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Navigating Heat Exchangers: Design, Operation, and Maintenance Essentials

Muhammad Rehan

Heat exchangers, often referred to as the unsung heroes of industrial processes, play a pivotal role in managing heat transfer across various applications. In our journey through this article, we will delve into the intricate world of heat exchangers, exploring not only the technical intricacies of their design and operation but also the often-underestimated importance of long-term considerations such as cost-effectiveness, quality, and sustainability. From the challenge of balancing heat transfer efficiency and pressure drop to the critical role materials and design play in sustainability, we aim to provide a holistic understanding of these engineering marvels.

Typical challenges in heat exchanger design:

Heat exchanger design comes with its own set of challenges, but with careful consideration and innovative approaches, these challenges can be addressed effectively.

One of the primary challenges is achieving the desired heat transfer efficiency while minimizing pressure drop. Balancing these factors requires a deep understanding of fluid dynamics and thermodynamics. Computational tools, such as CFD simulations, can help optimize heat exchanger designs by iteratively refining geometry and fluid flow patterns to strike the right balance.

Fouling is another significant challenge in heat exchanger design. Over time, deposits can accumulate on heat transfer surfaces, reducing heat transfer rates and efficiency. Designers can address this challenge by incorporating features that facilitate cleaning and maintenance. For example, removable tube bundles or plates in heat exchangers simplify the cleaning process.

Materials selection is crucial. Compatibility with the fluids being processed and resistance to corrosion are vital factors. Challenges related to materials can be addressed by staying updated on advances in material science and selecting materials with proven performance in specific applications.

Space constraints can be a challenge, especially in retrofitting or expanding existing facilities. Designers should consider compact heat exchanger designs that maximize heat transfer surface area within limited space. Plate heat exchangers, for instance, are known for their space-efficient designs.

Addressing environmental concerns is a challenge and an opportunity. Heat exchanger designers should explore materials and designs with lower environmental impacts. This includes considering recyclable materials and energy-efficient designs to reduce carbon footprints.

Designers' contribution to sustainability and energy efficiency:

Designing heat exchangers with a focus on sustainability and energy efficiency is of paramount importance in today's engineering landscape. Heat exchanger designers can make significant contributions to sustainability in the following ways:

Sustainability in heat exchanger design is often centered around maximizing energy efficiency. The heat recovery potential of heat exchangers can play a crucial role in reducing the overall energy consumption of industrial processes. This is particularly relevant in industries such as chemical processing, power generation, and HVAC systems. By recovering and reusing heat that would otherwise be wasted, designers can contribute to substantial energy savings and reduced greenhouse gas emissions.

Materials selection is another key aspect of sustainability. Heat exchanger designers should opt for materials that are not only corrosion-resistant but also environmentally friendly. Choosing materials with a low environmental impact and high recyclability is essential. Additionally, considering the entire lifecycle of materials, from production to disposal, is vital in reducing the environmental footprint.

Furthermore, heat exchanger designers can explore innovative designs that minimize pressure drops and enhance heat transfer efficiency. Compact heat exchangers, such as plate and fin-tube exchangers, are excellent examples of designs that offer both efficiency and sustainability benefits. These designs often require less space and lower fluid volumes, reducing the overall environmental impact.

Collaboration with experts in fluid dynamics and thermodynamics can help in optimizing the design for better energy performance. Computational Fluid Dynamics (CFD) simulations and heat transfer analysis can aid in achieving the most energy-efficient configurations.

Heat exchanger designers can also keep sustainability in mind by minimizing fouling potential. Fouling can significantly reduce the efficiency of heat exchangers over time. Designing for ease of cleaning and maintenance can lead to longer operational lifespans and less frequent replacements, contributing to sustainability.

Lastly, a focus on sustainability should include compliance with industry standards and regulations related to energy efficiency and environmental impact. Heat exchanger designers should stay informed about evolving standards and strive to exceed them in their designs.

Understanding Life Cycle Cost and Cost of Quality in Heat Exchanger Design:

It's a common practice for many heat exchanger designers to prioritize the upfront capital expenditure (CapEx) cost, as it appears to be the most apparent financial consideration. However, it's important to recognize that the lowest CapEx cost does not necessarily translate to the most cost-effective solution over the entire lifecycle of a heat exchanger. The true cost of a heat exchanger includes factors beyond its initial purchase price, such as maintenance, repair, and operational expenses.

To help clients better understand the concept of life cycle cost and the importance of considering the cost of quality, let's break down this perspective:

1. Initial Investment vs. Long-term Costs: Heat exchangers with lower upfront costs might seem appealing, but they may be constructed with less durable materials or design compromises that could lead to increased maintenance, repairs, and even premature replacement. Clients should be encouraged to view their investment in heat exchangers as a long-term commitment, where spending a bit more initially can result in substantial cost savings over the equipment's lifecycle.

2. Cost of Quality: Quality in heat exchanger design encompasses factors like material selection, construction quality, and adherence to industry standards. Low-cost heat exchangers may cut corners in these areas, compromising quality. Such compromises can lead to issues like leaks, reduced heat transfer efficiency, and safety concerns, which can incur substantial costs in terms of downtime, repairs, and even regulatory fines.

3. Total Cost of Ownership (TCO): Encouraging clients to calculate the Total Cost of Ownership, which considers the initial purchase price, operational costs, maintenance expenses, and potential repairs, provides a holistic view of the heat exchanger's cost over its lifetime. This approach highlights the significance of considering long-term value rather than focusing solely on the initial investment.

In summary, heat exchanger designers should collaborate with clients to shift their perspective from initial cost savings to long-term value and cost-effectiveness. Emphasizing the importance of investing in quality and reliability can help clients make more informed decisions that ultimately lead to substantial savings and a more efficient, trouble-free operation over the heat exchanger's entire lifecycle.

Heat Exchanger Response to Vibration:

One often overlooked aspect in HEX design and operation is vibration. Understanding and analyzing vibration during the design phase is of utmost importance, as it can have a profound impact on heat exchanger performance, safety, and longevity.

During the operation of a heat exchanger, it is subjected to various sources of vibration, including mechanical and fluid-induced vibrations. The response of a heat exchanger to vibration is a complex interplay of its structural properties, fluid dynamics, and mechanical forces. Key factors include:

Natural Frequencies: Every heat exchanger system has specific natural frequencies at which it is prone to resonate. These are determined by the geometry and material properties of the exchanger. Vibrational energy imparted at or near these frequencies can lead to resonance, which can be destructive.

Mode Shapes: Heat exchangers exhibit characteristic mode shapes when subjected to vibration. Understanding these mode shapes is critical in identifying areas of potential stress concentration or failure.

Vibration-Induced Issues: Vibration can result in several issues for heat exchangers. These include fatigue failure of tubes, reduced heat transfer efficiency, fretting wear at tube-to-tube support locations, and even complete structural failure in severe cases.

Drawing from practical experience, it is essential to highlight the significance of vibration analysis during the design phase. In one instance, an industrial plant installed a heat exchanger that frequently experienced leakages. Upon review of the engineering design and vibration analysis, it was discovered that the exchanger suffered from tube vibration issues. The root cause of these issues was traced back to a lack of appropriate baffling. Baffles are essential components within heat exchangers. They serve to guide the flow of fluids and prevent destructive vibration. In this case, the addition of the right baffling not only resolved the tube vibration issue but also significantly improved the heat exchanger's overall performance and reliability.

There are common strategies to address vibration issues in heat exchangers:

Baffling: Adequate baffling is crucial to controlling fluid-induced vibrations. Properly designed baffles help redirect fluid flow to reduce turbulence and mitigate vibration issues.

Tube Supports: Tube-to-tube support configurations play a significant role in vibration control. Using proper support structures and materials can prevent fretting wear and fatigue failures.

Damping Materials: The use of damping materials can help reduce the transmission of mechanical vibrations. This is particularly relevant in situations where heat exchangers are in proximity to other vibrating equipment.

Structural Analysis: Performing structural analysis and finite element analysis (FEA) during the design phase can identify potential trouble spots and guide modifications to the heat exchanger's design.

Flow Analysis: Computational Fluid Dynamics (CFD) simulations can help optimize the flow patterns within the exchanger to reduce fluid-induced vibrations.

Monitoring and Maintenance: Regular monitoring of heat exchangers can identify vibration-related issues as they arise. This allows for proactive maintenance and repairs, reducing the risk of unplanned downtime.

Monitoring Heat Exchanger Heat Duty:

Monitoring the heat duty of a heat exchanger is a critical aspect of ensuring its optimal

performance and efficiency. There is a growing trend in the industry towards leveraging digital technologies for monitoring and enhancing heat exchanger performance. Plant operators are increasingly considering outsourcing their heat exchanger monitoring services to third-party providers as part of the broader digital transformation and Industrial Internet of Things (IIoT) initiatives.

In the coming years, the adoption of Software as a Service (SaaS) and Platform as a Service (PaaS) for heat exchanger monitoring is expected to experience significant growth. The primary focus of these initiatives is to achieve several key objectives. These objectives include increasing energy savings, extending the life of heat exchanger equipment, improving operational efficiency, and avoiding issues such as heat exchanger stall and surge.

To support solutions based on Artificial Intelligence (AI) and Machine Learning (ML), it is essential to gather data with improved sensor quality and embedded systems. The accuracy and reliability of the signal measurements play a pivotal role in the effectiveness of heat exchanger performance and condition monitoring.

Heat exchanger performance and monitoring rely on a combination of hardware and software capabilities. The key to obtaining reliable readings begins during the design phase of the heat exchanger. The strategic placement of instrumentation on the piping and equipment, along with the quality of support structures and civil foundation, significantly impact the quality of data acquired during operation.

Vibrational disturbances and potential radio or electromagnetic interference (depending on whether digital or analog sensors are used) can introduce noise into the signals, affecting the accuracy of heat duty measurements. Therefore, it is crucial to maintain an appropriate sampling frequency and ensure signal integrity to generate high-quality data for further post-processing using software methods.

It is important to emphasize that while AI and ML can offer powerful tools for analyzing data and identifying patterns, they cannot compensate for shortcomings in the design and hardware performance of heat exchangers. A well-designed and properly instrumented heat exchanger is the foundation for reliable heat duty monitoring, making it essential to get it right from the start to achieve the best results in terms of performance and efficiency.

Role of maintenance in ensuring the longevity and efficiency of heat exchangers:

Maintenance is pivotal in ensuring the longevity and efficiency of heat exchangers. Proper maintenance can extend the operational life of heat exchangers and maintain their performance at optimal levels. Here's how maintenance planning plays a crucial role:

Scheduled Inspections: Regular inspections of heat exchangers are essential to detect early signs of fouling, corrosion, or damage. By identifying issues in their nascent stages, maintenance teams can take corrective actions before they escalate into significant problems.

Cleaning and Fouling Prevention: Maintenance planning should include cleaning schedules. Depending on the application, heat exchangers can accumulate fouling deposits, reducing heat transfer efficiency. Periodic cleaning, either by mechanical means or chemical processes, is necessary to maintain performance.

Repairs and Replacements: Maintenance planning involves budgeting for repairs or replacements as necessary. Over time, heat exchangers may experience wear and tear. A well-thought-out maintenance plan ensures that repairs are executed promptly, preventing downtime and operational disruptions.

Monitoring Performance: Modern technologies enable real-time monitoring of heat exchanger performance. Maintenance planning can integrate predictive maintenance techniques that use data and analytics to predict when maintenance is required based on actual performance metrics.

Sealing and Gasket Replacement: Gaskets and seals in heat exchangers are critical components. Maintenance planning includes the periodic replacement of gaskets to prevent leaks and ensure the integrity of the heat exchanger.

Safety Measures: Maintenance planning should encompass safety protocols for personnel involved in maintenance tasks. Safety is paramount, and proper planning ensures that maintenance is carried out without incidents.

Documentation and Records: Effective maintenance planning involves detailed documentation of maintenance activities, including dates, types of maintenance performed, and any observed issues. This documentation provides a historical record that can be used for trend analysis and future planning.

Spare Parts Inventory: Maintenance planning should include maintaining an inventory of

critical spare parts. This ensures that necessary components are readily available for timely repairs, minimizing downtime.

Training and Expertise: Ensuring that maintenance personnel are adequately trained and possess the necessary expertise is a vital aspect of maintenance planning. Well-trained teams can perform maintenance tasks more efficiently and safely.

By incorporating these elements into their maintenance planning, organizations can significantly enhance the longevity and efficiency of their heat exchangers, reducing operating costs and ensuring reliable performance over time.

Maintenance-Induced Failures in Heat Exchangers

Sometimes, well-intentioned maintenance and installation activities can inadvertently lead to failures of heat exchangers. These are commonly referred to as "maintenance-induced failures."

1. **Damage to Tube-to-Tubesheet Joints:** One of the most critical components in a heat exchanger is the tube-to-tubesheet joint. This joint is responsible for maintaining the integrity of the heat exchanger by ensuring a leak-proof seal between the tubes and the tubesheet. During maintenance activities, such as cleaning or retubing, mishandling or improper tools can damage this joint. Even a small distortion or crack in the joint can lead to leakage, reducing heat exchanger efficiency and potentially causing safety concerns.

2. **Structural Damage During Rigging:** The removal and installation of heat exchangers often involves rigging and lifting. In some cases, improper rigging methods or equipment can lead to structural damage. This may include bending or distorting the heat exchanger frame, which can affect its structural integrity.

3. **Misalignment and Piping Stresses:** Heat exchangers are interconnected with the process piping system. Misalignment during installation or improper support can result in excessive stress on the heat exchanger. This can lead to issues such as tube bending or tube-to-tubesheet joint failures.

4. **Fouling and Erosion During Cleaning:** Routine cleaning is essential to maintain the efficiency of heat exchangers. However, aggressive cleaning methods or the use of abrasive materials can lead to fouling or erosion of tube surfaces, reducing heat transfer efficiency.

5. **Welding-Related Failures:** Welding may be required during maintenance or repair activities. However, improper welding practices, such as inadequate weld quality or improper material selection, can lead to failures in the heat exchanger's structural components.

In my own experience, I encountered a heat exchanger at my plant with a history of frequent leakages. The root case analysis was found to be lifting and tailing activity of the exchanger during installation which was causing severe stress on cold-rolled TTS joints.

As we conclude our exploration of heat exchangers, it becomes evident that these devices are far more than mere components within industrial processes. They represent a fusion of scientific expertise and engineering precision. From the critical juncture of design challenges to the longevity and efficiency ensured by meticulous maintenance, every facet of a heat exchanger's lifecycle is vital. With sustainability and energy efficiency at the forefront, the role of heat exchanger designers is evolving, shaping a more responsible and eco-friendly industrial landscape. By prioritizing quality, understanding the true cost of ownership, and embracing innovation, the industry can harness the full potential of these heat exchangers while minimizing their environmental footprint. In the complex dance of vibrations, monitoring, and maintenance, heat exchangers reveal their intricacies, and the importance of thoughtful design becomes apparent. We've also shed light on the unintended consequences of maintenance-induced failures, emphasizing the significance of precise execution. Our journey through these diverse aspects of heat exchangers underscores the importance of striking a balance between technology and pragmatism, ensuring that these essential devices continue to drive efficiency and sustainability in the industries they serve.

