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Letter from the Editor: Levels of Wealth



There are many levels of wealth and most everyone has different things that are important to them. To some people money is the most important thing, and they will sell their soul to the devil to gain money.

"Whoever loves money never has enough; whoever loves wealth is never satisfied with their income. This too is meaningless." Solomon

Like most people I am also money motivated, but my largest driver might be respect. I have tried to be respected as an engineer and person. Like most people, I have succeeded and failed in my efforts. Let us look at different levels of wealth.

Zero Level of Wealth

The zero level of wealth is where you do not have the basic needs of life. 1) Food, 2) Shelter and 3) Health Care. There are many people in the USA and all over the world that are in the zero level of wealth. In the world this might be as high as 20%.

Where I live in Florida there are many homeless people. Over the years I have given food to homeless shelters, but I rarely give money. When I worked in Indonesia I would buy orange juice, milk, and fruit to give to the children begging on the streets.

It is easy to be critical of the homeless and beggars, but remember they are the sheep and Satan (who sometimes by using us) is the wolf that is wounding the sheep. When you see a sheep that is wounded, let us try to help instead of being critical.

Level One

Level one is where you have the basic needs of life. In level one you are only a few days of hard luck away from level zero. Most of the world families bond together to help stabilize themselves. In the USA we are so blessed that we have hurt our family structure to the detriment of our children.

Level Two

Level two is where you are able to have more than the basic needs of life. A genuinely nice house, money in savings, and excellent job and a car. For most of the world this involves some luck and arduous work.

Level Three

Level three is where you have an excellent job, large savings account and you do not continually look at what food and other basic needs cost. You buy better food at the store to be healthier. You buy things to make your house look better. In many parts of the world to own a car is only a dream.

Level Four

Level four is where you have multiple house and cars. This is an exceptionally low percentage in the world, and the amazing thing is the study show that large wealth does not bring great happiness.

"Contentment makes poor men rich; discontent makes rich men poor." Benjamin Franklin

Most of us would like to improve our level. One way that lower-level people improve is by gaining knowledge. We believe that IACPE would be a terrific way to gain practical knowledge to help you to climb the ladder. Remember once you climb the ladder, help those below.

All the best in your career and life,
Karl

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How to Change Phase a Non-renewable Industry to a Bio & Renewable Industry in Oil, Gas & Petrochemical in Downstream Sectors

Hamid Reza Seyed Jafari, Mohammad Ali Tork, Dr. Ahmad Shariati, Dr. Seyed Morteza Seyed Jafari, Seyed Mohammad Reza Seyed Jafari

ABSTRACT

UN says: "To preserve a livable climate, greenhouse-gas emissions must be reduced to net zero by 2050. By changing our habits (especially in industries ...) we can tackle the climate emergency & build a sustainable world. Greenhouse gases come from transportsations, industries, cities, farms... ". The present article briefly discusses few technical process engineering practical ways to reduce greenhouse gases (mainly carbon dioxide) in the downstream oil & gas refining and petrochemical industries of oil and gas sectors with the construction and operation of renewable production units for the production of renewable oil & gas and petrochemical products. Methodology of decarbonized path as converting an oil or gas refinery or petrochemical plant with fossil hydrocarbon feedstock is so-called change phasing a non-renewable refinery or petrochemical plant to a renewable refinery or petrochemical plant whose products are large-scale compatible with environment production processes and avoiding climate change and proceeding to net zero carbon emission globally.

Keywords: Climate change, Renewable feed, Non-renewable feed, Refinery, Petrochemical plant, Greenhouse Gas (GHG), Oil & Gas, Downstream and Hydrocarbon, Decarbonized path

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PREFACE

Before entering the main discussion of the article, to realize the importance of the issue in the first part of the article, we will briefly talk about some of the main points raised by the United Nations (UN), which have been described on its website, about climate change and global warming and its roadmap about net zero carbon emission. Subsequently, in the

second part, we will introduce some process technical solutions to the decarbonized and net zero carbon emission to change phase non-renewable oil & gas & petrochemical downstream industry to a renewable one. Finally, in part three, we will briefly describe ways to reuse carbon dioxide produced by industries to manage greenhouse gas emissions.

PART ONE

1. The global coalition for net-zero emissions is growing

Along with companies, cities, and financial institutions, more than 130 countries have now set or are considering a target of reducing emissions to net zero by mid-century. While net zero is a critical longer-term goal, steep emissions cuts – especially by the largest greenhouse-gas emitters – are imperative in the next 5 to 10 years to keep global warming to no more than 1.5 °C and safeguard a livable climate. Of the 191 Parties to the Paris Agreement, more than 150 Parties have so far submitted a new or updated national action plan – called Nationally Determined Contributions (NDCs) – as required by the agreement. Their planned combined emissions reductions by 2030 still fall far short of the level of ambition needed to achieve the 1.5 °C goal,(For more information: see UNFCCC NDC synthesis report).

2. Most emissions come from just a few countries

The following statistics and chart were extracted from the official website of the United Nations in February 2022 and show the share of a few countries and the largest consumers of fossil fuels and greenhouse gas emitters in the world.

3% Contribution of the 100 least-emitting countries

68% The 10 largest greenhouse gas emitters

contribute over two-thirds of global emissions

46% The top 3 greenhouse gas emitters contribute 16 times the emissions of the bottom 100 countries

3. Net zero decarbonized approach

Perhaps the most important question is whether net zero carbon emissions are possible for all sectors related to fossil fuel consumption? Yes, the answer is yes (This is the response of the United Nations). But it needs committing of every country in the world to net zero emission.

There are many ways to reach net zero carbon emission target in different sectors (industry, transportation...) to protect environment and control climate change because of global warming due to the activities of these sectors arising GHG emission.

4. The roadmap to net zero

2015: 196 countries adopted the historic Paris Agreement to reduce global warming and build resilience to climate change. Its overall goal: limit warming to no more than 1.5 degrees Celsius.

2015-2017: Parties to the agreement began submitting climate action plans known as nationally determined contributions (NDCs). Initial commitments, even if fully implemented, would only be enough to slow warming to 3 degrees. Urgent calls for action and ambition gained momentum as the plans would not stop catastrophic impacts.

2020-2021: In the lead-up to the COP26 climate talks, countries have begun revising their NDCs to strengthen climate action. With science affirming a shrinking window of opportunity, the plans must include urgent actions to cut carbon emissions and reach net zero by 2050.

2030: To keep warming to 1.5 degrees, countries must cut emissions by at least 45 per cent compared to 2010 levels.

2050: The transition to net-zero emissions must be fully complete.

PART TWO

In this part, we will briefly introduce several renewable process techniques and briefly mention some practical examples of its investments around the world.

1. How to change a crude fossil oil to a biofuel refinery

To convert a non-renewable fossil fuel refinery into a bio refinery, the simplest way is to blend non-fossil and non-renewable oil products (such as gasoline, diesel, kerosene and fuel oil) with renewable bio products in standard proportions regarding to governmental regulations of each country. They are known as for example E5, E10, E20, B5, B10, B20, B40, SAF and renewable marine liquid fuel oil. Renewable for the production of diesel / ethanol / SAF / fuel oil, they could be purchased from market or installation of respective renewable plants are built near the crude oil refinery with different feedstock such as: Sugarcane and crops waste / Edible and non-edible vegetable oils / Algae / Plastic and tires waste

Some examples of technology suppliers in this regard are:

- Neste corporation; Finland in which provides technologies to produce pure biodiesel (B100) and sustainable air fuel (SAF)
- Clariant AG company; Switzerland in which provides technology to produce pure bioethanol(E100)
- Green fuel company; United Kingdom in which provides technologies to produce different types of biofuels
- Calumetspecialty company; USA in which provides technology to produce pure biodiesel(B100)
- Suncor company: Canada in which provides technology to produce biojet (SAF) and Bioethanol(E100)
- Honeywell-UOP; USA in which Runs a bio refinery project with the capacity of 400,000 tpa of bio products (Diesel, Gasoline, Naphtha) for Total company
- Indonesia and Malaysia: Production plants of Biodiesel B10, B20, B30, B40
- Agbion company; Australia in which provides technology to produce Bio Jet

2. How to change a petrochemical fossil complex to a bio petrochemical complex

One way to achieve the production of bio-petrochemical products is to use renewable feeds instead of using fossil hydrocarbon feeds. This category can be used to use biogas (renewable natural gas) produced from organic biomass and green hydrogen produced from the electrolysis of water and electricity produced from renewable solar, wind,

hydropower ... systems in a petrochemical complex and finally bio petrochemical products such as green ammonia, green methanol, green ethanol ... produced.

- Covestro company and Burealis Company: Germany and Austria to produce bio polymer (poly carbonate)
- Spain and South Korea: Production of bio petrochemical products

3. How to change a non-renewable grid network natural gas to a renewable grid network

Two ways that are currently used in some parts of the world to replace the use of fossil natural gas as follows:

- A. Production and use of biogas by renewable anaerobic digestion (AD) reactor processes that includes about 60% to 65% of it, and even in the case of highly advanced technologies, up to 90% of bio methane (RN :renewable natural gas) and the rest is carbon dioxide mainly from solid or liquid of organic waste materials (crop waste, industrial waste water, Fruit waste, waste of Slaughterhouse effluent and dairy and fruit industries, Animal and poultry manure , Urban organic waste ...)
- B. Green hydrogen production: Of course, in both cases, clean renewable gases can be obtained either used alone or by injection of them regarding the necessary standards to the existing grid network of city gas for domestic, industrial and transportation consumption.
 - Finland: Production of biogas from urban organic waste in AD plants
 - England: Production of biogas from crops organic waste and manure in AD plants
 - Philippine: Production of biogas from pineapple waste in AD plants
 - Netherlands: Production of green hydrogen in biggest project by Shell in Rotterdam by renewable electrolysis plant
 - EU: Plan of production of green hydrogen in European countries
 - Italy: Production of biogas from olive ponace waste in AD plants
 - England (Arcon, Scotland): Injection of Hydrogen to the pipeline of natural gas grid network
 - Turkey: Injection of Hydrogen to the pipeline of natural gas grid network

- The Netherlands: Plan of injection of Hydrogen to the pipeline of natural gas grid network
- Turkey (Sutas co.): Production of biogas from dairy wastewater in AD plant to produce electricity
- Canada: Production of biogas from food wastewater in AD plants
- Merus company; Finland in which provides technology to produce green Hydrogen
- Tecnifpmc company ; UK in which provides technology to produce green Hydrogen
- Attero company; The Netherlands in which provides technologies to produce biogas from any organic waste material
- Bmp greengas company; Germany in which provides technologies to produce biogas from agricultural biomass

PART THREE

Another of the most technical ways of Net Zero Emission management is to reuse CO2 gas (GHG) in production of green petrochemical, green gas, green fuel products and electricity instead of using decarbonization processes as follows:

- A. Gathering and injection of CO2 gas known as, carbon capture usage storage (CCUS) in oil & gas fields to enhance recovery of oil and gas Carbon capture and storage (CCS) is a combination of technologies designed to prevent the release of CO2 generated in suitable underground storage reservoirs
- B. Production of renewable petrochemical and bio-oil products such as renewable methane, Renewable methanol, renewable ethanol ... for example from reaction of syn gas (CO produced from CO2) with green Hydrogen in which produced from electrolysis of H2O using wind, solar ... electricity. Renewable and non-renewable Petrochemical products are used to manufacture analgesics, antihistamines, antibiotics, antibacterial, rectal suppositories, cough syrups, lubricants, creams, ointments, salves, and many gels. Processed plastics made with oil are used in heart valves and other esoteric medical equipment.
 - England: C4U project, changing CO2 to H2
 - Norway: Injection of CO2 to oil & gas fields to improve them (enhance oil & gas recovery)

- CGG company; Australia in which provides technology to capture and storage carbon dioxide to net zero emission

CONCLUSION

It can be seen that using the existing natural renewable capacities in any countries and with the possibility of making the necessary planning, the necessary direct investment or with the support of financial institutions friendly to environmental projects and plans around the world to implement various decarbonization projects with net zero carbon emission policy along the policy of UN roadmap by 2050 in the short , medium and long term in the oil , gas and petrochemical industries around the world take actions to preserve the planet's survival and the normal daily lives of its people to deal with the environmental impacts consequences of global warming due to climate change due to greenhouse gas emissions.

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Dr. Seyed Morteza Seyed Jafari is a graduated in PhD degree in Cellular Biomedical Sciences from Switzerland University with about 8 years' experience in his medical and clinical field and interested idea and knowledge in renewable medicine production (such as: bio glycerol).

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Seyed Mohammad Reza Seyed Jafari is a B.Eng. Chemical Engineer from Iran Azad University (IAU), MBA strategic planning from Tehran University and IT student of master's degree and has experiences about 6 years in consulting engineering companies as HSE engineer, and knowledgeable technical data in the execution of oil, gas and petrochemical downstream EPC projects and is an IT specialist.



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How Effective Leadership Can Develop a Learning Culture – Building a Team

Dr. Tina Persson

Quotes: Definition of a team

"A small number of people with complementary skills, who are committed to a common purpose, set of performance goals, and shared approach for which they hold each other mutually accountable." - Jon Katzenbach

"...And which has ways of effectively meeting and communicating that raise morale and alignment, effectively engaging with all the team's key stakeholder groups and ways that individuals and the team can continually learn and develop." - Peter Hawkins

INTRODUCTION

A team is commonly described as a group of people working together toward a common goal. A team is different from a group in many aspects, but the most notable differences are:

- A team shares a common goal and mission, but each member of a group works towards their individual goals.
- Team members work interdependently, connected in the team by their unique skillsets.
- Each team member offers unique support to the team.
- A team is part of a larger structure in the company and organization.
- A team takes both collective and individual responsibility for its mission, while members of a group are only individually accountable.

Creating a learning culture and tolerance for failure in any purpose-driven team are vital aspects of generating an innovative and psychologically-safe work environment. Team members who feel uncertain in the workplace are highly likely to hinder team processes. This includes team members who struggle to make decisions (or are afraid of making the wrong decision), team members who fear failure, feel insecure in their current position, or are worried about losing their jobs. Insecurities such as these can lead to your team transforming into a loose group of individuals with separate goals and ambitions.

Very few professionals are self-born leaders, but by developing their people skills and building awareness around their shortcomings, blind spots, and self-management, anyone can grow to a great leader.

However, it's far more logical for STEM professionals to prioritize and focus on the technical aspects of leadership. Let's change that!

This article will share some ideas on creating an environment for learning within a team. In any healthy, purpose-driven team, the learning process is a natural part of daily life, and team members should share their failures and celebrate their victories together.

ARTICLE

If there is a culture of learning in any workplace, then the whole team will continuously progress and develop, becoming better and better over time. Team members will be able to hone their current skills and learn new ones. This will allow them to contribute to the success of the team as a whole. On the other hand, in the absence of a learning culture, the team members' skillsets will stagnate. They can sink into a monotonous routine and lose their motivation and productivity.

A leader must seek to promote the establishment of a learning culture if he/she wants their team to be successful. A learning culture refers to an environment where people are encouraged to learn new skills, gain more knowledge, and be innovative. Once you have a team that is constantly learning and developing, your success rate will increase exponentially. A learning culture will promote creativity, resourcefulness, and innovation in your team. A good leader understands the importance of building a team based on people's specific skillsets and needs, on both a technical and personal level. As a leader, you play a vital role in kickstarting the development of a learning culture in your team. You can take steps to ensure that your team is continuously expanding its capacity so that its future can be brighter. Listed below are some ways your effective leadership can develop a learning culture:

Provide Learning Opportunities

Your team members might want to learn new skills, but they do not have the opportunity to do so. You need to ensure you are providing your team with suitable opportunities to improve on their current skillsets, learn new skills, and grow in their careers. If you invest in your team, the benefits are astounding.

Virtual learning is an excellent way for your team members to learn and grow their skillset. Virtual learning can be extremely effective and is relatively easy to provide. You need to encourage your team members to adopt a learning attitude. If you can, adopt and apply a mindset where you are a coach, a teacher, and a leader so that your team is more willing and excited to learn from you. To develop an effective learning culture within your team, you need to lead by example. Try to learn and grow your skillset so that your team members are inspired to follow suit. If they have readily available means to learn and expand their skillsets, then it is likely that they will be happy to do so. If a team member expands their knowledge and skills, it will benefit not only them, but the team as a whole. Your team members might be ready to learn, and all they are lacking are the means to do so. Provide them with the means to learn, and it will result in a successful and resourceful team.

Keep in mind that it is not enough to simply provide your employees with learning opportunities; they need to be able to utilize them. What good will it do if your team knows what to learn and where they can learn it, but they are unable to undergo the training? There can be many factors that can contribute to your team members being unable to learn and expand their skill sets even when they have the means readily available. One of the most common reasons is lack of time.

Barriers to your team's skill development need to be tackled head-on. You can help in the following ways:

1. Ensure that your team has time to acquire new skills and to learn. This can be done by adjusting their workload or allocating them a specific time to complete their learning.
2. Keep an open line of communication and be flexible wherever you can be.
3. Let them come to you with any problems they might be having that are hindering them from learning.
4. Offer constructive and motivational feedback.

5. Ensure you, as their leader, are ready to take the team's feedback. Showing you are willing to learn from them

Once you address these issues, a learning culture will develop almost naturally in your team.

Make Learning Rewarding

One of the reasons you might be having trouble developing a learning culture in your team is that your team members have no incentive to learn. As a leader, you need to make learning something rewarding so that your team members are enticed and motivated to develop their knowledge and skills.

Don't just focus on short-term results either. Some leaders wrongly think that if their employees are learning, then they are not working. They believe this to be the case because they are only focusing on the short-term results. Now, it is important to note that some employees might have the same view. A good leader knows that if there is a learning culture in place, then it will ensure great results in the long run.

If your employees view learning as unrewarding and something that will get in the way of their work, they will not contribute to establishing a learning culture. The incentive being discussed here is not just praising and giving promotions to those who display an effort to develop and learn. It is also about creating a climate that nurtures thinking and learning. An effective leader will create this climate which will, in turn, help develop a learning culture. As a leader, do not stifle the voices of your team members. Instead, let them speak up and challenge authority even if it results in some discord, because it is in situations like these that innovation is born.

Make Failure Acceptable

If people are too afraid to make mistakes, they will most likely fail in the long run or be left behind. A good leader understands that failures are just as important as successes. For the development of a learning culture in a team, the leader needs to make failures acceptable and share constructive ways your team can learn from their mistakes going forward. If your team members are too afraid of failure, they will not leave their comfort zone and learn. However, if you approach failures and mistakes in a constructive way and show your employees that, sometimes, failing is okay because it means they are learning, they will be more willing to try. This

acceptance of failure will lead to employees going out of their comfort zone and exploring the ideas they previously would have avoided. If your team members go out of their comfort zone in the pursuit of new ideas, it can result in either success or failure, but it can also result in innovation. Promote the view of seeing failure as positive and as a learning process so that a learning culture can be developed.

Get to Know Your Team

Getting to know your team will allow you to be a much more effective leader. Get to know what drives every individual in the team and what makes them happy. Doing so will allow you to provide more effective learning opportunities to them. If you know your team members, then you can recognize and take steps against any obstacle stopping them from learning. It will also allow you to figure out ways to help your team develop a learning culture.

