is greater than 25 ppm. (Ref. 9). To adjust the pH to the require values the use of ammonia, neutralizer or combination of both can be used.

NEUTRALIZER INJECTION

Ammonia is the least expensive solution for neutralization in the overhead system. Some refiners use ammonia gas and others use aqueous ammonia. In both cases, the control of the pH is very difficult due to the properties of the ammonia: being very volatile it will neutralize only at the end of the condensation and not as required during the whole condensation. The ammonia neutralization curve is very sharp and a small amount of ammonia in excess can change the pH drastically.

Neutralizing amines are also commonly used. The neutralizing amines are blends of amines, which give a very good pH profile during the condensation and it is relatively simple to control the pH range, due to the buffering capacity which produces a smooth increase of ph. The disadvantage is the higher cost.

In some units, ammonia is used for a baseline of neutralization and then neutralizing amine is used to fine tune the ph. In some systems the use of ammonia and neutralizing amines have reduced the cost 60% compare with the use of neutralizing amine only.

For a designer, if the crude is light a base recommendation to control the pH in the range 6-7 is a good guideline, but has to be corrected when the system is in operation. For heavy crudes, do not exceed 6.0 but use H2S correlation (Ref. 13) as a first approach and then correct during operation.

FILMIC INJECTION

Filming amines provide added insurance against corrosion by forming a protective film on the metal surfaces. In towers with relatively low top temperatures, the filming amines are often injected into a reflux line going into the tower. In hotter towers, they are injected into the overhead line, but not into the same injection point as the neutralizer.

As a general rule Overhead pH control, call your chemical supplier and ask for their advice, ask them to run their models and discuss the results. This is a process engineer responsibility and the Process engineer should participate in the team to discuss the solutions to the problem, it is not only metallurgical engineer responsibility.

The system must be studied in detail, the traditional approach that indicates that HCl is the only source of corrosion in the overhead system is not valid anymore, especially when running opportunity crudes (heavy or shale oil).

CONCLUSIONS

Managing corrosion control in a Crude Unit is not an easy task, many factors are involved as described in this paper; operators must move away from “fix solutions” (Ref. 16) and “one-size-fits-all” and develop their own solutions.

Using the principles of Process Safety Management: knowing the risk, understand the risk and learn from previous experiences had been accomplished in this paper. Now it is up to the reader to commit and continuous improvement to prevent corrosion related accidents and avoid unnecessary shutdowns.

A good managed Corrosion Plan provide safer and extended operation without unwanted “surprises”

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Comparative Study of Physio-Chemical Specifications & Free Fatty Acids of Canola (Rapeseed) & Used Cooking Palm Oil to Produce Biodiesel & Glycerine

Hamid Reza Seyed Jafari, Morteza Seyed Jafari, &
Seyed Mohammad Reza Seyed Jafari

Annually a huge amount of non-edible used cooking oil (UCO) and a few edible (Corn , Palm , Rapeseed , Sunflower ,…) and non-edible (Jatropha) seeds oil and animal fat are used to produce pure biodiesel(B100) in developed countries as commitment to the global programme of CO2 control emission in transportation fuel sector. This article compares the physical & chemical specifications and free fatty acids of canola (rapeseed) and used cooking palm oil to produce biodiesel (biofuel) and glycerol. There are valuable glycerine (glycerol) and different types of fatty acid (FA) in these neat agriculture oilseed crops and waste cooking vegetable oils. We actually did a lab test by ourselves to produce pure biodiesel and crude glycerol from edible canola (rapeseed) oil and mixing used cooking oil .But we have used the data too for our comparative analysis study from the relevant experimental papers in which are published.

Key words: Glycerine (Glycerol), Waste Cooking Oil (WCO), Agriculture Crops Vegetable Seed Oil (Bio-Oil), Biotechnology, Fatty Acids (FA), Transesterification, Non-edible , Edible , Fatty Acid Methyl Ester(FAME , known as: Biodiesel) , Free Fatty Acid(FFA) , Renewable & Biofuel , Palm Oil

INTRODUCTION

Vegetable oils (neat or waste) consist of organic fat molecules .As usual an organic fat molecule is made up of two main components, glycerine and fatty acids. Glycerine is an alcohol with three carbons, five hydrogens and three hydroxyl (OH) groups, $C_3H_8O_3$ [CH $(CH_2)_2(OH)_3$]. Because vegetable oil organic fat molecules are made up of three fatty acids (FA) and one glycerin (glycerol), they are also called triglyceride. The reaction of fatty acids component of a vegetable oil or used cooking oil with methanol in the presence of base catalyst (NaOH , KOH ,…) could also produce fatty acid methyl ester (FAME) knows as biodiesel. Pure biodiesel could blend with fossil diesel to produce biofuel which is sustainable with global environmental regulations such as B5, B10, B20, B40, and B100 and can be used for transportation vehicle, marine, train … as renewable clean fuel.