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Sustainability – First Things First

Karl Kolmetz, KLM Technology Group

Introduction

Sustainability is a societal goal that broadly aims for humans to safely co-exist on planet Earth over a long time. The quality of causing little or no damage to the environment and therefore able to continue for a long time. These are great goals, to reduce the impact on the environment. There are many current buzz words used in sustainability discussions. These include:

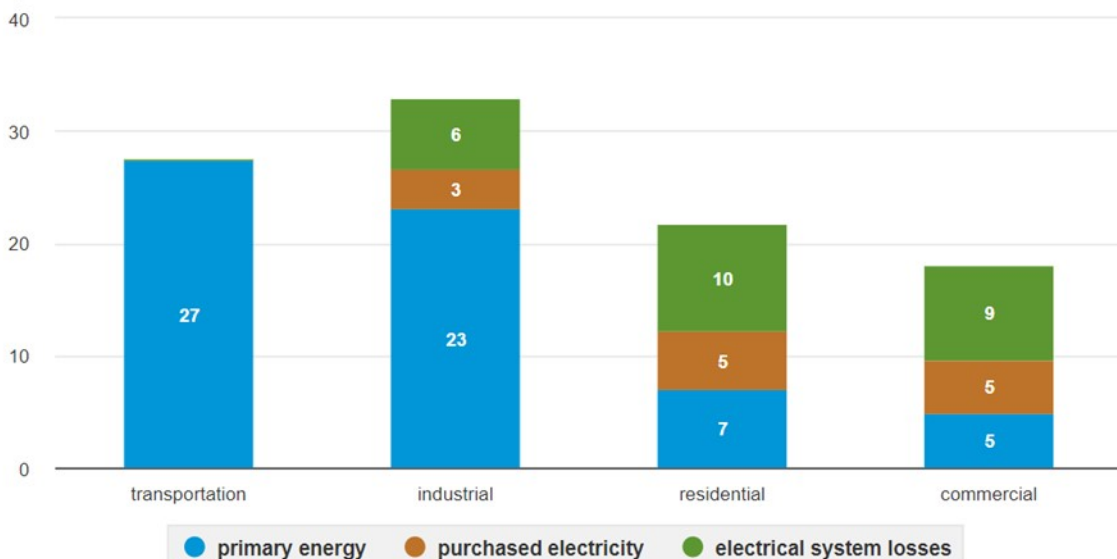
- Green Energy – Wind, Solar and Hydrogen
- Electric Cars
- Blue Energy – From the sea
- Renewable Kero and Diesel
- Bio Diesel
- Ethanol in Gasoline
- Recycling
- Conservation

What should be the first one of these we focus upon? Any logical study would decide conservation should be first, but we do not spend our energies or funding on conservation because it is too simple and logical, we like to focus on the new and exotics. We have spent millions on Green Energy, Electric Cars, and Renewable Energies, which are good to some extent, but should not be the main effort.

Here is a table by the USA Energy Information Administration showing Total Energy Consumption by End Users. Transportation is 27%, Industrial Manufacturing 32%, Residential 22% and Commercial 19%. An interesting thing to note is the green portion, electrical system losses associated with the generation, transmission, and distribution of purchased electricity which is 25% of all energy used. Estimates are 10% are lost in generation and 15% are lost in transmission. Renewables will reduce the loss of generation, but the transmission loss will remain the same until research develops better transmission systems.

Total energy consumption by end-use sector, 2022

quadrillion British thermal units



Data source: U.S. Energy Information Administration, *Monthly Energy Review*, Tables 2.2 to 2.5, April 2023, preliminary data
 Note: Electrical system losses are energy losses associated with the generation, transmission, and distribution of the purchased electricity.

Therefore, for each 1% we can reduce in electrical consumption, the actual savings are 1.25%. Conservation should be our first priority for sustainability. Most residential and commercial buildings just assume the electrical usage is a cost of doing business, they do not understand the long-term impact to the environment.

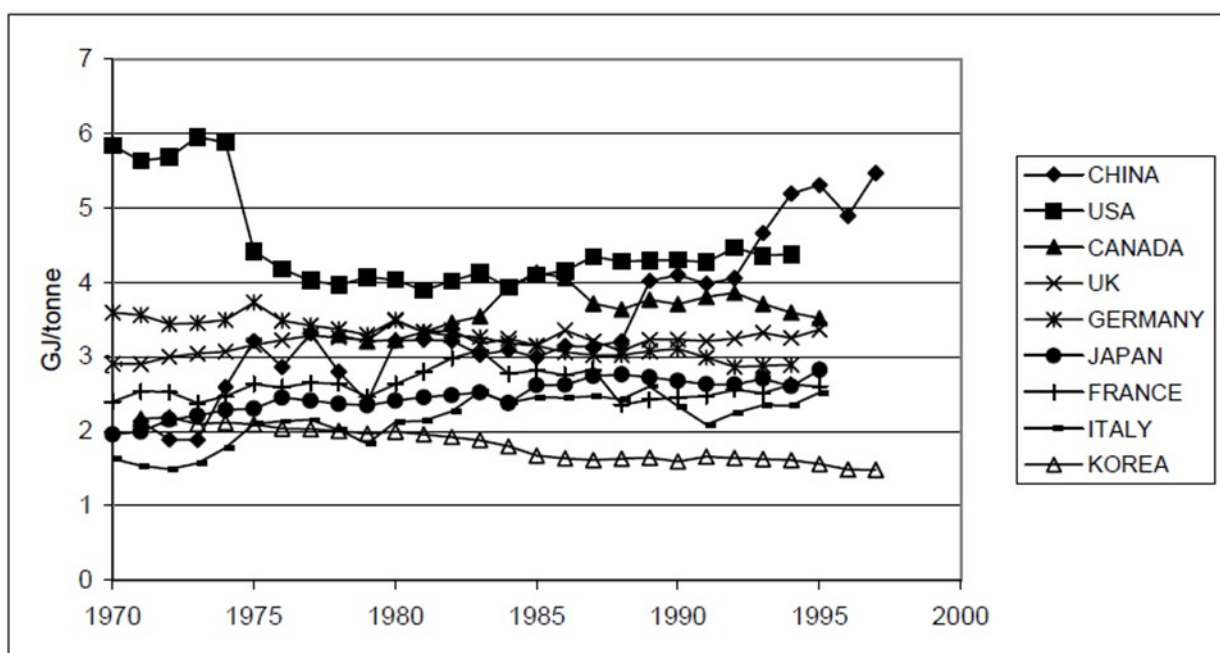
Residential and Commercial buildings consume 41% of total energy utilized, which is the largest, yet most homes and commercial buildings I visit have poor energy usage and no real energy reduction programs. But this is not new and exotic, we have known this a long time and have not really made any improvements. These are simple improvements to make – doors, windows, and insulation. We are spending millions on the exotic, and we do not attack the largest users first. In 2021 KLM Technology Group developed an Engineering Design Guideline on the Energy Management of Buildings.

The second largest user is industrial manufacturing, which is 32%. I have mostly worked in refining, ethylene, and natural gas industries. Refining and ethylene contracts are structured where they must purchase all their feedstocks, so they work to reduce energy consumption and flaring due to economics.

Some natural gas contracts are structured where they are only paid for the finished product, not what they take from the wells, so there is not the same economic incentive to reduce energy consumption and flaring. Everyone remembers the pictures of North Dakota flares at night. Not good for the environment and not good for the producers, but great for the midstream processor. This is an area where the oil and gas well producers and environmentalists need to review.



Ammonia is the largest producer for fertilizer, refining is second and ethylene is third in total tons produced. Refining and Ethylene are large energy intensive industries, and they have been studied to reduce total energy consumption. The energy per ton has been greatly reduced in the last 50 years. Attached is a graph of refinery energy.



Source: IEA, 2000.

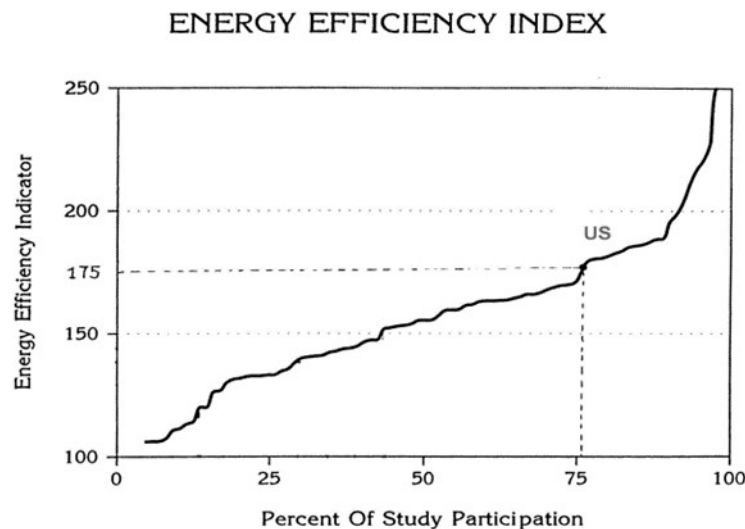
Many of the countries are still trending up which is amazing due to the high cost of energy today compared to the 1970s. If you review the Korea data – they saw a 20% reduction in energy from 1970 to 2000 – about 0.6% per year and this was starting at a low number already. This is the average of all the refineries in Korea, the best performing plants can see 3% or greater per year. There is a large variation in the performance of the different plants.

Below is an Energy Efficiency Indicator of 85% of North American Ethylene plants from 1995 (3)

The average ethylene plant has an Efficiency Indicator of 175, while many are below 150, and the top tier plants are greater than 200. There is always a large variation in how each plant performs on energy. You need to reduce energy at 0.6% per year (actual 30-year average) or better – remember the best plants are reducing 3% per year. In 2021 KLM Technology Group developed an Engineering Design Guideline on the Energy Management of Process Plants.

Twice in my career we have formed teams and reduced energy consumption by over 5% in a two-year period. This is possible, we have accomplished this twice - Steps to reduce energy consumption.

1. Forming an energy reduction team and tracking past performance and current performance. It is important to assign cost to energy. No one cares if you save BTU or KW. In one of the plants, we saved USD 10.0 million, and everyone noticed. KLM can assist in training and consulting for your energy team.
2. When you replace equipment, you replace it with higher efficiency equipment. Equipment designed today has higher efficiencies than even 10 years ago. Take advantage of current designs.
3. Current distillation equipment has higher capacity and efficiency than sieve deck trays, which most towers have installed. Distillation is a very high component of energy, for some plants 50% of energy usage. Even a small energy saving is a large monetary amount, several million USD per year. You need to know what your current tower efficiency and what energy saving in USD a small revamp might bring. Tray revamps are relatively low cost, compared to the current energy prices. You should at least calculate the numbers. KLM can assist with assessing your current distillation efficiency and what an upgraded design might bring in energy savings.



4. Heat exchangers are designed poorly, because they are awarded to the low-cost bidder, leading to low energy recovery and higher energy consumption in the adjacent heaters. When you replace a heat exchanger do not replace in kind, upgrade to a fouling resistance, higher efficiency design. This may be several million USD per year. Many times, heat exchangers set the maintenance schedule, and a few extra months is several million USD for large plants, and this is almost pure profit. KLM can assist with assessing your heat exchanger efficiency and what an upgraded design might bring in energy savings and USD.
5. Pump and Motors designed 20 years ago had about 80% efficiency. Current designs have greater than 90% efficiency. KLM can assist in providing high efficiency equipment for your team. Because we buy many pumps per year, KLM might be able to provide higher efficiency pumps, maybe at a lower price than you are paying for lower efficiency pumps.

Conclusions

Sustainability is an important concept. In any important concept we need to reduce the largest users first. Buildings are the largest users, but they are not new and exotic – Doors, window, insulation, and improved utility systems can lead to large savings in energy. We should look at poor income areas and assist in replacing doors and windows, but this is not new and exotic – just needed.

Industrial Manufacturing is second in total energy usage. More complex than buildings, but the principles are well understood, and top tier companies are reducing energy by more than 3% per year. At least matches the 0.6% twenty-year average.

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- STHE : TEMA, API 660, ASME Sec VIII Div 1&2
- Storage Tank : API 650, API 620, AWWA D100
- Piping System : ASME Sec I, ASME B31.3, B31.4, B31.8
- Condenser : HEI (Heat Exchanger Institute)
- LP Heater
- HP Heater
- Deaerator

Certifications

- ASME U, U2, S
- The National Board of Boiler and Pressure Vessel Inspectors (NB & R)
- ISO 9001 : 2008
- HTRI Member



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Octane Boosting Routes – Cleaner and High-Performance Gasoline

Dr. Marcio Wagner da Silva

Introduction

Despite the trend of reduction in transportation fuels demand, these derivatives are still responsible by great part of revenues in the downstream industry and are fundamental to sustain the economic development of the nations, especially in development economies, according to Figure 1, the demand for gasoline tends to be sustained by in development economies in the short term.

Another example of market with great dependence of transportation fuels is the Brazilian domestic market. The country is the seventh world largest crude oil derivative consumer, and a major part of this consumption is related with transportation fuels leading to the country reach the third position in this category, demanding mainly middle distillates (diesel and kerosene) and, according to the Brazilian Petroleum Agency (ANP), the Brazilian demand for crude oil derivatives will rise 20% until 2026 against the current 2,4 million barrels per day.

Minimizing the consumption and the environmental impact of transportation fuels is a constant objective of researchers and some refining technologies were developed over the years aiming to improve the performance and

reduce the environmental footprint. Gasoline is one of the most consumed crude oil derivatives in the world and is normally composed by a blend of naphtha aiming to comply with strict regulations like sulfur content and octane number. An adequate octane number can optimize the performance of the gasoline in Otto cycle engines and minimize the consumption, in the refining hardware the refiners normally rely on dedicated refining technologies to improve the octane number of the final gasoline though the management of naphtha molecules.

The streams normally involved in the gasoline production process are straight run naphtha, cracked naphtha (after hydrodesulfurization), coke naphtha (after hydrotreatment) and reforming naphtha.

Reformed naphtha, produced in the catalytic reforming unit is one of the streams that contribute to raising the octane number in the final gasoline. However, due the severe restrictions related to the carcinogenic aromatic emissions, mainly benzene, some refiners have avoided the application of this stream to formulate gasoline, directing the reformed naphtha preferably to petrochemical

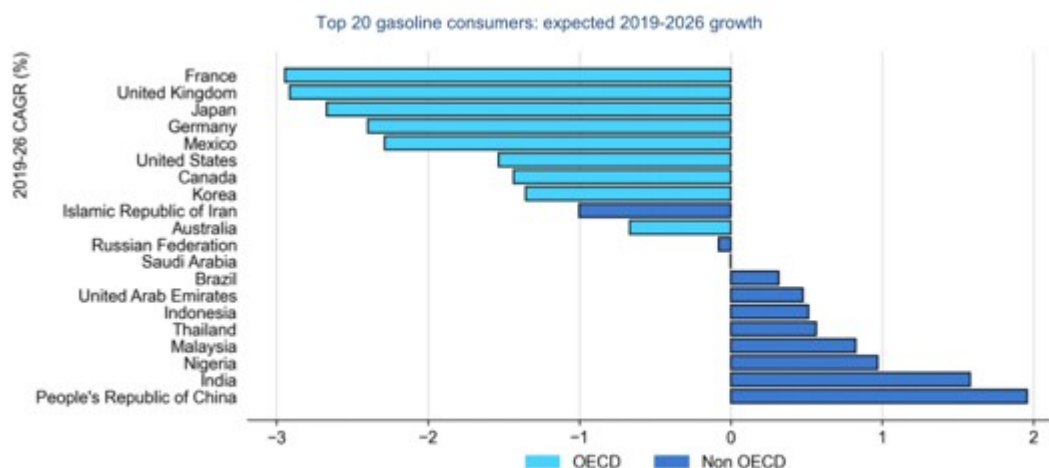


Figure 1 – Growth of Gasoline Demand (IEA, 2021)

intermediates production in aromatics complexes.