Utilize Digital Tools

The utilization of digital tools is crucial for the development of a learning culture nowadays. Digital tools have become a part of our everyday lives, not only personally but at work as well. They provide ease and flexibility as well as a multitude of platforms where you and your team members can learn. Utilize these tools to make learning more readily available to your team members and provide them with flexibility in how and when they want to learn new skills and knowledge. Not utilizing digital tools will result in you and your team being left behind in the competitive business landscape. So, make sure you have the latest digital tools available to every team member and have measures in place to ensure everyone can use them effectively.

Follow these ideas to develop a productive and successful learning culture in the workplace.

AUTHOR



Tina Persson, PhD spent 20 years in academia as a scientist and leader, then she entered the corporate world for over eight years as a Headhunter, Branch Manager, and Consultant Manager. Alongside her corporate career, her entrepreneurial spirit and business mindset created an opportunity. She proudly serves as

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As a coach, Tina has supported 1000+ higher professionals and performed 500+ assessments to entangle and pave the way for their career success stories. Tina's multifaceted background, creativity, and experience as a coach allow her to guide and transform her clients. She has developed an approach aimed at growing her clients' skills and building a long-lasting trust in their abilities and goal-setting capabilities so they can become successful leaders in any organization.

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Update for the Southeast Asia (SEA) Oil & Gas industry

March 2021

KEY DRIVING FACTORS

- Russia-Ukraine escalation creates anxiety of crude supply pushing crude oil prices past US\$110/ barrel. OPEC+ hasn't decided to increase output significantly.
- Omicron variant sweeps through most of SEA posing downward pressure on demand. Most authorities restraining on implementing overly strict restrictions.
- Singapore budget touched on Carbon taxes.
- Countries financial governing bodies incorporate Environmental Social Governance (ESG) component.
- All National and Supermajors companies have set Carbon and circular targets by 2030-2050.
- Executives' remunerations have started to include sustainability component.

KEY COMPANY / COUNTRY ACTIONS

Singapore

Singapore will increase its Carbon tax by five-fold by 2024 and ten-fold by 2030. Singapore main national carrier Singapore International Airlines (SIA) will start consuming sustainable aviation fuel from 3Q 2022 in a pilot involving ExxonMobil and Neste.

Singapore Green plan includes circular economy and Shell decide to invest on Plastic to Fuel technology as part of its goal to get to 1million tons of plastic recycled chemically.

Malaysia

Petronas Pengerang refinery is expected to be back to full operations in late first quarter 2022. In SEA only Petronas Pengerang had turnaround/shutdown plans for the 1st Quarter 2022. Vitol fuel oil refinery plans to start commissioning early 2022.

Petronas embarks on circular economy in partnership with Plastic Energy and are potentially looking at a pilot plant. They have carbon capture investments to help them towards Net Zero Carbon Emissions NZCE50.

Indonesia

Pertamina carries on investing as part of its refinery expansion at 5 of their 6 refineries. In the Refinery Development Master Plan (RDMP) Balongan is planned in the next few years and subsequently integrated Refinery and chemical project in Tuban.

Thailand

Stock Exchange of Thailand (SET) announced that 41 Thai companies were recognized with S&P Global Sustainability Awards by S&P Global, making Thailand the world's fourth highest by number. Compared to the preceding year, number of Thai companies in the S&P Global Sustainability Yearbook 2022 rose by 12.

Vietnam

SCG group target start-up of its olefin plant Long Shon Petrochemicals in 1st half 2023. In tandem Hyosung Petrochemicals have started its Propane Dehydrogenation Unit (PDH).

Philippines

Philippines fuel security concerns we put at bay once again with Petron restarting its operations in 2nd. Q 2021.

ASEAN

Supermajor ExxonMobil that has significant operations in Singapore and Thailand has restructured global operations by combining its Refining and chemical business and elevated its Energy transition business on same footing as its traditional businesses.

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
- is a supplier-independent tool. There are no preferred product placements or promoted designs
- considers static dimensions, manways and fastenings
- offers an interactive 3D-view for all designs
- can be used for single stage, profile and data validation calculations
- has a unique, logical and multi-lingual user interface, with multiple input and output options
- applies hundreds of online queries to check the feasibility and limits of the calculated designs
- is a well introduced software many companies have relied on for more than 20 years
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Zero Sulfur in Steam Cracker Plants

Joseph C. Gentry

INTRODUCTION

The petrochemical industry is pressured. Environmental regulations dominate investment budgets, and often take the top priority in operating expenditures. Mandates on compliance rule over all else and must be adhered to as a license to operate regardless of the logic or cost/benefit analysis. The Gas Processing Industry faces some of the same challenges and has found different ways for managing H₂S that are prudent to consider in the downstream industry.

The current buzz of attention is about anything ‘green’. For steam cracker plants, this is mainly reflected in a) taking unconventional feeds or recycled polymers or biofuels, or b) making products that are recyclable or environmentally friendly. But traditional issues such as waste reduction and energy efficiency remain important as well. This paper is a sequel to the article Zero Sulfur in Refineries, which prompts some re-thinking about sulfur management in the downstream industry based on practices learned in the Gas Processing Industry.

THE SULFUR CONUNDRUM

Issues with sulfur are mainly related to crackers processing naphtha or heavier feedstocks, as ethane and LPG feedstocks contain little sulfur.

On a macro scale, sulfur comes in from:

- Liquid hydrocarbon feedstock. This includes H₂S that has been sequestered by triazine in the loading and transporting of naphtha by barge.
- Furnace tube pre-sulfiding
- Chemical additives
- Pre-sulfiding agents for catalysts

Sulfur leaves the cracker plant in:

- Products [Pyrolysis Gas Oil (PGO), Pyrolysis Fuel Oil (PGO), and Pyrolysis Gasoline (pygas), including C₄ and C₅ cuts]
- Waste Caustic
- Soluble salts in process wastewater

As in refineries, sulfur is not our friend. There are many ill-effects from sulfur in steam cracking plants, including:

- Catalyst poison
- Equipment corrosion
- Severe health hazards
- Interferences with process chemistry
- Specification issues in finished products
- Process line freezing in the Cold Box

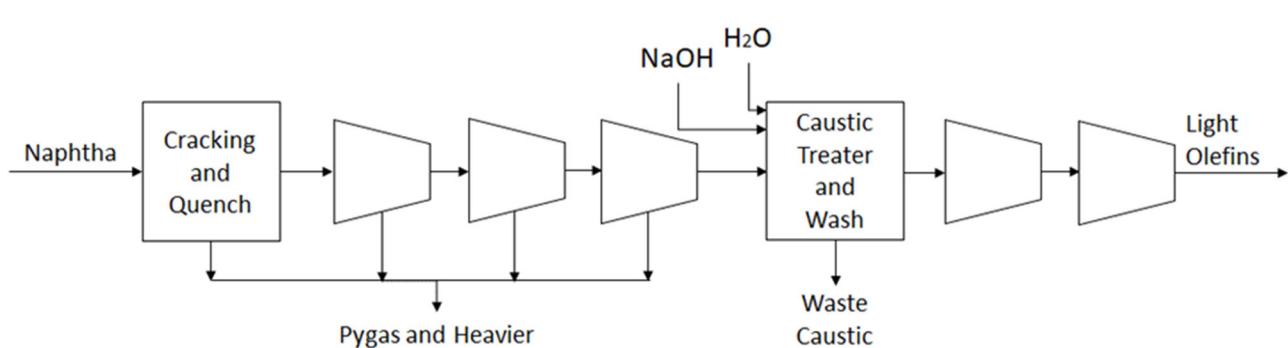


Figure 1. Caustic treater within the cracker compressor train

Let's look at the most important means for removing sulfur, which is the caustic treater and wash tower. This is usually positioned after the third stage of charge gas compression and has the purpose to remove H₂S and CO₂ before continuing into the Cold Fractionation section of the cracker. At this point in the process, some of the sulfur is in the form of H₂S resulting from the severe thermal conditions at the cracker furnace. CO₂ derives from decomposition of oxygenated products in the cracker hot section. In any case, both need to be removed to ppm level of concentration.

In the caustic treater, H₂S reacts with NaOH to form NaSH and a few other sulfonated products. Caustic is used in excess to ensure that no H₂S leaves to go further downstream unconverted, then water washed to remove remaining sodium hydroxide. The stream typically goes to wet air oxidation to reduce the COD, and is neutralized with hydrochloric acid or sulfuric acid, which creates water-soluble salts from the acid and base.

The other dominant acid gas, CO₂, reacts with caustic to form sodium carbonates, which entail the same further treatment.

What causes headaches? Almost universally, cracker operators will note that waste caustic handling is a chronic nuisance they wish would go away. The operation is prone to complications, with many operational steps required that do not directly relate to producing ethylene.

There is:

- Cost of the fresh caustic
- Red oil generated in the caustic treater, which needs disposal and causes hydrocarbon yield loss
- Cost of wet air oxidation to reduce the COD
- Cost of acid to neutralize the waste caustic
- Cost of wastewater treatment or ultimate disposal of waste caustic
- Environmental impact of sodium sulfate salts and sodium carbonate added to wastewater

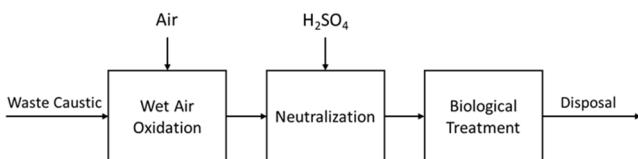


Figure 2. Process Steps for Waste Caustic Treatment

Anything that can be done to reduce the load on the caustic wash system will be advantageous for the cracker operator by improving the safety and environmental impact in the waste water treatment system. Additionally, there will be OPEX savings associated with less waste disposal.

HEAVY SULFUR SPECIES

One method for reducing the operating costs in the caustic treater is to eliminate the loading that comes from the heavy sulfur species. In the Hot Section fractionation of the cracker, the sulfur species are segregated by their boiling points into PFO, PGO, and the C5+ pyrolysis gasoline fraction.

The PGO and PFO leave the system directly with their sulfur and are not the topic for discussion here.

The sulfur components in the pygas are hydrotreated into H₂S in 2-stage hydrotreatment units. The H₂S is recycled back to the charge gas ahead of the caustic wash tower for removal by conventional means. At this point in the process, the recycle gas stream is free of impurities except the H₂S, which can be removed by adsorption in a SweetTreat™ 1 vessel or direct treatment system. The acid gases in this recycle would therefore bypass caustic treating and have a proportional reduction in operating costs. H₂S from the pygas of naphtha crackers represents a significant quantity of the total hydrogen sulfide that must be removed.

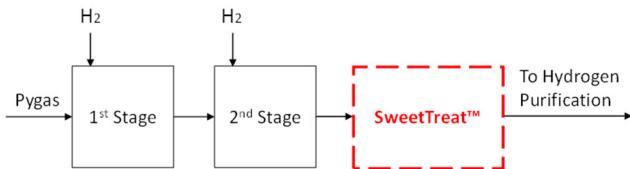


Figure 3. Alternate H₂S Removal from Pygas Hydrotreatment System

C4 and C5 Cuts - Sulfur removal in the C4 and C5 cuts uses a different method, as these are carbonyl or sulfide species and not reactive with basic amines or caustic. The raw cuts of these heavy olefins are not subject to hydrotreatment on account of the need to preserve the butadiene, isoprene, and hydrocarbon resin reactivities. Other strategies using selective adsorption of sulfur species can be used to remove these trace components.

CONCLUSION

The sulfur problem in petrochemical plants

can be solved piece by piece, eventually bringing about notable improvements. One item is introduced here:

1. Use an adsorption system or direct treatment of H₂S on the pygas hydrotreater off-gas to intercept the H₂S that would otherwise go to the caustic wash system. The load on the caustic treatment system is reduced and there is a proportional reduction in OPEX along with reduced waste.

Other solution pathways will address the fundamentals of caustic treating altogether, along with specific sulfur-reducing adsorbents and techniques for the various sulfur species.

Looking beyond compliance requirements and operating costs, ESG scores play an important role in the cracker's viability. Reducing waste products from the caustic treater will demonstrate environmental commitment and establish the cracker operator as a leader that is sensitive to environmental issues.

REFERENCE

SweetTreat™ is a system which removes H₂S from gas streams using adsorption or direct conversion of H₂S into sulfur or sulfur products.

AUTHOR



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The Importance of Thermodynamics on Process Simulation Modeling

Timothy M. Zygula, Eric Roy, Pamela C. Dautenhahn, Ph.D., P.E.

ABSTRACT

This paper will demonstrate the importance of choosing the correct thermodynamic package when using a process simulator to model a distillation column. The authors will present a brief background of how thermodynamics are used in distillation design. The authors will then present a test case comparing operating data and design details of a commercial hydrocarbon column with results from three different process simulation packages. The test case will be used to demonstrate the steps to obtain a good model using a process simulator. Finally, the authors will provide guidelines to select the correct thermodynamic method when using a process simulation package to model a distillation column.

INTRODUCTION

There are many factors to consider when modeling or designing a distillation column using a commercial process simulation package. One of the biggest concerns is correctly choosing the thermodynamic package to use in simulation design work.

This paper will present some guidelines for selecting the correct thermodynamic method when using a commercial process simulation package to model distillation equipment. The authors will present a test case comparing operating data from a commercial hydrocarbon column with results from three different process simulation packages. These cases will be used to demonstrate the steps to obtain a good model using a process simulator.

SIMULATION MODELING

Thermodynamic Properties

Thermodynamic properties are critical to the success of a simulation model. The accuracy of a model depends on the ability of the thermodynamic package used to estimate the physical properties of the components in the system. Sometimes poor physical property data may prevent your simulation model from converging. (1) Although many typical

problems in the thermodynamics may arise from having missing physical property parameters for the compounds in the system, this paper is going to concentrate on using the simulation packages without any adjustments for these missing parameters. The purpose of this paper is to compare results of various thermodynamic packages for a specific system. The thermodynamic packages were chosen on the expectation that they would be either good or not so good methods for the compounds being used in the commercial column.

Vapor-Liquid Equilibrium

In the analysis of distillation columns and other vapor-liquid separation processes the compositions of multicomponent vapor and liquid mixtures in equilibrium must be estimated. The basis for vapor-liquid equilibrium calculations is the following relationship.

$$f_i^L(T, P, x_i) = f_i^V(T, P, y_i)$$

where: T- temperature, °F

P- pressure, psia

x_i- liquid phase mole fraction

y_i- vapor phase mole fraction

f_i- fugacity of a species in a mixture

To calculate the fugacity of a species in the vapor phase an equation of state must be used. However, there are two distinct methods for calculating the fugacity of a species in the liquid phase. An activity coefficient model or an equation of state can be applied. (2)

The activity coefficient model can be used for liquid mixtures of all species. The activity coefficient model does not incorporate the density of the liquid and does not do a good job of describing an expanded liquid that occurs near the vapor liquid critical point of the mixture. Problems can also occur when using two different models for the liquid phase and the vapor phase. For example, when using an activity coefficient model for the liquid

phase and an equation of state for the vapor phase the properties of the two phases may not become identical. When this occurs the vapor liquid critical region behavior is predicted incorrectly. (2)

When using an identical equation of state to calculate vapor and liquid phase properties good phase equilibrium predictions can be made over a wide range of temperatures and pressures. These equations also do very well predict conditions at the critical region. Not only can the phase compositions be predicted from an equation of state, but other physical properties can be predicted as well. Some of the properties that can be predicted using an equation of state are densities and enthalpies. However, this is only possible for hydrocarbon mixtures, inorganic gases, and a few other materials. (2)

The most common method is to use an equation of state to predict vapor phase compositions and properties and using an activity coefficient model to predict liquid phase compositions and properties. This way ensures that the physical properties for both the liquid phase and the vapor phase can be calculated with reasonable accuracy.

Equations of State

The mathematical relationship between pressure, temperature, volume, and composition is called the equation of state. Most equations of state are pressure explicit. (3) Thermodynamic properties can be predicted over a wide temperature and pressure range, including the critical region, by equations of state. When molecules are relatively small and nonpolar, they have been proven to be effective for vapor-liquid equilibrium calculations. However, the equations of state tend to be inaccurate for strongly hydrogen-bonding mixtures or substances with more complex molecular structure. (4,5) Many of the equations of state give similar results in estimating the vapor-liquid equilibrium. Bubble point pressure estimations of hydrocarbons and gases have been found to be within five percent and estimations based on binary interaction parameters have been within about 15 % accuracy. (4) In general, the variations in accuracy between the equations of state are subtle. One equation might be best for a narrow range of applications, while another equation might be more appropriate for another range of applications. (4)

Activity Coefficient Method

An ideal mixture can either be liquid or gaseous which is defined by the following relationships:

$$\underline{H}_i^{IM}(T, P, x_i) = \underline{H}_i(T, P)$$

$$\bar{V}_i^{IM}(T, P, x_i) = \bar{V}_i(T, P)$$

where: T- temperature, °F

P- pressure, psia

x_i- liquid phase mole fraction

\bar{V}_i - Partial Molar Volume, ith Component

\underline{H}_i - Enthalpy Per Mole, ith Component

\underline{H}_i^{IM} - Enthalpy Per Mole, Ideal Mixture

\bar{V}_i^{IM} - Partial Molar Volume, ideal Mixture

In an ideal liquid solution, the liquid fugacity of each component in the mixture is directly proportional to the mole fraction of the component. The ideal solution assumes that all molecules in the liquid solution are identical in size and are randomly distributed. This assumption is valid for mixtures containing molecules of similar size and character. (3)

In general, you can expect non-ideality in mixtures of unlike molecules. Either the size or shape or the intermolecular interactions between components may be dissimilar. These differences are called size and energy asymmetry. Energy asymmetry occurs between polar and non-polar molecules and also between different polar molecules. An example is a mixture of alcohol and water. (3)

The activity coefficient represents the deviation of the mixture from ideality. The activity of a component at some temperature, pressure and composition is defined as the ratio of the fugacity of the component at actual conditions over the fugacity of the component at standard conditions. (3)

$$a_i(T, P, x) = f_i(T, P, x) / f_i(T, P^o, x^o)$$

where a_i – component activity
 T – temperature at actual conditions
 P – pressure at actual conditions
 x – liquid mole fraction at actual conditions.

Note: The superscript “o” indicates at standard state.

The liquid activity models are designed to have more flexibility by having more adjustable parameters and allow the free energy curve to be accurately tuned for magnitude and skewness. One of the key features of these models is treating liquids differently than vapors. The liquids are evaluated as deviations from ideal-solution behavior, whereas the vapors are evaluated as deviations from ideal-gas behavior. (4)

Peng Robinson Equation

The Peng Robinson equation is an equation of state that is generally good for ideal hydrocarbon systems not operating near the critical region. The Peng Robinson equation does not do a good job of matching the experimental data in the critical region. The equation calculates a larger two-phase region than what was generated through experimental data. One reason that might explain this deviation is in the critical region density fluctuations contributes strongly to thermodynamic properties. These fluctuations are ignored in the Peng Robinson equation. To incorporate this into this equation would be extremely difficult. (3)

NRTL & Van Laar Equations

The NRTL (Non-Random Two Liquid) equation is a three-parameter equation that can be used for both liquid-liquid and vapor-liquid equilibria correlations. The strength of the NRTL equation is for highly non-ideal systems. The NRTL equation often provides a good representation of highly non-ideal mixtures, polar compounds and partially immiscible systems. The NRTL equation provides good representation of experimental data if care is exercised in data reduction to obtain the adjustable parameters in the equation. (3)

The Van Laar is a two-parameter equation that is good for moderately non-ideal systems. The Van Laar equation should be used for relatively simple non-polar liquids. However, this equation has been empirically fit to represent the activity coefficients of complex liquids. The Van Laar equation is a popular equation to use because it is easy to mathematically manipulate. (3)

For moderately non-ideal systems, the NRTL equation does not offer a significant advantage over the Van Laar and the three-suffix Margules equation.

