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In This Issue

Volume 8 | Number 34

SPECIAL FEATURES

- 04** **Facing the Challenges of the Downstream Industry with Versatile Technologies | The FCC Alternative**
Dr. Marcio Wagner da Silva
- 15** **Gas Compression Stages | Process Design & Optimization**
Jayanthi Vijay Sarathy
- 20** **How to... RANDOM PACKINGS How to Calculate Hydraulics of Random Packings**
Dr.-Ing. Volker Engel
- 28** **Fourth Quarter 2022 Update for the South East Asia (SEA) O&G industry**
- 30** **Rock Bottom View**
Ronald J. Cormier
- 33** **Whitepaper Sampling Sulfuric Acid | An Engineered Solution for Safer Sampling**
BIAR Sampling Systems

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Facing the Challenges of the Downstream Industry with Versatile Technologies | The FCC Alternative

Dr. Marcio Wagner da Silva

INTRODUCTION AND CONTEXT

The downstream industry faces a transition period where the focus of the players is changing from transportation fuels to petrochemicals aiming to ensure maximum added value to processed crude oils as well as to allow the growth of low carbon energies in the global energetic matrix.

The growing market of petrochemicals have been led some refiners to look for a closer integration between refining and petrochemicals assets aiming to reach more adherence with the market demand, improve revenues, and reduce operation costs. In this business environment, flexible refining technologies like Fluid Catalytic Cracking (FCC) reach highlighted position in the strategy of the refiners to reach competitiveness in the market.

Facing these challenges, search for alternatives that ensure survival and sustainability of the refining industry became constant by refiners and technology developers. Due to his similarities, better integration between refining and petrochemical production processes appears as an attractive alternative. Although the advantages, it's important take into account that the integration between refining and petrochemical assets increase the complexity, requires capital spending, and affect the interdependency of refineries and petrochemical plants, these facts need to be deeply studied and analyzed case by case. In this business environment, flexible refining technologies like Fluid Catalytic Cracking (FCC) can ensure high competitiveness to refiners once are capable to produce high quality intermediates both to petrochemicals and transportation fuels, in markets with great demand by petrochemicals, the petrochemical FCC technologies can be an attractive option, despite the high capital spending. Refiners with restriction of capital investment can even maximize the profitability of FCC units through optimization actions aiming to maximize the yield of petrochemicals against transportation fuels.

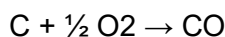
FLUID CATALYTIC CRACKING TECHNOLOGIES – AN OVERVIEW

Fluid Catalytic Cracking (FCC) is one of the main processes which give higher operational flexibility and profitability to refiners. The catalytic cracking process was widely studied over last decades and became the principal and most employed process dedicated to converting heavy oil fractions in higher economic value streams.

The installation of catalytic cracking units allows the refiners to process heavier crude oils and consequently cheaper, raising the refining margin, mainly in higher crude oil prices scenario or in geopolitics crises that can become difficult the access to light oils. The typical Catalytic Cracking Unit feedstream is gas oils from vacuum distillation process. However, some variations are found in some refineries, like sending heavy coke naphtha, coke gas oils and deasphalted oils from solvent deasphalting units to processing in the FCC unit.

The catalyst normally employed in fluid catalytic cracking units is a solid constituted by small particles of alumina (Al₂O₃) and silica (SiO₂) (zeolite). By the catalyst characteristics and the operational conditions in the catalytic cracking process (temperature higher than 500 °C), the process is inefficient to cracking aromatic compounds, therefore, how much more paraffinic is the feedstream, higher is the unit conversion. Figure 1 presents a process scheme for a typical Fluid Catalytic Cracking Unit (FCCU).

In a conventional scheme, the catalyst regeneration process consists in the carbon partial burning deposited over the catalyst, according to chemical reaction below:



The carbon monoxide is burned in a boiler capable of generating higher pressure steam that supplies others process units in the refinery.

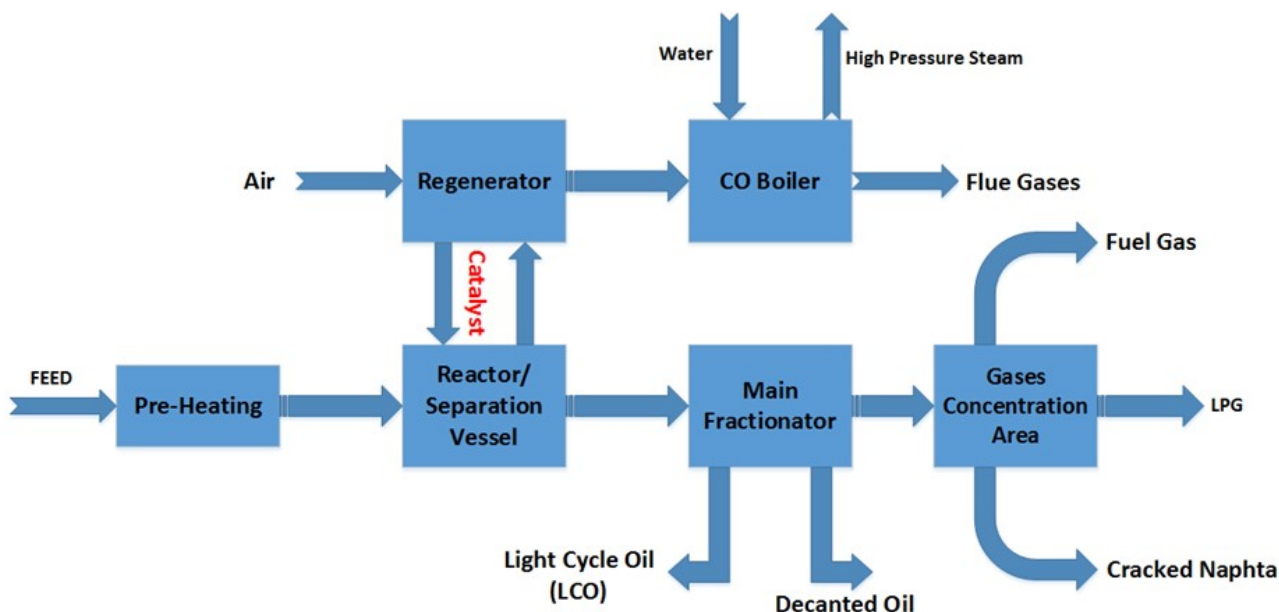


Figure 1 – Schematic Process Flow for a Typical Fluid Catalytic Cracking Process Unit (FCCU)

The principal operational variables in a fluid catalytic cracking unit are reaction temperature, normally considered the temperature in the top of the reactor (called riser), feed stream temperature, feed stream quality (mainly carbon residue), feed stream flow rate and catalyst quality. Feedstock quality is especially relevant, but this variable is a function of the crude oil processed by the refinery, so is difficultly can be changed, but for example, aromatic feedstocks with high metals content are refractory to cracking and conducting to a quick catalyst deactivation.

An important variation of the fluid catalytic cracking technology is the residue fluid catalytic cracking unit (RFCC). In this case, the feedstock to the process is basically residue from atmospheric distillation column, due to the high carbon residue and contaminants (metals, Sulphur, nitrogen, etc.) are necessary some adaptations in the unit like catalyst with higher resistance to metals and nitrogen and catalyst coolers furthermore, it's necessary apply materials with most noble metallurgy due the higher temperatures reached in the catalyst regeneration step (due the higher coke quantity deposited on the catalyst), that raises significantly the capital investment to the unit installation. Nitrogen is a strong contaminant to the FCC catalyst because they neutralize the acid sites of the catalyst which are responsible for the cracking reactions.

When the residue has high contaminants content, is common the feed stream treatment in

hydrotreating units to reduce the metals and heteroatoms concentration to protect the FCC catalyst.

Typically, the average yield in fluid catalytic cracking units is 55% in volume in cracked naphtha and 30 % in LPG. Figure 2 presents a scheme for the main fractionator of the FCC unit with the principal product streams.

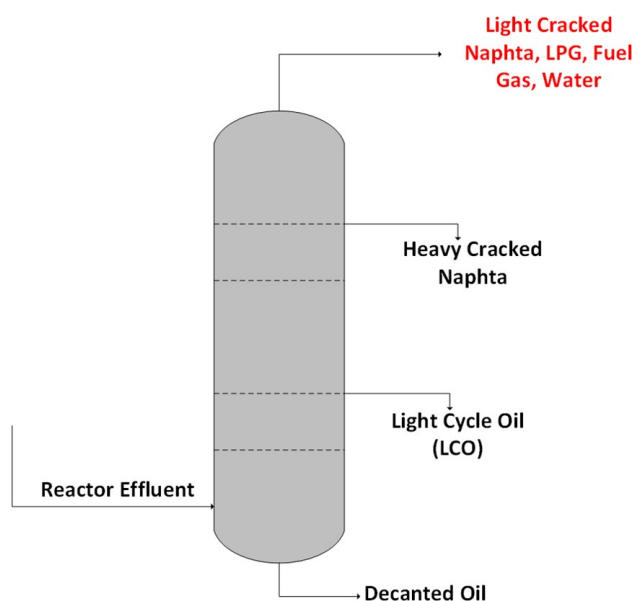


Figure 2 – Main Fractionator Scheme for a Typical Fluid Catalytic Cracking Unit

The decanted oil stream contains the heavier products and have high aromatic content, is common that this product are contaminated with catalyst fines and normally this stream is directed to use like fuel oil diluent, but in some refineries, this stream can be used to produce black carbon.

Light Cycle Oil (LCO) has a distillation range close to diesel and normally this stream is directed to treatment in severe hydrotreating units (due to the high aromaticity), after this treatment the LCO is sent to the refinery diesel pool.

Heavy cracked naphtha is normally directed to refinery gasoline pool, however, in scenarios where the objective is to raise the production of middle distillates, this stream can be sent to hydrotreating units for further diesel production.

The overhead products from main fractionator are still in gaseous phase and are sent to the gas separation section. The fuel gas is sent to the refinery fuel gas ring, after treatment to remove H₂S, where will be burned in fired heaters while the LPG is directed to treatment (MEROX) and further commercialization. The LPG produced by FCC unit have a high content of light olefins (mainly Propylene) so, in some refineries, the LPG stream is processed in a Propylene separation unit to recovery the propylene that has higher added value than LPG.

Cracked naphtha is usually sent to refinery gasoline pool which is formed by naphtha produced by other process units like straight run naphtha, naphtha from the catalytic reforming unit, etc. Due to the production process (deep conversion of residues), the cracked naphtha has high sulfur content and to attend the currently environmental legislation this stream needs to be processed to reducing the contaminants content, mainly sulfur.

The cracked naphtha sulfur removing represents a great technology challenge because is necessary to remove the sulfur components without molecules saturation that gives high octane number for gasoline (mainly olefins).

Over the last decades some technology licensors had developed new processes aiming to reduce the sulfur content in the cracked naphtha with minimum octane number loss, some of the main technologies dedicated for this purpose are technology PRIME G+™ from Axens, the processes OCTAGAIN™ and SCANfining™ from Exxon Mobil, the process S-Zorb™ from ConocoPhillips and ISAL™ technology from UOP.

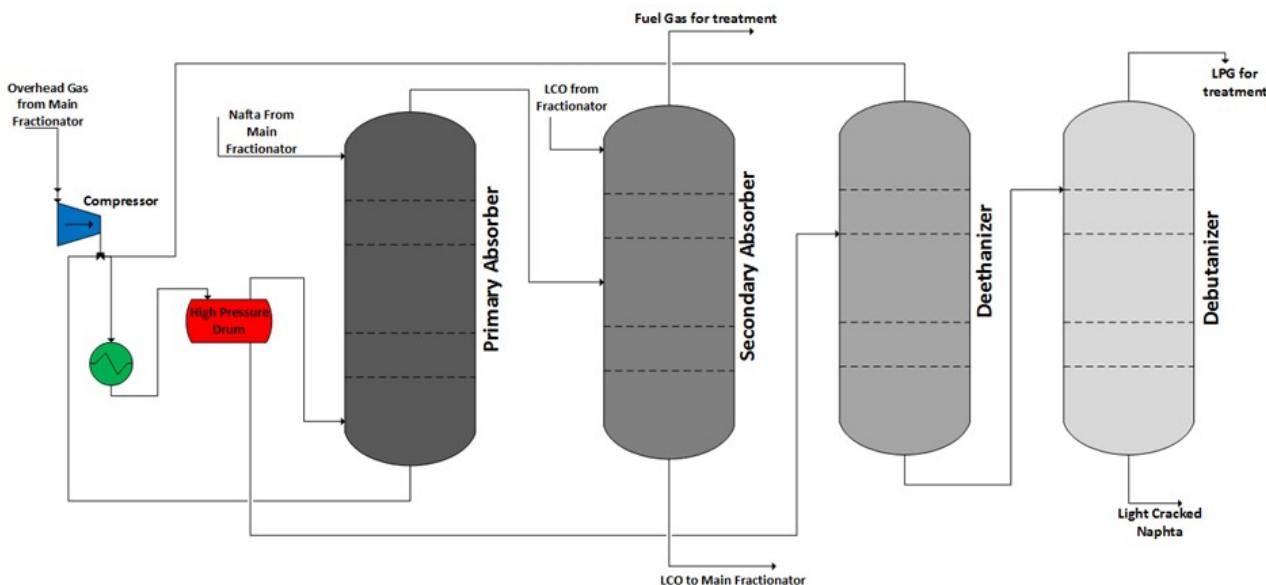
Usually, catalytic cracking units are optimized to aiming the production of fuels (mainly gasoline), however, some process units are optimized to maximize the light olefins production (propylene and ethylene). Process units dedicated for this purpose have his project and operational conditions significantly changed once

the process severity is strongly raised in this case.