EXPERIMENTAL PROCESS

You could do the laboratory experimental transesterification process with Rapeseed (Canola) oil and waste cooking oil (WCO) to reach pure biodiesel and crude glycerol (glycerine) as we did as follows of figure-1:

- Beginning
- Mix 100 ml of methanol (CH_3OH alcohol) with 1.4 g of strong base as catalyst (NaOH) at normal temperature Room for 15 minutes
- Prepare sample oil (rapeseed oil or WCO) in the amount of 500 ml
- Heat oil to 55 ° C and add the solution of methanol and catalyst to the oil.
- Stir the mixture of oil, methanol (about 20% oil) and catalyst (about 0.3 wt.% of total weight oil & methanol) for 30 minutes at the temperature at 50 ° C to run the reaction of transesterification to produce crude glycerine and pure biodiesel
- Pour the 2-phase liquids created in a separating funnel (Decanter) and give a residence time of 4 hours for separation of crude glycerine and pure biodiesel)
- Note: Due to the higher density of crude glycerine (about 1.21 gr/cm3) than pure biodiesel (about 0.86 gr/cm3), the lower phase is crude glycerine
- Separation of crude glycerine phase from the bottom of the separating funnel
- Note: After separation of pure biodiesel and crude glycerine, if it is needed to increase their purities of each them, you could do the conventional distillation methods
- Performing the laboratory tests of products quality
- Ending

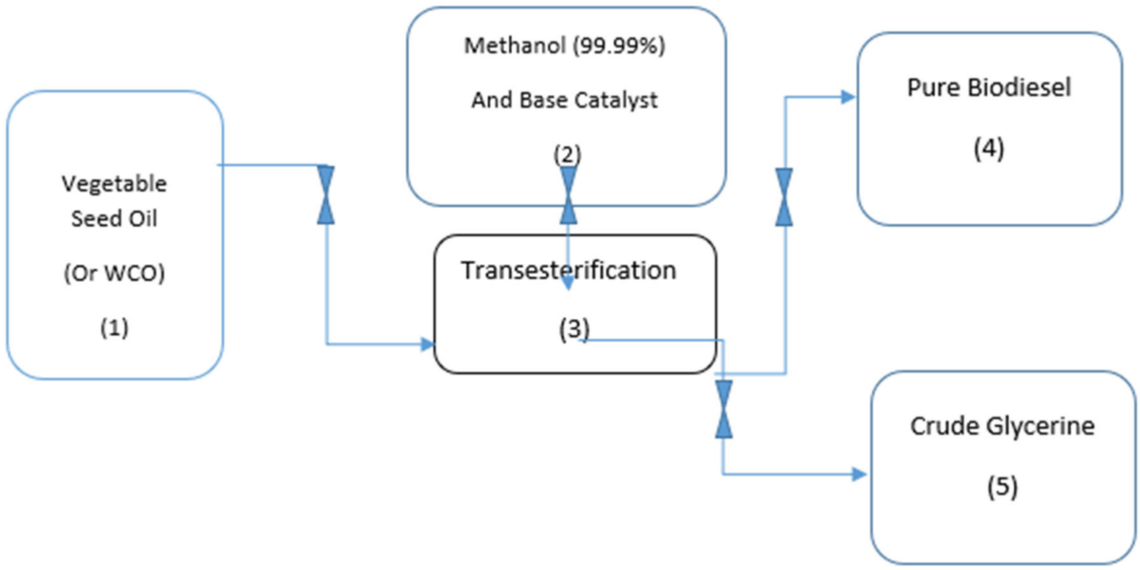
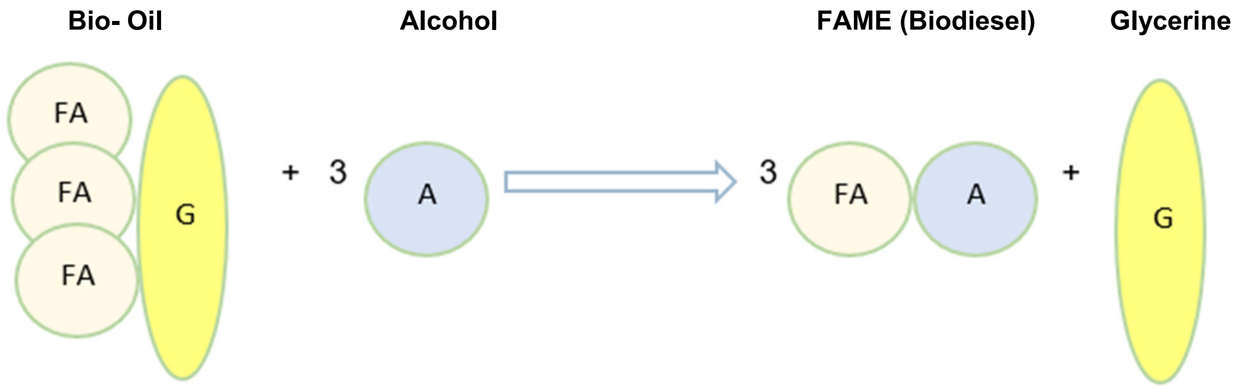


Figure 1– Block flow diagram to produce experimental Biodiesel & Glycerine
Figure 2- Transesterification process to obtain crude Glycerine & pure Biodiesel from Bio-oil



The transesterification reaction (process) of this experiment is above as (figure-2).