SIMULATION MODEL

Many times, when simulating a distillation column, the simulation model may not converge or, if it does converge, the model does not match plant data. After confirming that the input data are correct one may determine that the immediate answer to the problem is that “I have chosen the wrong thermodynamic package for my system”. Then you begin switching between thermodynamic packages to try to get your simulation model to work. However, once the simulation has converged or you have matched your plant data does not mean that your model is correct. Thermodynamic packages are constructed for specific applications. Some thermodynamic packages are good for highly non-ideal systems while others are not. The thermodynamic model used might be outside its recommended range. For example, the temperature or pressure range or both ranges are exceeded. In many cases thermodynamic models are extrapolated to ranges beyond the data they have for that model. However, any time a model is extrapolated outside its range the results are questionable until evaluated for validity.

Physical properties are critical to the success and accuracy of a simulation model. Poor physical property data may prevent your simulation model from converging or matching operating data. In this paper, three different thermodynamic packages are used for estimating the physical property data to match the data for a commercial hydrocarbon tower. In addition, three simulation packages are used to demonstrate how the results from the same thermodynamic packages may vary from simulator to simulator. The variations from simulator to simulator represent slightly different property estimations or values for the components in the system. The purpose of using different simulators is to demonstrate that there are variations, and one should always analyze the results from a simulator for accuracy and reasonableness. (7)

TEST CASE

The results from a test case, which is a commercial ethylbenzene recovery tower, will be examined. Plant data from this tower were compared with results from three process simulation packages using three thermodynamic

packages. For each of the thermodynamic packages, it was desired to match the external material and composition data reasonably well. Then the rest of the data, including the internal vapor and liquid flow rates, equilibrium data, and column diameter estimations were compared for similarities and differences.

The ethylbenzene recovery tower separates ethylbenzene from heavier materials. The feed was a 45% vapor mixture at 38.6 psia pressure. Since operational data were available the simulations were run to match the operational data. The desired products contained 99.4 percent ethylbenzene in the distillate and 85 percent heavy materials in the bottoms. Several thermodynamic models were chosen for use in the simulation runs on this tower. These models included Peng Robinson, Non-Random –Two-Liquid (NRTL) and Van Laar.

Feed Stage Optimization and McCabe-Thiele Diagram Development

To determine the optimum feed stage, simulation runs were performed at several different feed positions. In the simulation runs, the material balance, reflux ratio, and total number of stages were kept constant. The feed tray was varied and the light key component composition in the bottoms was determined. Then a concentration versus feed stage plot was created and is given in **Figure 1**. The optimum feed stage is where the minimum of the curve occurs. From **Figure 1** there are several stages in which the minimum value of the light key is approximately the same. Based on these data, the optimum feed stage was chosen as stage 30, which also corresponded to the expected efficiency for the column. All of the simulation results presented with the pseudo McCabe-Thiele diagram used stage 30 as the feed stage.

For each of the simulation runs a pseudo McCabe-Thiele diagram was developed. The pseudo McCabe-Thiele diagram was developed by using the mole fraction data for the light key and all lighter components calculated for each stage by the simulations. The equilibrium data and the operating lines were determined from these data. The pseudo McCabe-Thiele diagram helps one identify pinched

regions, mislocated feed points, over refluxing or reboiling, or where feed or intermediate heat exchangers are needed. (6)

Test Case Results

The results from the simulation runs were compared to the plant operational data. The feed pressure was specified as 38.6 psia and the feed vapor fraction was specified as 0.4544. The pressure profile was held constant in all simulation runs. In addition, the simulation runs held constant the feed rate at 67,995 lbs/hr, the reflux rate at 174736 lbs/hr, and the ethylbenzene (EB) composition in the bottoms at 0.671 weight percent. Theoretical stages were used, and the number was based on what is believed to be the overall efficiency of the tower. **Figures 2, 3, and 4** show the comparison of the simulation results of the commercial ethylbenzene recovery column.

Peng Robinson Simulation Runs

Figure 2 shows a comparison of equilibrium data from simulator A, B and C using the Peng Robinson model. The equilibrium data for simulators A and C are almost identical. The equilibrium curves as well as the operating lines lie on top of each other. This indicates that the results from the two simulation packages will be very close. The equilibrium curve for simulator B is consistently higher than simulators A and B. This shift in the equilibrium curve indicates that separation is easier and that the internal traffic in the column is lower. The operating line from simulator B is identical to the operating lines from simulators A and C.

A comparison of the simulated results using the Peng Robinson model is given in **Table 1**. The data in **Table 1** show good agreement between the plant data and the simulated results. There is only a one-degree difference between the overhead temperature measured in the plant and the temperature calculated in the simulation runs. The feed temperature calculated for simulator A and B is between one and two degrees less than plant data. The feed temperature calculated by simulator C is slightly more than two degrees cooler than plant data. There is some slight variation in the calculated results for the EB distillate composition and heavies' composition in the bottom. However, all of the results are considered to reasonably match plant data.

	Ovhd Temp °F	Btm Temp, °F	Reboiler Duty, mmb-tu/Hr	EB Comp. Distillate Wt%	Feed Temp, °F	Heavies in the Bottom Wt%
Plant Data	334	426		99.46	364	85.69
Simulator A	333	427	2.76	99.40	362.1	86.26
Simulator B	333	430	2.77	99.46	362.6	86.29
Simulator C	332	427	2.77	99.43	361.8	86.29

Table 1. Comparison of Key Data using Peng Robinson

NRTL Simulation Runs

Figure 3 shows a comparison of equilibrium data from simulator A, B and C using the NRTL model. The equilibrium data for simulators A and C are almost identical. The equilibrium curves as well as the operating lines lie on top of each other. This indicates that the results from the two simulation packages will be very close. The equilibrium curve for simulator B at the bottom of the column is below the equilibrium line for simulators A and C. Then as you go up the column it crosses the equilibrium line of simulators A and C. This shift in the equilibrium curve indicates that there is going to be big differences in the internal traffic above and below the feed in the results from simulator B. The operating line from simulator B is identical to the operating lines from simulators A and C.

A comparison of the simulated results using the NRTL model is given in **Table 2**. There is good agreement in the simulated results presented in **Table 2**. The overhead temperature, feed temperature, EB distillate composition and heavies' composition in the bottoms simulated results match plant data very well. The bottom temperature has the most variation with the temperatures ranging from -15 degrees to +15 degrees with respect to the plant measurement.

Van Laar Simulation Runs

Figure 4 shows a comparison of equilibrium data from simulator A, B and C using the Van Laar model. The trends in this diagram are the same as seen in the NRTL diagram. Simulators A and C give similar results while Simulator B varies like it did with the NRTL method.

A comparison of the simulated results using the Van Laar model is given in **Table 3**. The data in **Table 3** shows good agreement between the plant data and the simulated results. There is only a one-degree difference between the overhead temperature measured in the plant and the temperature calculated in the simulation runs for simulator A and B. Simulator C shows a two-degree difference in overhead temperature. There is an approximate ± 3-degree difference in feed temperatures calculated for simulators A and B with respect to the plant data. However, simulator C matched the feed temperature data almost exactly. There is some slight variation in the calculated results for the EB distillate composition and heavies' composition in the bottom. The results given by simulator B did not match the EB composition in the distillate as well as the others.

	Ovhd Temp °F	Btm Temp, °F	Reboiler Duty, mmb-tu/Hr	EB Comp. Distillate Wt%	Feed Temp, °F	Heavies in the Bottom Wt%
Plant Data	334	426		99.46	364	85.69
Simulator A	333	426	2.80	99.44	362.3	86.27
Simulator B	333	413	2.72	99.46	362.1	86.28
Simulator C	332	437	2.78	99.46	362.1	86.24

Table 2. Comparison of Key Data using NRTL

	Ovhd Temp °F	Btm Temp, °F	Reboiler Duty, mmB-tu/Hr	EB Comp. Distillate Wt%	Feed Temp, °F	Heavies in the Bottom Wt%
Plant Data	334	426		99.46	364	85.69
Simulator A	333	425	2.80	99.46	362.1	86.27
Simulator B	333	422	2.72	99.12	367.9	86.28
Simulator C	332	438	2.78	99.47	364.6	86.24

Table 3. Comparison of Key Data using Van Laar

Equilibrium Curve Discussion

Figures 5 –13 provide the equilibrium and operating curves for each of the individual runs. There appears to be a pinch point at the top of the equilibrium profile in all of the simulations. This pinch point is near the feed stage. The column does most of its separation below the feed. Typically this type of pinch indicates that there is a mislocated feed point. The feed point should be where the q-line intersects the equilibrium curve. This is generally the rule in binary distillation. However, it is not always true in multicomponent distillation. The optimum feed stage plot, **Figure 1**, suggested the optimum feed stage is used in the simulation runs. (6)

Therefore, a pinch point appears in the equilibrium diagrams that can't be explained by bad feed point location or system limitation. The pinch point tends to shift in simulator B when the Van Laar model is used. In ternary and higher component systems, the curvature in the operating lines will also sometimes cause curvature in the equilibrium

curve. This results from the discontinuity at the feed stage and the development of the equilibrium curves and operating lines from the same data. This curvature may produce the appearance of a mis-located feed when in actuality the pinch point is a function of the curvature of the operating line and the equilibrium curves. (1)

Great effort was taken to try to remove the

is consistent in all of the simulation runs. The authors have concluded that this phenomena must be associated with the simulation packages, the pseudo McCabe-Thiele diagram development, or a result of the separation of very close boiling point components occurring in the stages above the feed stage.

Test Case Column Sizing

Once the simulation runs for the test case was completed and the accuracy of the models was confirmed each process simulation package was used to size the diameter of the column. The default flood factor of .80 was used as the basis of the column sizing.

The results from the process simulators for the ethylbenzene recovery column are given in **Table 4**. Examining the results from the process simulation packages there is a large amount of variation in the results. Each package predicted about the same diameter column using the Peng Robinson Model. The column diameter calculated by process simulator B was a $\frac{1}{2}$ of a foot larger than what process simulators A and C calculated. This may indicate a different sizing criteria for simulator package B.

The diameters calculated by the NRTL models and Van Laar models are very different. Simulator B predicted a diameter one foot smaller in the bottom of the column. This is due to lower vapor/liquid traffic below the feed than what was predicted by the other two simulation packages. The vapor/liquid traffic predicted by simulators A and C were very similar. The actual tower is a constant 8.5 feet in diameter.

Column Dia., in Ft	Simulator A	Simulator B	Simulator C	Actual
Peng Robinson	8.5	9.0	8.5	8.5
NRTL Model	9.0	9.0 Above the Feed 7.5 Below the Feed	8.5	8.5
Van Laar Model	9.0	9.0 Above the Feed 7.5 Below the Feed	8.5	8.5

Table 4. Ethylbenzene Recovery Tower, Column Diameter Sizing Comparison

*****Note***** In designing a column, one should check the results by doing some basic hand calculations. The calculations for sizing a column by hand were provided in an earlier paper. Please refer to the paper entitled "Use of Process Simulation for Distillation Design" by Zygula, T. M., Dautenhahn, P. C. for complete details.

Conclusions

The results from these runs have shown that there will be variations between thermodynamic packages within a simulator and the same thermodynamic package between simulators. It is important to analyze the results for each system based on an appropriate thermodynamic method associated with the simulation package.

Recommendations

An equation of state can be used over a wide range of temperatures and pressures, including the subcritical and supercritical regions. Equations of state are typically used for ideal or slightly non-ideal systems, thermodynamic properties for both the vapor and liquid phases can be computed with a minimum amount of component data. Equations of state are suitable for modeling hydrocarbon systems with light gases. Equations of state are not capable of properly representing highly non-ideal systems, such as alcohol and water systems

For the best representation of non-ideal systems an activity coefficient model may be the best. One drawback of an activity coefficient model is that you may need to obtain binary interaction parameters from regression of experimental vapor-liquid equilibrium (VLE) data.

Table 5 provides some choices for deciding which thermodynamic model to try when modeling distillation columns. There are a few things to keep in mind when looking at this chart. Non-polar fluids may be modeled with an equation of state. Polar fluids are best modeled with a fitted activity coefficient model. Some systems have specific thermodynamic models designed especially for that kind of system. For example, there are some thermodynamic packages that specifically model electrolytic solutions. There are other thermodynamic packages that model alcohol systems and amine systems. These facts should be considered when trying to choose a thermodynamic model. (3)

System	Thermodynamic Model
All Gases, Non-Polar Solutions	Peng Robinson, SRK
Moderately Non-Ideal, Polar Solutions	NRTL, Wilson, Van Laar
Highly Non-Ideal, Polar Systems	NRTL, UNIQUAC

Table 5. Thermodynamic Model Selection Table (5)

*****Note***** When using the following equations, NRTL, Wilson, and Van Laar, you should make sure that all the Binary Interaction Parameters are present before using the equation to obtain the best results. (5)

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FIGURE 1, EB Column
Determination of Optimum Feed Stage