The reaction temperature reaches 600 oC and higher catalyst circulation rate raises the gases production, which requires a scaling up of gas separation section. Figure 3 presents a typical scheme for a gas separation section for a fluid catalytic cracking unit.

Figure 3 – Basic Process Flow Diagram for a Typical Gas Separation Section from FCC Unit

In several cases, due the higher heat necessity of the unit is advantageous to operate the regenerator with the total combustion of the coke deposited on the catalyst, this arrangement significantly changes the thermal balance of the refinery once it's no longer possible to resort the steam produced by the CO boiler.



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Over last decades, the fluid catalytic cracking technology was intensively studied aiming mainly the development of units capable of producing light olefins (Deep Catalytic Cracking) and to process heavier feedstocks. The main licensors for fluid catalytic cracking technology nowadays are the companies KBR, UOP, STONE & WEBSTER, AXENS, and Lummus.

RESIDUE FLUID CATALYTIC CRACKING (RFCC) TECHNOLOGIES – DEALING WITH HEAVY FEEDS

One variation of the fluid catalytic cracking that has been widely applied in the last years is the Residue Fluid Catalytic Cracking (RFCC). In this case, the feed stream to the process is basically the bottom stream from the atmospheric distillation column, called atmospheric residue, that have high carbon residue and higher contaminants content like metals, nitrogen, and sulfur.

Due to the feed stream characteristics, the residue catalytic cracking units require design and optimization changes. The higher levels of residual carbon in the feed stream led to higher temperatures in the catalyst regeneration step and a lower catalyst circulation rate to keep the reactor in constant temperature, this fact reduces the catalyst/oil ratio that leads to a lower conversion and selectivity. To avoid these effects, the RFCC units normally rely on catalyst coolers, as presented in Figure 4.

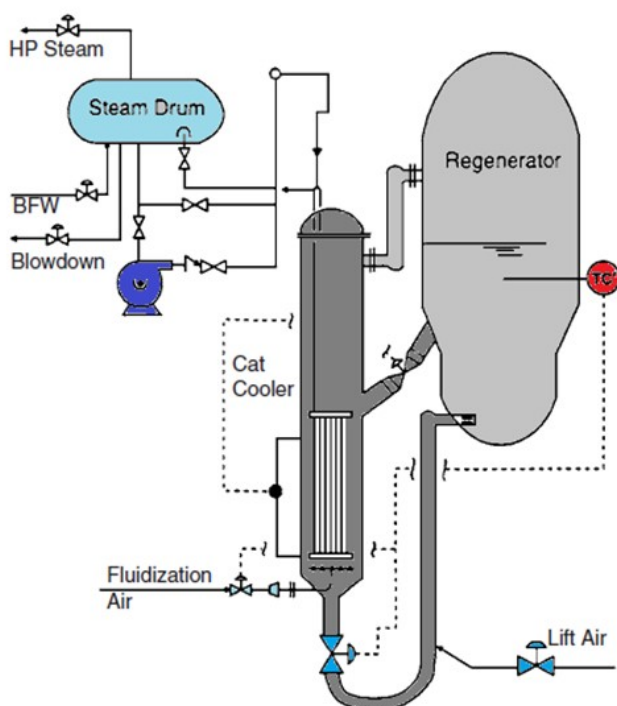
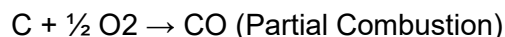
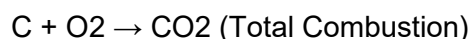


Figure 4 – Catalyst Cooler Process Arrangement for a Typical RFCC Unit (Handbook of Petroleum Refining Processes, 2004)

Installation of catalyst cooler system raises the process unit profitability through the total conversion enhancement and selectivity to noblest products as propylene and naphtha against gases and coke production, furthermore, helps the refinery thermal balance, once produces high-pressure steam. The use of catalyst cooler is also necessary when the unit is designed to operate under total combustion mode, in this case, the heat release rate is higher due to the total burn of carbon to CO₂, as presented below.



$$\Delta H = - 27 \text{ kcal/mol}$$



$$\Delta H = - 94 \text{ kcal/mol}$$

In this case, the temperature of the regeneration vessel can reach values close to 760 °C, leading to higher risks of catalyst damage which is minimized through catalyst cooler installation. The option by the total combustion mode needs to consider the refinery thermal balance, once, in this case, will not the possibility to produce steam in the CO boiler, furthermore, the higher temperatures in the regenerator requires materials with noblest metallurgy, this significantly raises the installation costs of these units.

As pointed earlier, the feed streams characteristics to RFCC units require modifications when compared with the conventional fluid catalytic cracking. The presence of higher content of nitrogen compounds leads to an accelerated process of catalyst deactivation through acid sites neutralization, the presence of metals like nickel, sodium, and vanadium raise the coke deposition on the catalyst and lead to a higher production of hydrogen and gases, besides that, reduces the catalyst lifecycle through the zeolitic matrix degradation. Beyond these factors, heavier feed streams normally have high aromatics content that are refractory to the cracking reactions, leading to a higher coke deposition rate and lower conversion.

Due to this operation conditions, the residue fluid catalytic cracking units presents higher catalyst consumption when compared with the conventional process, this fact raises considerably the operational costs of the RFCC units. However, the most modern units have applied specific catalysts to process residual feed streams, in this case, the catalyst has a higher porosity aiming to allow a better adaptation to the high aromatics content, furthermore, the catalyst needs to have a higher metals tolerance.

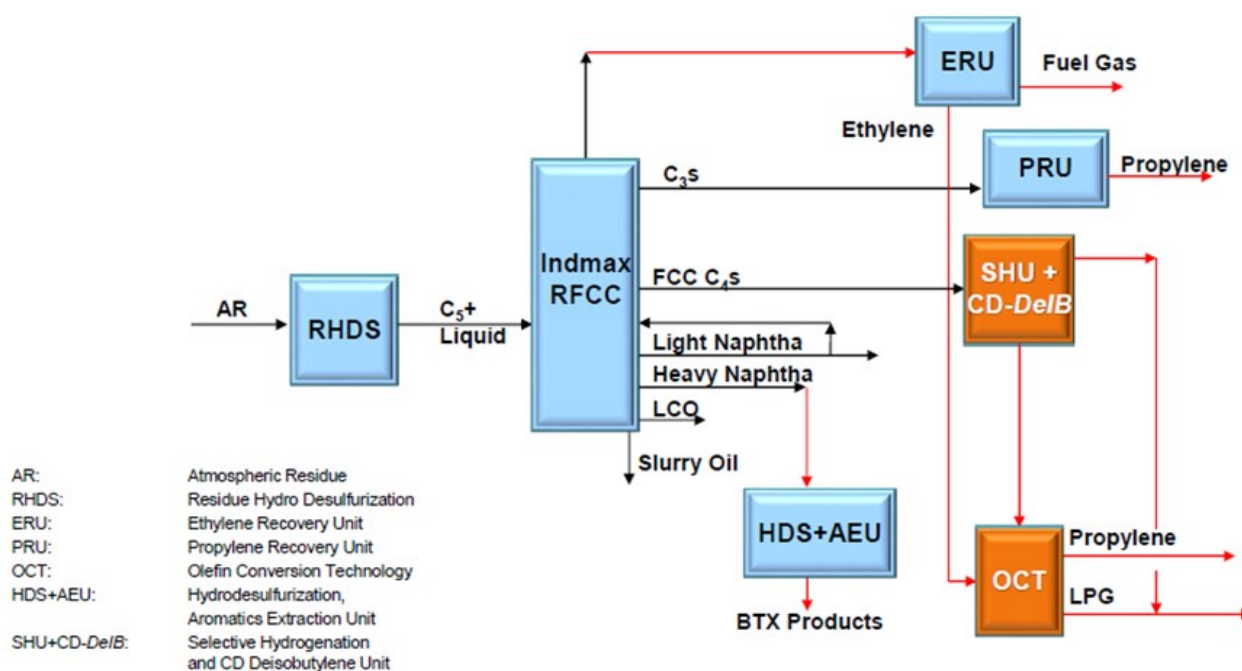
The control of contaminants content in the feed stream or his effects is a fundamental step to the residue fluid catalytic cracking process. Sodium content can be minimized through an adequate crude oil desalting process and the effects of nickel (dehydrogenation reactions) can be reduced by dosage of antimony compounds that act like neutralizing agent of the nickel dehydrogenation activity, reducing the generation of low added value gases, in its turn, the vanadium effects can be controlled through the addition of rare earth to the catalyst, like cerium compounds. The addition of these compounds needs to be deeply studied once significantly raises the catalyst cost.

The use of visbreaking units to treat the feed streams to RFCC units is a process scheme adopted by some refiners, in these cases, the most significant effect in the reduction in the residual carbon, however, due to his higher effectiveness, the tendency in the last decades is to treat the bottom barrels streams in deep hydrotreating or hydrocracking units before to pump for RFCC units, with this processing scheme it's possible to achieve lower contaminants content, mainly metals, leading to a higher catalyst lifecycle. Furthermore, the hydroprocessing has the advantage of the reduction of the sulfur content in the unit intermediate streams, minimizing the necessity or severity of posterior treatments, a clear disadvantage of this refining scheme is the high hydrogen consumption that significantly raises the operational costs.

Like to the conventional FCC units, the main operational variables to RFCC units are the reaction temperature, normally considered in the highest point in the reactor (also called riser), feed stream temperature, feed stream quality, feed stream flow rate and catalyst quality. It's relevant to quote that the conventional FCC units can process atmospheric residue as the feed stream, however, it's necessary to control the contaminants content, mainly metals, which requires processing lighter crudes with higher costs that raise the operational costs and reduces the flexibility of the refiner in relation of the crude oil supplier.

Some of the most relevant residue fluid catalytic cracking technologies available commercially are the R2R™ by Axens Company, the INDMAX™ process licensed by Lummus Company and the RxPro™ process developed by the UOP Company. Figure 5 presents a block diagram showing a case study demonstrating how the petrochemical FCC unit, in this case the INDMAX™ technology by Lummus Company, can maximize the yield of petrochemicals in the refining hardware.

Figure 5 – Olefins Maximization in the Refining Hardware with INDMAX™ FCC Technology by Lummus Company (SANIN, A.K., 2017)



It's interesting to note that, in the case presented in Figure 5 the refiner can maximize olefins production from atmospheric residue, as aforementioned, due to the feedstock characteristic is necessary to apply a residue hydrotreating unit upstream to the FCC unit (the RHDS unit) to control the contaminants content to the FCC catalyst.

THE FCC CATALYST – CONVERTING RESIDUES TO ADDED VALUE DERIVATIVES

A key factor in the FCC operation is the catalyst applied in the process. The catalyst normally employed in fluid catalytic cracking units is a solid constituted by small particles of alumina (Al_2O_3) and silica (SiO_2) (zeolite). By the catalyst characteristics and the operational conditions in the catalytic cracking process (temperature higher than 500 oC), the process is inefficient to cracking aromatic compounds, therefore, how much more paraffinic is the feed stream, higher is the unit conversion.