It is clear that, there are different amounts & types of fatty acids (FA) in neat vegetable seed oils in comparison of used vegetable cooking oils .Also there is free fatty acid (FFA) in waste cooking oils (WCO) because of degrading of neat vegetable oil due to heating and cooking as an impurity such as water. But the products of transesterification reaction of these bio-oil are the same but in different yields, for example: about 80%-90% of FAME and 10%-20% of crude glycerine in different types of WCO and neat vegetable seed oils.

The usage of WCO of any edible oils, as feedstock of FAME (biodiesel) transesterification reaction has been found to be economically beneficial than the neat edible oils (palm, rapeseed, sunflower…) and non-edible oil (jatropha). Using of WCO is along with the results of:

- Reduction of the operation cost of biodiesel
- Problem solutions in which associated with the disposal of WCO to the landfill
- Eliminations the pollutants in which associated with contamination of environment
- Prevention of blocking of drains and pipelines as a result of kitchen disposal
- Generation of income from production of crude glycerine and pure biodiesel (FAME) such as neat vegetable oils (edible & non-edible seedoil)

RESULTS AND DISCUSSION

Waste cooking oil and vegetable edible and non-edible oils such as: canola (rapeseed), palm, jatropha , sunflower, corn, soybean… are included into saturated fatty acids (SFA) and unsaturated fatty acids (UFA) and glycerol. Waste cooking oil comes from edible vegetable oil and animal fat. The main chemical composition of used cooking oil is the higher fatty acid glyceride. Fatty acids are from various carbon chains and included with unsaturated chemical bonds such as: oleic acid, linoleic acid, … and without unsaturated chemical bonds such as: palmitic acid and stearic acid, etc. in which are named lipid numbers such as:, C18: 1, C18: 2 , C16: 0, C18: 0 too .There are different weight composition (%) of fatty acids (unsaturated & saturated) in waste cooking oils and vegetable edible and non-edible oils regarding to the type of vegetable oil seeds and it is possible to separate them from fatty acid glyceride molecules. Because, for example oleic acid (a type of unsaturated fatty acid, UFA) is most commonly used for preventing heart disease and reducing cholesterol or Alpha-linolenic acid(a type of unsaturated fatty acid, UFA) is popular for preventing and treating diseases of the heart and blood vessels. It is used to prevent heart attacks or the main uses of palmitic acid (a type of saturated fatty acid, SFA) is in soaps because of its ability to help keep skin smooth. The table below shows the comparison organic chemical fatty acid weight composition (%) of canola (Rapeseed) and used cooking oil (UCO).

The tables - 1&2 of the study shows us that some results such as that:

Saturated fatty acids (SFA) % of waste palm cooking oil are higher than SFA % of canola neat vegetable oil.

Unsaturated fatty acids (UFA) % of canola neat vegetable oil are higher than UFA% of waste palm cooking oil.

Of course in few cases, it has exceptions too. For example, the amount of SFA % for neat vegetable sunflower oil is greater than the SFA% of its waste (sunflower) cooking oil (i.e.: neat SFA% of sunflower oil is equal to 71.48% and waste sunflower oil SFA% is equal to 32%).[5]

Table 1- Comparison of wt. (%) of organic chemical fatty acids properties of canola and WCO

Fatty Acid Title	**Lipid number**	**Canola(Rapeseed)**	**WCO (waste palm oil)**
Sp. Gr. (gr/cm3)	-------	0.912	0.91-0.93
Oleic acid(UFA)	C18:1	50-65	14.31
Linoleic acid(UFA)	C18:2	20	13.58
Palmitic acid(SFA)	C16:0	1.5	35.22
Stearic acid(SFA)	C18:0	4.6	5.11

Reference: [6&4&7&11&5]

Another type of comparison weight composition (%) of organic chemical saturated and unsaturated fatty acids properties between canola oil and waste cooking oil of some neat vegetable oils are as follows, Table-2:

Table 2- Comparison of Wt. (%) UFA&SFA properties of canola and WCO of some neat vegetable oils

Fatty Acid Title	**Canola(Rapeseed)**	**WCO (Sunflower oil)**	**WCO (Palm oil)**
UFA %	Min. 80%	68%	20%
SFA %	Min. 7%	32%	80%

Reference: [4]

Table 3- Comparison properties of canola and WCO to produce biodiesel (FAME) & Glycerine

Physical Properties	**Canola (Rapeseed) Biodiesel**	**WCO (Palm oil) Biodiesel**	**Diesel (Petrol)**
*Density, gr/cm3 @15C	0.88	0.869	0.836
Viscosity, mm2/sec @ 40C	2.7	4.64	4.2
*Cetane index	51.6-61.5	Min. 53.0	55.8
Flash point,C	182	165	55
Pour point,C	-8	-11	Min.-21&Max.-13
Ester Content (%)	98.9	97.18	-

Reference: [6&7&8&9]

(*) Note: these two properties of biodiesel prepared are measured too by means of laboratory practical tests by author for Canola (Rapeseed) oil samples as properties: Canola [sp.gr. 0.8612 gr/ml @ 15C - Cetane index: 51.4].