The North American market is an interesting case study which perfectly describe the challenges of produce low sulfur and high-performance gasoline. Since 2020 the Tier 3 gasoline specifications put under pressure the USA refiners once imposes a maximum sulfur content in the gasoline of 10 ppm at same time which requires better performance (high octane numbers), in practice these restrictions creates more difficulties to the refiners to use their cracked naphtha (Naphtha from FCC) in the gasoline pool once it's necessary to hydrotreat a higher amount of olefins with octane losses, leading the refiners to look for more selective catalysts and improve their hydroprocessing capacity.

Gasoline Production Process

The final gasoline is composed by a blending of different naphtha streams, as presented in Figure 2.

The use of straight run and reformed naphtha is normally minimized, aiming to direct these streams to petrochemical intermediates market due to the higher added value of these streams in this market.

Cracked naphtha (Naphtha from FCC) contributes positively to the octane number of the final gasoline, however, due to the current restrictions related to the sulfur content in the gasoline (maximum of 10 ppm), the use of cracked naphtha without treatment step is limited. Refineries that have catalytic alkylation units in his refining scheme normally direct this stream to produce aviation gasoline that have higher market value when compared with automotive gasoline, for this reason, the participation of the alkylation naphtha is minimized in the composition of this fuel.

Isomerization naphtha has low contaminants content (sulfur and nitrogen) and high octane number and, for these reasons, the participation of this stream in the formulation of gasoline is maximized in refineries that have isomerization units in the refining scheme. In markets with high demand for gasoline, refiners can add butanes to gasoline pool, however, the participation is limited due to the high vapor pressure of this stream that can lead to break quality requirements (Reid Vapor Pressure – RVP). Normally, butanes are added to LPG pool, respecting the limits to avoid breaking the mixture quality related to heavy limitations.

Nowadays, due to the environmental and quality regulations over the gasoline the hydrodesulphurization of cracked naphtha is fundamental to be possible the refiners meet the sulfur content in the final gasoline that can be low than 10 ppm in most restrictive markets. In this short technical review, we introduce the available technologies to improve the quality of the gasoline pool.

Isomerization Technologies

An alternative to the reforming naphtha is the production of branched hydrocarbons (with high octane number) through processes as Catalytic Alkylation and Isomerization.

Isomerization process involves the conversion of normal paraffin to branched paraffin, keeping the carbon number in the reactant molecule. The reactions are carried out in the presence of hydrogen under pressure and temperature mild conditions. The presence of hydrogen aims mainly to avoid coke deposition on the catalyst.

Isomerization reactions (1) are slightly exothermic, that is, are favored under lower temperatures. To balance the kinetic

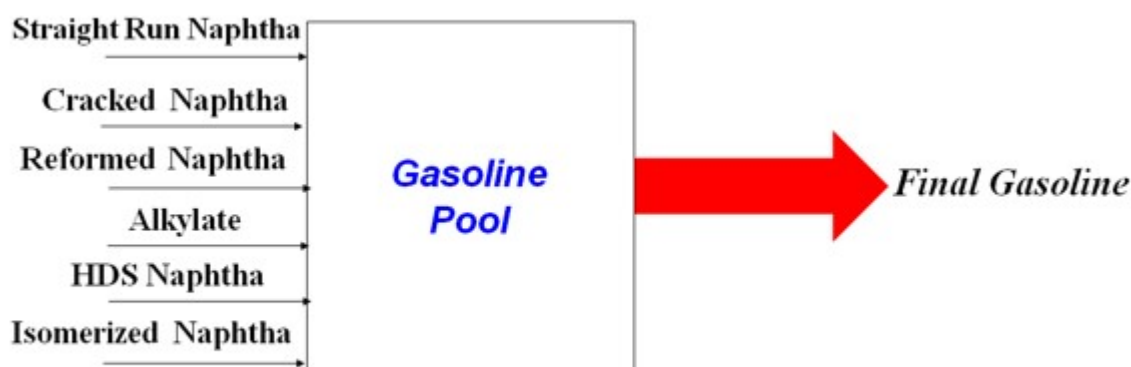


Figure 2 – Example of Process Streams Blending to Produce Gasoline

requirements and thermodynamic limits, are applied high activity catalysts which allow operating under lower temperatures.



The catalysts applied in the isomerization processes have bifunctional characteristics containing acids and metallic sites, the most employed catalysts are platinum impregnated chlorided-alumina, zeolitic and oxide-based catalyst.

Isomerization process produces a light stream that can contribute to raising the octane number to the final gasoline and is practically free of contaminants like nitrogen and sulfur, however, due the high content of lighter compounds, the isomerate stream negatively affects the gasoline fugitive emissions specification (high Reid Vapor Pressure), that is, the isomerate need be blend with heavier streams to formulate gasoline that meet the current specifications.

The typical feed stream to isomerization units is normally the lighter fraction (C5 – C6) of straight run naphtha when the objective is to produce isomerate naphtha which will be directed to gasoline pool. Another process that has great interest to the refining industry is the isomerization of N-butane to isobutane, this product can be directed to the feed stream to catalytic alkylation units or to produce MTBE (Metil-Tert Butyl Ether), in this case, the process feed stream is the heavier fraction of LPG

obtained in debutanizers columns. The isomerization catalyst is sensitive to contaminants as nitrogen and sulfur, and then normally the feed pass through a treating step to reduce the contaminant content (normally hydrotreatment).

Figure 3 shows a process flow diagram for a typical isomerization unit.

The feed stream is mixed with hydrogen and is pre-heated in heat exchangers, following is fed to the reactor, and the reactor effluent is cooled through heat exchange with the fresh feed and then is directed to a separation vessel where a major part of hydrogen is separated from the liquid phase. Hydrogen is sent back to the process by the compressor while the liquid phase is sent to a distillation column where the isomerate naphtha is the bottom product and the light products are removed in the top.

The main process variables of the isomerization processes are temperature, operation pressure, and space velocity. As aforementioned, the temperature is normally reduced and can vary between 120 and 250 oC depending on the activity of the employed catalyst, due to the isomerization reactions characteristics, seek to operate under lower temperatures.

Operating pressure is normally close to 30 bar, higher pressures conduct the higher catalyst cycle life, on the other hand, favor hydrocracking reactions that are undesirable. The space velocity in the reactor is a design

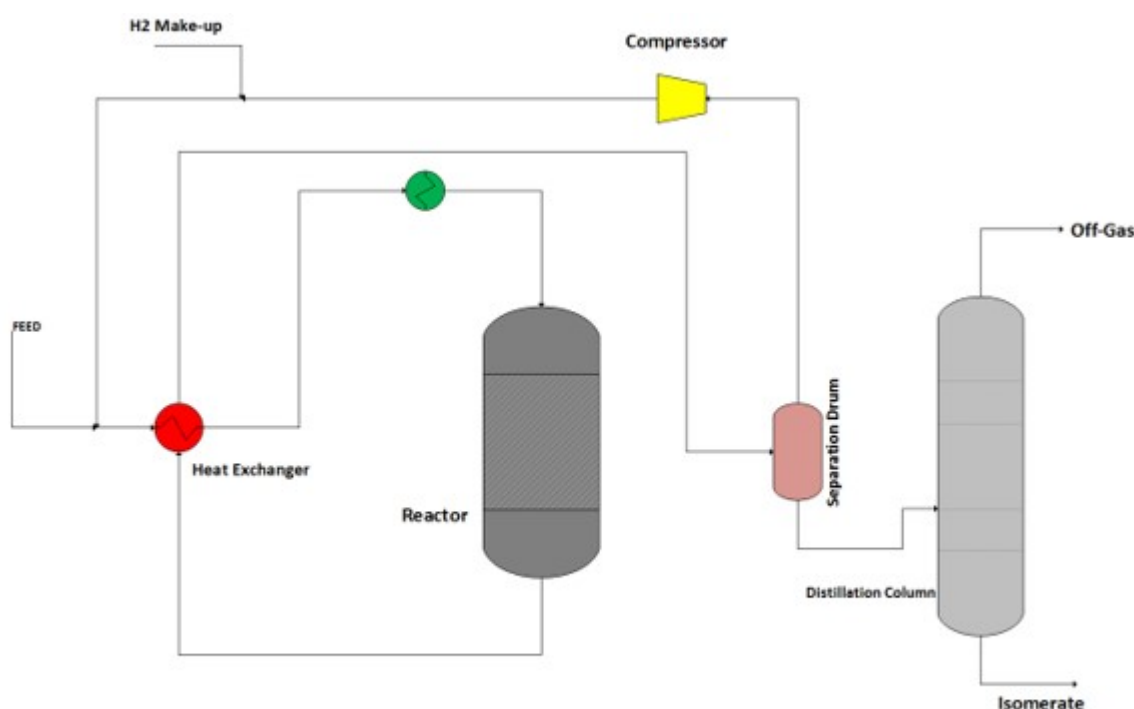


Figure 3 - Typical arrangement for Single reaction stage Isomerization Unit.

variable and expresses a relation among residence time and catalyst total cost, lower velocity results in higher catalyst mass and higher residence time which allow operates under lower temperature level.

One of the most known isomerization technologies is the PENEX™ process, developed by UOP Company that apply a platinum impregnated chlorinated alumina as the catalyst. Figure 4 presents a simplified scheme for this process.

PENEX™ technology applies dryer vessels containing molecular sieves aim to remove water from feed and hydrogen streams, preserving the catalyst.

The process applies two reactors in series and this arrangement allows one reactor while the other is under catalyst replacement or maintenance.

Another very employed isomerization technology is the PAR-ISOM™ process also developed by UOP Company, in this case, is applied a sulfated-zirconia catalyst with the possibility of regeneration in the processing unit.

GTC Technology Company developed the ISOMALK-2™ technology that also applies platinum impregnated sulphated-zirconia as the catalyst, the process still applies pre-fractionating step and the recycle of poor octane index streams, the process is presented in Figure 5.

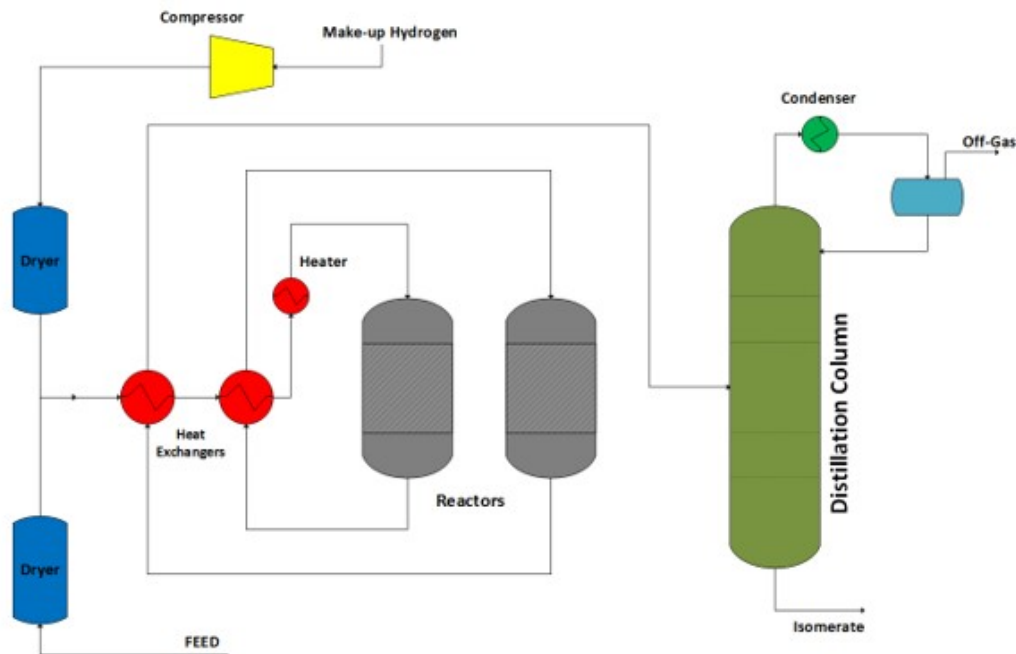


Figure 4 – Simplified Process Scheme to PENEX™ technology by UOP Company

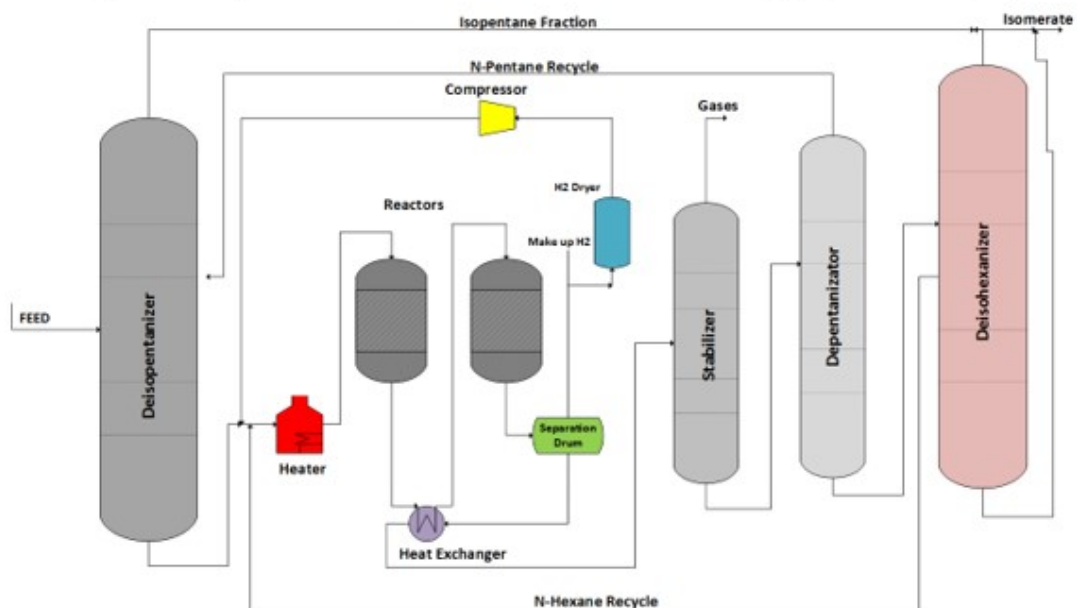


Figure 5 – Process Scheme for ISOMALK-2™ technology by GTC Technology Company.

Despite need higher investment, the ISOMALK-2™ technology can produce isomerase naphtha with higher octane index.

As the isomerization reactions are limited by equilibrium conversion, some technologies involve removing isoparaffin formed during the process from the recycle stream, shift the reactional equilibrium and raising the quality of final product. These technologies apply sophisticated separation processes like simulated moving bed and molecular sieves, the technologies IPSORB™ and HEXSORB™ developed by AXENS Company and technologies MOLEX™ e ISOSIV™ developed by UOP company are examples of these processes.

As mentioned above, the N-butane isomerization is economically attractive once the isobutane is applied like feedstock to catalytic alkylation processes, which is another process capable to produce high quality gasoline. Another use to isobutane is the MTBE production, however, face the current environmental regulations his use as a gasoline additive is falling down and in some countries is prohibited.

The main butane isomerization technology is the BUTAMER™ process, developed by UOP. Another available technology is the ISO C4™, developed by AXENS. The process is basically the same applied to C5-C6 fraction isomerization process as described above.

Isomerization processes show advantages in relation to others gasoline upgrading technologies because can produce low contaminant stream (nitrogen and sulfur), without aromatic compounds and productive process safer when compared with catalytic reforming and alkylation technologies, respectively.