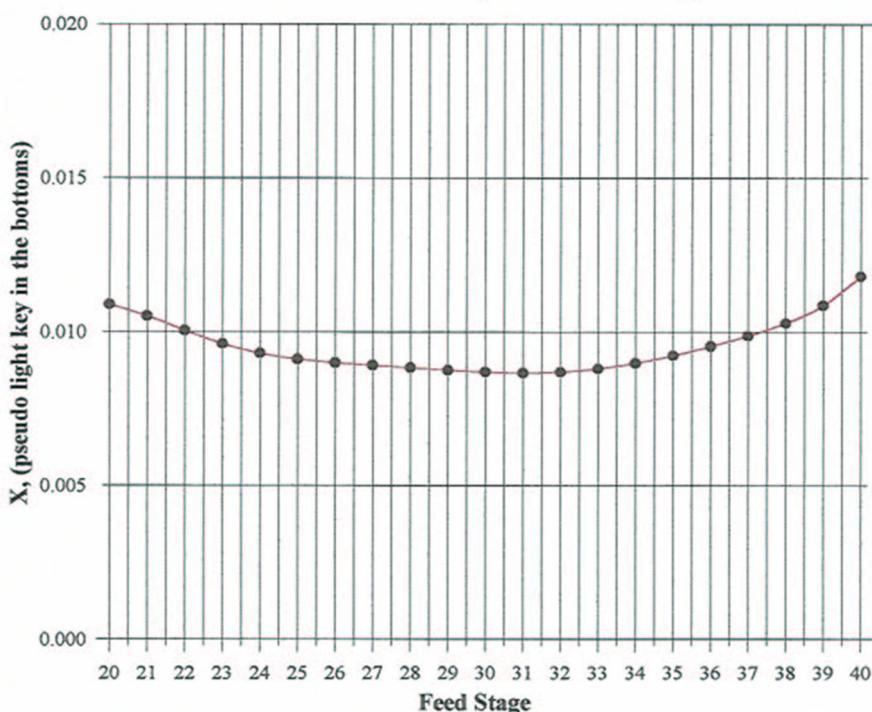


FIGURE 2
Ethylbenzene Column Simulation Comparison

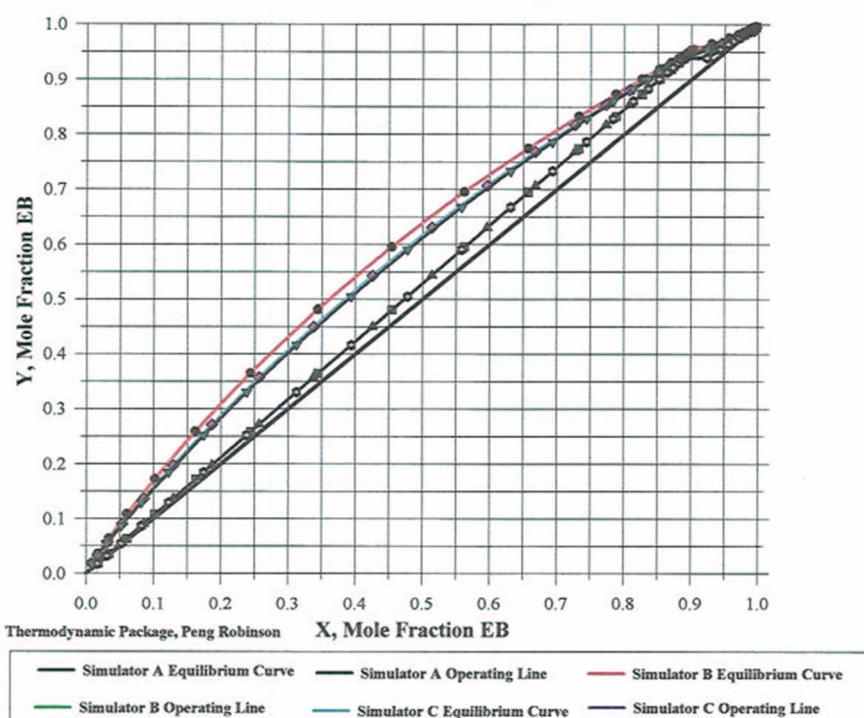


FIGURE 3
Ethylbenzene Column Simulation Comparsion

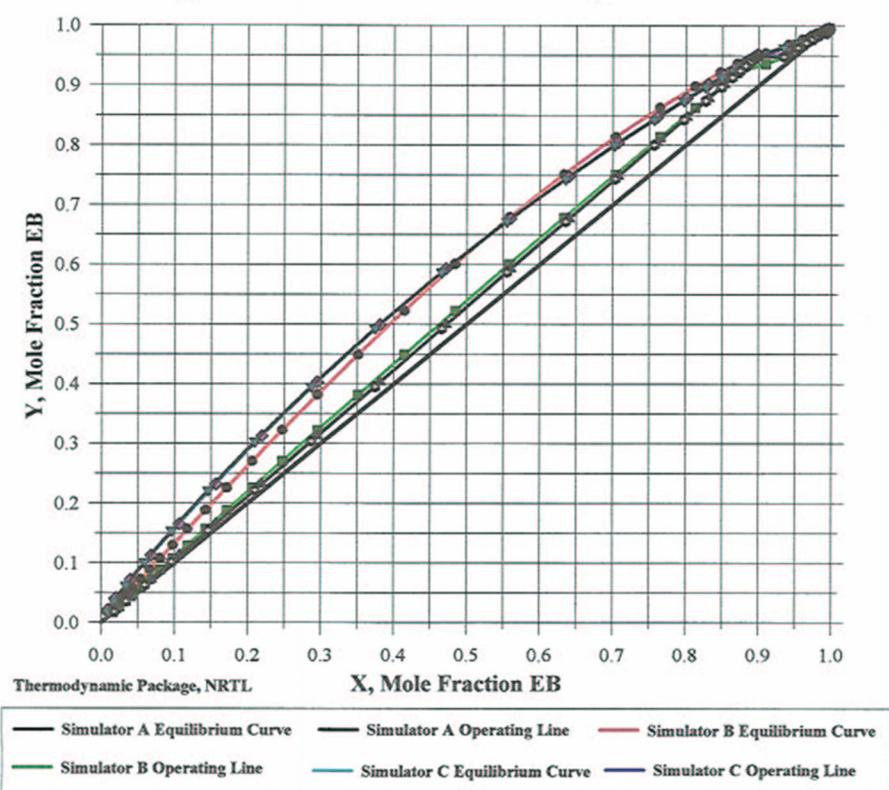


FIGURE 4
Ethylbenzene Column Simulation Comparsion

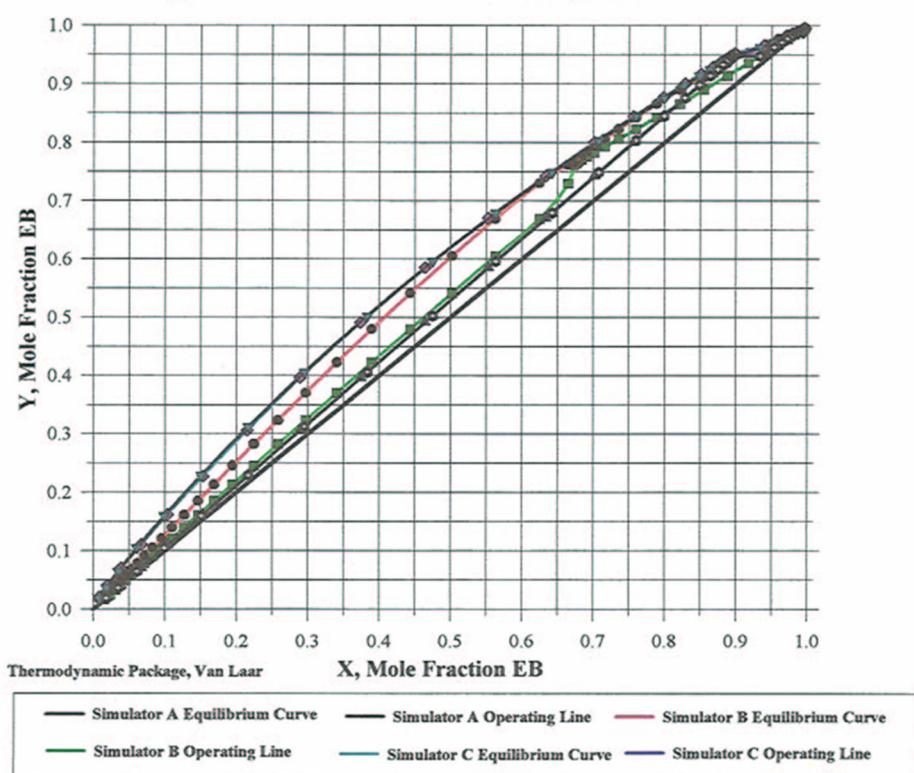


FIGURE 5
Ethylbenzene Column Simulation Comparsion

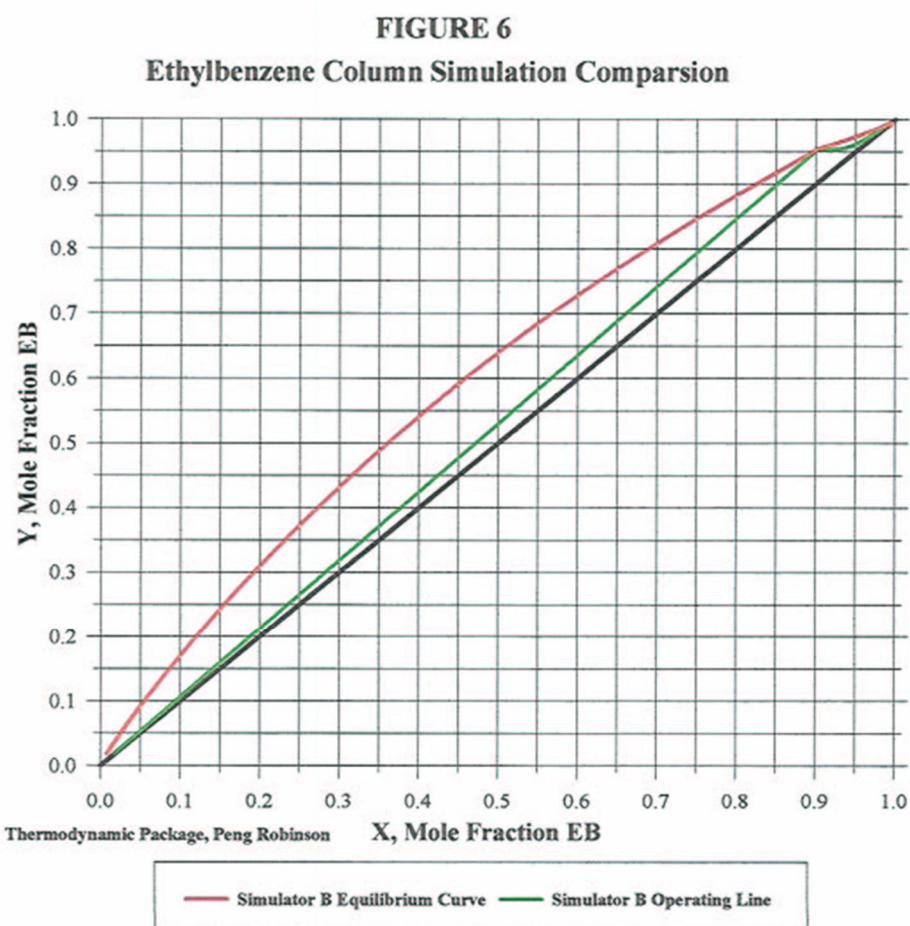
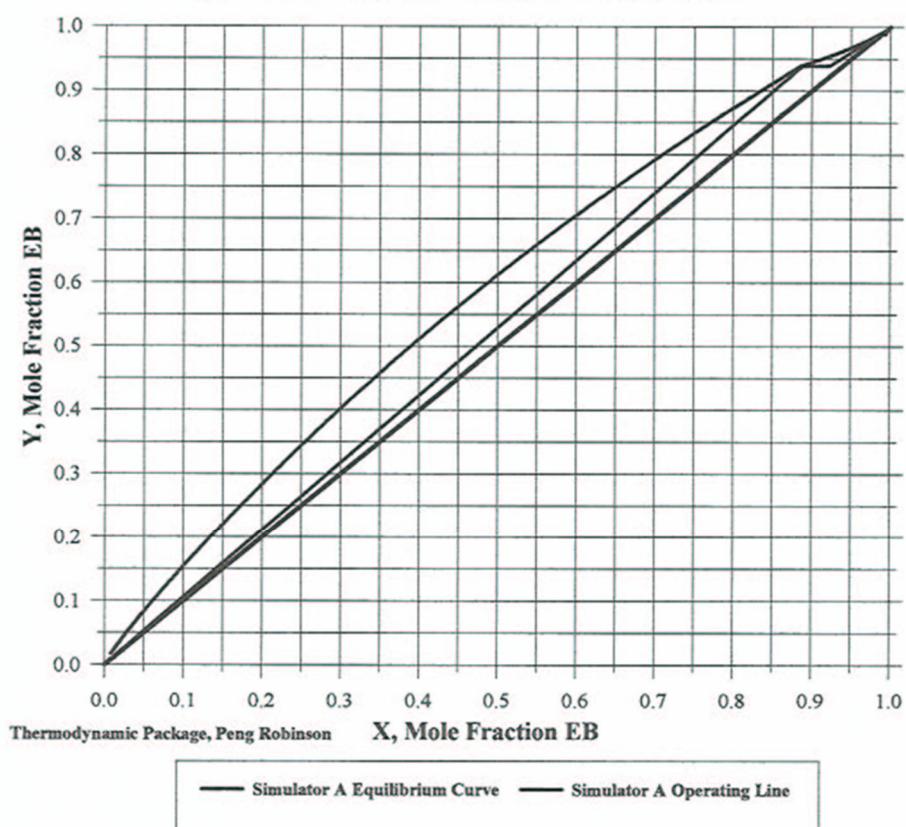