The active phase in the FCC catalyst is composed by the zeolite that is responsible by the catalytic activity and selectivity of the catalyst and by the alumina that is responsible by the cracking of heavier molecules allowing these molecules to reach the access to the zeolitic phase. The other components of the FCC catalysts are the inert (kaolim) and synthetic matrixes that are responsible to the mechanical resistance, hardness, and act as binder agent

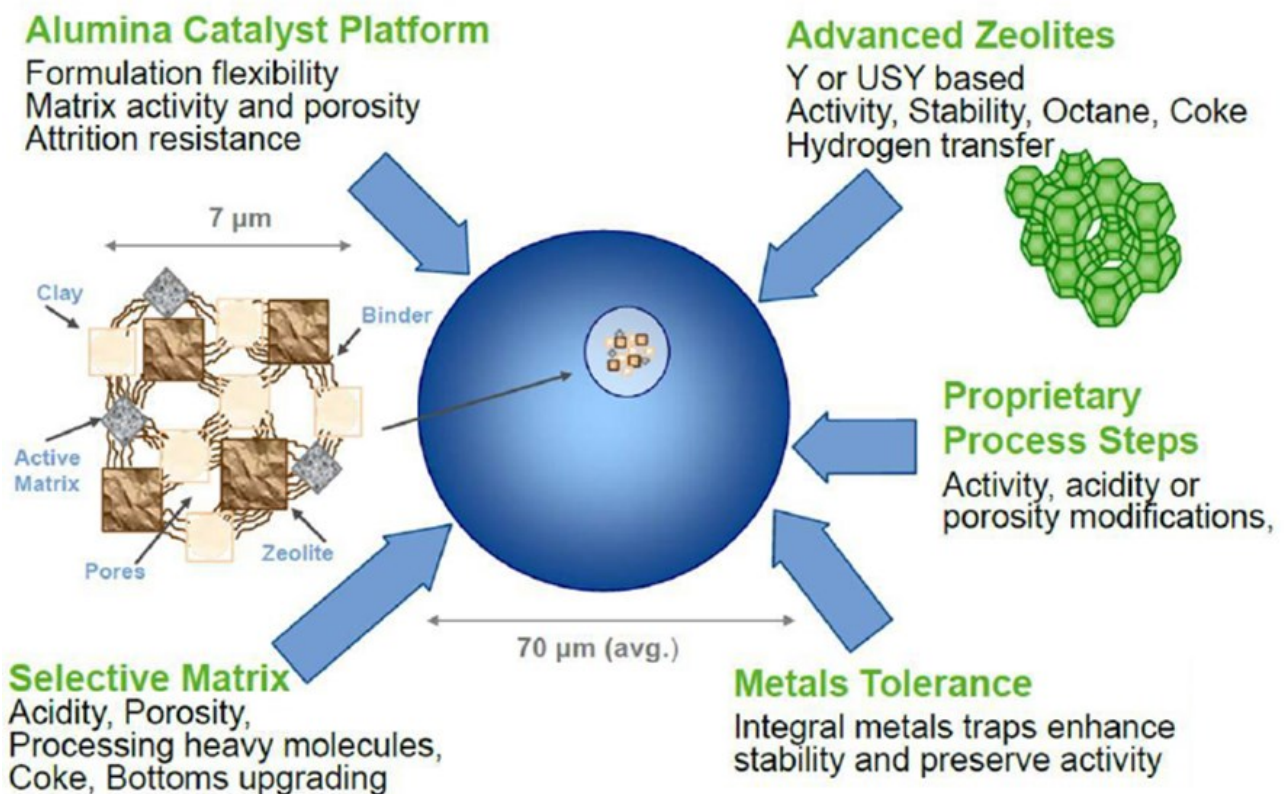
between the active phases and the matrix.

According to the process conditions, can be added some compounds to the catalyst with specific purpose. In refineries that processing feed streams with high amount of nickel it's common to add antimony as that act as passivator agent, another deleterious metal is the vanadium, in this case is applied some trap agent to minimize his effects. The Figure 6 presents an arrangement of a typical design of FCC catalyst.

Figure 6 – Typical Design of FCC Catalyst (Grace Company, 2015)

As aforementioned, the processing of heavier crude oils leads to a more challenging feedstocks to FCC units due to the higher concentration of residual carbon and mainly contaminants as Nickel and Vanadium. The nickel acts as dehydrogenation agent leading to the coke deposition over the catalyst and raises the hydrogen production, normally the refiners used to process heavier feeds apply metals passivators as boron to keep under control the deleterious effect of metals, the most common form to control the nickel effects is to inject Antimony in the FCC feed.

The vanadium effect over the FCC catalyst involves the degradation of the zeolite matrix leading to the reduction in the catalytic activity and his action is keep under control through vanadium traps. In the last years



some catalyst developers are focusing his research to study the effects of iron in the FCC catalyst, the high concentration of iron is a characteristic of the shale oils produced in the North America and the availability of these crudes raises significantly in the last years, especially after 2015, when the United States starts to exports his internal production. The iron is not catalytically active, but this compound can accumulate over the catalyst surface reducing the porosity reducing the activity and leading to dehydrogenation reactions as well as carbon monoxide (CO) promoter, furthermore the high concentration of Iron can raise the SOx emissions in the catalyst regenerator.

Another dangerous contaminant of FCC catalyst is the sodium, this compound promotes an irreversible deactivation of the catalyst through the chemical degradation of the zeolitic matrix. By this reason, an adequate control of the crude oil desalting process is fundamental to control the sodium content in the FCC feeds, preserving the catalyst lifecycle. Nowadays, some refiners are injected caustic soda in the crude to improve the desalting characteristics, and a stricter control is required in these cases. A less common contaminant founded in some crude oils is the copper, his effect is the promotion of dehydrogenation reactions, raising the yield of hydrogen and coke. The copper is present in some NOx reducing agents.

Aiming to improve the catalytic activity, some developers apply rare earth compounds to the FCC catalyst as Lanthanum and Cerium. These compounds raises significantly the activity and selectivity of the final catalyst, but his high cost made the refiners avoid his application, furthermore, the presence of rare earth in the catalyst improve yield of gasoline and reduces the light olefins production in FCC units, in the current scenario this is exactly the inverse that the refiners are looking for.

The trend of reduction in transportation fuels demand is making refiners to optimize his FCC units to maximize petrochemical intermediates against transportation fuels. To achieve this goal, normally the refiners are applying most severe conditions as higher catalyst/oil ratios, higher reaction temperature (TRX), and the use of ZSM-5 as additive to the catalyst.

The presence of ZSM-5 in the catalyst is capable to improve the yield of light olefins in the FCC unit by up to 8,0 %. One of the most important role of the refineries optimization teams is to analyze the FCC equilibrium catalysts to found the improvement alternatives based on the contaminants content and the

reached conversion of the unit as well as the degradation observed on the equilibrium catalysts. The volumetric conversion of an FCC unit is defined as Equation (1).

$$(1) \text{ Volumetric Conversion (\%)} = [\text{Feed} - (\text{LCO} + \text{Decanted Oil})] / \text{Feed} \times 100$$

The fraction LCO and Decanted Oil (DO) is considered non converted fractions.

The main FCC catalyst developers present in the market nowadays are, BASF Catalysts Company, Albermarle, and W. R. Grace Company.

MEETING THE MARKET DEMAND THROUGH FCC OPTIMIZATION

According to the market demand, the FCC units can be optimized to produce the most demanded derivatives. In traditional FCC units there are normally four operating campaigns:

1 – Maximum Gasoline – In Maximum gasoline campaigns the process unit operates under medium or high severity. The severity is limited by the octane number achieved in the cracked naphtha, in refining configurations where the refiners rely on octane boosting units like alkylation, catalytic reforming, and isomerization there are more flexibility to maximize the gasoline yield in the FCC operating in maximum gasoline mode.

The catalyst formulation to maximum gasoline campaigns involves high zeolite and active matrix once the presence of rare earth compounds tends to raise hydrogen transfer reactions, reducing the olefins content and consequently the octane number in the cracked naphtha. Another alternative to improve the yield of gasoline in the is operation mode is change the final boiling point of cracked naphtha to higher values, in this case the limitation is the quality requirements, mainly the sulfur content in the final derivative, according to the operating capacity in cracked naphtha hydrodesulfurization unit.

The main restrictions in the process unit in maximum gasoline mode are the gas separation section capacity, especially related to the cold area compressors as well as the debutanizer columns.

2 – Maximum LPG – In this operation mode the FCC unit operates under high severity translated to high operation temperature (TRX), high catalyst/oil ratio. The catalyst formulation taking into account higher catalyst activity through addition of ZSM-5 zeolite. There is the possibility to a reduction in the

total processing capacity due to the limitations in blowers and cold area capacity.

It's observed an improvement in the octane number of cracked naphtha despite a lower yield, due to the higher aromatics concentration in the cracked naphtha. In some cases, the refiner can use the cracked naphtha recycle to improve even more the LPG yield.

In the maximum LPG operation mode, the main restrictions are the cold area processing capacity, metallurgic limits in the hot section of the unit, treating section processing capacity as well as the top systems of main fractionating column.

3 – Maximum LCO – The maximum LCO (Light Cycle Oil) operation mode is applied by refiners with great demand by middle distillates, especially diesel, and adequate hydrotreating capacity to convert the LCO in high quality diesel. In this case, the FCC unit operates under relative low severity conditions with low TRX, low catalyst/oil ratios, and the catalyst formulation tends to minimize the catalyst activity.

In process units where is observed a restriction related to the cold area and blowers processing capacity, the maximum LCO operation mode can allow the raise in the total processing capacity of the unit. This fact can be positive, once allow lower time contact between catalyst and feed, improving even more the LCO and decanted oil (DO) yield.

It's important to taking into account the effect of the feed stream quality over the produced LCO. Paraffinic feeds tends to produce higher quality LCO, refiners operating FCC units in maximum LCO mode tends to minimize the final boiling point of cracked naphtha and maximize this parameter in the LCO aiming to improve the LCO yield, but this action is limited by the quality of the final diesel.

4 – Maximum Aromatic Residue – This is the less common operation mode in FCC units, where the main objective is to maximize the yield of decanted oil and achieve the quality requirements of aromatic residue. The aromatic residue is normally applied to produce carbon black, these derivative presents great demand in some markets.

The main difficult to comply with the aromatic residue specification is regarding to ash content in the decanted oil. This parameter is strictly related to the cyclones efficiency in the catalyst regeneration section, to achieve this objective some refiners apply additives to promote de ash decantation in the final tanks or

specific filtration systems that requires more capital spending.

Another key quality parameter to meet aromatic residue specification is the BMCI (Bureau of Mines Correlation Index) that is related to the aromaticity of the decanted oil, to achieve the current specifications of black carbon it's necessary to achieve a minimum BMCI higher than 120. The BMCI is calculated based on viscosity of the decanted oil at the temperature of 210 oF. The metals content in the decanted oil needs to be also controlled, especially, sodium, aluminum, and silicon.

The operating severity in maximum aromatic residue mode tends to be high with high TRX, high catalyst/Oil ratio, and high catalyst activity. As side effect is observed the raise of octane number in cracked naphtha due to the incorporation of aromatics compounds in this intermediate.

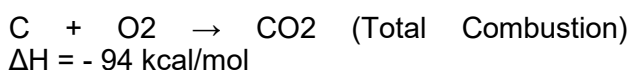
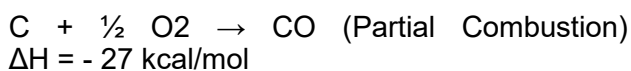
In maximum aromatic residue operation mode the main restrictions are the temperature of the bottom section in the main fractionators that can lead to coke formation, metallurgic limitations in the hot sections as well as the capacity of blowers and cold area compressors.

THE PETROCHEMICAL FCC ALTERNATIVE – RAISING COMPETITIVE ADVANTAGE

Considering the current scenario of the downstream industry and the last forecasts, it's observed trend of reduction in transportation fuels demand followed of a growing market of petrochemicals, leading the refiners to optimize his FCC units to maximum LPG yield aiming to improve the capacity to produce light olefins and promote closer integration with petrochemical assets. A major part of the catalytic cracking units is optimized to maximize transportation fuels, especially gasoline, however, face to the current scenario some units have been optimized to maximize the production of light olefins (ethylene, propylene, and butenes). As aforementioned, units focused on this goal have these operational conditions severely changed, raising the cracking rate.

The reaction temperature reaches 600 oC and higher catalyst circulation rate raises the gases production, which requires a scaling up of gas separation section. The higher thermal demand makes advantageous operates the catalyst regenerator in total combustion mode leading to the necessity of installation a catalyst cooler system.

Installation of catalyst cooler system raises the process unit profitability through the total conversion enhancement and selectivity to noblest products as propylene and naphtha against gases and coke production. The catalyst cooler necessary when the unit is designed to operate under total combustion mode due to the higher heat release rate as presented below.



In this case, the temperature of the regeneration vessel can reach values close to 760 oC, leading to higher risks of catalyst damage which is minimized through catalyst cooler installation. The option by the total combustion mode needs to consider the refinery thermal balance, once, in this case, will not the possibility to produce steam in the CO boiler, furthermore, the higher temperatures in the regenerator requires materials with noblest metallurgy, this raises significantly the installation costs of these units which can be prohibitive to some refiners with restricted capital access.

CONCLUSION

As discussed above, the FCC units offer great operation flexibility to refiners and can significantly raise the refining margins and, according to the local market demand, the process unit can be optimized to produce different kind of intermediates. Following recent trends, the synergy between refining and petrochemical processes raises the availability of raw material to petrochemical plants and makes the supply of energy to these processes more reliable at the same time ensures better refining margin to refiners due to the high added value of petrochemical intermediates when compared with transportation fuels.