These characteristics make the isomerization processes attractive to refiners inserted in markets with high demand for gasoline and petrochemical intermediates

Catalytic Reforming Technologies

The main objective of the Catalytic Reforming unit is to produce a stream with high aromatics hydrocarbons content that can be directed to the gasoline pool or to produce petrochemical intermediates (benzene, toluene, and xylenes) according to the market served by the refiner, due the high content of aromatics compounds the reformate can significantly raise the octane number in the gasoline.

A typical feedstock to the catalytic reforming unit is the straight run naphtha, however, in the last decades due to the necessity to increasing

the refining margin through installation of bottom barrel units, hydrotreated coke naphtha stream has been consumed like feedstock in the catalytic reforming unit.

The catalyst generally employed in the catalytic reforming process is based on platinum (Pt) supported on alumina treated with chlorinated compounds to raise the support acidity. This catalyst has bifunctional characteristics once the alumina acid sites are active to molecular restructuring and the metals sites are responsible for hydrogenation and dehydrogenation reactions.

The main chemical reactions involved in the catalytic reforming process are:

- Naphthene Compounds dehydrogenation;
- Paraffins Isomerization;
- Isomerization of Naphthene Compounds;
- Paraffins Dehydrocyclization;

Among the undesired reactions can be cited hydrocracking reactions and dealkylation of aromatics compounds.

The naphtha feed stream is blended with recycle hydrogen and heated at a temperature varying 500 to 550 oC before to enter in the first reactor, as the reactions are strongly endothermic the temperature fall quickly, so the mixture is heated and sent to the second reactor and so on. The effluent from the last reactor is sent to a separation drum where the phases liquid and gaseous are separated.

The gaseous stream with high hydrogen content is shared in two process streams, a part is recycled to the process to keep the ratio H₂/Feed stream the other part is sent to a gas purification process plant (normally a Pressure Swing Adsorption unit) to raise the purity of the hydrogen that will be exported to others process plants in the refinery.

The liquid fraction obtained in the separation drum is pumped to a distillation column wherein the bottom is produced the reformate and in the top drum of the column is produced LPG and fuel gas.

The reformate has a high aromatics content and, according to the market supplied by the refinery, can be directed to the gasoline pool like a booster of octane number or, when the refinery has aromatics extraction plants is possible to produce benzene, toluene and xylenes in segregated streams, which can be

directed to petrochemical process plants. The gas rich in hydrogen produced in the catalytic reforming unit is an important utility for the refinery, mainly when there is a deficit between the hydrogen production capacity and the hydrotreating installed capacity in the refinery, in some cases the catalytic reforming unit is operated with the principal objective to produce hydrogen.

The main process variables in the catalytic reforming process unit are pressure (3,5 – 30 bar), which normally is defined in the design step, in other words, the pressure normally is not an operational variable. The temperature can vary from 500 to 550 oC, the space velocity can be varied through feed stream flow rate control and the ratio H₂/Feed stream that have a direct relation with the quantity of coke deposited on the catalyst during the process. To semi-regenerative units, the ratio H₂/Feed stream can vary from 8 to 10, in units with continuous catalyst regeneration this variable can be significantly reduced.

Due to the process severity, the high coke deposition rate on the catalyst and

consequently the quick deactivation leaves short operational campaign periods to semi-regenerative units that employ fixed bed reactors.

To solve this problem some technology licensors developed catalytic reforming process with continuous catalyst regeneration steps.

The process Aromizing™ developed by Axens company apply side by side configurations to the reactors while the CCR Platforming™ developed by UOP apply the configuration of stacked reactors to catalytic reforming process with continuous catalyst regeneration. Figure 6 presents a flow diagram to Aromazing™ catalytic reforming unit.

Both technologies are commercial and some process plants with these technologies are in operation around the world. Figure 7 presents a basic process flow diagram to CCR Platforming™ developed by UOP Company.

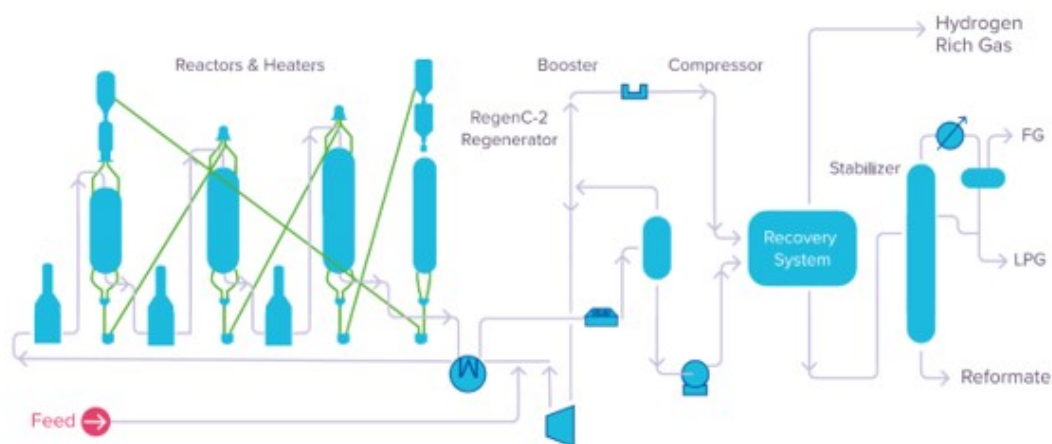


Figure 6 – Aromizing™ Reforming Technology by Axens Company

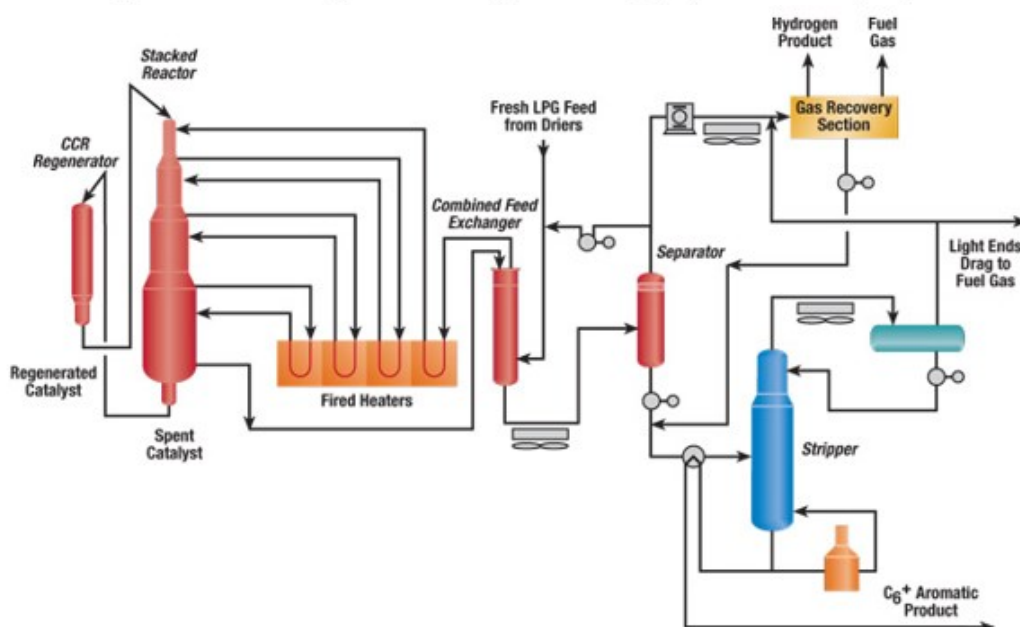


Figure 7 – CCR Platforming™ Reforming Technology by UOP Company

In the regeneration section the catalyst is submitted to processes to burn the coke deposited during the reactions and treated with chlorinated compounds to reactivate the acid function of the catalyst.

Despite the higher capital investment, the rise in the operational campaign and higher flexibility in relation to the feedstock to be processed in the processing unit can compensate the higher investment in relation of the semi-regenerative process.

The catalytic reforming technology gives a great flexibility to the refiners in the gasoline production process, however, in the last decades there is a strong restriction on the use of reformate in the gasoline due to the control of benzene content in this derivate (due to the carcinogenic characteristics of this compound). This fact has reduced the application of reformate in the gasoline formulation in some countries. Furthermore, the operational costs are high, mainly due to the catalyst replacement and additional security requirements linked to minimize leaks of aromatics compounds.

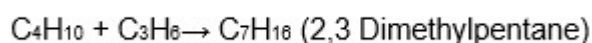
Face to the limitation of the aromatics content in the gasoline, mainly the benzene, the refiners has used alkylation or isomerization to produce streams capable of improving gasoline octane number in detriment of reformate naphtha. Like, some refiners have aromatics extraction plants in his refining scheme, in this case, the production can be directed to produce benzene, toluene, and xylenes as intermediates products to petrochemical industries, despite higher capital and operational investments this configuration can be economically attractive, these products have commercialization prices higher than gasoline and this fact can be potentialized in scenarios like saturation of gasoline market.

Alkylation Technologies

Another alternative to improve the naphtha octane number is the production of branched hydrocarbons (with high octane number) through Catalytic Alkylation Process.

The alkylation process involves the reactions between light olefins (C3 – C5) and isoparaffinic hydrocarbons like isobutane. The reaction product called alkylate is a mixture of branched hydrocarbons with higher molecular weight and higher-octane number.

An example of typical alkylation reaction is represented below:



The reaction is catalyzed in a strongly acidic reaction environment, the acids normally employed in the industrial scale technologies are Hydrofluoric Acid (HF) and Sulfuric Acid (H₂SO₄).

The main advantage of alkylation process is the production of a stream with high octane number, high chemical stability and practically free of contaminants as nitrogen and sulfur. These characteristics turn the alkylate a component attractive to the gasoline formulation to the automotive and aviation industries.

Alkylation process feed streams are generally obtained from LPG produced in deep conversion units, mainly Fluid Catalytic Cracking (FCC) and Delayed Coking. The LPG produced in these process units have high olefins content, ideal for the alkylation process. The isobutane stream is normally obtained through separation of LPG produced in the atmospheric distillation unit, FCC or Delayed Coking in deisobutanizer towers.

Like, the acids generally employed as the homogeneous catalyst to the alkylation process are HF and H₂SO₄. Figure 8 presents a process flow diagram to the alkylation process catalyzed by HF.

The feed stream goes through a pretreatment (generally molecular sieves or alumina) before being pumped to the reactor, the objective is to remove process contaminants mainly water, diolefins and sulfur and nitrogen compounds. Water is especially damaging to the process, once accelerates piping and equipment corrosion process, and beyond requires higher HF reposition.

After pretreatment the hydrocarbons streams are put in contact with the hydrofluoric acid in the reactor and the hydrocarbons mixture and HF solution is separated through gravity in a settler vessel, the hydrocarbon phase is sent to the fractionating section while the aqueous phase (containing the most of HF) is cooled and sent back to the reactor. As alkylation reactions are exothermic, the reactor is continuously refrigerated aim to keep the reaction ideal conditions.

A part of hydrofluoric acid is sent to the stripping column where the acid is stripped with isobutane. The top product is a mixture of HF and isobutene and sent back to the reactor while the bottom stream containing an azeotropic mixture of water and HF, beyond hydrocarbons, this step is responsible to keep the HF free of contaminants and with adequate concentration to the alkylation process.

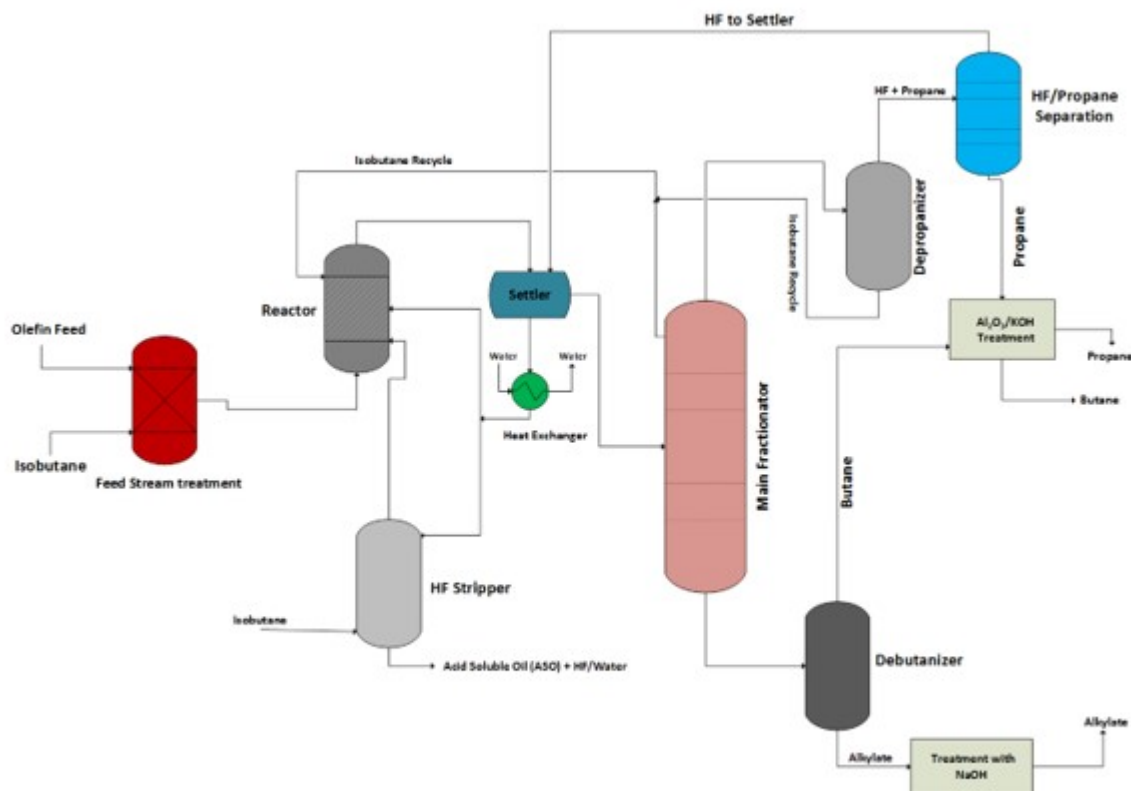


Figure 8 – Typical Process Flow Diagram to Catalytic Alkylation Unit using HF as Catalyst

After the separation columns, butane and propane streams go to a treatment with alumina aim to decompose organic fluorides and with KOH to neutralize the remaining acidity. The alkylate stream is treated with NaOH to neutralize the remaining acidity. Currently, the main alkylation technology licensors with HF are the companies UOP and CONOCO-PHILLIPS.

Alkylate stream is normally directed to the refinery gasoline pool to the production of high-octane automobile gasoline or aviation gasoline, however, in petrochemical plants this stream can be used as intermediate to produce ethyl-benzene (to produce Styrene), isopropyl-benzene (to produce Phenol and Acetone) and dodecyl-benzene used to produce detergents. Propane and butane streams can be sent to the LPG pool of the refinery or commercialized separately.

The alkylation process with sulfuric acid as catalyst has similarities with the hydrofluoric acid process, however, the sulfuric acid regeneration step is more complex and involves the H_2SO_4 decomposition in SO_2 and SO_3 and the subsequent condensation of concentrated sulfuric acid, this regeneration can be conducted in the processing site or in an external process plant, consequently the acid sulfuric consumption in the process is much higher than

HF, furthermore, the solubility of sulfuric acid in hydrocarbons is lower, requiring greater agitation to maintain the contact between the phases in ideal conditions to the process.