FIGURE 7
Ethylbenzene Column Simulation Comparsion

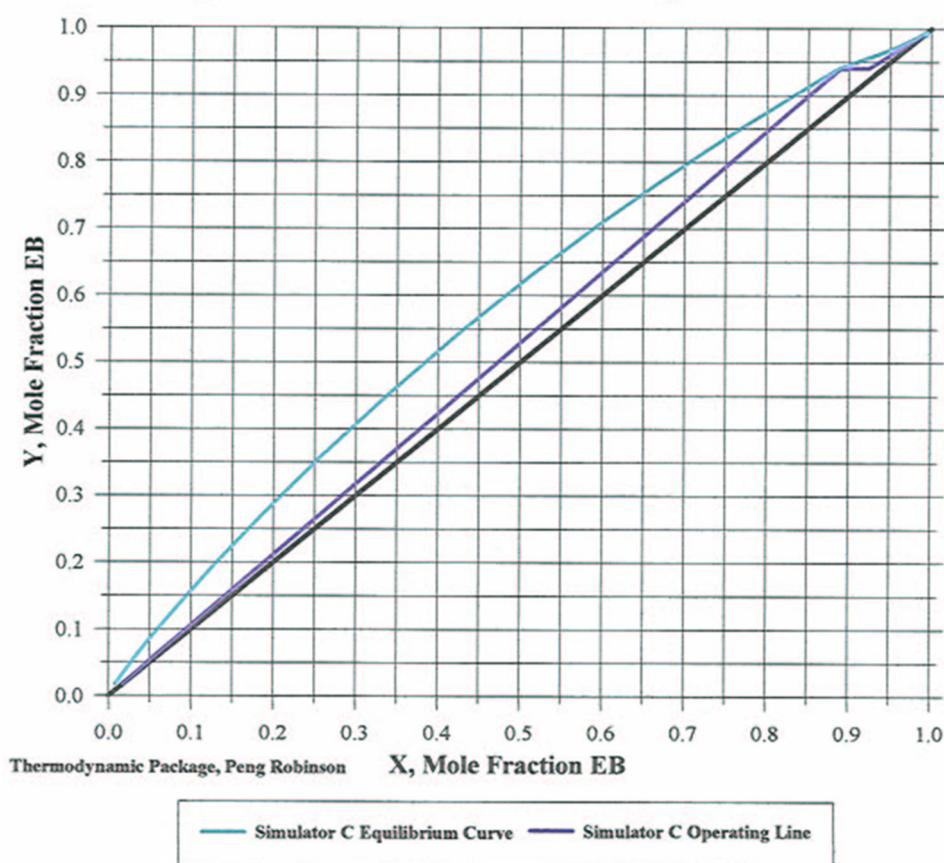


FIGURE 8
Ethylbenzene Column Simulation Comparsion

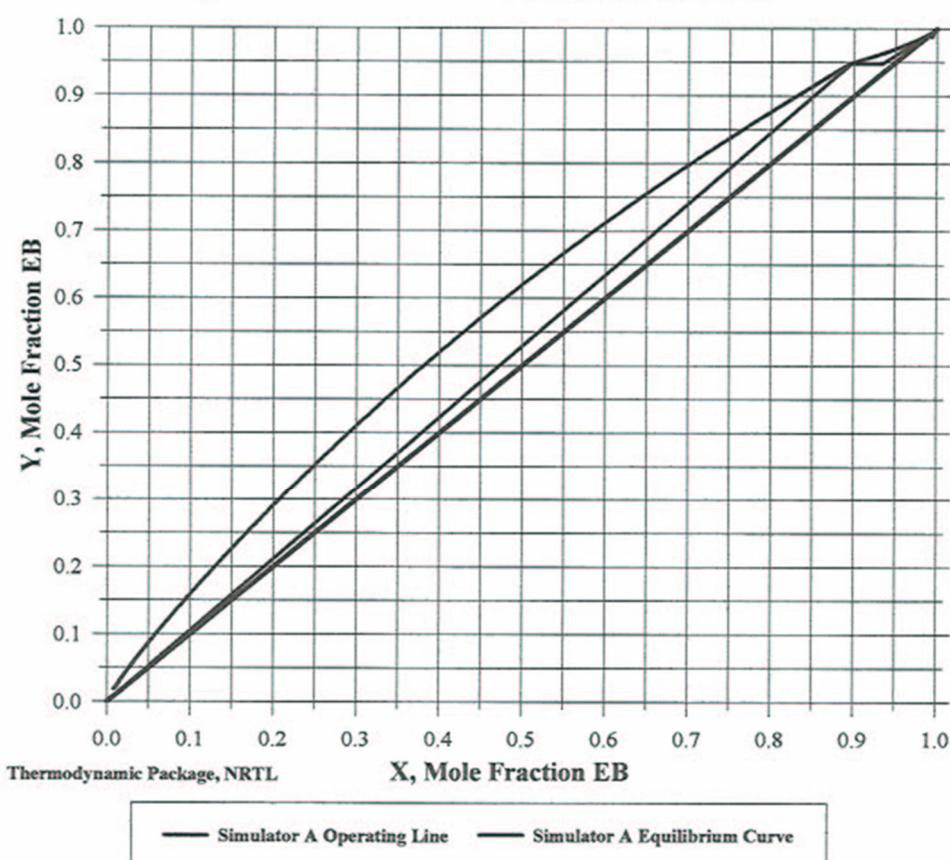


FIGURE 9
Ethylbenzene Column Simulation Comparsion

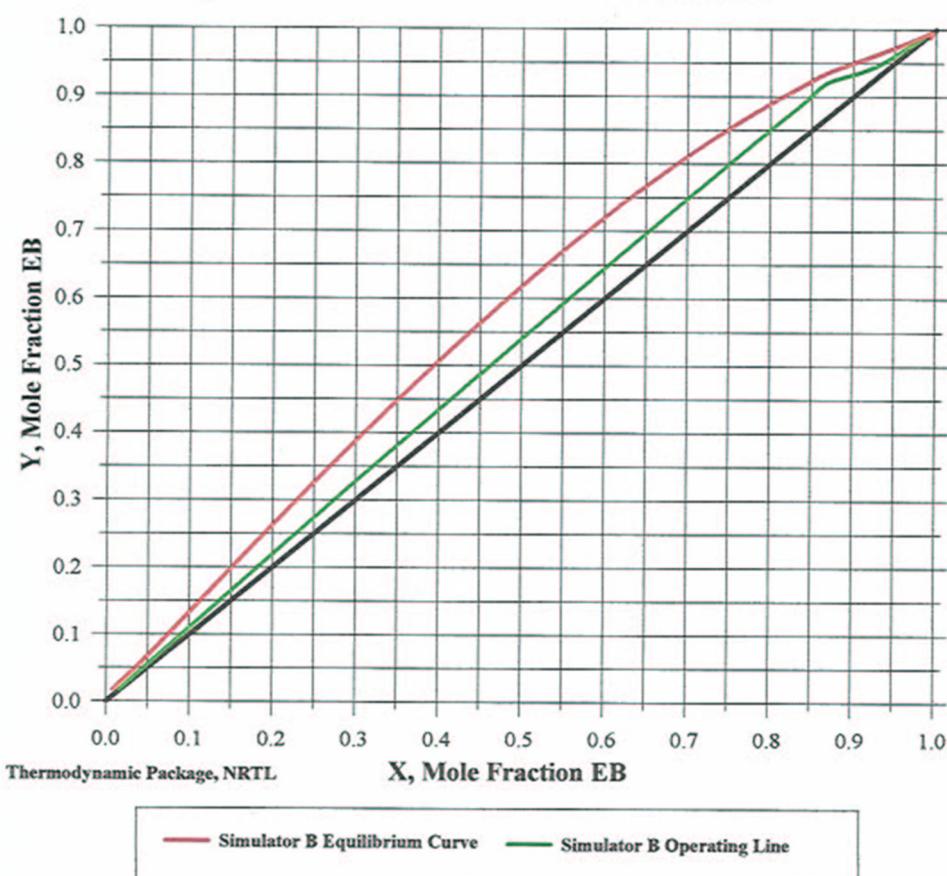


FIGURE 10
Ethylbenzene Column Simulation Comparsion

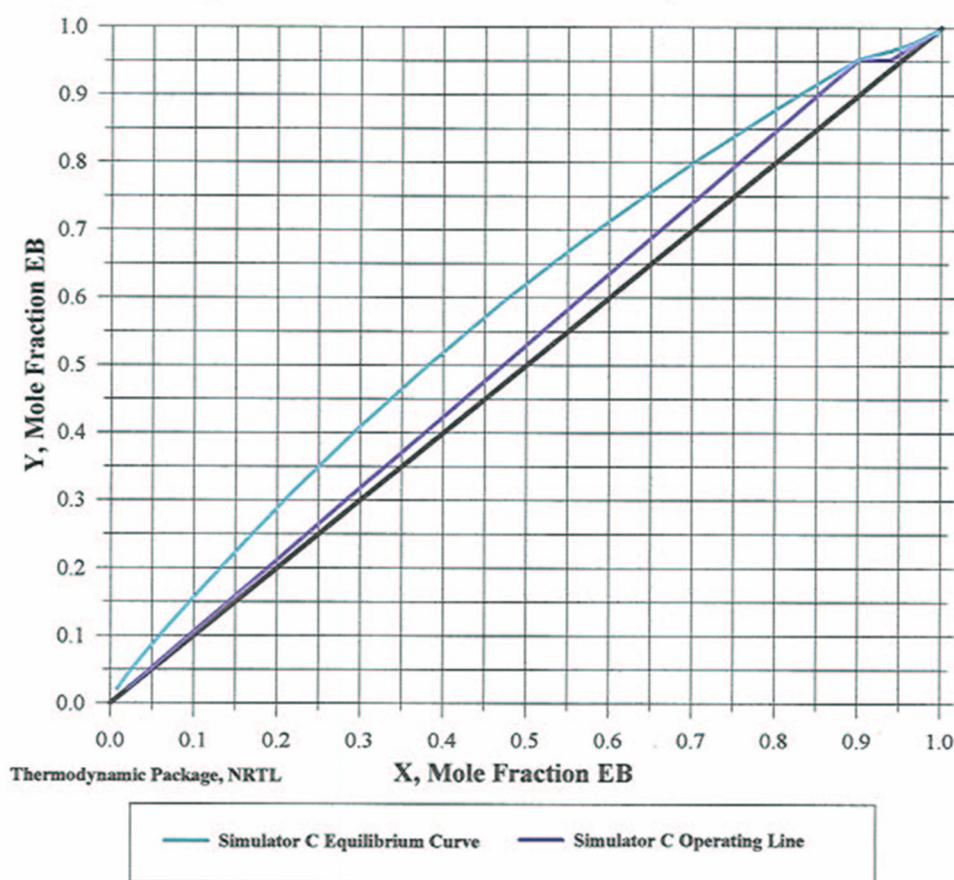


FIGURE 11
Ethylbenzene Column Simulation Comparsion

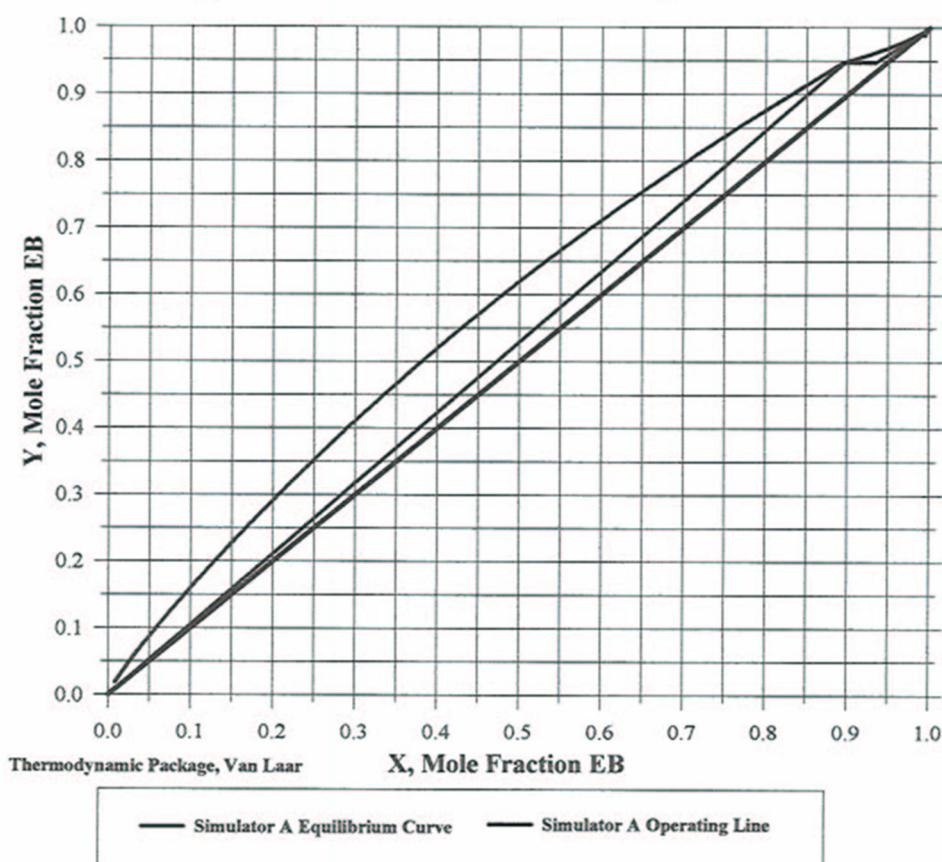


FIGURE 12
Ethylbenzene Column Simulation Comparsion

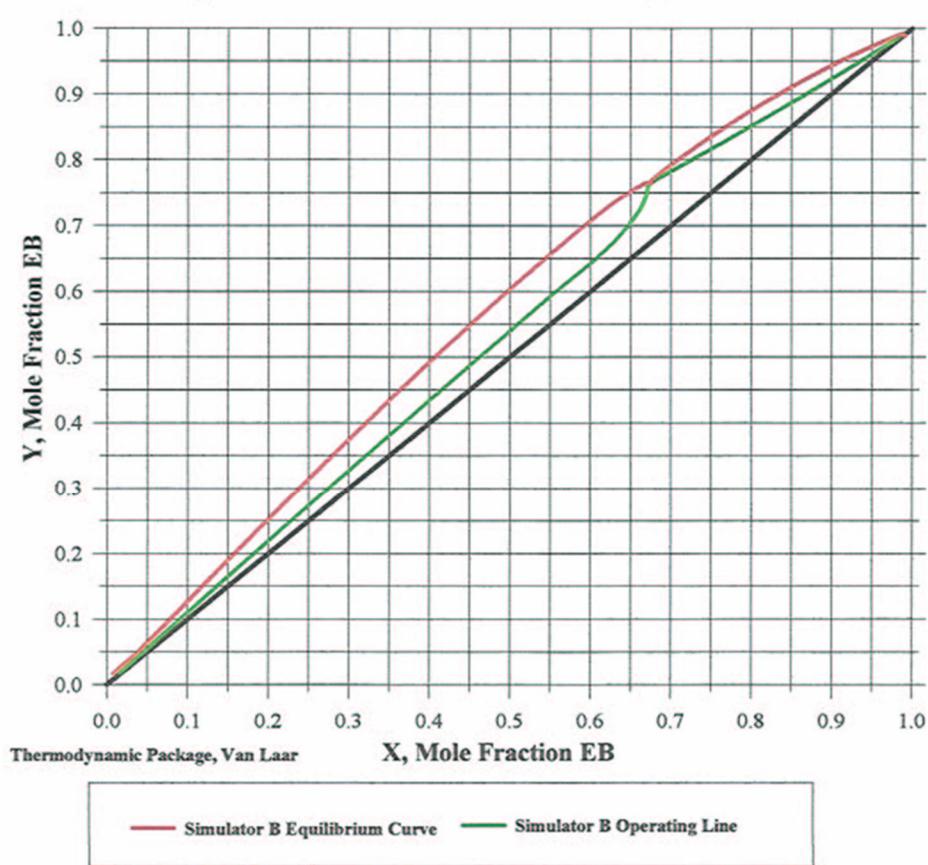
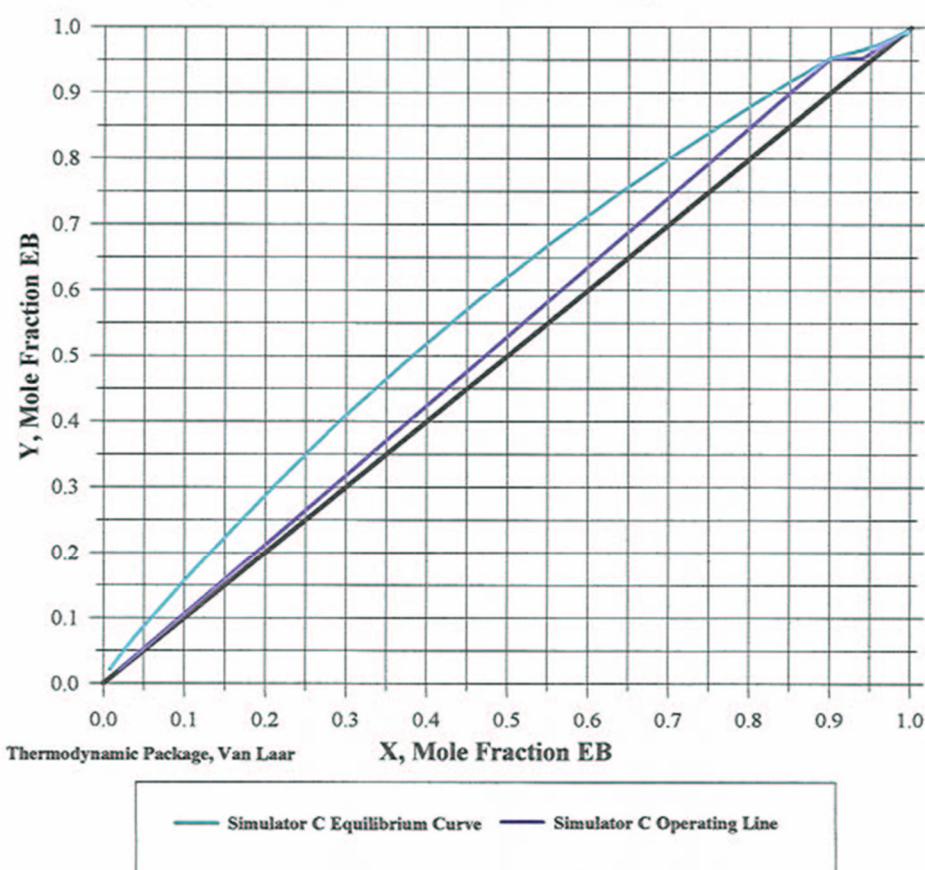


FIGURE 13
Ethylbenzene Column Simulation Comparsion



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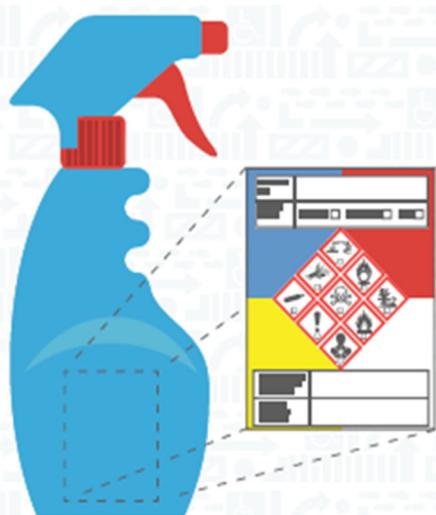
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Gas Condensate Separation Stages – Design & Optimization

Jayanthi Vijay Sarathy

The life cycle of an oil & gas venture begins at the wellhead where subsurface engineers work their way through surveying, drilling, laying production tubing and well completions. Once a well is completed, gathering lines from each well is laid to gather hydrocarbons and transported via a main trunk line to a gas oil separation unit (GOSP) to be processed further to enhance their product value for sales. Gas condensate wells consist of natural gas which is rich in heavier hydrocarbons that are recovered as liquids in separators in field facilities or gas-oil separation plants (GOSP).

The following tutorial is aimed at demonstrating how to optimize and provide the required number of separation stages to process a gas condensate mixture and separate them into their respective vapour phase and liquid phase – termed as “Stage Separation”. Stage separation consists of laying a series of separators which operate at consecutive lower pressures to strip out vapours from the well liquids & resulting in a stabilized liquid. Prior to any hydrocarbon processing in a gas processing plant or a refinery, it is imperative to maximize the liquid recovery as well as provide a stabilized liquid hydrocarbon. A schematic of a 2-Stage Separation Unit is as follows,

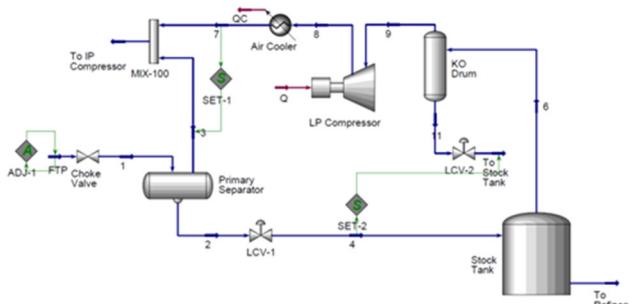


Figure 1. Two Stage Separation

A schematic of a 3-Stage Separation Unit is as follows,

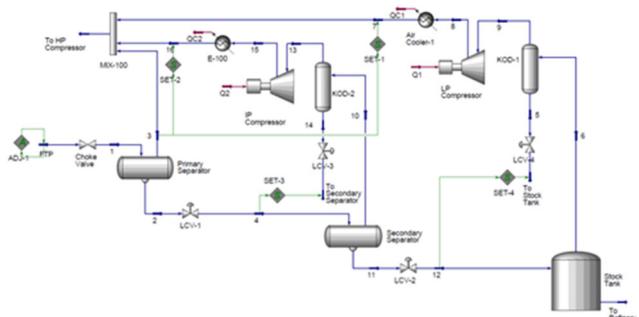


Figure 2. Three Stage Separation

General Notes

1. Stage Separation consists of series of separators which flash the incoming well fluids consisting of gas, oil and water into their respective constituents. The oil/condensates exiting the separation vessel is eventually routed to a storage tank, a.k.a, Stock Tank which operates at atmospheric conditions. The liquid in the stock tank is in turn termed as stabilized crude. To increase vaporization, sometimes a heater is installed in the liquid side of the separation stages.
2. The art of flashing well fluids in successive separation stages to increase liquid yield is not linear but inversely proportional to the number of stages. Therefore, the liquid recovery with an extra stage to a single stage system can be substantial. However, adding an extra stage to more than three stages does not produce a significant yield in liquid quantities. In theory, as the number of separation stages increase, so will the liquid yield increase and the gas and liquid reach equilibrium. In practice, a three-stage separation process is very efficient and cost effective to arrive at a stabilized stock.
3. In terms of terminology, a 2-Stage separation system means one separator and an atmospheric storage tank (stock tank) because the storage tank also acts as a separator. Similarly, a 3-Stage separator consists of a two separators & a stock tank.

4. The number of stages required to provide a gas and liquid at equilibrium conditions, referred to as flashing can be estimated by empirical correlations or using Equation of state (EoS). In this tutorial, the method of EoS is used.
5. Separator calculations primarily consist of optimum separator pressure and temperature, Gas-Oil Ratio (GOR), API Gravity of the Stock Tank Oil, Oil formation factor (a.k.a Formation Volume Factor, FVF/Bo) and the respective compositions.
6. The key to selecting the optimum number of stages is based on, Minimum GOR, Maximum API gravity & Minimum Oil FVF.
7. Minimum GOR implies maximum liquid yield. GOR is termed as the cumulative gas flow from all the separators including the stock tank divided by the amount of oil/condensate exiting the stock tank. Higher API gravity implies, higher is the commercial value of the oil/condensate. Oil FVF can be defined as the volume of reservoir fluid required to produce a barrel of stock tank oil. Therefore, lower Oil FVF implies more stock tank oil for a given volume of reservoir fluids. Oil FVF values typically range between 1 bbl/STB to 3 bbl/STB.
8. Since the process conditions of the stock tank are already fixed to be at atmospheric conditions while the primary separator is determined by the operating conditions required to avoid inhibiting well production, the only control had, are the operating pressures in the intermediate stages. Therefore, the intermediate pressure is controlled to optimize and obtain the highest amount of liquid yield.
9. 2-Stage separation is applicable for low GOR, low API gravity oils & low flowing tubing pressure (FTP) wells. 3-Stage Separation is for intermediate GOR, intermediate API gravity oils & intermediate FTP wells. 4-Stage Separation is for high GOR, high API gravity oils & high FTP wells.
10. Separation vessels also consist of gas control valve on the gas side which also serve the purpose of controlling the wellhead back pressure.
11. For effective operation, minimizing energy & costs, the primary separator pressure should be lower than the Wellhead FTP and higher than the gas pipeline export pressure. Failure to keep the primary separator pressure higher than the pipeline pressure would require the installation of gas compressors to boost gas pressure to export requirements.

Case Study

A Gas-Condensate well with an FTP of 14.48 bara [210 psia], 450C and liquid fraction of 1.0, flows to a gas oil separation unit at a production rate of 78,295 STBPD [533.3 Am3/h].

Assumptions

1. The stock tank pressure & temperature is constant at atmospheric conditions and weather remains unchanged.
2. The composition of the well fluids is taken to be constant for a given FTP.
3. Both Gas and liquid are assumed to be at complete equilibrium upon flashing.
4. The well fluids composition is chosen to be free from H2S, CO2, N2 and produced water. Presence of water would require a 3-phase separator. For this tutorial, a 2-Phase separator is used considering only gas and condensate.

The gas condensate composition is as follows,

Table 1. Gas Condensate Composition

Components	Mole Fraction	Units
Hydrogen Sulphide [H ₂ S]	0.0000	-
Carbon Dioxide [CO ₂]	0.0000	-
Nitrogen [N ₂]	0.0000	-
Methane [C ₁]	0.0385	-
Ethane [C ₂]	0.0391	-
Propane [C ₃]	0.0516	-
iso-Butane [iC ₄]	0.0145	-
n-Butane [nC ₄]	0.0575	-
Iso-Pentane [iC ₅]	0.0231	-
n-Pentane [nC ₅]	0.0346	-
n-Hexane [C ₆]	0.0491	-
Heptane Plus [C ₇₊]	0.6920	-
Total	1.0000	-
Heptane Plus [C ₇₊] SG	0.8576	
Heptane Plus [C ₇₊] MW	227	lb/lbmole

Methodology

The number of separators can be chosen by first arriving at a preliminary pressure estimate based on equal pressure ratio as,

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

Where,

$P_{primary}$ = Primary Separator Pressure [bara]

P_{Stock} = Stock Tank Pressure [bara]

n = Number of stages [-]

X = Maximum number of Stages [-]

Rewriting the expression,

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

$$n = \frac{\ln \left[\frac{P_{primary}}{P_{Stock}} \right]}{\ln X} \quad (3)$$

Or, The separation ratio is computed as,

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

The intermediate pressure is computed as,

$$P_i = \frac{P_{primary}}{R^i} \quad (5)$$

Where,

P_i = Intermediate Pressure at Stage ' i '

Therefore, considering a maximum number of stages of 3, with the well fluids data, for a two-stage separation unit, the primary separator pressure [P_1] and Separation ratio [R] is,

$$n = \frac{\ln \left[\frac{14.48}{1.01325} \right]}{\ln [3]} = 2.42 \sim 2 \text{ Stages} \quad (6)$$

$$R = \left[\frac{14.48}{1.01325} \right]^{1/2} = 3.7801 \quad (7)$$

$$P_1 = \frac{14.48}{3.7801} = 3.831 \text{ bara} \quad (8)$$

The stock tank becomes the second stage, and the operating pressure is $P_2 = 1.01325$ bara.

For a three-stage separation unit, the primary separator pressure [P_1] and secondary separator pressure [P_2] is,

$$R = \left[\frac{14.48}{1.01325} \right]^{1/3} = 2.4266 \quad (9)$$

$$P_1 = \frac{14.48}{2.4266} = 5.968 \text{ bara} \quad (10)$$

$$P_2 = \frac{14.48}{2.4266^2} = 2.459 \text{ bara} \quad (11)$$

The stock tank becomes the third stage, and the operating pressure is $P_3 = 1.01325$ bara.

Using these preliminary stage pressures, a vapour-liquid equilibrium (VLE) flash

Calculation can be performed to estimate GOR, API gravity and Oil FVF. For this tutorial, the Peng Robinson EoS is chosen. To arrive at the final separator pressures, the following iterative procedure is adopted.

1. Keeping all preliminary estimated pressures fixed, the primary separator pressure is varied for a pressure range to obtain GOR, Oil FVF & API gravity. Making a plot of the above values, the separator pressure corresponding to Min GOR, Max API gravity & Min FVF is chosen [1st Iteration of 1st Stage].
2. The primary separator initial estimate pressure is now replaced with the 1st Iteration's optimized pressure. Following further, the secondary separator pressure is also varied for a given range to similarly obtain an optimized pressure corresponding to Min GOR, Max API gravity & Min Oil FVF [1st Iteration of 2nd stage].
3. The secondary separator initial estimate pressure is now replaced with the optimized value, [1st Iteration of 2nd stage].
4. With the 1st iteration optimized pressures, flash calculations are repeated similar to Step 2 and Step 3, i.e., 2nd Iteration and so forth, until a converged solution is reached.

Results

With the flash procedure applied for the calculated initial estimates, the results of 2-Stage Separation and 3-Stage Separation for a compressor polytropic efficiency of 82% are,

Table 2. Separation Stage Pressures

Stages	Operating Pressure	Compressor Power
-	[bara]	[kW]
2-Stage Separation [Liquid Rate = 75,235 STBD]		
FTP	14.48	
Primary Separator	2.60	83.04
Stock Tank	1.014	
3-Stage Separation [Liquid Rate = 75,430 STBD]		
FTP	14.48	
Primary Separator	3.90	71.47
Secondary Separator	1.70	65.32
Stock Tank	1.014	

From the results between the 2-Stage and 3-Stage separation, the liquid yield increased by 195 STBD, i.e., 0.26%. The GOR, Oil FVF and API gravity for the separation stages are also tabulated below. Between both cases, the GOR decreases from 90.77 scf/STB to 86.68 scf/STB. API gravity increases from 37.93 to 38.08. The Oil FVF decreases from 1.0466 m³/m³ to 1.0435 m³/m³.