Another advantage is the risks reduction of transportation fuels oversupply, facing the current scenario of demand reduction and restriction of fossil fuels. It's important to consider that integrated processes lead to a higher operational complexity, however, given current and middle term scenarios to refining industry, a better integration between refining and petrochemical processes is fundamental to the economic sustainability of the downstream industry. In this scenario, the FCC technologies can ensure higher added value to processed crude oils through the maximization of petrochemical intermediates, like propylene, in the refining hardware. Another important variation of the FCC technologies is the unit focused to processing residues, the Residue Fluid Catalytic

Cracking (RFCC) that can allow even more added value to bottom barrel streams, especially for refiners processing heavier crudes.

Like a flexible refining technology, the Fluid Catalytic Cracking (FCC) units have a highlighted role in the future of the downstream industry, especially considering the transitive period, where the FCC units can help to supply the demand by petrochemicals without shortage of transportation fuels.

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Gas Compression Stages | Process Design & Optimization

Jayanthi Vijay Sarathy

The following demonstrates how to estimate the required number of compression stages and optimize the individual pressure ratio in a multistage centrifugal compression system. A schematic of a 2-Stage compressor unit is,

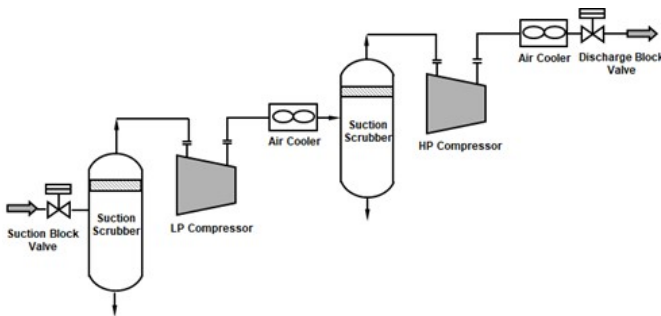


Fig 1. Two Stage Compressor Unit

A schematic of a 3-Stage Compressor Unit is,

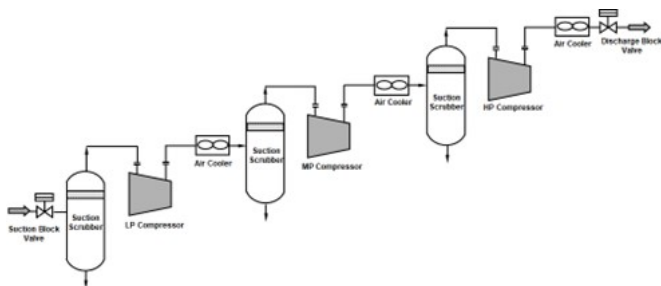


Fig 2. Three Stage Compressor Unit

GENERAL NOTES

1. When vapours are compressed, its temperature increases & therefore requires provisions for gas cooling.
2. High gas temperatures can affect lube oil characteristics causing them to carbonize and turn in sludge. This results in fouling causing the bearing pads and seals to wear out and performance degradation.
3. As per API 617 (7th Edition, 2002), Clause 2.7.1.3, it states, As a design criteria, bearing metal temperatures shall not exceed 100°C (212°F) at specified operating conditions with a maximum inlet oil temperature of 50°C (120°F). Vendors shall provide bearing temperature alarm and shutdown limits on the datasheets. However, clause

No. 2.7.1.3.1 of the said document also says, In the event that the above design criteria cannot be met, purchaser and vendor shall mutually agree on acceptable bearing metal temperatures.

4. During gas recycling, (either by cold recycling or hot recycling), the compressor discharge temperature rises above the temperature pertaining to normal running conditions. Quantitatively, the rise in temperature depends on the pressure ratio of each stage. The maximum discharge temperature is typically limited to, in the range of 1500C to 1600C to avoid damage to the bearings and seals. To ensure these limits are not crossed, the compressor discharge temperature at normal running conditions must be operated at lower temperatures with a margin of 200C to 250C. This means typical compressor discharge temperatures (under normal running conditions) should be limited to the range of 1200C to 1350C.
5. Individual compressor pressure ratios must also be optimized to obtain the lowest amount of power required to meet the final discharge pressure. This also enables to reduce the suction scrubber volumes and air cooler duties to save on material and operating costs.

CASE STUDY

A multistage compression system receives 30 MMScfd of hydrocarbon vapours at 2 bara, 300C and is required to be raised to 15 bara. The Polytropic efficiency [h] for all LP compressors is assumed to be 82%. An optimization study is performed for a 2-Stage and 3-Stage centrifugal compression system. The vapour composition is as follows,

Components	Mole Fraction [-]
Methane [C ₁]	0.5232
Ethane [C ₂]	0.3001
Propane [C ₃]	0.1096
iso-Butane [iC ₄]	0.0106
n-Butane [nC ₄]	0.0346
Iso-Pentane [iC ₅]	0.0076
n-Pentane [nC ₅]	0.0092
n-Hexane [C ₆]	0.0052
Total	1.0000
MW [kg/kmol] [PR EoS]	26.53
Density [1 atm, 15.6°C] [kg/m ³]	1.128

Table 1. Gas Composition

Methodology

The number of compressors can be chosen by first estimating preliminary discharge pressures based on equal pressure ratio as,

$$X^n = \left[\frac{P_{Last}}{P_{First}} \right] \quad (1)$$

Where,

P_{First} = First Compressor Pressure [bara]

P_{Last} = Last Compressor Pressure [bara]

n = Number of stages [-]

X = Maximum number of Stages [-]

Rewriting the expression,

$$n \times \ln X = \ln \left[\frac{P_{Last}}{P_{First}} \right] \quad (2)$$

$$\text{Or, } n = \frac{\ln \left[\frac{P_{Last}}{P_{First}} \right]}{\ln X} \quad (3)$$

The separation ratio is computed as,

$$R = \left[\frac{P_{Last}}{P_{First}} \right]^{1/n} \quad (4)$$

The intermediate pressure is computed as,

$$P_i = P_{first} \times R^i \quad (5)$$

Where,

P_i = Intermediate Pressure at Stage 'i'

Therefore, considering a maximum number of stages of 3, for a two stage compressor unit, the first compressor discharge pressure [P_1] and Pressure ratio [R] is,

$$n = \frac{\ln \left[\frac{15}{2} \right]}{\ln [3]} = 1.83 \sim 2 \text{ Stages} \quad (6)$$

$$R = \left[\frac{15}{2} \right]^{1/2} = 2.7386 \quad (7)$$

$$P_1 = 2 \times 2.7386^1 = 5.48 \text{ bara} \quad (8)$$

For a three-stage compressor unit, the LP compressor discharge pressure [P_1] and MP compressor discharge pressure [P_2] is,

$$R = \left[\frac{15}{2} \right]^{1/3} = 1.9574 \quad (9)$$

$$P_1 = 2 \times 1.9574^1 = 3.91 \text{ bara} \quad (10)$$

$$P_2 = 2 \times 1.9574^2 = 7.66 \text{ bara} \quad (11)$$

Using these preliminary values, to arrive at optimized discharge pressures, the following iterative procedure is adopted.

1. Keeping all preliminary estimated discharge pressures fixed, the LP compressor discharge pressure is varied for a range to obtain total absorbed power & total cooler duty of all compressors and sizing each suction scrubber. Making a plot of the above values, the discharge pressure corresponding to the lowest duty is chosen [1st Iteration of LP Compressor].
2. The LP compressor initial estimated discharge pressure is now replaced with the 1st Iteration's optimized pressure.
3. Following further, the MP compressor discharge pressure is also varied for a given range to similarly obtain an optimized discharge pressure corresponding to the lowest total compressor duty and cooler duty. [1st Iteration of 2nd stage].
4. The MP compressor initial estimate pressure is now replaced with the optimized value, [1st Iteration of 2nd stage].
5. With the 1st iteration optimized pressures, calculations are repeated similar to Step 2 Step 3 & Step 4, i.e., 2nd Iteration and so forth, until a converged solution is reached.

RESULTS

With the procedure applied for the calculated initial estimates, the optimized results of 2-Stage & 3-stage system [LP hp = 82%] is,

Table 2. Optimized Compressor Stage Pressures

Stages-Pressure	Discharge Pressure [bara]	Pressure Ratio [-]
2 Stage LP [2S-LP]	8.12	4.060
2 Stage HP [2S-HP]	15.00	1.847
3 Stage LP [3S-LP]	6.15	3.075
3 Stage MP [3S-MP]	8.25	1.341
3 Stage HP [3S-HP]	15.00	1.818

The plots of total compressor absorbed power, total cooler duty for two stage design and three stage design is as follows,

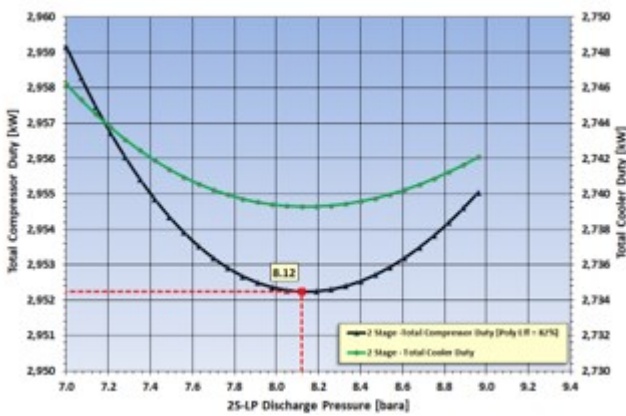


Fig 3. Two Stages – Total Compressor & Cooler Duty

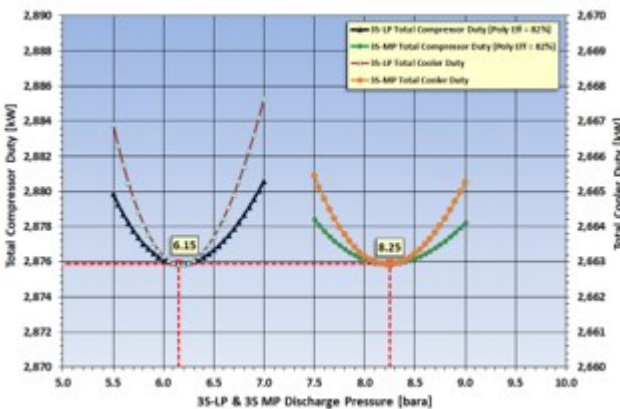


Fig 4. Two Stages – Total Compressor & Cooler Duty

Based on the optimized compression ratios, the savings on the total compressor duty and total air cooler duty is 1.59% and 1.68% for 2 stages respectively. For 3 stages, the respective savings is 1.86% and 2.03%.

Table 3. Savings on Compressor & Air Cooler Duty

Parameter	2 Stage	3 Stage
Before Optimization		
Total Comp. Duty [kW]	3,000	2,930
Total Cooler Duty [kW]	2,786	2,717
After Optimization		
Total Comp. Duty [kW]	2,952	2,876
Total Cooler Duty [kW]	2,739	2,663
% Savings [Compressor]	1.59%	1.86%
% Savings [Air Cooler]	1.68%	2.03%

Based on the optimized compression ratios, the suction scrubber sizes for both cases are,

Table 4. Suction Scrubber Sizes

Suction Scrubber [H/D = 3.0]	Head Design [2:1 Elliptical]		
	D [mm]	H [mm]	Vessel Volume [m ³]
2S-LP/3S-LP	2,400	7,200	34.08
Before Optimization			
2S-HP	1,900	5,700	17.11
3S-MP	2,100	6,300	22.98
3S-HP	1,800	5,400	14.59
After Optimization			
2S-HP	1,800	5,400	14.59
3S-MP	1,900	5,700	17.11
3S-HP	1,800	5,400	14.59

For 2S-HP & 3S-MP cases, the vessel volume decreases by 14.7% and 25.5% respectively.

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2. www.checalc.com

AUTHOR



Vijay Sarathy holds a master's degree in Chemical Engineering from Birla Institute of Technology & Science (BITS), Pilani, India and is a Chartered Engineer from the Institution of Chemical Engineers, UK. His expertise over 16 years of professional experience covers Front End Engineering, Process Dynamic Simulation and Subsea/Onshore pipeline flow assurance in the Oil and Gas industry. Vijay has worked as an Upstream Process Engineer with major conglomerates of General Electric, ENI Saipem and Shell.



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How to... RANDOM PACKINGS How to Calculate Hydraulics of Random Packings

Dr.-Ing. Volker Engel

Random Packings ("Rings") are universal all-rounders: they are not expensive, have good separation performance, low pressure drop, adapt to the column diameter and are available in many sizes, types and materials. They have been in technical use for more than 100 years.

A Random Packing is a volume of dumped hard-ware where the liquid is wetting the hard-ware and in this way provides a mass transfer area (Fig. 1).

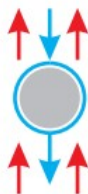


Fig. 1: Principle of Random Packings

This principle is well known since hundreds of years. Brushwood tufts were used to concentrate brine and were piled up in so-called graduation houses and sprinkled with brine. The water evaporates and the brine concentrates, reducing the amount of fire wood needed to vaporize the brine. Random Packings were therefore already successfully used for mass transfer and energy saving 500 years ago!