The alkylation technologies with sulfuric acid most applied in industrial scale are the processes STRATCO Effluent Refrigerated Alkylation Process™, licensed by STRATCO Engineering Company and EXXON MOBIL Cascade Auto refrigerated Process™, licensed by EXXON MOBIL Company. Figure 9 shows a simplified process flow diagram to the alkylation technology with H_2SO_4 , licensed by STRACTO Engineering.

Olefins feed stream go to a coalescer to remove water, after the mixture with isobutane recycle, in the sequence the mixture is sent to the reactor. The mixture of hydrocarbons and acid follow to a settler where the phase separations occur, organic phase is sent back to reactor, a control valve promotes the necessary pressure reduction to vaporize the lighter hydrocarbons and remove heat from the reactor, controlling the equipment temperature which raises due the exothermic characteristics of alkylation reactions.

The hydrocarbons blend is sent to a flash drum where the lighter phase is directed to a compressor to condense in an accumulator

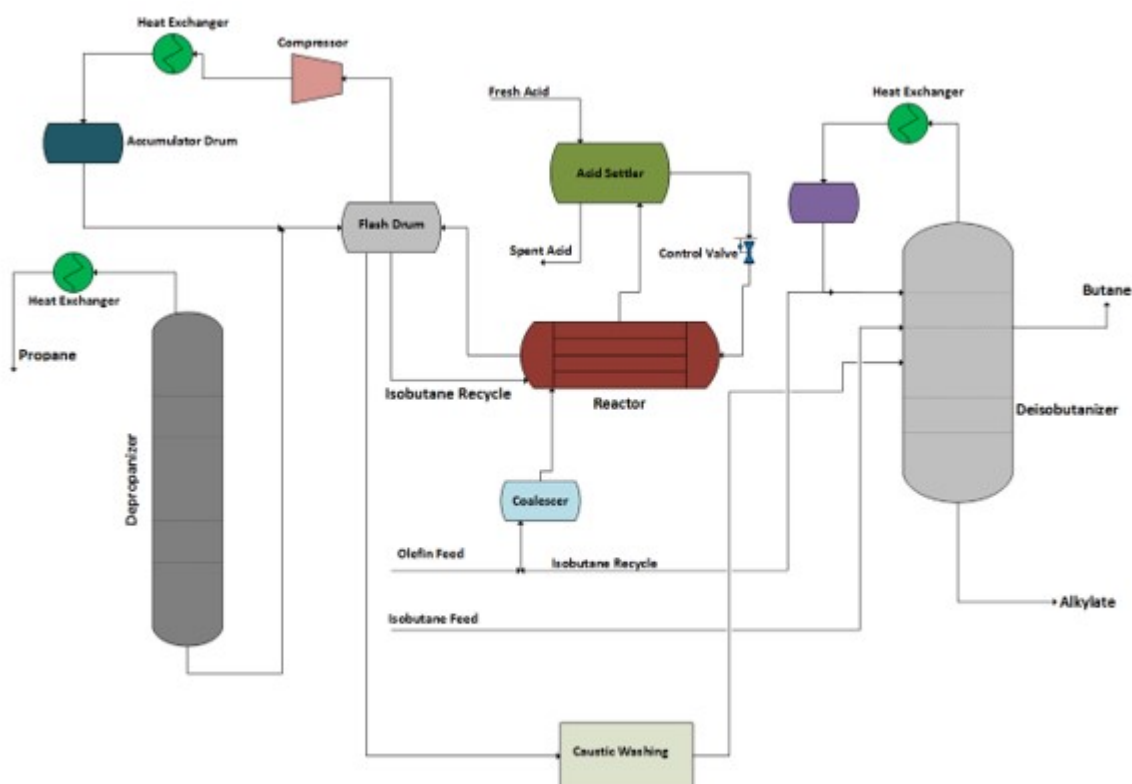


Figure 9 – Basic Process Flow Diagram to the Alkylation Process Catalyzed by H_2SO_4 , developed by STRATCO Engineering Company.

vessel and the propane is recovered in the depropanizer tower while the heavier hydrocarbons (essentially isobutane) are recycled to the reactor. The stream containing the alkylate is directed to a caustic treatment and posteriorly to a deisobutanizer column where the alkylate are removed in the bottom.

As aforementioned the need of catalyst replacement is higher in the process with sulfuric acid, however, the HF process needs higher Isobutane/Olefins ratio, which means a greater separation system. Over the last decades, the refiners have opted to the HF alkylation technologies due to the higher simplicity of this process and the lower need of catalyst replacement that leaves to lower operational costs.

However, regulatory pressures have led some refiners to convert her their HF alkylation units to operate with H_2SO_4 , due the high volatility and higher risks presented by the hydrofluoric acid, some licensors developed technologies to convert HF units to operate with sulfuric acid like the ALKYSAFE™ technology, licensed by STRATCO Engineering Company and the ReVap™ process, developed by the companies EXXON MOBIL and CONOCO-PHILLIPS which uses additives to reduce the HF volatility, making the unit operation safer.

Acid purity must be maintained higher as

possible through the removal of ASO (Acid Soluble Oil), water and dissolved reactants in the HF case and through fresh acid replacement in processes with acid sulfuric as the catalyst.

The main disadvantage of the alkylation processes with homogeneous catalyst (HF or H_2SO_4) is the need to handling strong acid highly concentrated, that leave a greater process safety risks and high maintenance costs, mainly related to avoid corrosion in piping and equipment and, as aforementioned, equipment failures with contention losses can have dramatic consequences.

Aiming to eliminate these risks, some licensors have dedicated his efforts to develop heterogeneous catalysts that can replace the strong acids in the alkylate production processes, the UOP Company developed the process called ALKYLENE™, that apply a solid catalyst with continuous regeneration during the process. Among other technologies can be cited the processes LURGI EU-ROFUEL™, developed by Lurgi Engineering Company in cooperation with SUD-CHEMIE, the ALKYCLEAN™ process, developed by the companies ABB-Lummus and Akzo Nobel and the process FBA™, developed by Haldor Topsoe.

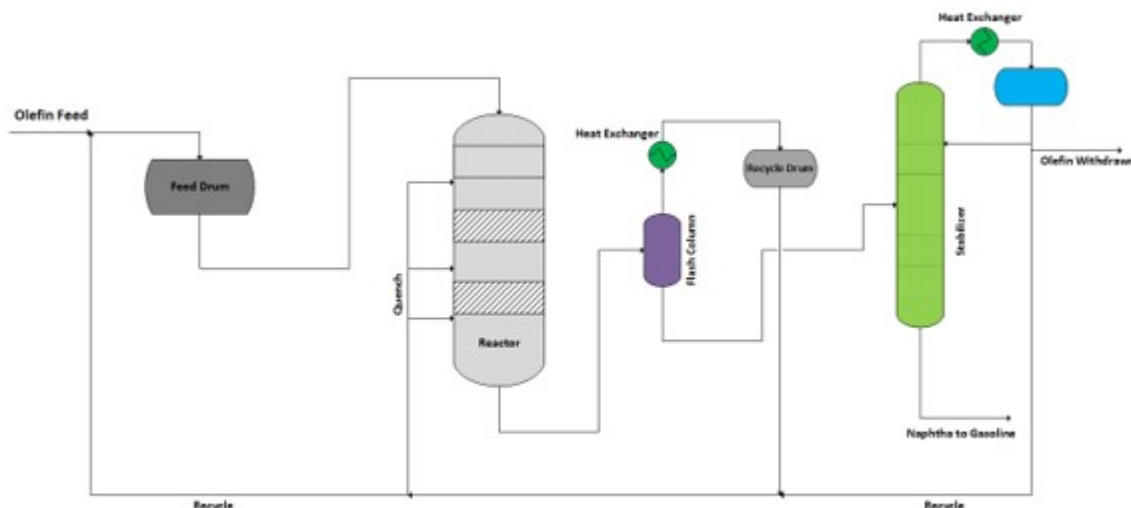
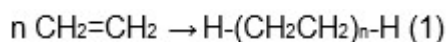


Figure 10 – Typical Process Flow Diagram for Light Olefins Condensation Process to produce Gasoline.

Light Olefins Condensation

The process consists in an olefins combination and the consequent production of high molecular weight olefins, as presented as following.



This process is controlled to maintain the products in the gasoline distillation range.

The reactions are carried out under mild temperature conditions (between 15 and 25 oC) and pressures that vary between 10 and 80 bar, according to the process feed stream. The condensation reactions are exothermic and the reaction is controlled by heat removal from the reactor, normally through cold streams injection between the catalytic beds (quench streams). The process can be conducted under thermal or catalytic conditions; however, the commercial units normally apply the catalytic route using acid catalyst, mainly phosphoric acid deposited on an adequate carrier.

Raw material (light olefins) for the process is normally from fluid catalytic cracking units (FCC), catalytic dehydrogenation or thermal cracking units.

A typical process flow diagram for a gasoline production unit through olefins condensation is presented in Figure 10.

The feed stream passes through a process to remove contaminants, mainly sulfur compounds that are catalyst poisons. From the feed drum, the olefinic stream is pumped to the reactor where the temperature control is realized by the injection of reactants under a reduced temperature between the catalytic beds, as aforementioned.

After the reaction step, the reactor effluent is separated in a flash distillation column where the bottom product is sent to a stabilizer column that aims to removing the light compounds from the naphtha stream and the top product is recycled to the process. Normally the gasoline produced by this route is called polymerization gasoline.

This process is capable to produce high octane gasoline, however, the high olefin content makes the polymerization gasoline chemically unstable, leading to gum producing in the short term. The polymerization gasoline is normally directed to the refinery gasoline pool and mixed with the others naphtha streams to contribute to raising the octane index of the final gasoline, however, his adding is limited too by his high volatility (high Reid Vapor Pressure). The remaining olefins stream can be directed to petrochemical intermediates market or to the refinery LPG pool.

The gasoline production process by olefins condensation or polymerization, lost space to other technologies like isomerization, alkylation and catalytic reforming that can produce more chemically stable naphtha with the same octane index (in some cases higher).

Nowadays, light olefins are intended to consumption as petrochemical intermediates due the higher profitability offered to the refiner, however, refiners inserted in markets with high gasoline demand can apply this process to quickly raise the high-quality gasoline production.

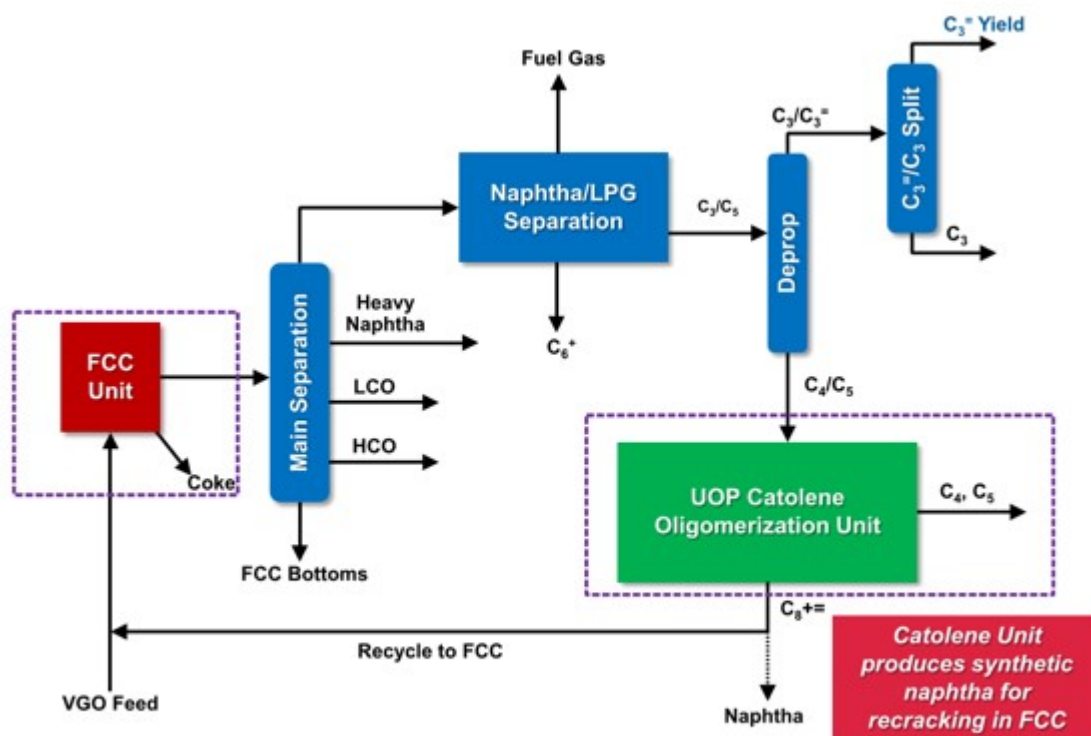


Figure 11 – Processing Scheme Relying on UOP Catolene™ Olefins Polymerization Technology

Some important technology developers as UOP Company and Shell Global Solutions developed contributions to improve the olefins condensation process. Among the commercial technologies dedicated to produce naphtha from olefins polymerization we can quote the Catolene™ process by UOP Company and the Polynaphtha™ technology developed by Axens Company. Considering the growing demand by petrochemicals, the naphtha polymerization units are being applied to improve the yield of light olefins through the recycling of polymerized naphtha to an FCC unit, as presented in Figure 11.

As aforementioned, polymerization or olefins condensation can contribute an agile and relatively cheap way to raise gasoline production, mainly in extreme scenarios of the shortage of derivatives. In some refining configurations, these processing units can also be applied to produce diesel.

Etherification Processes – The Oxygenated Alternatives

Among the additives that were widely applied in the gasoline formulation, it's possible to highlight oxygenated compounds as the ethers MTBE (Methyl Tert Butyl Ether), ETBE (Ethyl Tert Butyl Ether), and TAME (Tert-Amyl Methyl Ether).

These additives are produced through etherification reactions, which consist in the addition of an alcohol to olefins producing ethers. The MTBE and TAME are produced from Methanol while the ETBE is produced from Ethanol.

Due to its characteristics (total miscibility whit hydrocarbons, high octane number, and low volatility), MTBE is the ether most widely employed. The MTBE production chemical reaction is presented in Figure 12.

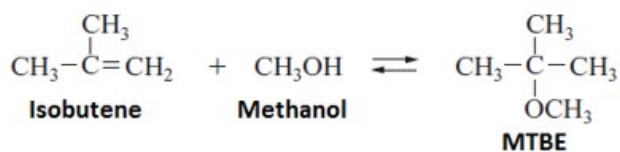


Figure 12 – MTBE Production Chemical Reaction

The reaction is catalyzed by acid catalyst with cationic resins as the carrier.

In refineries with MTBE producing units, the Isobutene is normally obtained through fractionating of LPG from Fluid Catalytic Cracking Unit (FCC). MTBE production reaction is exothermic and is carried out under mild conditions, normally the pressure varies from 10 to 20 bar and the temperature is controlled from 40 to 70 oC. Figure 13 shows a typical process flow scheme for MTBE production.