Table 3. GOR, Oil FVF and API Gravity

Stages	GOR	Oil FVF	API Gravity
-	[scf/STB]	[m ³ /m ³]	[°API]
2	90.77	1.0466	37.93
3	86.68	1.0435	38.08

The plots of Total GOR, API Gravity & Oil FVF for two stage design and three stage design are as follows,

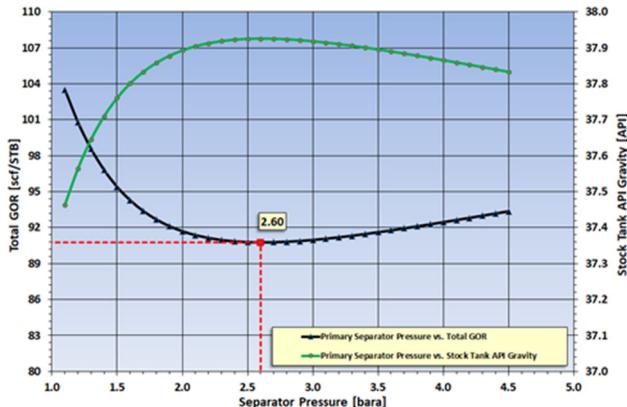


Figure 3. Two Stages – GOR & API Gravity

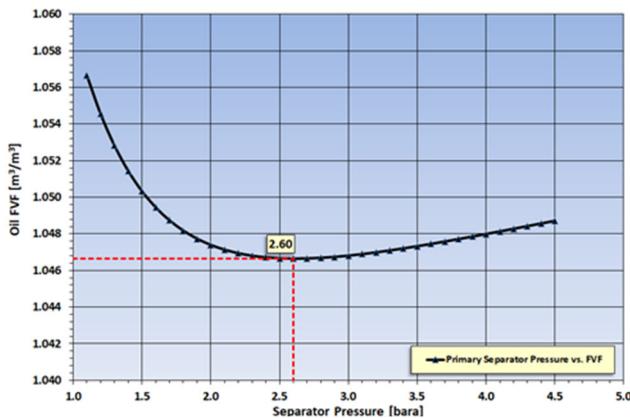


Figure 4. Two Stages – Oil FVF

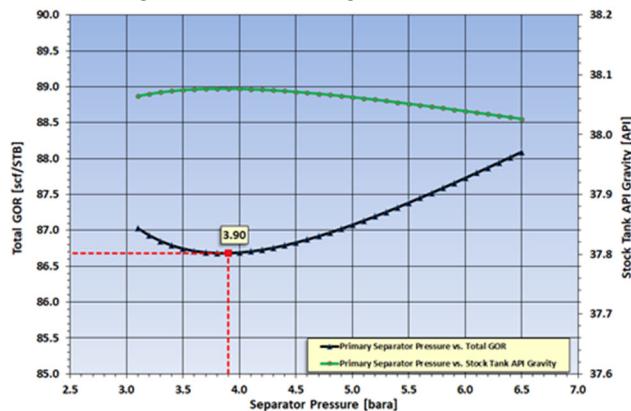


Figure 5. Three Stages – Primary GOR & API Gravity

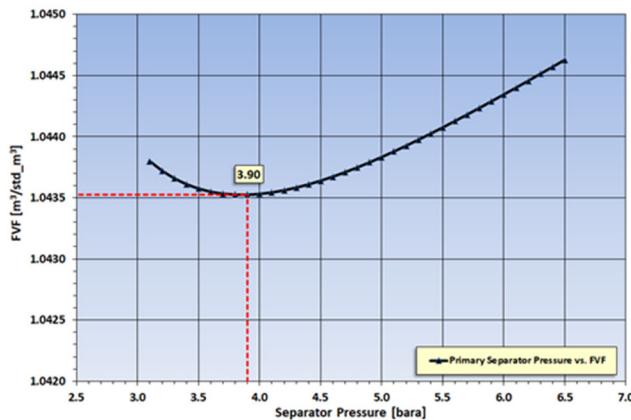


Figure 6. Three Stages – Primary Oil FVF

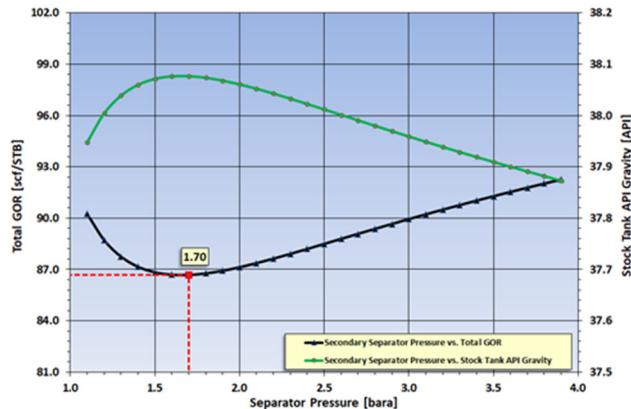
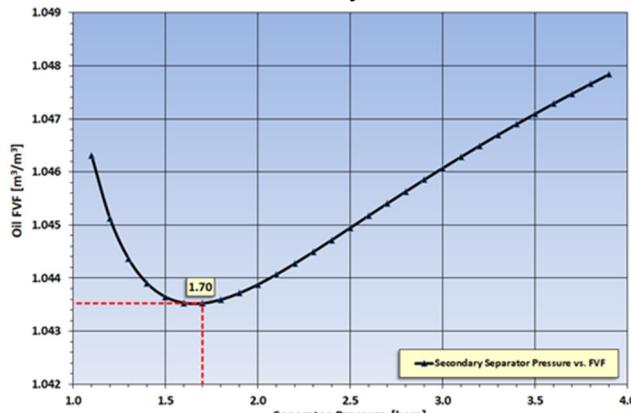


Figure 7. Three Stages – Sec. GOR & API Gravity



CONCLUSIONS

From the calculations made, a three-phase separator offers the advantage of higher liquid yield. The Gas-Oil Ratio (GOR) can also be decreased which allows to recover more liquids and thereby offering higher commercial value. Although a 4th stage can be added to increase liquid yield, since well pressures are low at ~15 bara, 3 stages would suffice. It is also seen that with increase in number of stages, the LP compressor power requirements also decreases.

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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 12 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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Guidelines for Alarm Identification Methods & Training Content for Alarm Management Systems

Praveen Nagenderan C

ALARM IDENTIFICATION METHODS

Alarms may be identified by a range of good engineering practices or regulatory requirements. Some combination of identification methods can also be used to determine potential alarms.

- Below are recommended identification methods to be used to determine alarm:

- Process Hazard Analysis (PHA)
- Hazard and Operability Study (HAZOP)
- Layer of Protection Analysis (LOPA)
- Root Cause Failure Analysis (RCFA)
- Failure Mode and Effect Analysis (FMEA)
- Risk Assessments
- Incident Investigation Recommendations
- Operating Procedure Review
- Piping and Instrumentation Diagram (P&ID)
- Development and Review
- Process Modifications
- Safe Operating Limits
- National and International Standards and
- Regulations
- Technical Literature
- Project Documentation (or) Basic Design
- Engineering Packages
- Manufacturers/Vendor recommendation
- Packaged Equipment Manufacturers
- Recommendations
- Company Policy
- Environmental Limits
- Quality Review

- Generally, below mentioned cases shall not be considered as an alarm:
 - Signals without a defined operator response

- Process variable or plant status changes that
- Do not require operator attention
- Events that are recorded in an alarm/ event log, but which operator does not need to see
- Signals which confirm successful operator action
- Signals which duplicate another alarm
- Generally, setpoint can be determined by
 - Allowable Response Time
 - Complexity of the operator response
 - Time necessary to complete operator action
 - Normal operating range
 - Operating or Design Boundaries
 - Knowledge of process operation or history
- Any new alarm requirement raised should be from the recommendations of any one of the above-mentioned alarm identification methods.
- Identification method for the new alarm to be mentioned in the “Request form”.
- Identified new alarms will have to go through the Alarm Rationalization process for incorporation.
- System/Instrument Engineer is responsible for incorporating new alarm in the system as per the request form.
- Production operations team to mention required alarm attributes in the request form for incorporation.
- Any new alarm requirement outside the recommended alarm identification methods shall not be taken up for implementation by System/Instrument Engineer.
- Any Alarm set point to be changed shall go through the rationalization process and determination of the setpoint method to be mentioned in the request form by the Production operations team for incorporation in the system by System/Instrument

Engineer.

- Any alarm to be removed from the system shall go through the rationalization process, and rationale for removal to be mentioned in the request form by the Production operations team for removal from the system by System/Instrument Engineer.
- System/Instrument Engineer to update master alarm database summary list upon any inclusion or modification, including new alarm point addition in the system or removal from the system or any setpoint changes.

TRAINING CONTENT

Training shall be conducted for all direct and indirect user department personnel to familiarize the facilities alarm system functions and management. Every person working in the direct and indirect user departments shall undergo training every year. Training content is as mentioned below:

- Familiarization of Alarm management philosophy
- Alarm Rationalization
- Alarm Master Database document
- Details about Key Performance Indicators of Alarm system
- Alarm system performance monitoring methods and reporting
- Change process for Alarm set point
- Use, designation, and distinction of Alarm Priority
- Change process and request process for addition/removal of alarm or changes in alarm attributes
- Features of the control system's alarm presentation, annunciation, and management
- Permissible and Non-permissible changes to the alarm system by operations personnel's
- Usage of Advanced Alarm handling strategies
- Procedures regarding handling and reporting of nuisance alarms
- Methods for silencing and acknowledging an alarm
- Usage of alarm HMI features
- Methods for alarm shelving and suppression
- Methods for removing alarm from service

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Praveen Nagenderan C is a Chemical Engineer with experience in the field of Oil & Gas production & processing facilities and Refinery process units. Professional experience covers Production operations, Facility surveillance, Technical safety, Technical Services - Process, and Projects. Praveen has worked with major Oil & Gas companies in India, namely Nayara Energy, formerly known as Essar Oil Limited and Cairn Oil & Gas.

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Design Guidelines for Chemical Treatment Distillation Columns

Karl Kolmetz



INTRODUCTION

Distillation is the application and removal of heat to separate hydrocarbons by their relative volatility or boiling points. This necessary addition of heat normally in the feed stream or at the tower bottoms via a re-boiler can also lead to unwanted consequences such as polymerization, corrosion and reverse solubility. The removal of heat can lead to sedimentation, solubility effects, corrosion and precipitation. The concentration of certain constituents by the distillation process can cause corrosion, polymerization, sediment fouling and flow phenomena effects. A properly designed distillation column can reduce the effects of these consequences, but in certain applications the polymerization, corrosion and other effects are very prominent leading to reduced separation efficiency in the column. This reduced separation efficiency increases the need for column maintenance and unit down time. In these applications a review of tower internal design and process chemical treatments should be initiated. Previously a review of tower internal design was published (1), whereas this article will discuss the application of chemical treatments in distillation columns.

DISTILLATION ECONOMICS OF FOULING

Distillation is the most widely utilized separation technique and there are basically two main types of chemical treatments in distillation columns; one is for corrosion control and the second is fouling control. Distillation can be utilized in very clean services such as ethylene fractionation which, might fractionate for greater than ten years with no loss in efficiency due to corrosion or fouling - to very highly corrosive and fouling services. In Butadiene distillation, which is a highly fouling application, some fractionation applications are measured in days. There are at least four types of chemical treatments in the process industry distillation

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

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

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

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

Reducing the corrosion and fouling of a distillation column will reduce turnaround frequency. In one case at an ethylene plant the DeEthanizer reboiler cleanings averaged 21 days, and with proper chemical treatments went to 8 months. The increased run length will reduce maintenance costs with the added benefit of reducing personnel exposure to carcinogenic chemicals found in fouling deposits while cleaning the tower or reboiler. Some species like butadiene and benzene have

been shown to be carcinogenic. The species can be released when cleaning the tower and reboilers leading to unnecessary exposure to personnel. This benefit extends beyond the typical return on investment.

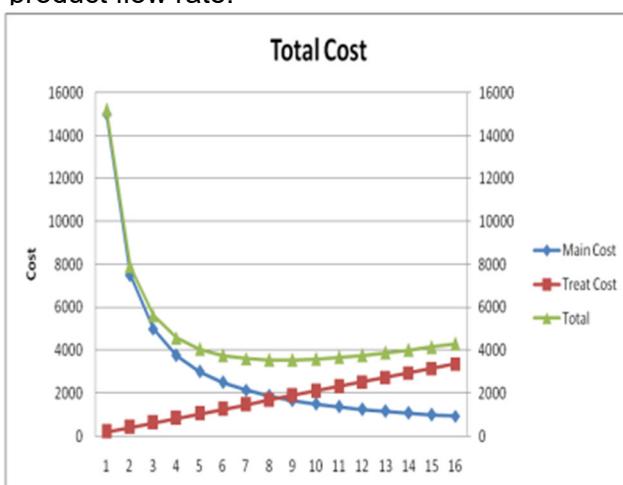
A typical return on investment for a chemical treatment programs should be 100%. If you extend your run length from one month to 8 months it can be as high as 1000%.

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

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

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

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



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

CORROSION CONTROL

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

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

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

Crude Distillation

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

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

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

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

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

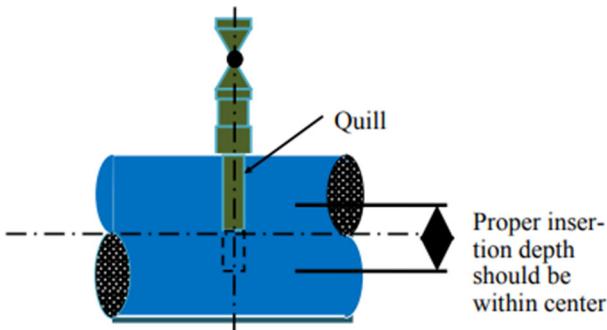
Refinery crude feeds contain water and inorganic salts (sodium, magnesium, and calcium chloride).

Hydrolysis of calcium and magnesium chlorides (MgCl_2 and CaCl_2) occurs when crude oil is heated in the pre-heat exchangers and fired heaters. (2) Many refiners inject caustic into the crude feed to the crude unit distillation tower to control condensation of hydrochloric acid downstream of the distillation tower in the overhead line. Caustic injection is carefully balanced with chloride levels measured in the overhead receiver.

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

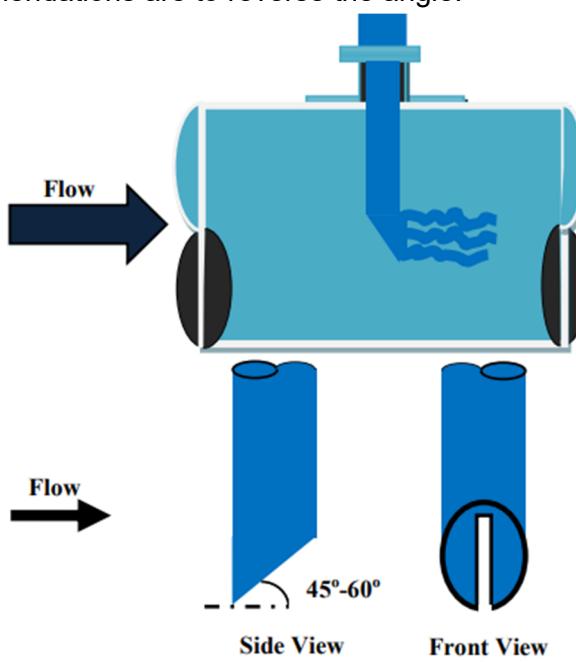
Caustic treatment has been ongoing for many years and the lessons learned from caustic

treatment can be applied to other types of chemical treatments. How the chemical treatment is introduced to the process is very important to the success of the treatment. A typical injection quill might look like the following example.

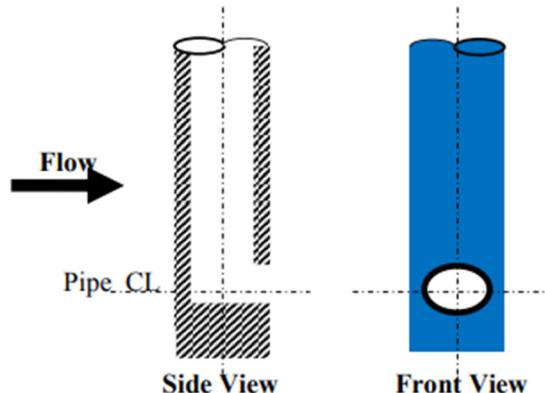


Generally, the most effective position for chemical injection is at the center of the pipe. The highest fluid velocity is normally at the center of the line, therefore, injection at this point is intended to prevent concentration of the chemical at the edge where the velocity is low due to friction and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

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



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



Naphthenic Acids in Crude and Vacuum Tower

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

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

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

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

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

Higher Levels of Organic Acids in Crude Unit Overhead Systems

Processing crudes high in calcium naphthenates, as with many high TAN (Total Acid Number) crude oils, can result in higher loadings of low molecular weight organic acids and CO₂ in the upper portions of the crude and vacuum columns and overhead condensing systems. The amount and distribution of lower molecular weight acids and CO₂ in these systems is a function of the distribution of organic acid molecular weights in the crude oil, plus heater outlet, side cut, and column overhead temperatures.

The higher loadings of organic acids and CO₂ in crude unit distillation towers and overheads from processing high TAN crude oils may cause higher than desired corrosion activity in these areas.

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

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

Increased High Temperature Naphthenic Acid Corrosion Activity

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

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

- The naphthenic acid content of the hydrocarbon streams, typically measured by TAN (mg KOH/gram sample). Naphthenic Acid based corrosion is either reduced or augmented depending on:
 - a. Wt. % sulfur
 - b. Whether TAN is high or low
 - c. Whether fluid phase is liquid or vapor
- The temperature of the metal surfaces being contacted by the corrosive hydrocarbons
 - a. Naphthenic acids concentrate above 260 C boiling range
 - b. Highest concentration in 316-427 C boiling range
 - c. Lowest temperature where attack occurs ~200 C (400 F)
 - d. Above 450 C (825 F) disintegrates into lower molecular weight acids
 - e. Naphthenic acids corrosion activity is often high in location where acids condense out of the vapour phase
- The shear stress of the hydrocarbon moving across the metal surface (a function of velocity and turbulence of the flowing stream)
 - a. At low velocity, acid concentration caused by boiling and condensing causes attack. Small erosion effect on corrosion if velocity is between 1.2-6.5 ft/sec. .
 - b. At high velocity, multiphase stream rapid corrosion can occur due to erosion-corrosion. Naphthenic acid corrosion is accelerated in furnaces and transfer lines where the velocity of the liquid/vapor phase is increased. High turbulence areas have severe corrosion.
 - c. Turbulence and cavitation in pumps may result in rapid attack
- The type of alloy in use where hydrocarbon TAN, surface temperature and shear stresses make the system susceptible to naphthenic acid corrosion attack
 - a. Metallurgy - 316SS, 317SS and materials with higher alloys (more molybdenum) are more resistant to naphthenic acid corrosion.

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

1. Are exposed to hydrocarbon fluids that contain corrosive levels of naphthenic acids (Generally considered to be any stream with TAN > 0.5 mg KOH/g, though lower thresholds apply in some cases)
2. Operate at temperatures of 220 – 400°C (425 – 750°F), and:
3. Are constructed with metallurgy not generally considered to be resistant to naphthenic acid corrosion attack. 316, 316L, 317 or 317 L stainless steels are generally considered to be resistant materials.

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

- Hot crude preheat exchanger network
- Atmospheric heater tubes
- Atmospheric tower transfer line
- Lower section of atmospheric tower (lining, trays) and associated atmospheric gas oil (AGO) pump around/product draw system
- Atmospheric tower bottoms line and any bottoms heat exchangers (if not integrated with vacuum unit)
- Vacuum heater tubes
- Vacuum tower transfer line
- Vacuum tower (lining, trays, packing) and associated LVGO, and HVGO pump around/product draw systems
- Vacuum tower over flash draw and “pump back” lines and associated equipment
- Vacuum tower bottoms line and heat exchangers

Other areas of the unit may also be susceptible depending on crude blend properties, unit design, operating conditions and actual materials of construction. One of the greatest concerns refiners face when processing high TAN crudes is the potential for high temperature naphthenic acid corrosion attack. However, years of experience in this area have yielded several strategies that can be implemented to identify susceptible areas of the unit, to successfully mitigate naphthenic acid corrosion, and to effectively monitor this type of corrosion activity.