The technical development of Random Packings started with the patent of Fritz Raschig in 1915. He defined a cylindric ring with equivalent height and diameter (Fig. 2). By this the classical „Ra-schig Ring“ was born and – probably – since this time Random Packings are also called „rings“.

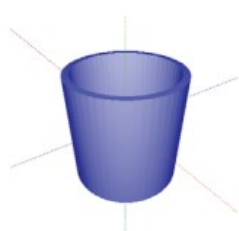


Fig. 2: Basic Raschig Ring

In the last 100 years several new types of

packings were invented, tested and came in use. Roughly estimated, there are about 200 Random Packings, taking into account the material classes (ceramic, metal, plastic) and the different sizes and shapes.

One can classify the Random Packings based on the basic geometry of the packing element as well as its type of shell surfaces.

The development can be classified in so-called „generations“. The first generation is represented by the patent of Fritz Raschig: the shell of the basic geometry (in case of the classic Raschig Ring the cylinder) is solid. In this case the pressure drop of a packing element is very dependent on its orientation. If the axis of the cylinder is perpendicular to the gas flow, the body blocks the gas flow. If its axis is in flow direction, the body acts like a pipe and has almost no pressure drop.

In order to reduce this positional dependency and to reduce the pressure drop of the entire packing bed, the shell surface of the packing elements was designed with openings in the 2nd generation.

In the 3rd generation, this development was then continued and the shell surfaces were reduced to web surfaces and the inner volume of the body was provided with additional surfaces.

While in the first generation the liquid formed a film by flowing over the surface, the 3rd generation also relies on the formation of droplets and their contribution to mass transfer.

Some suppliers advertise 4th and even 5th generation Random Packings. Whether the features implemented in these types of packing justify the definition of a new generation is questionable.

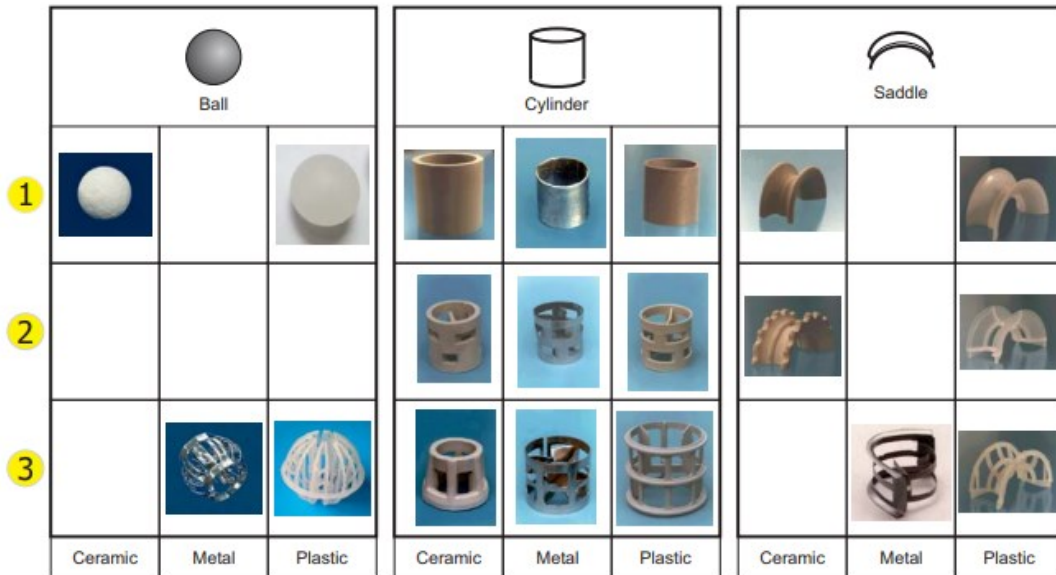


Fig. 3: Generations of Random Packings development

Fig. 3 shows a survey of the variation of the three basic geometries „ball“, „cylinder“ and „saddle“ in the three generations. The table is filled with pictures of corresponding representatives. Since there are restrictions regarding the formability of the respective materials, not all cells of the table are occupied.

In the past 20 years some high capacity rings were presented. Their basic geometry is a block (cuboid). The latest development of Random Packings came from Raschig by the patented Raschig Super Ring Plus. Actual this is the high end packing for maximum capacity. The work horse of the metal packings is still the saddle and a still often used packing type is the Pall ring (2nd generation cylindrical ring).

All Random Packings are basically described by their specific geometrical surface area (a_{geo}) and void fraction e . The shape of the packing elements can be characterized by the dry pressure drop. All this data is normally

provided by the packing supplier.

The qualitative pressure drop characteristic of a counter-current two-phase flow through a packed bed is shown in Fig. 4: In the double-logarithmic scaled diagram the pressure drop is a straight line, where liquid and gas can pass each other without hydraulic interaction. By increasing gas load there is the so-called loading, where liquid is accumulated by the counter-current gas: liquid holdup rises and the pressure drop increases disproportionately. This interaction between gas and liquid is conducive for mass transfer conditions.

By further increase of gas load, the liquid is accumulated to such an extent that a liquid layer is formed and the gas becomes disperse phase. The liquid flow rate through the bed is thus reduced, flooding occurs. The pressure drop of the bed also increases drastically. At this flooding point, the counter-current of the phases breaks down.

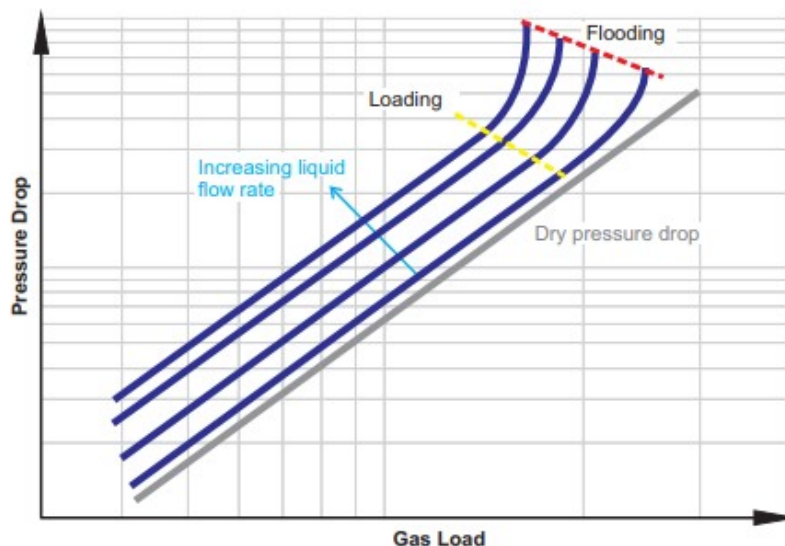


Fig. 4: Qualitative hydraulic characteristic of Random Packings

MODEL STRUCTURE

To predict the hydraulics of Random Packings, we have to use a suitable model structure to transfer the complexity and randomness of the dumped bed and its effects on the flow of liquid and gas.

The idea of a model is to reduce complexity to structures whose calculation is possible and known. The better a model is suited for the description, the fewer fitting parameters are necessary.

There are a variety of models that have been developed over the last 100 years. However, many of them are purely empirical, graphical or built on several fitting parameters that can only be determined experimentally. Thus, these models are not necessarily applicable for newly developed or non-measured types.

Therefore, the use of model-based approaches is strongly recommended.

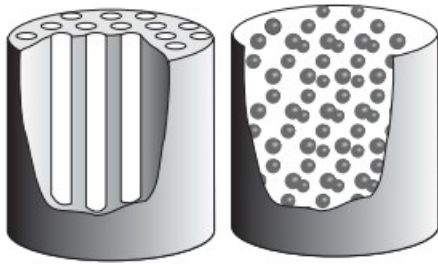


Fig. 5: Model structure „Channel“ and „Particle“

To model the structure of Random Packings, two structures are mainly used (Fig. 5). One is based on parallel channels, the other on particles. Both models transfer Random Packings to a regular structure, which can be calculated by basic principles. In case of the „Channel model“ one can use the pipe flow calculation, for the „Particle model“ the investigations of fluidized beds can be used.

In both model structures the Random Packings are transferred to a model based on the same surface area as well as the same hardware volume: In the Channel model to a certain number and diameter of the channels, in the Particle models to a certain number and diameter of particles.

In the first step, the models are validated by calculating the dry pressure drop. In the next step, the liquid holdup is implemented in the model structure and its impact on the calculation has to show up the hydraulic behavior of Random Packings.

HOLDUP

The liquid holdup is normally expressed as a relative value based on the tower volume:

$$h_L = \frac{V_L}{V} \quad (1)$$

The liquid holdup and its change with increasing liquid and gas load is the driving force of the hydraulic behavior of Random Packings.

Fig. 7 shows qualitatively liquid holdup vs. gas load for various liquid loads in a double-logarithmic diagram. The liquid holdup stays almost constant for a certain liquid load till at the loading point it starts increasing.

When shutting down the liquid, not all liquid will leave the Random Packings. Due to capillary forces and structural reasons, some liquid will stay within the bed. This part of the liquid holdup is called „static holdup“ (Fig. 6). The total holdup during operation is therefore the sum of this static holdup and the so-called „dynamic holdup“:

$$h_{L,tot} = h_{L,static} + h_{L,dyn} \quad (2)$$

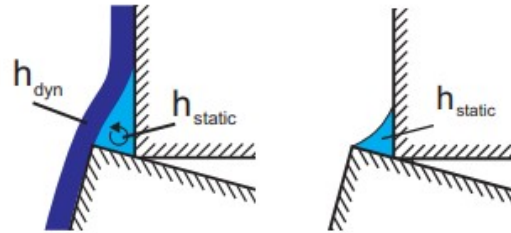


Fig. 6: Parts of liquid holdup

According to ENGEL 1999 the static holdup can be calculated by:

$$h_{L,static} = 0.333 \cdot \exp\left(-0.22 \cdot \frac{g \cdot \rho_L}{\sigma \cdot a_{geo}^2}\right) \quad (3)$$

To calculate the dynamic liquid holdup below the loading h_{dyn0} , eq. (4) can be applied:

$$h_{dyn0} = 3.6 \left(\frac{u_L^2 \cdot a_{geo}}{g}\right)^{0.33} \left(\frac{\eta_L^2 \cdot a_{geo}^3}{\rho_L \cdot g}\right)^{0.125} \left(\frac{\sigma \cdot a_{geo}^2}{\rho_L \cdot g}\right)^{0.1} \quad (4)$$

To properly account for the liquid holdup above the loading h_{dyn} , the pressure drop of the packing must be included in the calculation. This leads to an iterative process in calculation, since the pressure drop is a function of the liquid holdup as well:

$$h_{dyn} = h_{dyn0} \cdot \left[1 + 36 \cdot \left(\frac{\Delta p_{irr}}{H \cdot \rho_L \cdot g}\right)^2\right] \quad (5)$$

PRESSURE DROP

The basic equation for the dry pressure drop of Random Packings can be written as eq. (6). It describes a line within a double-logarithmic scaled diagram.

$$\frac{\Delta p_{dry}}{H} = 10^n \cdot F^m \quad (6)$$

By modeling Random Packings by the particle structure, the pressure drop correlation of a fluidized bed can be used [STICHLMAIR 1989]:

$$\frac{\Delta p_{dry}}{H} = \frac{1}{8} \cdot \zeta_0 \cdot a_{geo} \cdot \frac{\rho_G \cdot u_G^2}{\varepsilon^{4,65}} \quad (7)$$

To account for the liquid component in the particle structure, the liquid holdup is superimposed as particle structure (Fig. 8).

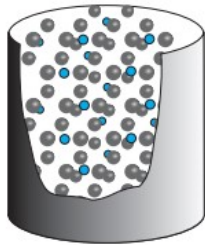


Fig. 8: Liquid holdup in Particle model

The liquid reduces the void fraction of the packing and enlarges the geometric area of the packing. Both effects are invoked in the pressure drop correlation:

$$\frac{\Delta p_{tot}}{H} = \frac{1}{8} \cdot \zeta_0 \cdot (a_{geo} + a_L) \cdot \frac{\rho_G \cdot u_G^2}{(\varepsilon - h_{dyn})^{4,65}} \quad (8)$$

The liquid area contributed by the liquid holdup can be calculated by eq. (9).

$$a_L = \frac{6 \cdot h_{dyn}}{d_L} \quad (9)$$

By eq. (1) to eq. (9) one can calculate the total pressure as well as the liquid holdup of Random Packings. As input parameters the geometric area, the void fraction and the dry pressure drop of the packings are needed – no additional packing-individual fitted parameters!