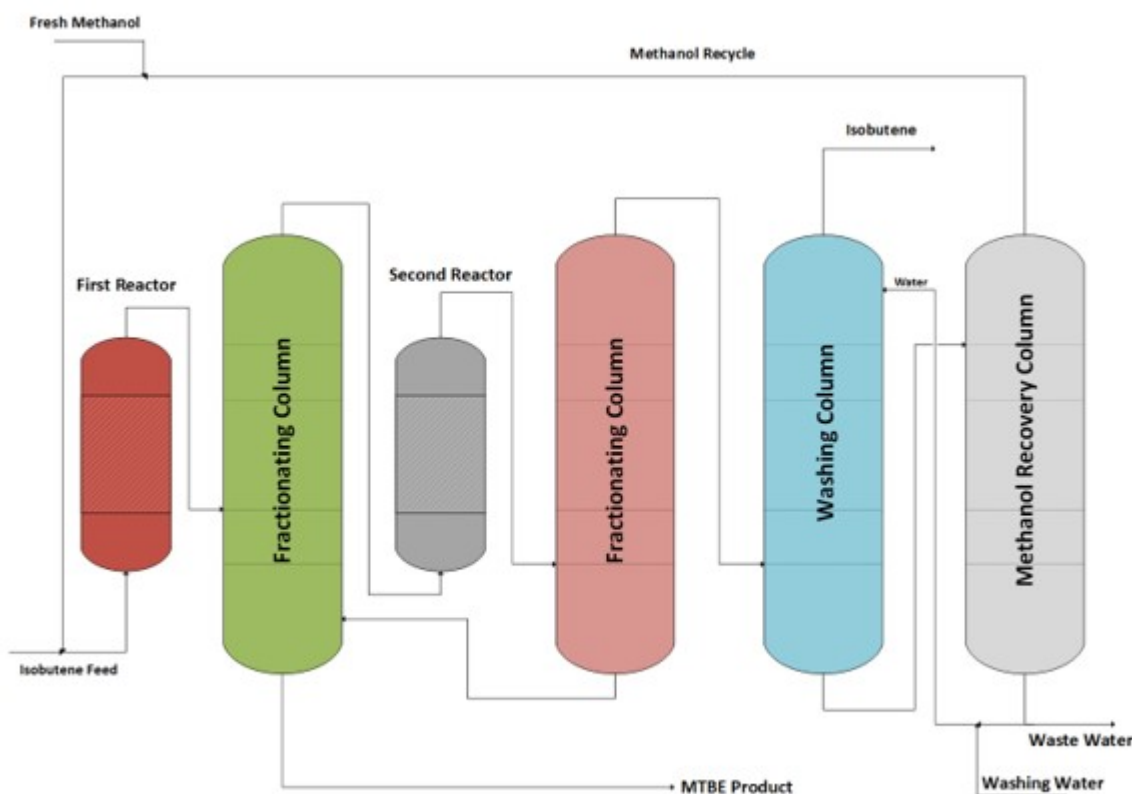


Figure 13 – Typical Process Arrangement to MTBE Production Process Unit

The methanol fresh feed is mixed with the recycled methanol and posteriorly mixed with the isobutene stream before entering the first reactor. The first reactor effluent is sent to a fractionating tower where the bottom product is the MTBE and the top stream is directed to the second reaction stage, the effluent of this reactor is pumped to another distillation column where the MTBE is removed from the bottom and the top is directed to a water washing column. In this column, the remaining Isobutene is removed in the top and the Methanol/Water mixture is removed in the bottom. This mixture is separated into another fractionating column and the remaining Methanol is recycled to the process while the water is removed to treatment or partially recycled to the washing tower.

The principal process variables for MTBE production process are the pressure and temperature that need to be controlled at the lower possible level to attend the compromise between the kinetic requirements and the exothermic characteristics of the reaction.

Main process technology licensors developed technologies to produce oxygenated additives for gasoline, mainly MTBE.

One of the main commercialized technologies is the ETHERMAX™ process developed by UOP Company, this process is presented in Figure 14.

This process is capable of producing MTBE, ETBE, and TAME according to the raw material applied, this fact gives a great flexibility to the process which is a considerable advantage. A major part of the etherification reactions occur in the reactor and the remaining alcohol is partially converted in the reactive distillation column.

As aforementioned, some of the main technology licensors developed processes aiming to produce oxygenated additives, mainly in the 80s and 90s with the objective to maximize the production of these compounds in substitution of lead-based additives. Among the main commercially available technologies we can cite the CDMTBE™ process, developed by McDermott Company and the CATA-COL™ technology developed by Axens Company.

Conclusion

As aforementioned, high-quality gasoline still presents great demand especially in growing economies. The octane boosting technologies can help refiners to comply with the market requirements at same time that reduce the consumption and environmental impact of fossil fuels that is an urgent requirement of our society. Flexible refining technologies capable to be directed to petrochemicals like catalytic reforming units gives competitive

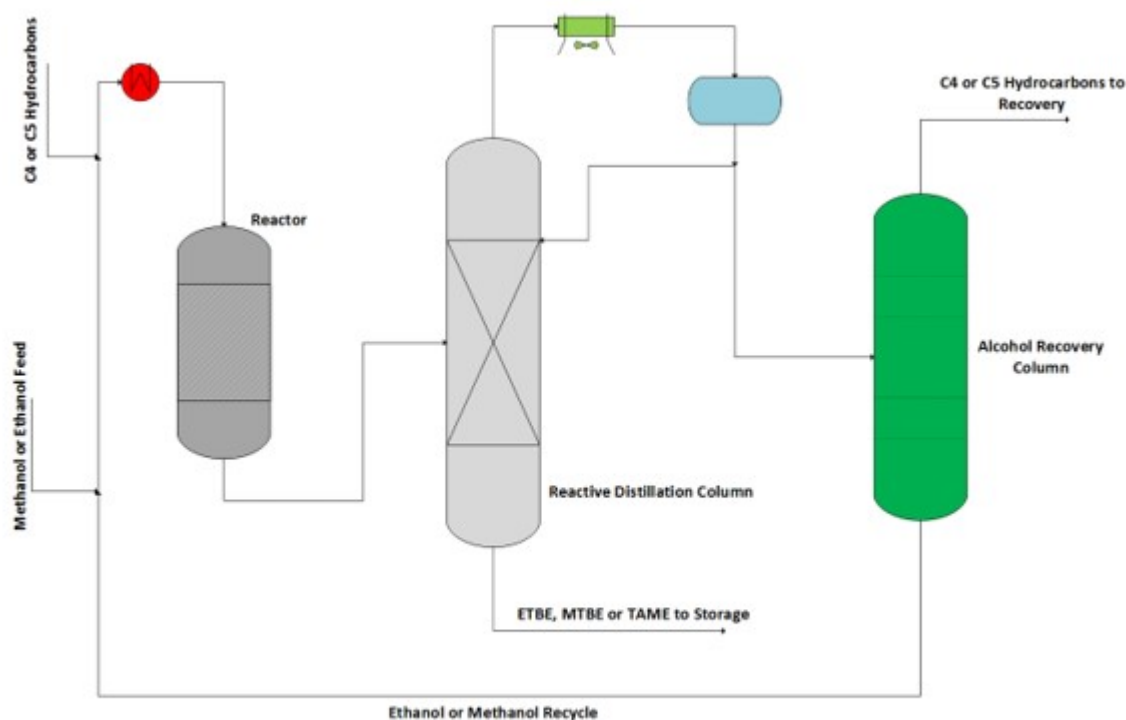


Figure 14 – Simplified Process Flow Diagram for ETHERMAX™ technology by UOP Company

advantage to refiners considering the growing demand by petrochemicals, especially light aromatics, but the remain octane boosting technologies can still offer great contribution to the refining margins according to the market supplied to the refiners.

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Hydrotreater Catalyst Sulphiding with Sulphur Spiking Agent

Shahzeb H.M Ismail, Arsalan Saleem

BACKGROUND

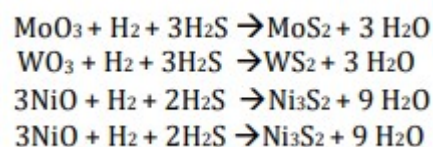
The need of spiking agent arises in case of lower content of sulfur in Hydro feed less than 100 ppm during the startup or when skimming is carried out where around 10-15% of the catalyst is also removed from the reactor's upper layer and catalyst is added to make up for the volume, the chemical Injection of Sulfur via spiking agent is to be accomplished to meet theoretical H₂S requirement for Hydrotreater catalyst. The online injection of sulfur rich agent like Dimethyl disulfide (DMDS) or di-*t*-butyl polysulfide (DBPS) is proven and being used worldwide, where both can be used with its own pros & cons.

INTRODUCTION

Typically, a catalyst used in all hydro processing or hydro treating facilities in a refinery requires sulfiding in order to get it activate. It consists of active species like Molybdenum or Tungsten Sulfides promoted by Cobalt or Nickel sulfides. Sulfide catalysts are pyrophoric in nature, therefore they are transported as Oxides and activated via reductive sulfiding in presence of hydrogen at elevated temperatures & pressures. On account of the fact, Catalyst is inactive/indolent in state when received. The catalyst is sulfided by reaction of its active metals with hydrogen sulfide, which is produced in-situ from a reaction between available sulfur in the feed stream (HSN) & hydrogen, or more commonly from sulfur in the sulfiding agent when it decomposes and makes H₂S alongside byproduct. A defined quantity of sulfur is required to activate the catalyst that depends upon the volume of catalyst, Reduction time & results of Recycle gas SO₂. When Lighter Crude is processed (LSN), amount of Sulphur in hydro feed is less, that hinders the catalyst activation as the Sulphur requirement is not fulfilled. In order to fulfill Sulphur requirement, Dimethyl disulfide or any other spiking agent injection is required to maintain the catalyst activity. Alternatively,

high sulfur feed is required, but there is a consequence of coking at high temperatures of Reduction prior to decomposition.

Dimethyl Disulfide (DMDS): DMDS is a Sulfiding agent, which is used along with reducing agent hydrogen to transform metal oxides to metal Sulfides. DMDS decomposes into H₂S which reacts with metal oxides in the presence of hydrogen as shown in the reactions below.



DMDS is ideal for Sulfiding because of following reasons:

- It has high sulfur content (68%) which reduces the amount of DMDS required for converting oxides to active metal sulfides.
- No exotherms from the Sulfiding reaction
- No considerable sour water make.
- By-Products are lighter Limited amount of H₂S (which is excess & not converted) circulates through the reactor, protecting the sulfur sensitive catalyst downstream of bed and contributing to indicate SO₂ in Recycle gas for estimation of completion of Sulfiding.
- It is thermally stable and has low viscosity, higher volatility ensures a good vaporization & distribution upstream of reactor
- It also has low decomposition temperature of 175-205 °C that prevents the risk of reducing the metal oxides prior to Sulfiding and favors its decomposition to H₂S at low temperature.

However, it has also major disadvantages like

- There are several hazards associated with DMDS injection because of its low flash point (16 °C) that presents a potential fire hazard in refinery usage. Therefore, it is mandatory to store DMDS under nitrogen.
- It can decrease the partial pressure of H₂ in recycle gas making excess of methane, so considerably calculated amount of it should be used.
- May need additional Hydrogen in order to make up for the purity.
- It requires purge out the H₂S that creates Sox contamination.

Alternative Method DBPS:

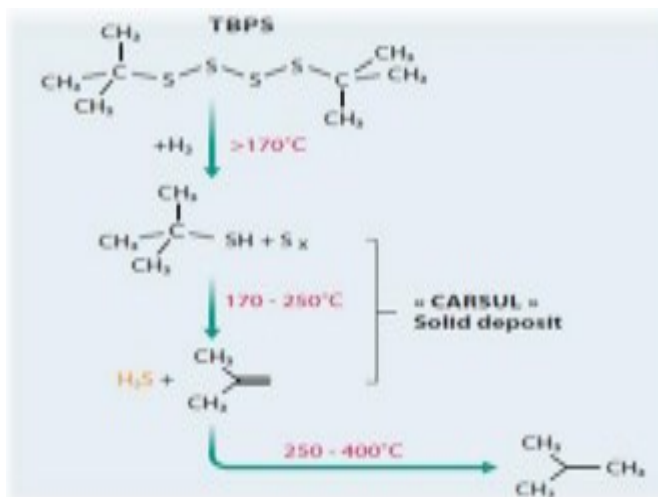
A Sulfur rich material di-t-butyl polysulfide (DBPS), consists of linear polysulfide chain with tertiary butyl end groups. It has the advantage of having virtually very few of the negative aspects or hazardous properties as associated with applying DMDS.

Advantages can be counted as:

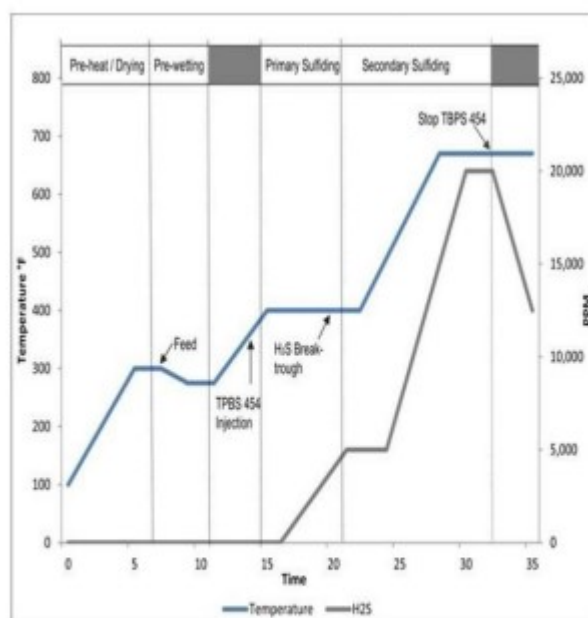
- DBPS flashpoint is high 100 °C – reduces fire hazard.
- Decomposition at lower temperatures as indicated in graph A, which allows to start sulfiding at lower bed temperatures.
- DBPS can be stored at the refinery regular containers.
- No wearing of special clothing beyond what is normally required for handling any chemical in a refinery.
- No hard odor, diesel-like smell associated with the products chemistry.
- DBPS hydrocarbon byproduct is isobutane, which normally exits the high-pressure separator with the liquid hydrocarbons and does not dilute hydrogen in the recycle gas.

However, it also has some disadvantages like

- Decomposition is relatively less clean and comes with elemental sulfur as intermediary element up till 250o Celsius.
- Additionally, the combination of olefins & sulfur can occur forming Carsul (solid deposit) at 170 – 250 oC.



- By-Product is heavier & can have a pressure drop if precipitation of intermediary element occurs.



Decomposition profile of Di-t-butyl polysulfide. Graph A.

Comparative study:

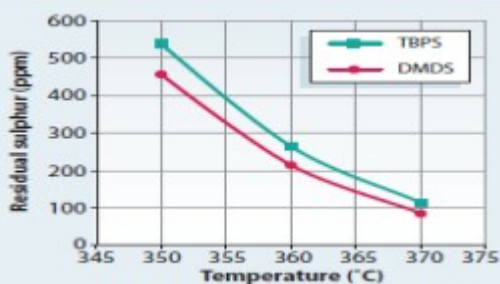
Comparative study was conducted in order to analyze the behavior of catalyst sulfided by DMDS & DBPS. Both showed relatively symmetrical results in terms of hydrodesulfurization.

- A minor pressure drop observed across reactor bed. whereas, no plugging or scaling found in downstream exchangers.
- The decomposition of DBPS is at lower temperatures than DMDS (160 0C)

- Furthermore, lesser sulfiding times were recorded as comparison to DMDS, lower temperature decomposition also helped in refraining irreversible reduction of catalyst with hydrogen due to exotherm.
- One major point noted that quantity needed for sulfidation increased to 20% when DBPS was used.
- DMDS yields methane which accumulates in the recycle gas, decreasing partial pressure for H₂ and sometimes it needs to be purged that accompanies the valuable H₂ & H₂S alongside that can cause SOX contamination.
- Additional makeup is required for H₂, when using DMDS. Whereas, DBPS produce isobutane as a byproduct that can easily be separated from recycle gas and contributes as a valuable stream for alkylation downstream.
- Coriolis Mass Flow Meters - the most accurate and dependable meter available.
- Empty Pipe Detector - Shuts off flow to the process once the delivery trailer is emptied, preventing cavitation of the feed pump.
- Materials - DMDS is a powerful solvent. All seats, trim and gaskets are specifically chosen to meet the rigorous demands of pumping this chemical.
- Safe Line Breaks – We purge all lines and equipment with diesel at the completion of the job, ensuring that line breaks are not made with residual DMDS in the lines.