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

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

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

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

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

Fouling Control

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

The column operating temperature affects fouling rates. In a refinery the crude unit and hydrotreater units might have towers that run under a vacuum to reduce the bottoms operating temperature to reduce fouling and product degradation. In an ethylene unit a DePropanizer tower might have the overhead

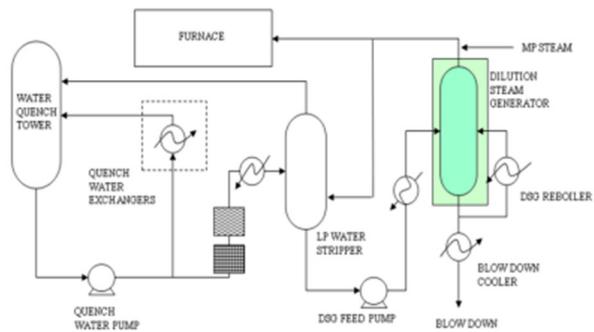
cooling be refrigeration to reduce the tower bottom temperature. The goal would be to operate the column below the fouling initiation temperature of the contained fouling species.

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

Olefin and Diene Polymerization in Ethylene Units

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

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



Olefin Unit Distillation

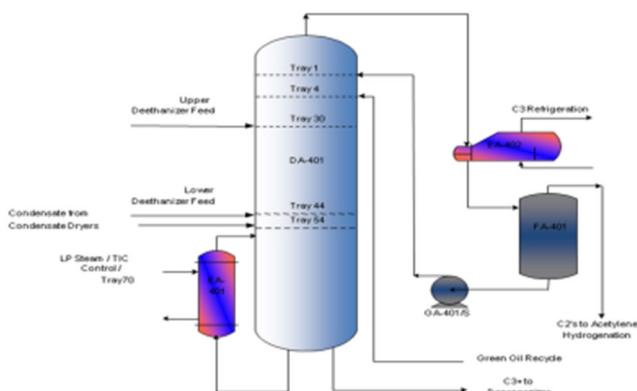
Olefin unit distillation is a series of tower separating the species. Each olefin vendor has their preferred flow sequence. Some will have the DeMethanizer first and some will have the DePropanizer first.

DeMethanizers

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

DeEthanizers

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



DePropanizers

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

polymerization potential. Some designs utilize a single DePropanizer that has refrigeration in the overhead to reduce the polymerization potential.

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

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

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

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

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

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

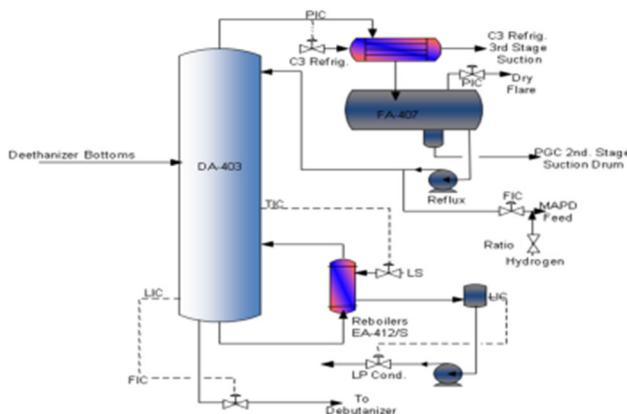


DeButanizers

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

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

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



As the tray efficiency decreases the fouling species travels down the column and fouls the trays and reboiler. The tray efficiency guideline is important to review during start up and low feed rate scenarios. Monitor the tower bottoms chemical treatment during start up and other non routine scenarios to insure the higher temperature of the tower bottoms is protected from fouling during these events.

Butadiene fouling in an overhead condenser



Styrene Applications

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

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

Radial Bed Reactor Overview

The feedstock, ethylbenzene, is catalytically dehydrogenated to styrene in the presence of steam in a fixed bed, radial flow reactor system. The dehydrogenation reaction is favoured by low pressures and is generally conducted under deep vacuum. Toluene, benzene, and some light compounds are formed as by-products. The overall reaction is endothermic with heat supplied by steam in the adiabatic

reactors. Reactor effluent waste heat is recovered through heat exchange with combined feed and by generating steam which is utilized in the process. The off gas stream is compressed, processed through the off gas recovery section, and used as fuel in the steam super heater. The condensates from the condenser and off gas recovery section flow into the separator where hydrocarbon and water phases separate. The dehydrogenated mixture is fractionated to recover the styrene monomer product and recycle ethylbenzene, as well as benzene and toluene by-products. Inhibitors are added to prevent styrene polymerization in the process equipment.

The energy needed for the reaction is supplied by superheated steam (at about 720 °C) that is injected into a vertically mounted fixed bed catalytic reactor with vaporized ethylbenzene. The catalyst is iron oxide based and contains Cr₂O₃ and a potassium compound (KOH or K₂CO₃) which act as reaction promoters. Typically, 2.5-3 kg steam is required for each kilogram of ethylbenzene to ensure sufficiently high temperatures throughout the reactor. The superheated steam supplies the necessary reaction temperature of 550-620 °C throughout the reactor. The ethylbenzene conversion is typically 60- 65%. Styrene selectivity is greater than 90%. The three significant by-products are toluene, benzene, and hydrogen. Styrene Distillation Overview After the reaction, the products are cooled rapidly (perhaps even quenched) to prevent polymerization. The product stream (containing styrene, toluene, benzene, and un-reacted ethylbenzene) is fractionally condensed after the hydrogen is flashed from the stream. The hydrogen from the reaction is used as fuel to heat the steam (boiler fuel).

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

EB / SM Splitter Column

The purpose of an ethyl benzene (EB) / styrene splitter is to separate ethyl benzene from styrene. The distillate EB is recycled to Styrene reactors and the bottom product Styrene Monomer (SM) is sent to the Styrene

Finishing column for heavy key removal. The EB impurity in the SM should be in the range of 100 ~ 500 ppm.

EB/SM Splitters are operated under vacuum due to the polymerization potential of styrene at elevated temperature. Polymers are undesirable in the monomer distillation column and can lead to plugging of distributors or packing and unit outages. The rate of polymerization is directly proportional to time and increases exponentially with temperature. Both residence time and temperate must be minimized to reduce polymerization deposits. Current guideline is to keep the tower bottoms temperature below 120°C.

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

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

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

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

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

Several high temperature commodity chemicals exist and function as retarders such as dinitrophenols, phenylenediamine, and hydroxylamines. They include DNP (Di-Nitrophenolic), DNBP (2-Sec-butyl4,6-dinitrophenol), DNPC, and dinitrocresol

(DNC) compounds, which again has environmental and safety concerns, but they are less than TBC. A challenge of the nitrogen based inhibitors is that the tar residual is sometimes burned as fuel. These nitrogen based inhibitors can produce NOx as they are combusted.

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

The retarder acts as a safety net for an extended tower outage. Retarders have slower reaction rates to inhibit the polymerization. They react at 103 to 105 ranges providing extended protection during power failures. The retarder can be recycled for extended usage. A normal retarder dosage might be to maintain 400 to 600 ppm in the recycle stream. True inhibitors have very fast reaction rates to inhibit the polymerization rates. An example would be nitroxyl stable free radical. A true inhibitor tends to react in the 107 to 108 ranges and typically only provides a few hours of protection.

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

CONCLUSIONS

Proper chemical treatment in distillation systems involves understanding distillation principles such as residence time, internal vapor and liquid flows, reboiler design and the chemistry of the process. Economics of chemical treatments and other engineering projects are very important and should be calculated for each application and project. Sometime the actual calculation will surprise you by being not what you expect. A successful application of chemical treatment must include how the chemical is added to the process and potentially removed. Chemical treatments need to be reviewed on several levels including corrosion or fouling abatement within economic and environmental constraints.

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Adding Value to High Sulfur Crude Oil Reserves – Deep Hydroprocessing Technologies

Dr. Marcio Wagner da Silva

INTRODUCTION AND CONTEXT

In the last decades, the crude oil transformation industry has suffered pressure from society to reduce the environmental impact of his processes. These pressures were translated in more restricted regulations leading to higher restrictions in the concentration of contaminants in the crude derivatives, especially nitrogen and sulfur.

This scenario raised the hydroprocessing technologies to a strategic level to refining industry, currently, it's practically impossible to produce marketable crude derivatives without at least one hydroprocessing step. Nowadays, the hydroprocessing capacity is fundamental to the competitiveness of any refining hardware, especially to refiners processing heavier crude oils.

HYDROPROCESSING TECHNOLOGIES

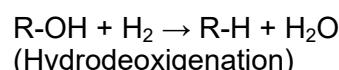
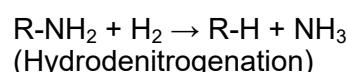
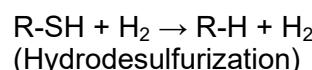
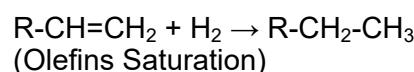
Normally, the hydroprocessing is applied to distillates streams like naphtha, kerosene, and diesel, however, the growing of heavier (and high contaminants content) crude oil reserves have been led to a higher relevance of the hydroprocessing of bottom barrel streams to the downstream industry.

The hydrotreating process (less severe hydroprocessing) involves a series of chemical reactions between hydrogen and organic compounds containing the contaminants (N, S, O, etc.). According to the target contaminant of the hydrotreating, the process can be called hydrodesulfurization (removing S), hydrodenitrogenation (removing N), hydrodeoxygenation (removing O) or hydrodearomatization when the main objective is to saturate of aromatic compounds, among others.

The most common hydrotreating forms are hydrodesulfurization (where the objective is to remove compounds like benzothiophene, dibenzothiophene, etc.) and the hydrodenitrogenation (removing porphyrins, quinolines, etc.) These compounds, besides provoke emissions of SOx and NOx when are burned,

produce in the derivates acidity, color, and chemical instability.

The main chemical reactions associated with the hydrotreating process are represented below:



Where R is a hydrocarbon.

The hydroprocessing of residual streams presents additional challenges when compared with the treating of lighter streams, mainly due to the higher contaminants content and residual carbon (RCR) related with the high concentration of resins and asphaltenes in the bottom barrel streams. Figure 1 shows a schematic diagram of the residue upgrading technologies applied according to the metals and asphaltenes content in the feed stream.

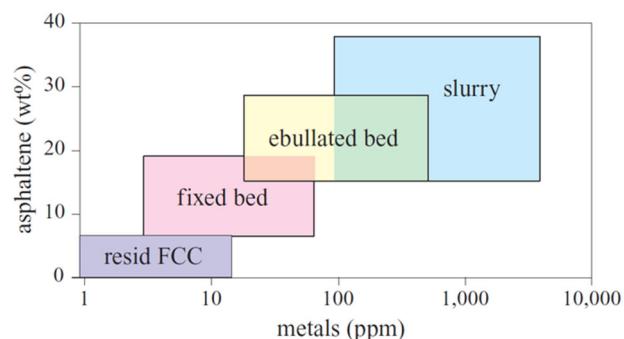


Figure 1 – Residue Upgrading Technologies According to the Contaminants Content (Encyclopedia of Hydrocarbons, 2006)

Higher metals and asphaltenes content lead to a quick deactivation of the catalysts through high coke deposition rate, catalytic matrix degradation by metals like nickel and vanadium or even by the plugging of catalyst pores produced by the adsorption of metals and high molecular weight molecules in the catalyst surface. By this reason, according to the content of asphaltenes and metals in the feed stream are adopted more versatile technologies aiming to ensure an adequate operational campaign and an effective treatment.

To demonstrate the mechanism of catalyst plugging, Figure 2 presents a scheme of reactants and products flows involved in a heterogeneous catalytic reaction as carried out in the hydroprocessing treatments.

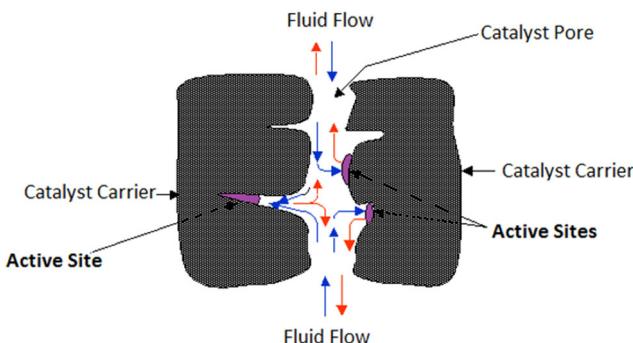


Figure 2 – Reactants and Products Flows in a Generic Porous Catalyst

To carry out the hydroprocessing reactions, it's necessary the mass transfer of reactants to the catalyst pores, adsorption on the active sites to posterior chemical reactions and desorption. In the case of bottom barrel streams processing, the high molecular weight and high contaminants content require a higher catalyst porosity aiming to allow the access of these reactants to the active sites allowing the reactions of hydrodemetallization, hydrodesulfurization, hydrodenitrogenation, etc. Furthermore, part of the feed stream can be in the liquid phase, creating additional difficulties to the mass transfer due to the lower diffusivity.

To minimize the plugging effect, in fixed bed reactors, the first beds are filled with higher porosity solids without catalytic activity and act as filters to the solids present in the feed stream protecting the most active catalyst from the deactivation (guard beds).

The process conditions are severer in the residue hydrotreating. The feed stream characteristics lead to a strong tendency of coke deposition on the catalyst requiring higher hydrogen partial pressures (until 160 bar to fixed bed reactors) and higher temperatures (400 – 420 oC).

Bottom barrel streams hydroprocessing can be applied aiming to prepare the feed stream for another deep conversion processes like FCC and RFCC, it's also common apply high severity hydrotreating process units to reduce the contaminants content to the processing in hydrocracking units, with the objective to protect the hydrocracking catalyst. The gas oil hydrotreating is very common in the preparation of feed stream to fluid catalytic cracking units (FCC) aiming to control the content of sulfur, metals and nitrogen as well as promote the opening of aromatics rings that are refractory of the catalytic cracking reactions. Figure 3 presents a basic process flow diagram for a typical high severity hydrotreating unit.

The hydrotreating process is normally conducted in fixed bed reactors and the most applied catalysts are Cobalt (Co), Nickel (Ni), Molybdenum (Mo) and Tungsten (W), commonly in association with then and supported in alumina (Al_2O_3). The association Co/Mo is applied in reactions that need lower reaction severity like hydrodesulfurization, while the catalyst Ni/Mo is normally applied in reactions that need higher severity, like hydrodenitrogenation and aromatics saturation. To the hydrotreating of bottom barrel streams (vacuum gas oil, delayed coking gas oil, etc.), due to the higher severity needed, is applied Nickel-Molybdenum (Ni-Mo) catalysts.

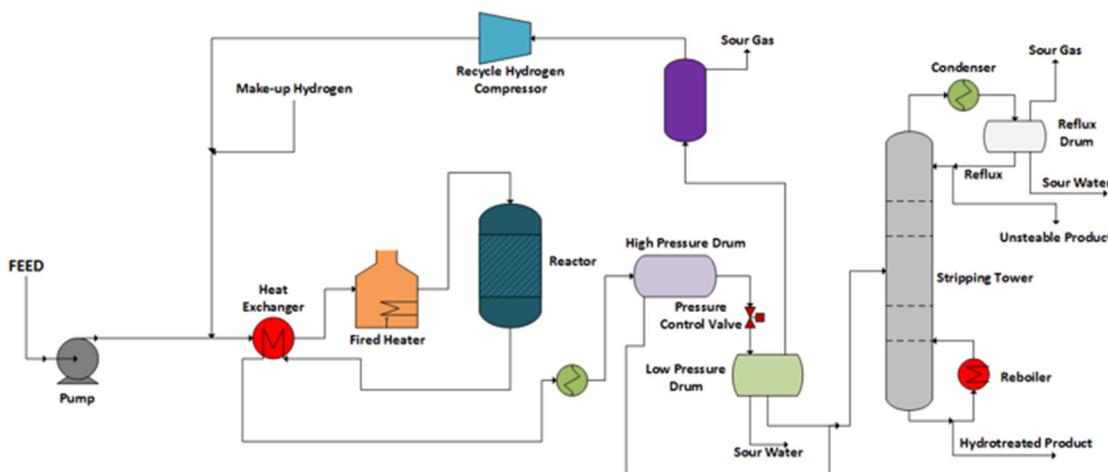


Figure 3 – Basic Process Flow Diagram for High Severity Hydrotreating Process Units

Among the bottom barrel streams hydrotreating technologies we can quote the process Aroshift™ developed by Haldor Topsoe Company, the Unionfining™ process developed by UOP Company, the Hyvahl™ technology by Axens Company and the RHU™ process by Shell Company.

The residue hydroprocessing also can be realized through hydrocracking process units according to the feed stream characteristics and the chosen refining configuration. Table 1 presents the main differences between the hydrotreating and hydrocracking processes.

As presented in Figure 1, streams with higher contaminants content, especially metals, requires treatment by hydrocracking. As aforementioned, in some refining schemes, hydrotreating units can be applied to prepare the feed stream to hydrocracking units aiming to control the concentration of metals and nitrogen and protect the hydrocracking catalysts that normally have high cost. Figure 4 presents a typical hydrocracking process unit with two reaction stage.

The process unit presented in Figure 4 relies on intermediate separation of gases between the reaction stages. This configuration is adopted when the contaminants content (especially nitrogen) is high, in this case, the catalyst deactivation is minimized through the reduction of NH₃ and H₂S concentration in the reactors. Among the main hydrocracking process technologies available commercially we can quote the process H-Oil™ developed by Axens Company, the EST™ process by ENI Company, the Uniflex™ Processes by UOP, and the LC-Fining™ technology by Chevron Company.

Catalysts applied in hydrocracking processes can be amorphous (alumina and silica-alumina) and crystalline (zeolites) and have bifunctional characteristics once the cracking reactions (in the acid sites) and hydrogenation (in the metals sites) occurs simultaneously. The active metals used to this process are normally Ni, Co, Mo, and W in combination with noble metals like Pt and Pd. The hydrocracking process is normally conducted under severe reaction conditions with temperatures that vary to 300 to 480 oC and pressures between 35 to 260 bar.