Table 4: Legal physical & chemical properties of biodiesel according to ASTM D6751 Standard

Property	ASTM (EN)Method	Limits	Units
Flash point	D 93	93 min	°C
Alcohol Control	-	-	-
1. Methanol content	EN14110	0.2 max	% mass
2. Flash point	D 93	130 min	°C
Water & Sediment	D2709	0.05 max	% vol
Kinematic Viscosity, 40°C	D445	1.9-6.0	mm^2/sec
Sulphur	-	-	-
S 15 Grade	D5453	0.0015 max (15)	% mass (ppm)
S 500 Grade	D5453	0.05 max (500)	% mass (ppm)
Copper Strip Corrosion	D130	No. 3 max	-
Cetane Number	D613	47 min	-
Cloud Point	D2500	Report	°C
Carbon Residue (100% sample)	D4530	0.05 max	% mass
Acid Number	D664	0.50 max	mg KOH/g
Free Glycerine	D6584	0.020 max	% mass
Total Glycerine	D6584	0.240 max	% mass
Phosphorus Content	D4951	0.001 max	% mass
Distillation, T90	D1160	360 max	°C
Sodium/Potassium, combined	EN 14538	5 max	ppm
Oxidation Stability	EN 14112	3 min	Hours

To ensure quality biodiesel produced from waste cooking oil or edible & nonedible neat vegetable oils, there are standards for testing the fuel properly to see that it meets specifications for use in diesel engines such as: ASTM D6751 or EN 14214. Table– 4 shows the test methods necessary for all the expected standards for biodiesel regarding to standard ASTM D6751.

Note: There are environmental chemical advantages to use biodiesel (FAME) as a biofuel compared to ultra-low sulphur diesel of the crude oil refinery. It has a higher lubricity, low sulphur content, and low hydrocarbon emissions from the diesel engine exhaust than petrol-diesel. This makes it too nice to blend with petrol-diesel (with high sulphur content) to produce biodiesel B5, B20, B40, B100. But biodiesel has also few physical disadvantages than petrol-diesel such as higher flash point, poor pour point properties. (Reference: www.biodiesel.org)

Any away, the table- 3 of the study shows us that some results such as that:

- The cetane index of biodiesel produced from waste palm cooking oil (CI =53) is lower than the cetane index of canola neat vegetable oil (CI =51.6 to 61.5).
- The flash point of biodiesel produced from waste palm cooking oil (FP=165 C) is lower than the flash point of canola neat vegetable oil (FP =182 C).
- The pour point of biodiesel produced from waste palm cooking oil (PP=-11 C) is lower than the pour point of canola neat vegetable oil (PP =-8 C).
- The ester content of biodiesel produced from waste palm cooking oil (Ester% =97.18%) is lower than the ester content of canola neat vegetable oil (Ester% =98.9%).
- The density of biodiesel produced from waste palm cooking oil (sp.gr. =0.913) is lower than the density of canola neat vegetable oil (sp.gr. =0.92).
- Only, the viscosity of biodiesel produced from waste palm cooking oil (viscosity =4.64) is higher than the density of canola neat vegetable oil (viscosity =2.7).

CONCLUSIONS

This study has shown that the physio- chemical specifications of Canola (Rapeseed) as a neat vegetable oil and waste cooking Palm oil to produce biodiesel (FAME) are near to each other regarding to the standard of ASTM D6751 (EN 14214), but the amount of their SFA & UFA wt. % of organic fatty acids (FA) composition of Canola neat vegetable oil and used cooking Palm oil are actually very different. The crude glycerol (glycerine) in which produced in the transesterification reaction of canola oil and WCO of palm oil could both refined to produce technical and pharmacopeia grades of glycerine as a high valuable by-product too.

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Safety Talk

Eye Safety

Chris Palmisano

Safety glasses protect your eyes and will save your sight - if you wear them. They offer no protection in your back pocket, your truck or if left at the house. People who wear glasses quickly become used to them. Unfortunately, people who don't wear glasses have never developed these habits. When it comes to eye protection, too often people forget, and safety glasses and goggles grow dusty laying around, unused.

The most common complaint about eye protection is that it's uncomfortable. That's why such equipment must be carefully fitted. Frames must be light, straight and properly adjusted. The lens size should be correct for the wearer, as should the fit of the bridge of the nose and at the temple.