One considerable con of DBPS is that its sulfur content is lower (54%) than DMDS (68%). This requires an extra dosage of DBPS compared to DMDS to make same amount of sulfur available to the catalyst.

*Below showing in graph that to reach the same performance for hydrotreaters, the start-up using DBPS requires to run at slightly higher temperatures than DMDS.

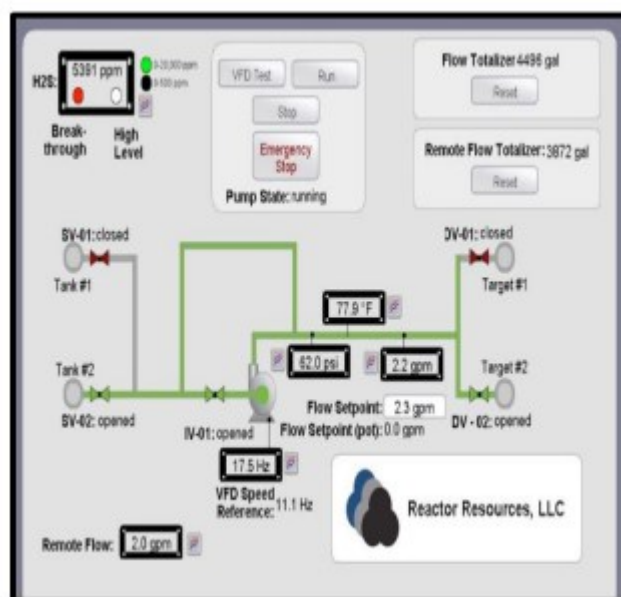


AUTOMATIC SKID FACILITY:

Reactor Resources has introduced the first and only patented Smart Skid DMDS Injection System for DMDS injection in Hydrotreater as safely and accurately as possible. It allows customers to constantly monitor flow rate, total quantity injected, pressure, temperature, and valve position via a secure web link. It also allows remote operation.

Other advantages of Smart Skid system are:

- Remote Operation - In the event of a unit evacuation, the injection system can still be controlled remotely. In addition, all of the pump operation parameters can still be viewed on the web.
- Replace N₂ environment with H₂ and keep temperatures to 120-150 oC, while draining from lowest points, keep circulating H₂ with minimum 80% purity and stay at the mentioned temperatures unless water stop appearing in separator, do not decrease further temperatures.



SULFIDING PROCEDURE & MONITORING:

GENERAL PROCEDURE:

Before the sulfiding is commenced the catalyst should be dried & free from oxygen, whether it is taken in service after regeneration or freshly used. We will be discussing about regenerated catalyst that should be sulfided after regeneration.

- Pulling the vacuum to remove any Oxygen that left over during burning and then purging with N₂ to make sure no Oxygen is present inside the HP system, confirm from analyses of gas, while keep draining from lowest points.
- Replace N₂ environment with H₂ and keep temperatures to 120-150 oC, while draining from lowest points, keep circulating H₂ with minimum 80% purity and stay at the mentioned temperatures unless water stop appearing in separator, do not decrease further temperatures.

- When water disappears & oxygen is found nil or very minimal start injecting 1-2 % of DMDS at same temperature and look for H₂S break through wave, temperatures will be rising keep monitoring to avoid any exotherm, in case of emergency stop injection and lower temperatures, if needed use N₂.
- If the H₂S from Recycle gas remains constant increase temperatures 315- 345 oC while monitoring the H₂S it will decrease in Recycle Gas first and then will increase up to the quantity it is being injected. At this point it is assumed to be completed & thus normal operation can be adopted.

MONITORING PARAMETERS:

Injection rate should be closely monitored as quantify and calculated from catalyst metal oxide data provided by Vendor Recycle Gas Purity must be monitored not to fall below 80% and preferred to be kept at higher side also keep checking H₂S from Separator top or Compressor Suction. Reactor Temperature must be carefully dealt with as sudden rise in temperature may lead to premature coking. Sour Water is by-product of sulfiding keep monitoring level and drain it to refrain traces from circulation back to reactor, its essential indication for completion of Sulfiding.

TROUBLESHOOTING EXPERIENCE:

Catalyst at normal conditions contain 2-5% moisture due to hygroscopic nature, it must be less than 1% or preferably traces else during rising temperature it may convert into steam causing damage to Catalyst. Additionally, most common problem encountered during DMDS injection is that the quantity to be injected is not adjusted as per the recommended flow rate in order to complete the step. Both higher rates and lower rates are handy, while the integrity of catalyst can be at risk. We experienced Low flow rate with higher temperature can cause the conversion of oxygen to water that can reduce the metal catalyst, the level in separator boot will start rising while H₂S starts diminishing and if not identified can permanently deactivate it. Meanwhile the temperatures are increasing and malfunctioning of injection for higher flow rates can produce a heat wave as its exothermic in nature when decomposed to from H₂S, you can see a premature coking, you can cut off the injection, heat source, check for recycle gas H₂S and replace the environment with N₂ if necessary & normalize activity once resolved.

CONCLUSION:

With respect to the online addition of the Sulfur spiking agent, DBPS is most suitable as

compare to DMDS but more quantity will be required. DMDS is also proven and widely used with hazard control strategies implementation and there are also specialized skids in the market for precision and control of dosing and reduction of human involvement. Furthermore, for Hydro desulfurization, sulfiding with DBPS have almost same impact as of DMDS & can be used as a substitute having privilege under many circumstances, however for achieving more fine results rise in temperature is required but still it remains minor factor. Additionally, other indicators like decomposition temperature, density, flash point and by products remains prominent distinction from rest.

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Dynamic Decoupling in Gas Compressors

Jayanthi Vijay Sarathy

Centrifugal Compressors are unlike positive displacement compressors which has a strong coupling between mass flow, speed, and pressure. Compressors are not only operated as single stage machines, but also with two or more machines in series or parallel. This represents a situation where due to any process disturbances, the action of one controller can cascade to create a change in another control loop and result in oscillatory behaviour in the overall compression system.

A factor that contributes to how a compression loop responds depends on the amount of piping and equipment volumes. For example, systems like scrubbers or similar vessels that have large liquid volumes flowing into them, take a longer time to reach equilibrium, which means they are capacitive in nature.

For systems with high capacitance, the loop coupling interactions is relatively less. However, in systems which have low capacitance and fast and responsive controllers, the controller loops would be more dynamically coupled, mandating the need to decouple the control loops faster. This is known as Feed forward loop decoupling, a.k.a, Dynamic Decoupling.

Loop Decoupling Example 1

To explain, a fixed speed drive with suction throttling is taken as an example.

In Figure 1 is a suction throttle valve [STV] with a pressure controller [PIC], placed inside the anti-surge loop. In a low flow situation, the anti-surge controller [UIC] recycles flow to the suction to avoid surge, thereby pressurizing the suction scrubber.

To relieve excess pressure, the suction throttle valve opens causing more flow to pass through the suction, followed by UIC initiating anti-surge valve [ASV] closure. However, the cycle keeps repeating where, every time UIC operates, PIC is also initiated (after some dead time) causing oscillatory instability in the loop.

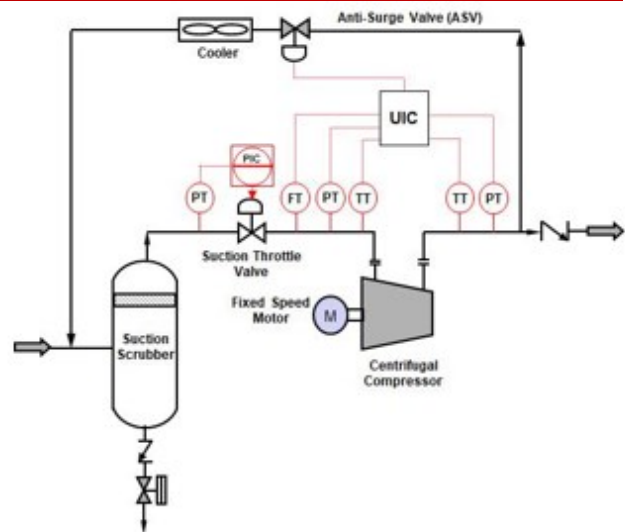


Figure 1. No UIC output to control PIC

But in figure 2, by giving the UIC output to the PIC, the suction throttle valve opening is controlled by the UIC output, thereby preventing any suction scrubber pressurization. Therefore, Loop decoupling is achieved by ensuring relatively constant scrubber pressure & throughput while UIC operation is unaffected by the actions of PIC.

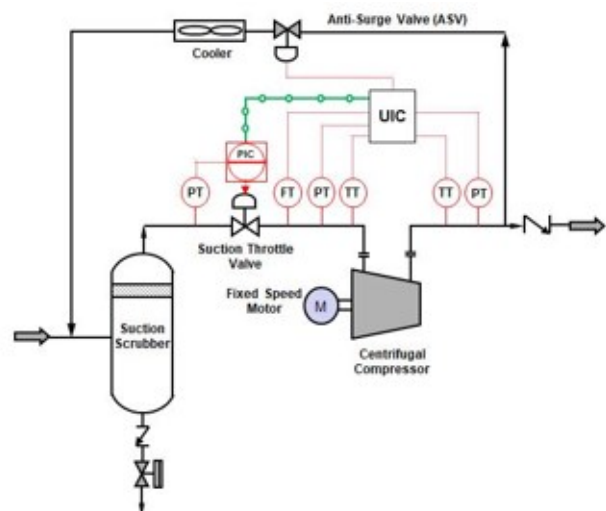


Figure 2. Suction Header Speed Control Method

In this case, it is advisable to provide a mechanical stopper on the STV, because at low flow conditions, the STV needs to maintain a minimum opening to prevent the compressor from completely being starved of any gas. A minimum opening of 15% can be implemented, although the actual value is determined during commissioning.

Loop Decoupling Example 2

In the case of variable speed drive [VSD] as shown below,

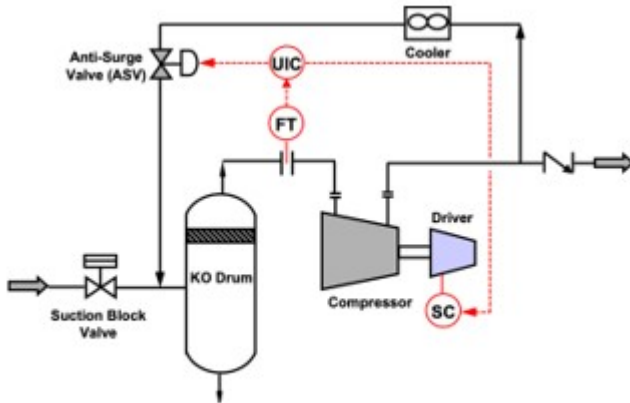


Figure 3. Suction Header Speed Control Method

When the suction gas flow decreases, the speed controller [SC] detects a fall in gas flow rate and decreases the compressor speed. As the speed decreases, the operating point moves closer to the surge control line [SCL]. At this junction, the anti-surge controller [UIC] opens the anti-surge valve (cold recycle) to ensure sufficient suction flow and keep the operating point away from the SCL.

However, this can result in the operating point cycling around the surge control line because the anti-surge controller is trying to increase flow to the suction, while the speed controller is trying to match the decreased flow to the compressor suction.

To circumvent the cycling issue, the output of the anti-surge controller [UIC] can be added to the control response / output of the speed controller [SC]. This can ensure the operating point moves back into the operating envelope without crossing the surge limit line [SLL].

Loop Decoupling Example 3

In the case of series compressors driven by a turbine with a common shaft as shown below,

When the ASV of the second compressor [K-102] opens, the suction pressure of K-102 also rises. However, in doing so, the discharge pressure of the first compressor [K-101] also increases.

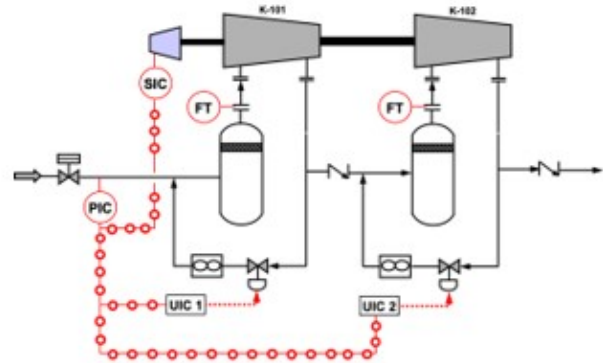


Figure 4. Suction Header Speed Control Method

This would cause ASV controller, UIC-1 to open the first compressor's [K-101] ASV, thereby again altering the discharge pressure of the first compressor [K-101]. This way both control loops are coupled & results in oscillatory and unstable behaviour.

To circumvent the loop coupling issue, a feed forward control algorithm can be implemented, such that a portion of the output from UIC -1 can be fed to output of UIC-2. UIC-2 would then perform its control action before it begins to see the disturbance caused by output from UIC-1.

Alternatively, when UIC-1 opens the ASV of K-101. This results in decreased flow to K-102 causing UIC-2 to open the ASV of K-102, thus ensuring both compressors are operating away from the surge line.

Loop Decoupling Example 4

Taking the case of parallel compressors using the equidistant from surge line method, the aim is to ensure the deviation between the operating point and the surge control line [SCL] in both trains is equidistant.

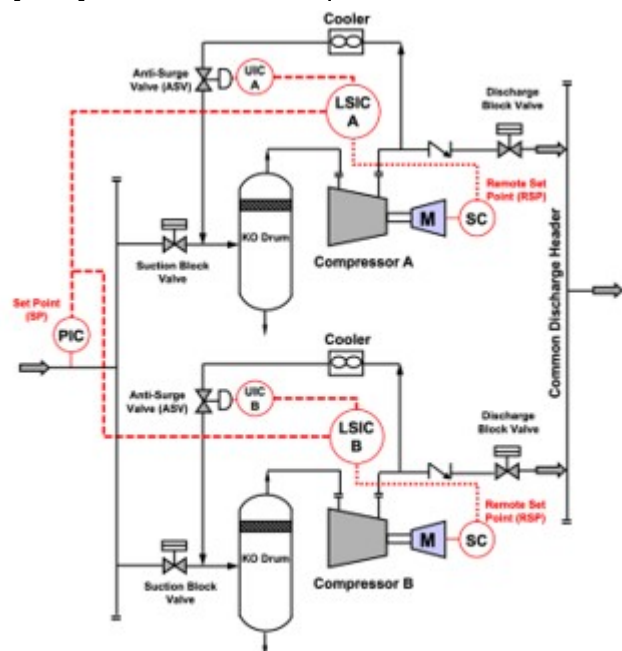


Figure 5. Equidistant to Surge Line Operation

In this configuration, neither the throughputs through each compressor or the operating compressor speed is the same, but only the deviation between the operating point and SCL. It may also be noted that the load sharing function (LSIC A/B) that alters the compressor speed, is not fed with the signal from the suction flow transmitter, but instead the anti-surge controller (UIC A/B) and the master pressure controller (PIC) installed on the common suction header. This would mean, both UIC A/B and LSIC A/B must coordinate in real time.