Hydrotreating	Hydrocracking
Contaminants Removal (S, N, O, Metals, etc.) and C-C bonds saturation	Contaminants Removal (S, N, O, Metals, etc.) ,cracking of C-C bonds and reduction in molecular weight
Minimum Cracking	High Cracking rate
Low Conversion (< 20%)	High Conversion (> 50%)
Feed stream preparation for Conversion Units - FCC / RFCC, Catalytic Reform, Hydrocracking, etc.	Production of Final Products – Transportation Fuels (Diesel and kerosene) and lubricants.
Ni/Co/Mo Typical Catalysts	Ni/W/Pt/Pd Typical Catalysts (Dual Character)

Table 1 – Hydrotreating and Hydrocracking Processes Comparison

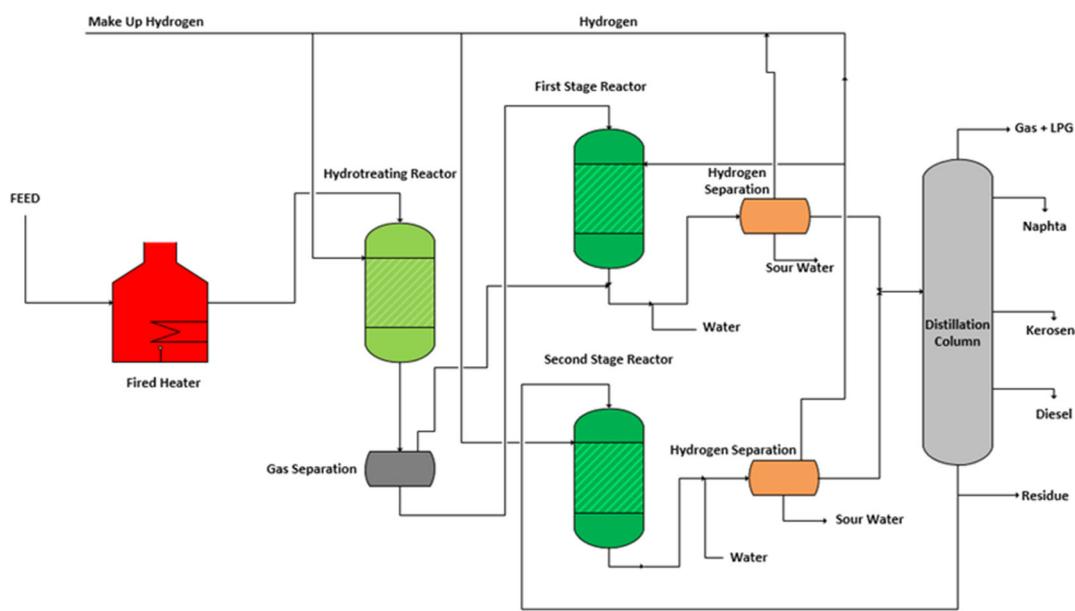


Figure 4 – Typical Arrangement for Two Stage Hydrocracking Units

It's necessary a synergic effect between the catalyst and the hydrogen because the cracking reactions are exothermic and the hydrogenation reactions are endothermic, so the reaction is conducted under high partial hydrogen pressures and the temperature is controlled in the minimum necessary to convert the feed stream. Despite these characteristics, the hydrocracking global process is exothermic, and the reaction temperature control is normally made through cold hydrogen injection between the catalytic beds as well as occurred in the hydrotreating processes.

Due to the severe operational conditions, the operational costs tend to be higher to the bottom barrel hydroprocessing units when compared with units dedicated to treat distillate streams (Diesel, Kerosene, and Nafta). The most intense hydrogenation process led to most robust catalytic bed cooling systems (quench), higher hydrogen replacing rates and complexes phase separation systems (multiple stages).

ATMOSPHERIC RESIDUE DESULFURIZATION – AN ESPECIAL CASE

With the start the validity of the new regulation over the quality parameters of marine fuel oil (BUNKER), some refiners and crude oil producers still question what will be the market behavior face to the new regulation. The IMO

2020 requires a deep reduction in the sulfur content of the marine fuel oil from the current 3,50 % in mass to 0,50 % in mass, leading to a necessity of changes in the production process of this derivative or higher control of sulfur content in the processed crude slate by the refiners.

To refiners with adequate bottom barrel processing capacity, the new regulation tends to don't be a great threat and can represent a good opportunity to raise the profitability, considering the competitive advantage which the high complexity refining hardware gives to these refiners. The eventual devaluation of high sulfur crude oil can suffer due to the IMO 2020 can be translated in higher refining margins to refiners capable to process these crudes.

One of the technologies that have been widely considered in the downstream industry in the IMO 2020 scenario the desulphurization of atmospheric residue, aiming to allow not only the compliance with the new regulation but the quality improvement of the other derivatives and reliability of the downstream process units like FCC or hydrocracking. As presented in Figure 5, the atmospheric residue corresponds to the bottom stream of the atmospheric crude oil distillation column.

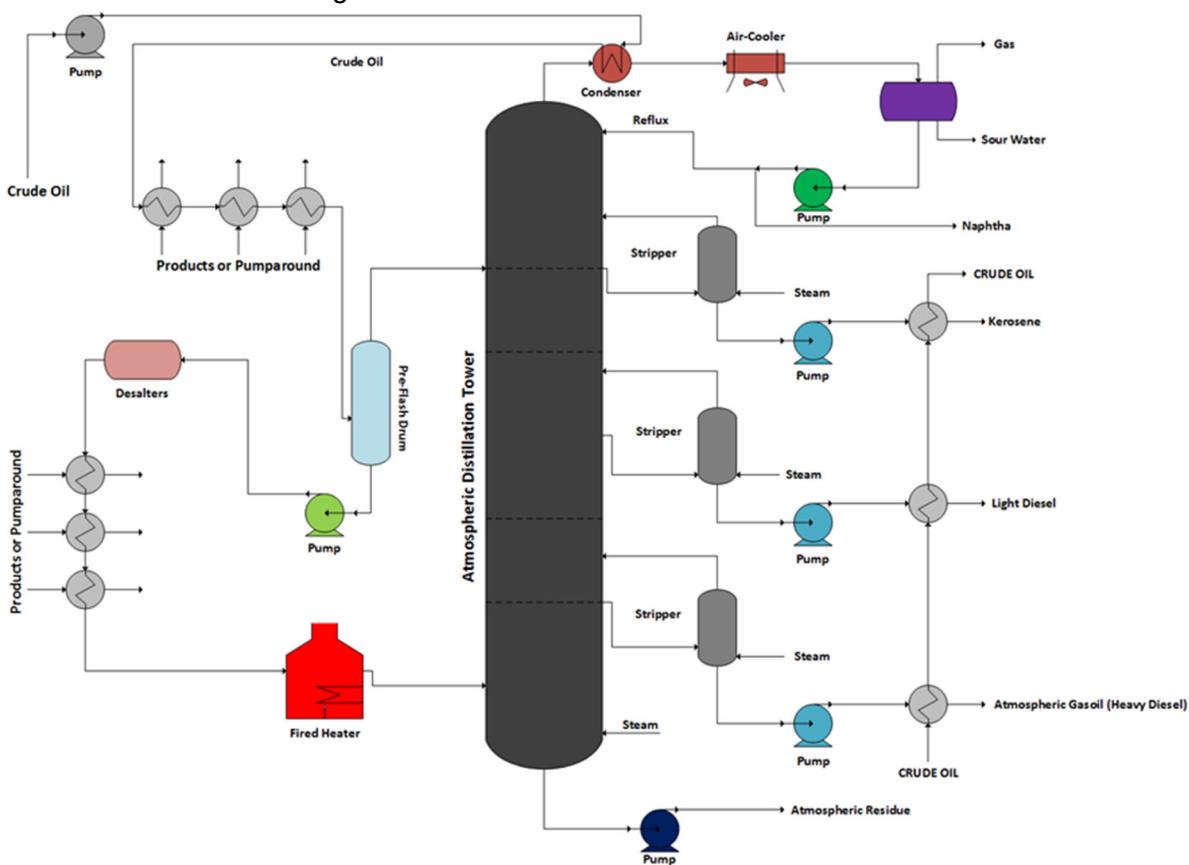


Figure 5 – Typical Process Arrangement of Atmospheric Crude Oil Distillation Unit

Once heteroatoms like sulfur, nitrogen, and metals tend to concentrate in the heavier fractions of the crude oil, the atmospheric residue drags a major part of the contaminants present in the crude oil. Considering the current quality and environmental requirements over the derivatives, posterior treatments are required aiming to reduce the contaminants content (mainly sulfur and nitrogen) in the derivatives.

Before January of 2020, the production of marine fuel oil (BUNKER) involves basically the dilution of vacuum residue (bottom barrel stream from vacuum distillation column) or deasphalted oil (to refiners that rely on solvent deasphalting unit in the refining scheme) with lighter streams like LCO (Light Cycle Oil) and gas oils, as presented in Figure 6.

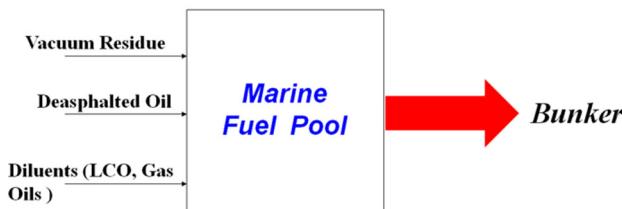


Figure 6 – Marine Fuel Oil (BUNKER) Production Process

The IMO 2020 makes necessary a better control of the sulfur content in the streams applied as diluents in the BUNKER production, to refiners with high bottom barrel conversion capacity the control of the sulfur content in the vacuum residue through the atmospheric residue applying hydrodesulphurization minimizes the necessity of treatment of other streams as well as can avoid the use of noblest streams like diesel and jet fuel as diluents in the BUNKER production.

The hydrodesulphurization process of atmospheric residue presents additional technologic challenges when compared with the hydrotreating process applied to final derivatives like diesel and gasoline, considering the high contaminants content, mainly metals, and the residual carbon due to the high concentration of resins and asphaltenes in the feed stream. Beyond the sulfur removal, the main goal, the atmospheric residue hydrodesulphurization unit promotes the partial removal of metals, nitrogen, and residual carbon (CCR) through catalytic hydrogenation mechanism.

Among the available atmospheric residue hydrodesulphurization technologies, we can quote the RCD Unionfining™ process developed by UOP Company, the process Hyvahl™ by Axens Company, the technology RHU™ by Shell Company, and the RDS™ technology commercialized by McDermott.

Figure 7 present the basic process flow diagram for the RCD Unionfining™ technology by UOP Company.

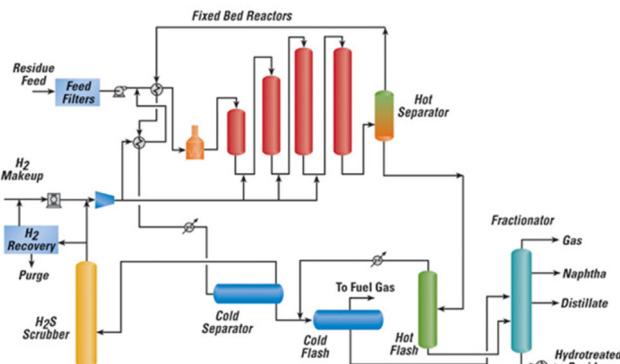


Figure 7 – UOP RCD Unionfining™ Atmospheric Residue Hydrodesulphurization Technology (UOP Company Website, 2019)

The role of the atmospheric hydrodesulphurization unit in the refinery goes beyond allowing the production of low sulfur fuel oil, in high complexity refineries the unit is applied as feedstock treatment step to conversion units as FCC/RFCC, hydrocracking, and delayed coking. The reduction of contaminants content and residual carbon promoted by the atmospheric residue hydrodesulphurization unit significantly raises the quality of derivatives produced by downstream units as well as raises the catalyst lifecycle of deep conversion processes like FCC and hydrocracking, contributing to reduce the operation costs.

The process conditions tend to be more severe in the case of atmospheric residue hydroprocessing. The feedstock characteristics lead to a strong tendency of coke deposition over the catalyst requiring then higher hydrogen partial pressure (until 180 bar to fixed bed reactors) as well as higher temperatures (380 to 420 oC).

The hydrotreating process of atmospheric residue is normally conducted in fixed bed reactors and the most employed catalysts are Cobalt (Co), Nickel (Ni), Molybdenum (Mo), and Tungsten (W), normally in association between them and supported over alumina (Al₂O₃). The combination Co/Mo is normally more active to hydrodesulphurization reactions while the Ni/Mo combination is responsible for hydronitrogenation and aromatics saturation reactions.

A typical atmospheric residue hydrodesulphurization unit can achieve 95 % of conversion in hydrodesulphurization reactions and 98 % in hydrodemetallization reactions, furthermore, it's possible to achieve a reduction

of 65 % in residual carbon according to the employed technology. Normally, atmospheric hydrodesulphurization units rely on catalytic beds focused to remove metals also called guard beds aiming to protect the catalysts in the downstream reactors and improve the operational lifecycle.

Due to the severe operating conditions, the operation costs of atmospheric residue desulphurization units are higher when compared with hydrotreating units dedicated to processing distillates (Diesel, Jet fuel, and Naphtha). The most intense hydrogenation process leads to a necessity of more robust quenching systems of catalytic beds, higher hydrogen make-up rates and more complex phase separation systems (multiple stages).

Despite the relatively high capital cost, the implementation of atmospheric residue hydrodesulphurization units allows refiners greater operational flexibility and high sulfur oil producers, greater value addition to crude oil. Countries with high production of high sulfur oil such as Kuwait have made a great capital investment to install atmospheric residue hydrodesulphurization units to add even more value to their crude oil reserves as well as to ensure the production of low sulfur fuel oil. The Al-Zour Refinery Enterprise from KNPC and KIPIC Companies relies on the biggest atmospheric residue hydrodesulphurization units in the world aiming to ensure market compliance and high added value to the Kuwait crude oil reserves even in the IMO 2020 scenario.

Where:

KNPC – Kuwait Petroleum National Company
KIPIC – Kuwait Integrated Petroleum Industries Company

CONCLUSION

Despite the operational costs, the hydroprocessing of bottom barrel streams can ensure higher reliability and profitability to refiners through the reduction in the global operational costs related with shorter operational campaigns due to early catalyst deactivation as aforementioned, another advantage is the capacity to processing heavy and discounted crudes that can allow a significant rising in the refining margins.

Beyond this, the relevance of residue hydroprocessing technologies raised, even more, after the start of the new regulation on Bunker (Marine Fuel Oil), the IMO 2020. Once the low sulfur crude oils are scarce, the refiners need to look for alternative routes to add value to his crude oil reserves as well as to supply the new marine fuel oil, ensuring participation in a profitable market.

The capacity to add value to the bottom barrel streams is a competitive differential in the refining industry and this differential tends to be even more relevant in the market scenario with the IMO 2020, especially in markets with easy access to high sulfur crude oils. Under this condition, as aforementioned, the presence of deep hydroprocessing units in the refining scheme can ensure a considerable competitive advantage to refiners, even considering the high capital spending.

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Rock Bottom View

Into a Clearing, But Not Out of the Woods Just Yet...

Ronald J. Cormier, *Engineering Practice Contributing Author*



Hello all. Welcome to EPM's March 2022 edition and greetings from this old screen porch at Rock Bottom Ranch in Central Texas, USA. Since we last discussed, global intrigue affecting our industry in January's edition, much has taken place extremely quickly, accelerating the pace of change since the end of 2021. Most notably, supply chain pressure on all types of commodities, as well as consumer goods, continued to increase, prefacing heightened tensions from Russia's unprovoked attack on Ukraine.

While war continues to rage as of this writing, transport fuels, oil/gas heating fuels, and hence electricity supplies, are under threat, causing prices to soar globally. While auto companies and the public are driving real traction with electric vehicle adoption, changeover from ICE is still in its infancy; many investors in historic parts of the energy chain now see fit to wait on the sidelines or bow out, anticipating possible longer-life ROI's from new, frustrating technologies. To say the least, current times don't provide much light at the end of a truly murky tunnel. In the meantime, enough uncertainty, unknowns, and timing variability are driven by underlying geopolitical, environmental, and national security concerns.

In this month's VRB, our friends at Chiron Financial LLC have authored a wonderful article for their recent blog, which well illustrates investment conundrums for our business just now. Hopefully the view is enlightening and provides a clear explanation of current interplay. History has shown that capital investment during times of significant uncertainty may just provide first-mover organizations with high value-added outcomes, assuming the right research and intel.

As your firm's growth and capex project financing needs evolve, please contact Chiron for

discussion and expertise. The article is reprinted below with Chiron's permission. Thanks additionally to Mr. Chris Mudd, Managing Director, for aiding the content submission!

Chiron Responds: Russia's Invasion of Ukraine and the Impact on the Global Energy Industry



Chiron's Founders Scott Johnson and Jay Krasoff, along with Managing Director Tom McNulty, discuss how Russia's invasion of Ukraine will impact the energy industry...

"The Energy Industry is not just a global business. It is a business with substantial and meaningful geopolitical, environmental, and national security impacts. The events unfolding in Europe currently highlight the importance of supply diversification. And since America is among the leading producers of oil and gas, along with Saudi Arabia and Russia, it is from American energy companies that much of this crucial role needs to be filled.

Think of this in terms of numbers. The EU imports more than 95% of the crude oil and petroleum products that it uses, and more than 25% of this comes from Russia. 35% of the natural gas used in central and western Europe comes from Russia. Of similar significance, natural gas must be the fulcrum molecule in the energy complex

during the Energy Transition. It is the cleanest burning and fastest growing fossil fuel, now accounting for about a quarter of global electricity generation. Natural gas is widely believed to be the only fuel that has a practical ability to substantially replace coal during the next two or three decades of the Energy Transition, especially in underdeveloped and energy poor countries where the need for rapid expansion of power generation will take priority over zero carbon until minimum living standards are achieved. And natural gas-fired power plants are capable of producing secure and consistent base load electricity while at the same time being able to handle peaking demand situations.

Natural gas prices in Europe are very vulnerable to disruptions caused by open combat that can damage pipelines. The announcement that the start-up of the completed Nord Stream 2 pipeline is to be delayed means that gas volumes from it will not reach full volume levels until much later in 2022, assuming that this conflict is resolved fairly quickly. Gas prices in Europe will likely be sustained at uncomfortable high levels through all of 2022, and this means that electric power prices will be higher as well. The situation is mitigated in some markets where long-term price contracts are in place. But keep in mind that people must pay for energy, so higher energy prices will lower all kinds of discretionary spending.

Liquified Natural Gas, or LNG, has become a crucial supply factor because the technology allows for the transport and delivery of natural gas from source fields to markets that are often far away.

It is methane, with some ethane mixed in, and it is cooled to 260 degrees Fahrenheit where much greater quantities can be carried in a limited space. Specially-designed ships can carry this liquid form. Last year, the United States, Qatar, and Russia accounted for about 70% of Europe's total LNG imports, and the United States became the largest source of LNG in 2021 at 26%. In January the United States supplied more than half of all LNG imports into Europe.

The traditional model for LNG development has to be changed to make the process faster so that the US can export much more of its natural gas as LNG to help balance the global gas market. Energy is a physical business and adding more LNG supply into Europe is not an easy thing to do fast, because there is limited import capacity available now and there is strong competition from Asia for the gas.

Current high levels of energy costs threaten the health of global economies and the livelihoods of most of the world's population. The United States should work to exceed 100 Bcf per day of gas production as soon as possible, both to protect economies and to help displace much dirtier forms of energy production that are otherwise inevitable in the near term.

As for crude oil, the nature and duration of potential sanctions will determine the impact. It might be that Europe could need to find other suppliers to off-set about 2.5 mmb/d of crude oil and condensate it gets from Russia and about 1.5 mmb/d of petroleum products it gets from Russia. Part of the Druzhba pipeline goes through Ukraine and it remains to be seen if it will be shut or damaged.

Industry and government in the United States should aim for 15 mm bpd of crude oil production to ensure that energy cannot be weaponized. Those who say that we should immediately reduce our production should consider the likely impacts in terms of conflicts, energy deprivation, soaring energy prices, and widespread suffering. As a nation, we can encourage, support, and even subsidize the Energy Transition, but it cannot be done overnight and we should beware of unintended consequences.

Global underinvestment in the traditional energy complex can be dangerous. There is plenty of capital for old energy and new energy; they can coexist for the time being. Capital flows into the Energy Complex, from existing sources, and from new sources, must accelerate rapidly, and American producers of natural gas and crude oil should increase their activity. Now is not the time to starve the traditional energy business of capital, regardless of whether it's a public Fortune 100 company or a private middle-market company."

Until next time, be prosperous and safe!!



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