When your goggles or glasses are dirty, dusty or grimy, they can interfere with your vision - so take time to clean them. Don't touch the lenses with your fingers. never lay goggles or glasses down so the lenses touch something that could scratch or pit them.

Store eye protection so that the lenses will be protected. During hot weather, use a sweatband to help keep perspiration off your goggles. Lens "FOG" problems can be eliminated by using an anti-fog preparation.

Some people complain that goggles give them a headache. Here again, proper fit is important. Be sure goggles are worn correctly. The head strap on cup goggles should be adjusted for just enough tension to hold them securely and should be worn low on the back of the head.

Eye protection is important off the job as well. Here are some tips you can use both at work and at home. Study the label and instructions for eye protection before using cleaning products, pesticides, and herbicides.

Consult the chemical SDS "Safety Data Sheet" for the correct Personal Protective Equipment recommended. Be sure nozzles are directed away from you and hoses are in good condition.

Eye injuries are preventable. Take the time to keep your eyes safe on the job and off the job. And if you see a work colleague working without them, give a friendly reminder. It could save someone from the tragedy of an eye injury or even blindness.

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Evaporation Pond Process Design in Oil & Gas Industry

Jayanthi Vijay Sarathy

In the upstream oil & gas industry, produced water is a by-product of well production. Hydrocarbon wells initially produce less water but in late field life, the water content increases. Produced water can contain oil carryover and a host of salts with TDS ranging anywhere from 2,000 mg/L to 40,000 mg/L for which evaporation ponds are used to concentrate by evaporating the associated water.

The energy requirement consists of pumping concentrate to the pond and in some cases aeration is provided to enhance the rate of evaporation. The ponds are lined with synthetic liner material to prevent seepage of water into the soil. In case of any corrosive compounds in the water, the number of layers is increased. Landscape and topography play a role in setting up evaporation ponds and it is necessary to have a flat terrain to avoid any overflow of the contents.

Evaporation ponds must also ensure that the amount of water entering is minimized and avoid any flooding. As part of waste disposal, the ponds maybe designed to accumulate sludge over the life time of the operating wells or can be periodically removed. The below figure depicts an evaporation pond.

Figure 1. Evaporation Pond [2]

The following article focuses on estimating the rate of evaporation, water surface temperature and rate of heat transfer to the water in an evaporation pond.

METHODOLOGY

Similarities exist between mass, momentum & heat transfer phenomenon. Therefore, the empirical correlations for heat transfer are also applicable for mass transfer. Schmidt number plays a similar role to Prandtl number in convection heat transfer. The heat transfer to the water from the air supplies the energy required to evaporate the water,

$$q = mh_{fg} = hA[t_\infty - t_s] = h_m A h_{fg}[\rho_s - \rho_\infty] \quad (1)$$

Where,

h = Convective heat transfer coefficient [W/m^2.k]

h_m = Convective Mass Transfer Coefficient [m^2/s]

A = Surface Area [m^2]

m = Evaporation Rate [kg/s]

t_s,r_s = Surface temperature & vapour density [K, kg/m^3]

t_∞,r_∞ = Air Temperature & vapour density [K, kg/m^3]

The energy balance can be arranged as,

$$\rho_s - \rho_\infty = \frac{h}{h_m}\left[\frac{t_\infty - t_s}{h_{fg}}\right] \quad (2)$$

The heat transfer coefficient, h can be estimated based on Nusselt Number (Nu) as,

$$Nu = 0.664 Re^{1/2} Pr^{1/3}$$, For Laminar Flow (3)

$$Nu = 0.037 Re^{4/5} Pr^{1/3}$$, For Turbulent Flow (4)

The mass transfer coefficient, h_m can be calculated using Sherwood Number (Sh),

$$Sh = 0.664 Re^{1/2} Sc^{1/3}$$, For Laminar Flow (5)

$$Sh = 0.037 Re^{4/5} Sc^{1/3}$$, For Turbulent Flow (6)

Where,

$$h_m = \frac{Sh \times D_v}{L} \quad (7)$$

$$h = \frac{Nu \times k}{L} \quad (8)$$

Dividing both heat and mass transfer coefficients and substituting in Eq. (2) yields,

$$\frac{h}{h_m} = \frac{Nu\times k}{Sh\times D_v} = \left[\frac{Pr}{Sc}\right]^{1/3}\frac{k}{D_v} \qquad (9)$$

$$\rho_s - \rho_\infty = \left[\frac{Pr}{Sc}\right]^{1/3}\frac{k}{D_v}\left[\frac{t_\infty - t_s}{h_{fg}}\right] \qquad (10)$$

The above expression is solved for r_s and h_{fg} is evaluated at surface temperature [t_s]. Air properties, *k*, D_v, *Sc*, *Pr* are evaluated at film temperature [t_f], as an average of t_∞ and t_s.