FLOODING

To prepare the flooding calculations, eq. (7) and eq. (8) can be written as eq. (10):

$$\frac{\Delta p_{tot}/H}{\Delta p_{dry}/H} = \frac{a_{geo} + a_L}{a_{geo}} \cdot \left(\frac{\varepsilon}{\varepsilon - h_{dyn}} \right)^{4,65} \quad (10)$$

From the mathematical point of view, the slope of the pressure drop characteristics at flooding conditions tends to be infinity:

$$\left. \frac{\partial \Delta p_{tot}/H}{\partial \Delta p_{dry}/H} \right|_{\text{Flooding}} = \infty \quad (11)$$

The reciprocal representation of eq. (11) can be used to evaluate the flooding factor:

$$\left. \frac{\partial \Delta p_{dry}/H}{\partial \Delta p_{tot}/H} \right|_{\text{Flooding}} = 0 \quad (12)$$

There is an explicit numerical solution of this eq. (12) in ENGEL 1999. Therefore it is possible to calculate an operation diagram as qualitatively shown in Fig. 9 quite fast.

Beside the loading and flooding curve for the packing, one can add the system flood characteristics as an additional limit.

A design load should be at loading conditions for good mass transfer.

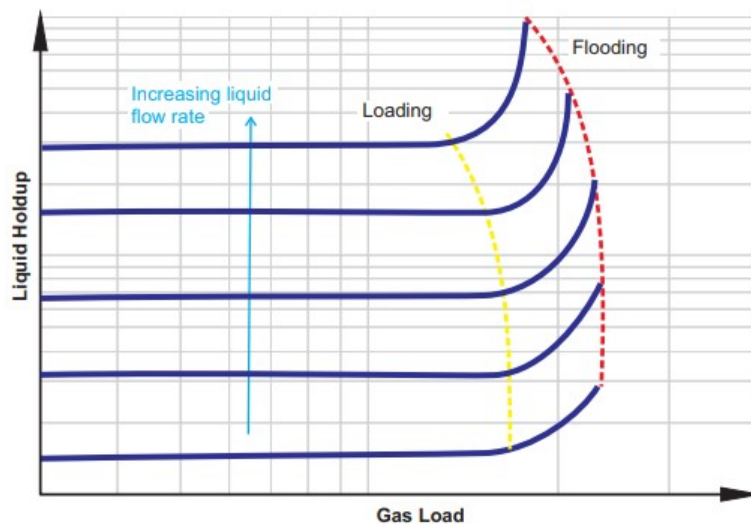


Fig. 7: Qualitative characteristic of liquid holdup

MALDISTRIBUTION

When liquid flows as a trickle through a packed bed, the liquid follows gravity but constantly changes its direction. This effect is partly random and dependent on the installation effects (therefore the packing is called Random Packing) and partly intrinsic due to the shape of the packing element.

In result, liquid can accumulate locally (e.g. in hotspots within the packing and at the tower shell). This effect is called maldistribution.

Even though the „mal-“ suggests a negative effect, maldistribution helps to evenly wet a bulk: starting from the liquid feed points, the liquid is distributed within the bulk. However, the same effect leads to uneven distributions in the liquid after a certain packing height. This worsens the conditions for mass transfer. To make up for this effect, the only thing left to do is to collect and redistribute the liquid.

To quantify the maldistribution effect, WELCHEM presented 2007 a cell model approach. The packing volume is modeled as a hexagonal cell volume (each cell represents a single Random Packing element). Each cell has individual information of its behavior concerning the transfer of liquid to neighboring cells (Fig. 10).

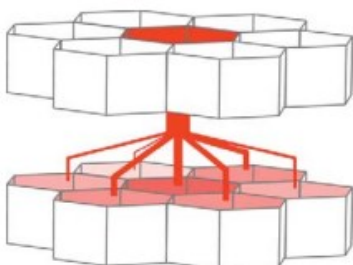


Fig. 10: Cell model for maldistribution

These parameters (called dispersion coefficients) are evaluated for each packing type. Because of the huge variety of shapes and sizes, this is not done by physical experiment, but by evaluation of 3D models of the packing elements. It is called „virtual irrigation“ and determines the deflection of streamlets into neighboring cells based on the orientation of the packing element within the cell (Fig. 11).

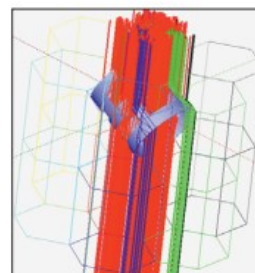


Fig. 11: Virtual irrigation of 3D packing element

In order to model the effects of the gas counter-current and its impact on the liquid distribution, an extensive measurement program was performed at the Technical University of Munich [Hanusch et. al 2017]. Based on these results, a very good agreement with the experiments could be obtained by modeling local hydraulics in a cell based on the equations presented in eq. (1) to eq. (9).

The presented maldistribution model is implemented in the software TrayHeart. Its database contains hundreds of packing elements and a large number of RandomPackings with these dispersion coefficients.

In the software the maldistribution calculation is connected to the layout of distributors. By this one can predict the development of maldistribution along the liquid run length of a

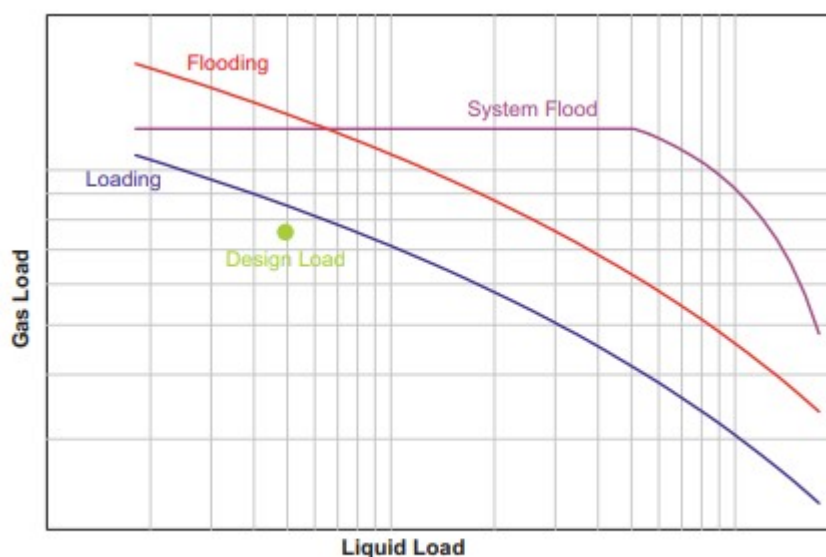


Fig. 9: Operation diagram

packing for a certain load (gas and liquid!). Fig. 12 shows an example of a 50mm metal saddle with an initial distribution by a trough distributor.

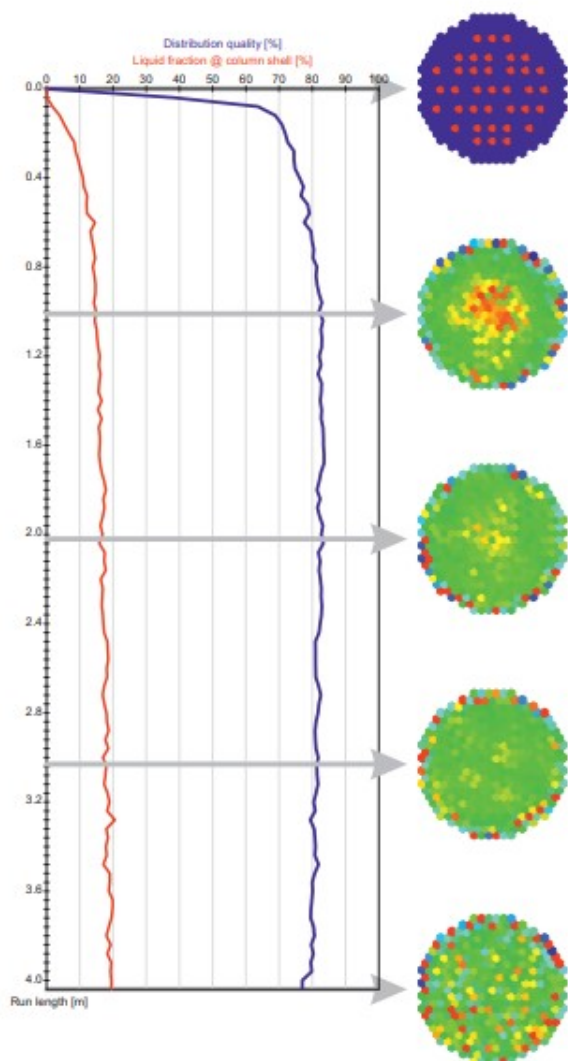


Fig. 12: Distribution quality vs. run length

By a detailed evaluation of this maldistribution one can determine criteria for the need of redistribution and the best interaction of initial distribution and Random Packings.

FILLING OF BEDS

To fill a certain volume with Random Packings, the supplier has to deliver the right quantity. This sounds easy — but it is not that easy to agree on the same volume: The supplier has counted the packing elements within a reference volume. But only for the diameter of this standard cylinder the specified number of pieces and thus the specific weight applies. If the packing is used in a different column diameter, the ordered volume must be adjusted. For this reason, all suppliers provide so-called „volume decrease curves“ to calculate the correct volume to fill a certain column volume.

Another effect of Random Packings is „settling“: Depending on the shape of the packing, the bed may settle during operation. Due to thermal and mechanical influences, packed beds arrange themselves in an optimized manner and thus take up less volume. The more the packings interlock, the less settling losses there are. The smoother the outer surfaces of the packing, the greater the settling losses (up to 10%).

CONCLUSION

Random Packings offer good options for normal pressure and high pressure applications due to their moderate pressure drop, reasonable prices, and the large variety of material, shape and size. They are comparable easy to calculate. General, reliable models are available.

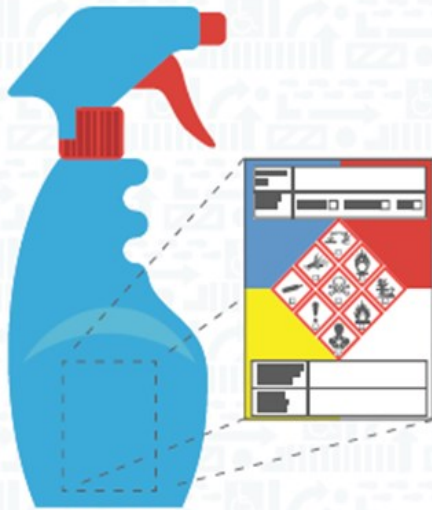
The efficiency of Random Packings is closely connected to the quality of initial liquid distribution and maldistribution effects.

ABOUT THE AUTHOR

Volker Engel studied process engineering at the Technical University of Munich and did his Ph.D. thesis on packed columns with Prof. Johann G. Stichlmair. Since 1998 he has been the managing director of WelChem Process Technology GmbH and head of the TrayHeart software. TrayHeart has developed into the state-of-the-art design tool for trays and internals in process technology.

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Fourth Quarter 2022 Update for the South East Asia (SEA) O&G industry

September 2022

KEY DRIVING FACTORS

- Refining and petchem spread getting thinner. Petchem loads getting trimmed back as margins thin. Seeing this across SEA.
- Manpower movement across industry makes hiring and keeping talents a more pressing problem.

HIGHLIGHTS

Shell's CEO Ben Van Beurden steps down, Wael Sawan to take over 1st Jan 2023.

Shell invest into Sustainable Aviation Fuel (SAF) at their Singapore site. SAF; a jet fuel alternative that's derived from waste products, biomass or cooking oil, and offers an 80 percent lifecycle emissions reduction compared to conventional fuel. Shell has partnered with Accenture and American Express Global Business Travel to launch Avelia, a platform that it hopes will bundle the sustainable fuel demand from corporate flyers into one easily trackable data set. The ultimate goal is to send a signal to fuel suppliers that it's worth investing in sustainable aviation fuel (SAF).

Singapore Tuas port opening and is the largest fully autonomous port.

ExxonMobil is targeting startup of its upgrading project to convert fuel oil and other bottom-of-the-barrel crude products into higher-value lube base stocks and distillates at ExxonMobil Asia Pacific's Singapore integrated manufacturing complex in 2025.

Petroleum Nasional Bhd's (Petronas) wholly-owned entity, Gentari Sdn Bhd, has signed 12 memorandums of understandings (MOUs) with international hydrogen sector players to leverage its advantages as the main driver of green energy.

Indonesian state oil and gas company Pertamina is accelerating moves to develop its capability for carbon capture, utilization and storage (CCUS) technology via multiple new tie-ups with companies ranging from ExxonMobil to Air Liquide of France and Japanese trading house Mitsui.

PTT Global Chemical Plc (PTTGC), a petrochemical flagship of PTT Group, has opened Thailand's first and Southeast Asia's largest high-quality and food-grade recycled plastic resin plant, aiming to process...