$$t_f = \frac{t_\infty + t_s}{2} \qquad (11)$$

The solution is arrived beginning with a guess value of surface temperature, t_s in Eq. (10) & iteratively solved until convergence. Relating saturated vapour pressure [P_s] with moist air temperature [T_∞, ^{0}C] using Arden Buck equation,

$$P_s[T_\infty > 0°C] = 6.1121e^{\left[\left(18.678-\frac{T_\infty}{234.5}\right)\times\left(\frac{T_\infty}{257.14+T_\infty}\right)\right]} \times 100 \qquad (12)$$

Where, P_s is saturated vapour pressure [Pa]

The vapour density [r_∞] for a given relative humidity [RH] is calculated as,

$$\rho_\infty = \left[\frac{P_s \times MW_{water}}{8314.447\times T_\infty}\right]\times\left[\frac{RH\%}{100}\right] \qquad (13)$$

The mass diffusivity of moisture in air [D_v] is estimated using Sherwood and Pigford, 1952 expression, valid for mass diffusivity of water vapour in air up to 1,100^{0}C

$$D_v = \left[\frac{0.926}{P_{amb}}\right]\times\left[\frac{T^{2.5}}{T+245}\right]\times\frac{1}{10^6} \qquad (14)$$

Where,

D_v = Mass diffusivity of moisture in air [m^2/s]

P_{amb} = Atmospheric pressure [kPa]

T = Ambient Temperature [K]

The Schmidt Number (*Sc*) is estimated as,

$$Sc = \frac{\mu}{\rho_{air}\times D_v} \qquad (15)$$

Where, m = Dynamic Viscosity [kg/m.s]

r_{air} = Air density [kg/m^3]

The Reynolds Number (*Re*) is estimated as,

$$Re = \frac{u_\infty \rho_{air} L}{\mu} \qquad (16)$$

Where, L = Pond Length along direction of air [m]

For the range 0^{0}C to 80^{0}C, the surface temperature [T_s] from curve fit data is,

$$T_s[K] = [(19.45777\times ln[\rho_s]) + 100.4106] + 273.15 \qquad (17)$$

CASE STUDY

Air at 25^{0}C & 101.325 kPa flows at 10 m/s along the length of an evaporation pond of L´W of 10m´2m. The relative humidity is 60%. The rate of heat transfer to water, rate of evaporation & the water surface temperature is to be estimated.

Evaluating the saturated vapour pressure,

$$P_s = 6.1121e^{\left[\left(18.678-\frac{25}{234.5}\right)\times\left(\frac{25}{257.14+25}\right)\right]}\times 100 \qquad (18)$$

$$P_s = 3{,}169\ Pa \qquad (19)$$

The vapour density at 25^{0}C is estimated as,

$$\rho_\infty = \left[\frac{3.169\times 18.02}{8314.447\times 298.15}\right]\times\left[\frac{60}{100}\right] = 0.013822\ \frac{kg}{m^3} \qquad (20)$$

Taking an initial guess of 15^{0}C, the t_f is,

$$t_f = \frac{15+25}{2} = 20°C = 293.15\ K \qquad (21)$$

Evaluating air properties at t_f = 20^{0}C, r_{air} =1.1975 kg/m^3, m=0.0000181 kg/m.s, k = 0.0257 W/m^{0}C, h_{fg} = 2,465 kJ/kg, Pr = 0.7094,

$$D_v = \left[\frac{0.926}{101.325}\right]\times\left[\frac{293.15^{2.5}}{293.15+245}\right]\times\frac{1}{10^6} = 2.5\times 10^{-5}\,\frac{m^2}{s} \qquad (22)$$

$$Sc = \frac{0.0000181}{1.1975\times 2.5\times 10^{-5}} = \sim 0.6063 \qquad (23)$$

$$\rho_s = \left[\frac{0.7094}{0.6063}\right]^{1/3}\times\frac{0.0257}{2.5\times 10^{-5}}\left[\frac{298.15-288.15}{2{,}465\times 1000}\right] + 0.01382 \qquad (24)$$

$$\rho_s = 0.01822\ kg/m^3 \qquad (25)$$

Estimating the surface water temperature [T_s] for r_s =0.0182 kg/m^3,

$$T_s = [(19.45777\times ln0.01822) + 100.4106] + 273.15 \qquad (26)$$

$$T_s = 295.62\ K = \sim 22.5°C \qquad (27)$$

Recalculating the air properties & iterating the calculations, T_s = 20^{0}C, r_s = 0.01601 kg/m^3, r_{air} = 1.1865 kg/m^3, m = 0.00001826 kg/m.s, h_{fg} = 2,454 kJ/kg and D_v = 2.54´10^{-5} m^2/s. The

Reynolds number & Sherwood number is estimated as,

$$Re = \frac{10 \times 1.1865 \times 10}{0.00001826} = \sim 6{,}497{,}679 \quad (28)$$

$$Sh = 0.037 \times 6{,}497{,}679^{4/5} \times 0.6058^{1/3} = 8{,}828 \quad (29)$$

The convective mass transfer coefficient is,

$$h_m = \frac{8{,}828 \times 2.54 \times 10^{-5}}{10} = 0.0224\ m/s \quad (30)$$

The rate of evaporation [m] is,

$$m = 0.022426 \times 20 \times [0.01601 - 0.013822] \quad (31)$$

$$m = \sim 0.000987\ \frac{kg}{s} = 85.3\ \frac{kg}{day} \quad (32)$$

The Rate of heat transfer [q] is,

$$q = mh_{fg} = 0.000987\ \frac{kg}{s} \times 2{,}454\ \frac{kJ}{kg} = 2{,}422W \quad (33)$$

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APPENDIX A

Evaporation Pond Calculations		
Air Properties		
Ambient Pressure [P]	101.325	kPa
Mean Wind Velocity [u_∞]	10	m/s
Dry Bulb/Air Temperature [T_∞]	25	^0C
	298.15	K
Relative Humidity [RH]	60	%
Saturated Vapour Pressure [P_s]	3169	Pa
Vapour Density [rho_inf] at 60% RH	0.01382	kg/m^3
Evaporation Pond Dimensions		
Pond Length [L]	10	m
Pond Width [W]	2	m
Direction of Wind	Along Length	m^2
Air Density [ρ]	1.1865	kg/m^3
Dynamic Viscosity [μ]	0.0000183	kg/m.s
Reynolds Number [Re]	6,497,679	-
Sherwood Number [Sh]	8,828	-
Convective Mass Transfer Coefficient [h_m]	0.0224	m/s
Rate of Evaporation [m]	**85.3**	kg/d
Rate of Heat Transfer to Water [q]	**2,422**	W

Iterations	Surface Temperature of Water [T_s]		Film Temperature [T_f]		Air Density [ρ]	Dynamic Viscosity [μ]	Thermal Conductivity [k]	Latent Heat of Vapourization [h_{fg}]	Prandtl Number [Pr]	Mass diffusivity of Mositure in Air [D_v]	Schimdt Number [Sc]	Vapour Density of Water Surface [ρ_s]
[-]	°C	K	K	°C	kg/m^3	kg/m.s	W/m.°C	kJ/kg	-	m^2/s	-	kg/m^3
1	15	288.2	293.2	20.0	1.1975	0.0000181	0.0257	2,465	0.7094	2.499E-05	0.6063	0.0182
2	22.5	295.6	296.9	23.7	1.1811	0.0000183	0.0260	2,448	0.7085	2.561E-05	0.6056	0.0149
3	18.6	291.7	294.9	21.8	1.1895	0.0000182	0.0259	2,457	0.7090	2.529E-05	0.6060	0.0166
4	20.7	293.8	296.0	22.8	1.1849	0.0000183	0.0259	2,452	0.7087	2.546E-05	0.6058	0.0157
5	19.6	292.7	295.4	22.3	1.1873	0.0000183	0.0259	2,455	0.7088	2.537E-05	0.6059	0.0162
6	20.2	293.3	295.7	22.6	1.1860	0.0000183	0.0259	2,453	0.7088	2.542E-05	0.6058	0.0159
7	19.9	293.0	295.6	22.4	1.1867	0.0000183	0.0259	2,454	0.7088	2.539E-05	0.6058	0.0161
8	20.0	293.2	295.7	22.5	1.1864	0.0000183	0.0259	2,454	0.7088	2.541E-05	0.6058	0.0160
9	19.9	293.1	295.6	22.5	1.1866	0.0000183	0.0259	2,454	0.7088	2.540E-05	0.6058	0.0160
10	20.0	293.1	295.6	22.5	1.1864	0.0000183	0.0259	2,454	0.7088	2.540E-05	0.6058	0.0160
11	20.0	293.1	295.6	22.5	1.1865	0.0000183	0.0259	2,454	0.7088	2.540E-05	0.6058	0.0160
12	20.0	293.1	295.6	22.5	1.1865	0.0000183	0.0259	2,454	0.7088	2.540E-05	0.6058	0.0160
13	20.0	293.1	295.6	22.5	1.1865	0.0000183	0.0259	2,454	0.7088	2.540E-05	0.6058	0.0160
14	20.0	293.1	295.6	22.5	1.1865	0.0000183	0.0259	2,454	0.7088	2.540E-05	0.6058	0.0160
15	20.0	293.1	295.6	22.5	1.1865	0.0000183	0.0259	2,454	0.7088	2.540E-05	0.6058	0.0160
16	20.0	293.1	295.6	22.5	1.1865	0.0000183	0.0259	2,454	0.7088	2.540E-05	0.6058	0.0160
17	20.0	293.1	295.6	22.5	1.1865	0.0000183	0.0259	2,454	0.7088	2.540E-05	0.6058	0.0160
18	**20.0**	**293.1**	**295.6**	**22.5**	**1.1865**	**0.0000183**	**0.0259**	**2,454**	**0.7088**	**2.540E-05**	**0.6058**	**0.0160**

Brief on the Process of Carrying Out Alarm Rationalization in the Process Plant

Praveen Nagenderan C

Rationalization encompasses several significant activities, including alarm justification, documentation, prioritization, and classification. In justification, existing or potential alarms are systematically compared to the criteria for alarms outlined in the alarm philosophy. If the proposed alarm meets the criteria, then the alarm type, setpoint, cause, consequence, and operator action are documented. The alarm is prioritized and classified according to the guidelines. Classification encompasses assigning alarms to a group defining certain administrative requirements. These activities are combined into a single rationalization activity. The objective of Rationalization is to ensure that every alarm is an indication of an abnormal condition requiring operator response and that every abnormal condition requiring operator action is appropriately alarmed.