RECENT EVENTS

Oil and Gas Asia 2022 (OGA) was held in conjunction with Petrochemical Sustainability Conference (PSC) by Malaysian Petrochemicals Association (MPA) on 13-15th September 2022 at Kuala Lumpur Convention Centre (KLCC).

Investing in Green Hydrogen 2022 was also recently concluded in Singapore between 15-16th September at the Marina Bay Sands Expo and Convention centre.

S&P's APPEC 2022 will be held physically in Singapore on September 26-28th at Raffles City Convention Centre



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Rock Bottom View:

“Man, it’s really hot outside!”

Ronald J. Cormier, *Engineering Practice* Contributing Author



Hello once again from this old ranch house porch in central Texas. Usually, I hear the soothing sound of rushing current in our Pedernales River, but no such luck this summer as the valley stopped flowing some 90 days ago, during relentless drought. As I penned to our readers back in July, this is still a hot and dry place to occupy on our fragile planet, Earth. Gratefully, signs of seasonal relief are creeping in, with temperatures in the 90’s (rather than 100s) and 2-3 inches of rain over the last 10 days. These conditions make fall in these parts much more tolerable, and for that we are hopeful.

In that July issue, we discussed projections regarding expected trends in energy sources/functionality over the next 20-30 years, required both to relieve stress on the planet, yet also maximize the luxuries of our civilized world. How it is that we live, dress, stay healthy, and transport ourselves plus materiel are, concisely, the learning challenge plus career basis for both current STEM university curriculum and entrepreneurial professional’s efforts. Improvement may indeed be frustrating (most meaningful change is), though positive effect on our “cost of lifestyle” hopefully results. In other words, Earth’s ability to support our continued existence remains possible.

Such accomplishments also include this week’s resumption of moon travel after some fifty years. Originally (1969), Apollo’s lunar engineering achievements had deep roots related to geopolitical prowess. At the same time (1970), the US Environmental Protection Agency was established during the Nixon administration. The quality of our air and water was increasingly suspect, coincidentally after seventy-five years of driving automobiles, producing modern petrochemicals, and inefficient disposal/recycling of finite-supply earthen materials.

With the evolution of NASA’s Artemis program, moon travel is again on the docket, but with

intent to perfect travel to Mars and beyond. The vision of conquering additional life-supporting places in the universe is certainly key, but even the presence of water, valuable minerals, and supporting environments for more economical production and material value-addition holds great hope, much to the relief to our own Earth.

After six decades, I can easily attest to hotter summers, colder winters, and more brutal unplanned events dealt by Mother Nature. These occurrences are real and now reoccur with shocking frequency, not limited to massive forest fires, floods, tornadoes, hurricanes, and earthquakes. Whether one supports the notion of global warming and its evidential occurrences, real outcomes today leave little time to argue association.

In the rear view mirror.....

Since the Industrial Revolution, the global annual temperature has increased in total by a little more than 1 degree Celsius, or about 2 degrees Fahrenheit. Between 1880—the year that accurate recordkeeping began—and 1980, it rose on average by 0.07 degrees Celsius (0.13 degrees Fahrenheit) every 10 years. Since 1981, however, the rate of increase has more than doubled: For the last 40 years, we’ve seen the global annual temperature rise by 0.18 degrees Celsius, or 0.32 degrees Fahrenheit, per decade.

The result? A planet that has never been hotter. Nine of the 10 warmest years since 1880 have occurred since 2005—and the 5 warmest years on record have all occurred since 2015. Climate change deniers have argued that there has been a “pause” or a “slowdown” in rising global temperatures, but numerous studies, including a 2018 paper published in the journal *Environmental Research Letters*, have disproved this claim. The impacts of global warming are already harming people around the world.

Now climate scientists have concluded that we must limit global warming to 1.5 degrees Celsius by 2040 if we are to avoid a future in which everyday life around the world is marked by its worst, most devastating effects. All people feel these effects in one way or another but are experienced most acutely by the underprivileged, the economically marginalized, and people of color, for whom climate change is often a key driver of poverty, displacement, hunger, and social unrest.

So, what causes the planet to react as observed? Global warming occurs when carbon dioxide (CO₂) and other air pollutants collect in the atmosphere and absorb sunlight and solar radiation that previously bounced off the earth's surface. Normally this radiation would escape into space, but these pollutants, which last for years to centuries in the atmosphere, trap the heat and cause the planet to get hotter. These heat-trapping pollutants—specifically carbon dioxide, methane, nitrous oxide, water vapor, and synthetic fluorinated gases—are known as greenhouse gases, and their impact is called the greenhouse effect.

Though natural cycles and fluctuations have caused the earth's climate to change several times over the last 800,000 years, our current era of global warming is directly attributable to human activity—specifically to our burning of fossil fuels such as coal, oil, gasoline, and natural gas, which results in the greenhouse effect. In the United States, the largest source of greenhouse gases is transportation (29 percent), followed closely by electricity production (28 percent, of which air conditioning plays a significant role, thus worsening the phenomenon) and industrial activity (22 percent).

Curbing dangerous climate change requires very deep cuts in emissions, as well as the use of alternatives to fossil fuels worldwide. The good news is that countries around the globe have formally committed—as part of the 2015 Paris Climate Agreement—to lower their emissions by setting new standards and crafting new policies to meet or even exceed those standards. The not-so-good news is that we're not working fast enough. To avoid the worst impacts of climate change, scientists tell us that we need to reduce global carbon emissions by as much as 40 percent by 2030.

For that to happen, the global community must take immediate, concrete steps: to decarbonize electricity generation by equitably transitioning from fossil fuel-based production to renewable energy sources like wind and solar; to electrify our cars and trucks; and to maximize energy efficiency in our buildings, appliances, and industries.

What does it mean to me/you....

Global warming is already taking a toll. And if we are not able to get a handle on our emissions, here's just a smattering of what we can look forward to:

- Disappearing glaciers, early snowmelt, and severe droughts will cause more dramatic water shortages and continue to increase the risk of wildfires in the American West.
- In the USA, rising sea levels will lead to even more coastal flooding on the Eastern Seaboard, especially in Florida, and in other areas such as the Gulf of Mexico. Thirty percent of the US population (100 million people) lives where sea level plays a role in flooding, shoreline erosion, and hazards from storms. Eight of the world's ten largest cities are near water and will be negatively affected accordingly.
- Forests, farms, roads, bridges, oil and gas wells, power plants, sewage treatment plants, and landfills will face troublesome new pests, heat waves, heavy downpours, and increased flooding. All of these can damage or destroy agriculture and fisheries.
- Disruption of habitats such as coral reefs and alpine meadows could drive many plant and animal species to extinction.
- Allergies, asthma, and infectious disease outbreaks will become more common due to increased growth of pollen-producing ragweed, higher levels of air pollution, and the spread of conditions favorable to pathogens and mosquitoes.

Though everyone is affected by climate change, not everyone is affected equally. Indigenous people, people of color, and the economically marginalized are typically hit the hardest. Inequities built into our housing, health care, and labor systems make these communities more vulnerable to the worst impacts of climate change—even though these same communities have done the least to contribute to it.

What can I/you do to help....

Fundamentally we must firstly recognize that critical climate change is not "a hoax". We must use our voices, hold government and industry leaders to account. Voice your support of climate-friendly and climate change preparedness policies. Insist that your governmental representatives equitably transition

from dirty fossil fuels to cleaner power, and that such should be a top priority—because it is vital to building healthy, more secure communities.

Make changes to daily habits. Reduce your own carbon footprint by taking a few simple steps:

- Make conserving energy a part of your daily routine and your decisions as a consumer. Use LED lighting, and repair even the slightest plumbing leaks. Recycle water and catch rain for irrigation. So long as it is sanitary, it is not in poor taste nor embarrassing to repropose plastic zipper bags for food and other storage. When you shop for new appliances like refrigerators, washers, and dryers, look for products with the government's ENERGY STAR® label; they meet a higher standard for energy efficiency than the minimum federal requirements. We are scientists and businesspeople.... calculate the return on investment with this energy consumption improvement. Most times you will find that savings well pay for themselves too, over the equipment's life.
- When you buy a car, go for highest mileage per gallon of fuel, or per kilowatt-hour, and lowest emissions. You can also reduce your emissions by taking public transportation or carpooling when possible.

- Encourage young people toward STEM education and “green” training. Stoke their interest, ingenuity, and skills development for design and commercialization of integral improvements serving humanity here on earth and in years to come, other parts of the universe. Just one example...clean water research and desalinization of sea water are burgeoning career fields.

Though not the best of human behavior, individuals tend to be lazy about the profound consequences of inaction. While new federal and state standards are a step in the right direction, much more needs to be done. You do not have to go it alone though. Movements around the world are showing how climate action can build community and be led by those on the front lines, toward meaningful impacts toward creating a future that is equitable, satisfying, and profitable for all.

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ABSTRACT

The primary aim of this document is to discuss how engineering controls are the most effective way to prevent accidental releases or injuries when sampling hazardous chemicals such as sulfuric acid. We also discuss how sample system design is a key factor not only in improving safety, industrial hygiene and quality, but in creating an inherently safer sampling process.

We can also see other benefits, such as reducing waste, improving efficiency and improving compliance with federal regulations. These are factors which influence day to day running costs and a plant's bottom line. We must bear in mind that sample stations are high risk locations where personnel run a higher risk of exposure to hazardous material. Where the risks of accidental releases are greater, it's in everyone's interest to ensure that the potential for chemical releases and accidents are kept to an absolute minimum, if not eradicated entirely. This article will be of interest to those that work with sulfuric acid and are interested in engineered solutions for reducing the exposure risk in the sampling process. It may also be of interest to those conducting PHAs', HAZOPs, Safety Audits, those involved in Process Safety Management and Continuous Improvement. As sulfuric acid is such a ubiquitous and vital component of the chemical industry, we need to utilize engineered solutions to protect workers and the environment from chemical releases.

THE CHEMICAL: SULFURIC ACID

Sulfuric acid (H_2SO_4) is an oily, colorless and odorless liquid composed of sulfur, hydrogen and oxygen also known as hydrogen sulfate, oil of vitriol, or sulphuric acid.

With a melting point of 10oC and a very high boiling point of just under 300o C, it reacts violently with water, organic and inorganic materials and can generate intense heat. Highly

corrosive to certain metals, it will also cause severe burns when in contact with eyes or skin and its vapors irritate the respiratory tract. Severe exposure can result in fatality.

Sulfuric acid is the most important chemical in the industry today, and by a large margin, the most consumed and produced chemical in the world. This is because sulfuric acid is a vital raw material for countless chemical products and processes. A large proportion of sulfuric acid is used to make phosphoric acid, and when reacted with ammonia, it produces ammonia sulfate. Both phosphoric acid and ammonia sulfate are key fertilizers in the agricultural industry. Concentrated sulfuric acid (93-98%) is used to manufacture detergents, explosives, dyes, and petroleum products. It also has an important function as a catalyst in the alkylation process in refineries, where light olefins such as propylene, butylene, amylene, and fresh isobutane are reacted to produce higher octane gasoline .

HAZARDOUS SUBSTANCE

Unfortunately, accidents and releases involving sulfuric acid are quite common.

In a study conducted by Aryana F. Anderson, who worked in the Agency for Toxic Substances and Disease Registry at the CDC¹, sulfuric acid was ranked in the top five dangerous chemicals by incident in nine states. The nine states examined were: Colorado, Iowa, Minnesota, New York, North Carolina, Oregon, Texas, Washington, and Wisconsin during the period 1998- 2008. Some interesting statistics regarding accidents and releases involving sulfuric acid are evident from the study:

- The highest percentage (30%) of injuries related to sulfuric acid were in the manufacturing sector.
- A high proportion of those injured (74%) were employees.

- Most of the injuries reported were burns.
- 41% of sulfuric acid releases were the result of equipment failure, while 34% were the result of human error, together a staggering 75%!

MITIGATING RISK IN THE SAMPLING PROCESS

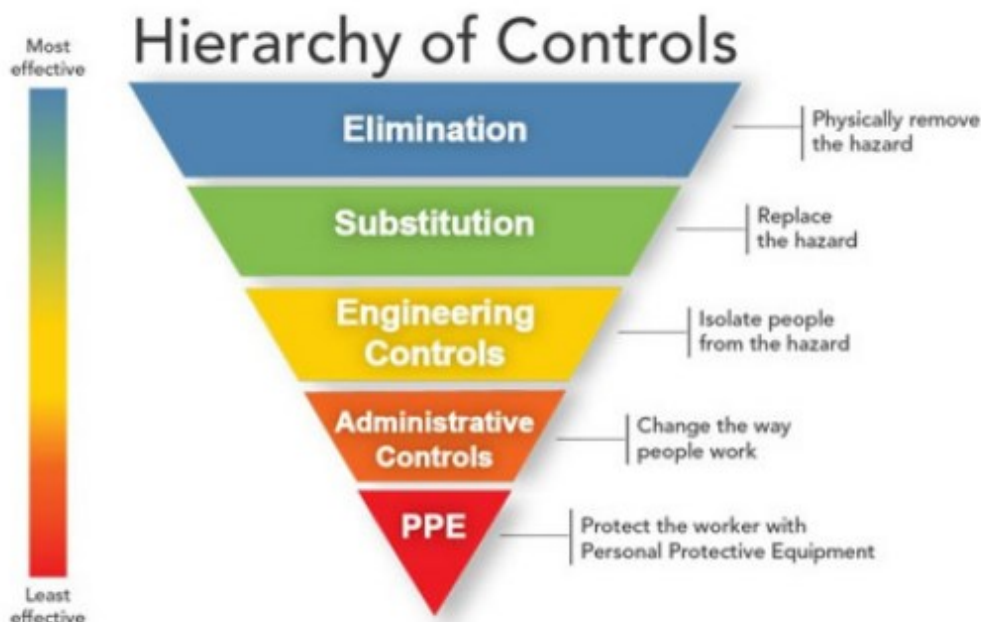
How can we reduce the risk of employee exposure and chemical releases during the sampling process?

If we consider the Hierarchy of Controls below, we see that the most effective ways are to either eliminate sulfuric acid completely from the process or substitute it with another chemical. As sulfuric acid is such an important raw material, and in some cases a safer alternative, (eg. as a substitute for HF in the alkylation process) substitution and elimination are impractical. The most effective way to mitigate risks associated with sulfuric acid is to isolate people from the hazard using engineering controls. Engineering controls are more effective than either administrative controls or PPE, as they remove or greatly reduce the risk at source.

SAMPLE SYSTEM DESIGN

What are the criteria we should consider when thinking about sample system design?

- **Simplicity:** The sampling process should be made as simple as possible so that the room for error is greatly reduced or eliminated entirely. This means that there should be as few procedural steps as possible to grab a sample.
- **Ergonomics:** The system should be designed in such a way that a sample can be extracted safely without unnecessary difficulty (eg. having to reach around a face shield with a bottle to grab a sample). Using the system should be as intuitive as possible so as to minimize the risk of error.
- **Minimize exposure:** Having to flush and purge into a receptacle before taking a sample exposes employees to unnecessary exposure risk. If the product cannot be recycled, it must be neutralized or disposed of. This generates waste and can represent a significant cost to the company. An inline solution will not only get rid of this process, meaning less risk of exposure and less cost, but also guarantee a representative sample everytime. If the new system is engineered to a high enough standard that ensures no dead space, it would ensure no product is left to influence the next sample.
- **Robust design:** The sample system should have a robust design to withstand the rigours of weather conditions and constant reuse. Small tubing and quick connects are not robust enough to handle continuous use and present potential leak points which must be replaced frequently.
- **Easily maintained:** Designing a system which is easily maintained is a key factor in sample system design. Ideally, a sample system should be relatively easy to maintain, and spare parts easily sourced, so that a regular Preventative Maintenance schedule can be carried out to ensure system integrity. Systems that are difficult to maintain run the risk of equipment failure and quickly fall into disrepair so that they are either bypassed or a cruder system is designed in its place.
- **Minimize Emissions:** There must be no release of sulfuric acid into the atmosphere. Where possible, valves which feature Certified Low Leak Technology should be installed.



EXAMPLES OF SAMPLE SYSTEMS CURRENTLY IN USE

Sample systems for sulfuric acid vary widely throughout the chemical industry.

Many plants have opted for homemade systems which consist of a double block and bleed system using ball valves. There are several flaws inherent in these systems which impact directly on safety, industrial hygiene and sample quality. Before a representative sample can be taken, a length of piping or tubing must be flushed by the Operator.

This not only increases the amount of sulfuric acid handled by the operator but it increases the complexity of the process, the exposure risk, as well as the amount of steps required to take the sample.

Additionally, if the process is not done correctly, the sample may also be compromised, which leads to poor quality samples. In an alkylation unit within a refinery where acid strength must be closely monitored, skewed results can have catastrophic consequences for both safety and the bottom line.

Let's look at a few examples.

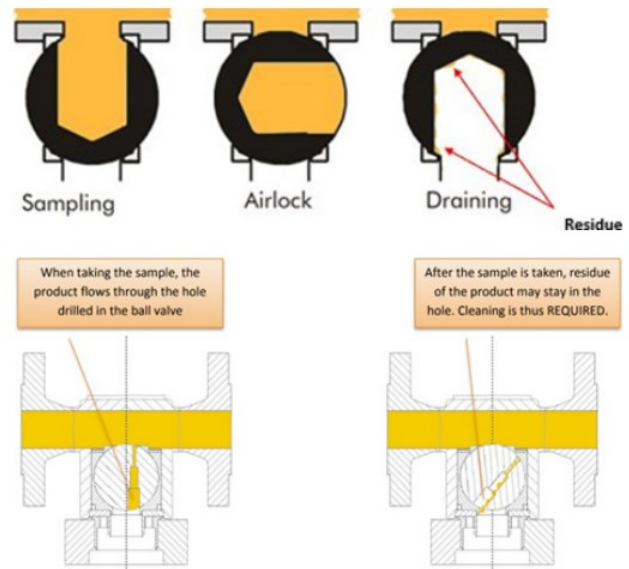


▲ A loose section of tubing connection from a sulfuric acid sample station responsible for the release of 84,000 pounds of sulfuric acid into the environment.⁴



▲ The picture is a home made system and consists of a pipe from the process line to a sulfuric acid sample box. The pipe from the valve (top right) to the sample box (bottom left) must be purged before a representative sample can be taken. This not only produces waste, but if not flushed correctly leftover residue may influence the next sample.

Some plants have opted for ball valve type inline sample systems for hazardous chemicals. While these are, in many cases, a better option in terms of safety compared to home made systems, they present their own issues relating to their individual designs. If we look at two types of inline ball valves commonly used for sampling hazardous liquids, we can clearly see the design flaws that render these types of valves unsuitable for sampling hazardous liquids.



Even if these systems are installed on a process line, they present Industrial Hygiene and sample quality issues. They must either be cleaned out or flushed out before the Operator can be confident that a representative sample can be collected.

MEETING THE CHALLENGE: SAMPLING SULFURIC ACID

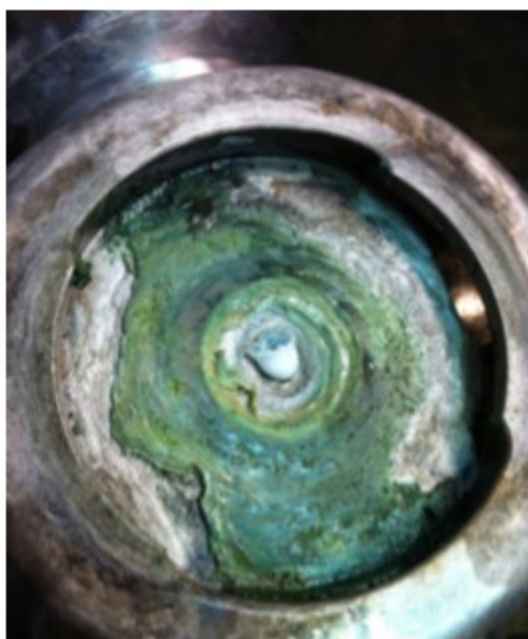
The particular characteristics of fuming acids such as sulfuric acid pose challenges which must be taken into consideration when considering sample system design.

- **Material of Construction:** Sulfuric acid in certain strengths and temperatures will react with stainless steel and cause excessive corrosion. If sulfuric acid comes in contact with the atmosphere, sulfate can form and will plug small diameters. As PFA is resistant to sulfuric acid corrosion it is an excellent substitute for the more expensive alloys that offer corrosion resistance to sulfuric acid. A PFA lined sample system is therefore a better option for high corrosion applications. When considering a system for sampling sulfuric acid, acid strength and temperature will determine the materials of construction most suitable for the process.

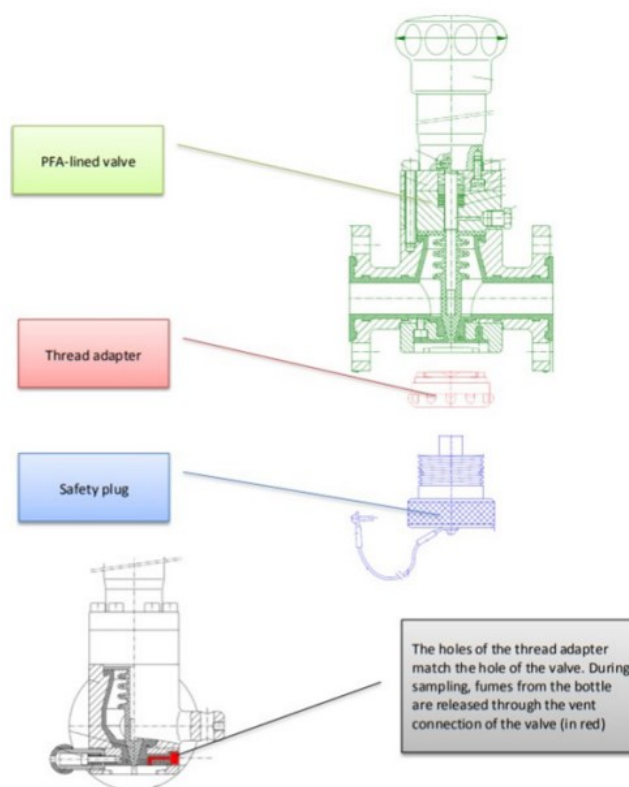


▲ Sulfuric acid corrosion on a stainless steel valve spindle

- **Minimize Exposure:** An engineered solution to reducing exposure risk is the most effective way to prevent sulfuric acid burns and exposure to acid mist. Sulfuric acid will react with moisture in the atmosphere and produce a highly visible acid mist which can lead to severe irritation of the eyes and respiratory tract in high concentrations. While collecting the sample, the operator must be protected from acid fumes at all times. Sampling systems which feature numerous connections and tubing are potential sources of leaks, particularly if they are not robust.



▲ Stainless steel valve outlet with sulfuric acid exposure



The diagram above shows a typical BIAR PFA-lined sample valve used for sampling sulfuric acid into a bottle. As it can be installed directly on the process line or a bypass /fast loop, the sample is directly representative and no flushing or purging is required. With this system the bottle is screwed directly onto the valve using the thread adapter. There is a vent connection on the valve which corresponds with the vent on the thread adapter which allows the air inside the bottle to escape so there is no build up of pressure in the bottle. These fumes can be vented away from the Operator by way of a vent line to a scrubber. When the sample has been taken, the safety plug can be screwed back onto the valve.

SUMMARY

The process of Sampling hazardous chemicals like sulfuric acid can be made safer with the 'effective implementation of inherently safer design and the hierarchy of controls'.

We have identified some of the risks associated with different types of sample systems and discussed a design that could potentially reduce the incidents of accidental exposure and releases into the environment. An engineered solution specifically designed to reduce emissions, waste and exposure risk which offers simplicity and reliability must be considered an inherently safer design.

Additionally, having an accurate representation of the process leads to better efficiency, less waste and less cost in the long run. Sample systems designed with piping or tubing which must be flushed before a representative sample can be taken introduces complexity to the process, and may lead to inaccurate samples. Whenever hazardous chemical sampling is a requirement, and a safer alternative is unfeasible, adequate engineering controls should always be considered as a safer alternative.

Personal Protective Equipment (PPE) should always be the last line of defence.

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ABOUT US

BIAR Sampling Systems was established in the early 80's by Guy Masson, a chemical engineer working with hazardous chemicals in Switzerland.

Tasked with finding a solution to safely sample hazardous chemicals, Guy invented the PRISEMASSON® sampling system which became the first sample system to feature a hand Wheel and conical seat. Now, with over 40 years of experience, we continue to pioneer innovations in the field of chemical sampling and produce a range of valve configurations with unmatched quality and precision. There is simply no shortcut when the health and safety of operators and the surrounding environment are at stake.

All our valves are fitted with a spring-to-close system to prevent any spillage should the operator suddenly step away from the valve. This may be in the form of a handwheel, lever, or pneumatic actuator, depending on the nature of the system. For example, for viscous liquids that are not under extreme pressure, the spring-to close lever actuator will provide a better solution than our standard spring-to-close hand-wheel. By taking the time to thoroughly characterize the specific details of a customers' application, we can provide them with the optimal sampling system tailored for their sampling needs.

Our valves are used in a myriad of challenging applications; liquids that pose thermal or toxic hazards, applications that demand an aseptic sampling environment or are atmosphere sensitive, to extremely toxic liquefied gases such as phosgene and chlorine. To meet such a wide ranging array of needs, we have established a strong global network that consists of a knowledgeable sales staff and distributors who work to customize each sampling valve to meet the customer's application. Aspects such as the chemical in question as well as the temperature, pressure, and pipe size of the given process system must be established in order to specify the correct valve type and its receptacle



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