- The facility should perform rationalization for all their existing configured alarms once a year.
- Signed off Alarm philosophy document to be in place as a prerequisite to start alarm rationalization process.
- Train rationalization Team: Before the commencement of the actual rationalization sessions, it is mandatory to conduct a brief training session on alarm rationalization to all likely participants. Training sessions should include the objectives and goals of the rationalization, actual process to be used during the sessions to be clearly explained which includes an explanation on existing and documented alarm philosophy, how the needs for the alarms are determined, how alarms are prioritized.
- Identify Team/Personnel: Rationalization should be performed by representatives with the knowledge and skills of process engineering, operations, process control, and experienced alarm rationalization facilitator, knowledge in alarm management principles and practices (optional). Scribe to be appointed for the rationalization process.
- The team should be supplemented with the skill set of safety and environment, maintenance/equipment reliability, electrical and rotating equipment engineers, metallurgy, knowledge of product quality requirements.
- Master Alarm Database summary list should be in place before starting the rationalization process.
- Results of rationalization should be documented and responsibility lies with System/Instrument Engineer to take up the job of implementation.
- Operational details of the process are needed including normal process variables and their tolerable limits.
- Major reference documents are typically used for rationalization include P&ID, PHA report, HAZOP reports, FMEA reports, LOPA reports and safety requirements specifications, safe operating limits, equipment's design parameters, C&E charts, environmental permits, production targets, quality targets, key operating procedures, HMI graphics, incident reports, access to processing historical data, process narrative or description and manufacture/licensor alarm recommendations. All the mentioned documents should be collected and in place while carrying out the rationalization process.
- Kick-off Meeting: A kick-off meeting session is used to acquaint management and all other interested parties as to the reasons for, method, and potential results of the rationalization process. Content should also include detailing the basis of alarm rationalization, as well as examples of past rationalization that will assist the group in understanding the overall intent of the effort. Requirements for participation by the specialist can be discussed if any special assistance is sought for the process.
- Roles and Responsibilities for the participants to be clearly explained and documented.
- Expectations of daily progress and overall effort duration should be set ahead of the rationalization session.
- Before starting the process, read out key items of the alarm philosophy related to the rationalization process to the participants.

- Every existing and proposed alarm is reviewed to ensure that it meets the basic requirements for an alarm such as the alarm indicates a malfunction, deviation, or abnormal situation, the alarm represents a situation requiring timely operator action in
- order to avoid defined consequences, the alarm is the best indicator of the cause of the abnormal situation i.e multiple alarms from the same condition should be avoided. Conditions can be assessed and compared with the existing alarm response procedure.
- When the validity check indicates an existing alarm is not needed, the rationale for deletion is documented.
- In case of a new alarm requirement,
  1. Document the immediate and proximate consequences of insufficient operator response to the alarm. The consequence should assume the condition alarmed continues or gets worse.
  2. Document the likely root cause of the process condition that would result in the alarm. The list of events should either be the likely events that this alarm is to identify or something unique about this alarm versus all others. Not every cause needs to be documented.
  3. Document the operator actions to take in response to the alarm. The actions should be objective using action verbs like start/stop or raise, lower or open, close. The actions can either be through the control system, through action in the field accomplished by the operator receiving the alarm, through instruction to field personnel, or consultation with others.
- Assign alarm priority as per the guidelines
- Determine alarm setpoint or logical condition
- Assess need for special handling for the alarm and specify the needs
- Requirements of alarm shelving to be assessed and mentioned.
- Assign classes and groups as per the guidelines provided in section
- In case of an existing alarm, the above-mentioned points shall be reviewed by the team. In case of any changes, amend and document the changes reviewed by the team.

The general activities of rationalization are Alarm Justification, Alarm Setpoint Determination, Alarm Prioritization, Alarm Classification, and Rationalization Review. Hence, Alarm rationalization shall determine and document the following for every alarm:

- Alarm Type
- Alarm Priority
- Alarm Class
- Alarm Set Point or Logical conditions
- Operator Action in case of Highly Managed Alarm category
- The consequence of action in the case of the Highly Managed Alarm category
- Probable Cause
- Alarm Identification Method
- Requirement of advanced alarming techniques
- The rationale of Setpoint

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