With a loop decoupling scheme, during a process disturbance (e.g., low suction flow), the load sharing controller [LSIC A/B] is decoupled from the anti-surge system (UIC A/B).

In case both are not decoupled, the load sharing scheme would work towards reducing the compressor speed while struggling to distribute the flow equally to both compressors. The UIC A/B on the other hand would open the ASV's to recycle flow and keep the operating point away from the surge control line [SCL] with the net result of the compressor operating point cycling around the SCL.

Some Design Considerations

1. The Master pressure controller which provides shared information across all compressors can often be subjected to harsh field conditions. To circumvent these issues, redundancy with multiple transmitters can be provided. This ensures not only maximum availability but also hardwiring the transmitters prevents any loss of signals to the Load sharing system.
2. Depending on the reliability of the control systems, controllers need to be replaced sometimes with third party OEM vendors, each with their own proprietary control systems. Hence load sharing systems must be able to integrate different vendors.
3. Real Time optimization (RTO) techniques based on regression models of steady state data have gained sufficient footing in recent years. Short Time RTO of the order of a few minutes & Long-term RTO of the order of a few days can be employed to determine the best load distributions between compressors.
4. With poor integration between performance controller and anti-surge controller, it can cause energy loss and unplanned compressor trip.

5. Since the dynamic characteristics of the performance controller and anti-surge controller can be quite different, any interaction between them tends to cause instabilities. For this reason, one of the loop must be made sluggish, i.e., typically the anti-surge loop with higher surge control margin and a slower acting PI controller.
6. An alternative is, during a process disturbance, the anti-surge controller can be allowed to take over recycling cold gas, while the performance controllers are left idling / standby till the operating point sufficiently moves away from the surge control line. However, the downside to this remedy is that, constant recycling wastes energy and increases the chance of flaring if the Anti-surge controller does not act fast enough, i.e., higher response time.
7. Therefore, the performance controller and the anti-surge controller have to be integrated in such a manner that both loops are optimized to save energy with the lowest surge margin possible, during a process upset.

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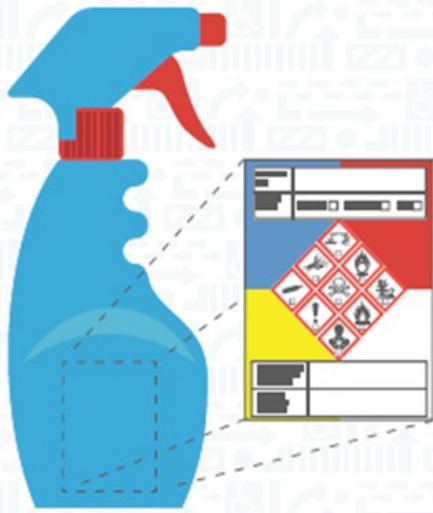
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Introduction

Algae biofuel is a type of renewable fuel source that uses algae as its source of energy-rich oils, according to search results to produce bio-gasoline, biodiesel, bio-jet fuels and in substitution of oil products from petroleum in combat of currently world climate crisis. Algae biofuel can be produced by different methods, such as transesterification, pyrolysis, gasification, or hydrothermal liquefaction. Algae biofuel can be used as an alternative to liquid non-renewable fossil fuels, such as gasoline, diesel, or jet fuel.

What is algal fuel & algal oil?

Algal biofuel, Algae fuel, or algal oil is a type of renewable fuel that uses algae as its source of energy-rich oils, and is an alternative to liquid fossil fuels that uses algae as its source of energy-rich oils. Algae biofuel can be produced by different methods, such as transesterification, pyrolysis, gasification, or hydrothermal liquefaction. Algae biofuel can be used as an alternative to liquid fossil fuels, such as gasoline, diesel, or jet fuel. Algae biofuel has some advantages over other biofuels, such as corn and sugarcane, because algae can grow in various habitats, consume carbon dioxide from the atmosphere, and produce higher yields of oil per acre. However, algae biofuel also may face some challenges, such as high production costs, low culture cell densities, and inefficient harvesting and processing methods. Algal oil is used as a source of fatty acid supplementation in food products, as it contains mono- and polyunsaturated fats, in particular EPA and DHA. Its DHA content is roughly equivalent to that of salmon based fish oil.

History

In 1942, European scientists Richard Harder and Hans von Witsch proposed the mass cultivation of diatoms to produce fat, which was urgently needed because of World War II.

Government researchers began exploring algae as a source of fuel in 1978 and continued experiments through later. Also, algae fuels are an alternative to commonly known biofuel sources, such as corn and sugarcane. When made from seaweed (macroalgae) it can be known as seaweed fuel or seaweed oil.

Process

Algae cultivation: Algae plant can be grown under multiple conditions. It can bloom in places where salty water, excessive sun exposure, and lack of vital nutrients inhibit growth of other crops. But the higher the concentration of algae cells, the lower the ability to absorb light. In heterotrophic conditions, the algae can use sugars, organic acids, and other organic carbons as carbon sources, replacing the need for light.

Converting the algae into bio-Fuel production: Converting wet algal plant biomass into combustible fuel is a challenge. After the algae is harvested, the biomass is typically processed in a series of steps, which differs based on the species and desired product. Often, the algae are dehydrated and then a solvent, like hexane, is used to extract energy-rich compounds, like triglycerides, from the dried material. Once extracted, the compounds can then be processed into fuel using standard industrial procedures. For example, the extracted triglycerides are reacted with methanol to create biodiesel via transesterification. (An alternative approach employs a continuous process that subjects harvested wet algae to high temperatures and pressures—350 °C and 21,000 kPa). Algal products include bio-oil products, which can be further refined into bio-aviation fuel, bio-gasoline, or bio-diesel renewable fuels. The test process converted between 50 and 70 percent of the algae's carbon into algal fuel. Other sub-products include clean water, fuel gas and nutrients such as nitrogen, phosphorus, and potassium.

Advantage & Disadvantage

Advantages

1. Versus petroleum (non-renewable) oil products: Algae fuel's carbon footprint is smaller than that of fossil fuels and it is renewable, making it more eco-friendly. Additionally, wastewater is a possible nutrient source for algae, making the use of freshwater less necessary and decreasing, rather than increasing, pollution.
2. Versus other biofuels (renewable): When compared to other biofuels, algae have a higher productivity rate, and does not compete with food sources because it does not need arable land to grow and is not a food crop. Microalgae can harvest radiant energy from the sun into valuable products at the expense of inexpensive natural resources like CO₂, contributing to global CO₂ reduction. Algae grow much faster than food crops, and can produce hundreds of times more oil per unit area than conventional crops such as rapeseed, palms, soybeans, or jatropha.
3. Ease of growth: One of the main advantages that using microalgae as the feedstock when compared to more traditional crops is that it can be grown much more easily. Algae can be grown in land that would not be considered suitable for the growth of the regularly used crops. [80] In addition to this, wastewater that would normally hinder plant growth has been shown to be very effective in growing algae. Because of this, algae can be grown without taking up arable land that would otherwise be used for producing food crops, and the better resources can be reserved for normal crop production. Microalgae also require fewer resources to grow, and little attention is needed, allowing the growth and cultivation of algae to be a very passive process.
4. Impact on food: Many traditional feedstocks for biodiesel, such as corn and palm, are also used as feed for livestock on farms, as well as a valuable source of food for humans. Because of this, using them as biofuel reduces the amount of food available for both, resulting in an increased cost for both the food and the fuel produced. Using algae as a source of biodiesel can alleviate this problem in several ways. First, algae are not used as a primary food source for humans, meaning that it can be used solely for fuel and there would be little impact in the food industry.

Second, many of the waste-product extracts produced during the processing of algae for biofuel can be used as a sufficient animal feed. This is an effective way to minimize waste and a much cheaper alternative to the more traditional corn- or grain-based feeds.

5. Minimalization of waste: Growing algae as a source of biofuel has also been shown to have numerous environmental benefits and has presented itself as a much more environmentally friendly alternative to current biofuels. For one, it can utilize run-off, water contaminated with fertilizers and other nutrients that are a by-product of farming, as its primary source of water and nutrients. Because of this, it prevents this contaminated water from mixing with the lakes and rivers that currently supply our drinking water. In addition to this, the ammonia, nitrates, and phosphates that would normally render the water unsafe serve as excellent nutrients for the algae, meaning that fewer resources are needed to grow the algae. Many algae species used in biodiesel production are excellent bio-fixers, meaning they can remove carbon dioxide from the atmosphere to use as a form of energy for themselves. Because of this, they have found use in industry to treat flue gases and reduce GHG emissions in decarbonization approach of combat to global warming.

Disadvantages

1. Commercial Viability: While the technology exists to harvest and convert algae into a usable source of biofuels, it still hasn't been implemented perfectly into a large enough scale to support the current energy needs in every developed countries. Further commercial research could be helpful to make the production of algae biofuels more efficient to substitute non-renewable petroleum oil products in energy transition. Anyway, in December 2022, ExxonMobil, the last large oil company to invest in algae biofuels, ended its research funding. Even in the best-case scenario, it was estimated that unextracted algal oil would cost \$59–186 per barrel, while petroleum cost about \$80 per barrel in 2023. In March 2023, researchers said that the commercialization of biofuels would require several billion dollars of funding, plus a long-term dedication to overcoming what appear to be fundamental biological limitations of wild organisms. Most researchers think that large scale

production of biofuels is either “a decade, or more likely two decades, away.” Although increasing interest in seaweed farming for carbon sequestration, eutrophication reduction and production of food has resulted in the creation of commercial seaweed cultivation since 2017. Reductions in the cost of cultivation and harvesting as well as the development of commercial industry will improve the economics of macro algae biofuels.

2. High water requirement: The process of microalgae cultivation is highly water intensive. Life cycle studies estimated that the production of 1 liter of microalgae-based biodiesel requires between 607 and 1944 liters of water. That said, abundant wastewater and/or seawater, which also contain various nutrients, can theoretically be used for this purpose instead of freshwater.

- Cultivation of algae: There are few types of algae cultivations as follows. After harvesting the algae, the biomass is typically processed in a series of steps, which can differ based on the species and desired product. (Photo 1)



Photo 1-Algae being harvested and dried from an ATS system.

- Closed loop system: The lack of equipment and structures needed to begin growing algae in large quantities has inhibited widespread mass-production of algae for biofuel production. Maximum use of existing agriculture processes and hardware is the goal. Closed systems (not exposed to open air) avoid the problem of contamination by other organisms blown in by the air. The problem of a closed system is finding a cheap source of sterile CO₂. Several experimenters have found the CO₂ from a smokestack works well for growing algae. For reasons of economy, some experts think

that algae farming for biofuels will have to be done as part of cogeneration, where it can make use of waste heat and help soak up pollution. To produce micro-algae at large-scale under controlled environment using PBR system, strategies such as light guides, sparger, and PBR construction materials required should be well considered.

- Photo bioreactors: Most companies pursuing algae as a source of biofuels pump nutrient-rich water through plastic or borosilicate glass tubes (called "bioreactors") that are exposed to sunlight (and so-called photo bioreactors or PBR). Running a PBR is more difficult than using an open pond, and costlier, but may provide a higher level of control and productivity. In addition, a photo bioreactor can be integrated into a closed loop cogeneration system much more easily than ponds or other methods. (Photo 2)



Photo 2-Photo bioreactor (closed-loop) from glass tubes.

- Open pond: Open pond systems consist of simple in ground ponds, which are often mixed by a paddle wheel. These systems have low power requirements, operating costs, and capital costs when compared to closed loop photo bioreactor systems. Nearly all commercial algae producers for high value algal products utilize open pond systems. (Photo 3)



Photo 3-Design of a race-way open pond commonly used for algae culture.

- Turf scrubber: The Algae scrubber is a system designed primarily for cleaning nutrients and pollutants out of water using algal turfs. An algal turf scrubber (ATS) mimics the algal turfs of a natural coral reef by taking in nutrient rich water from waste streams or natural water sources and pulsing it over a sloped surface. This surface is coated with a rough plastic membrane or a screen, which allows naturally occurring algal spores to settle and colonize the surface. Once the algae have been established, it can be harvested every 5–15 days, and can produce 18 metric tons of algal biomass per hectare per year. In contrast to other methods, which focus primarily on a single high yielding species of algae, this method focuses on naturally occurring polycultures of algae. As such, the lipid content of the algae in an ATS system is usually lower, which makes it more suitable for a fermented fuel product, such as ethanol, methane, or butanol. Conversely, the harvested algae could be treated with a hydrothermal liquefaction process, which would make possible biodiesel, gasoline, and jet fuel production. There are three major advantages of ATS over other systems. The first advantage is documented higher productivity over open pond systems. The second is lower operating and fuel production costs. The third is the elimination of contamination issues due to the reliance on naturally occurring algae species. The projected costs for energy production in an ATS system are \$0.75/kg, compared to a photobioreactor which would cost \$3.50/kg. Furthermore, because the primary purpose of ATS is removing nutrients and pollutants out of water, and these costs have been shown to be lower than other methods of nutrient removal, this may incentivize the use of this technology for nutrient removal as the primary function, with biofuel production as an added benefit. (Photo 4)



Photo 4-Algal Turf Scrubber (ATS) system

How to produce bio-oil products from algae?

There are different methods for producing oil products from algae, according to search results. Some of the common methods are:

- Oil press or mechanical press: This method squeezes out the oil from the algae paste using a nozzle. It can extract up to 70% of the oil but requires a dry algae feedstock.
- Hexane solvent method: This method combines pressing the algae with mixing the leftover algae with hexane, a chemical solvent that dissolves the oil. It can extract up to 95% of oil from algae but requires cleaning the oil from hexane residues.
- Supercritical fluids method: This method uses high-pressure carbon dioxide to extract the oil from the algae. It can extract almost 100% of the oil but requires high temperature and pressure.
- High temperature and pressure method: This method subjects wet algae to high temperatures and pressures (350 °C and 2,100 kpa) to convert them into crude oil, which can then be refined into various fuel products. It can convert 50 to 70% of the algae's carbon into fuel.

Algal Bio-fuel production

Algae can be converted into various types of fuels, depending on the production technologies and the part of the cells used. The lipid, or oily part of the algae biomass can be extracted and converted into biodiesel through a process similar to that used for any other vegetable oil, or converted in a refinery into "drop-in" replacements for petroleum-based fuels. Alternatively or following lipid extraction, the carbohydrate content of algae can be fermented into bioethanol or butanol fuel.

- **Algal Bio-Diesel:** Biodiesel is a diesel fuel derived from animal or plant lipids (oils and fats). Studies have shown that some species of algae can produce 60% or more of their dry weight in the form of oil. Because the cells grow in aqueous suspension, where they have more efficient access to water, CO₂ and dissolved nutrients, microalgae are capable of producing large amounts of biomass and usable oil in either high rate algal ponds or photobioreactors. This oil can then be turned into biodiesel which could be sold for use in automobiles. Regional production of microalgae and processing into biofuels will provide economic benefits to rural communities. One common way is called transesterification, which involves reacting the triglycerides with an alcohol (such as methanol or ethanol) and a catalyst (such as sodium hydroxide or potassium hydroxide) to produce biodiesel and glycerol.
- **Algal Bio-Gasoline:** Butanol can be made from algae or diatoms using only a solar powered bio refinery. This fuel has an energy density 10% less than gasoline, and greater than that of either ethanol or methanol. In most gasoline engines, butanol can be used in place of gasoline with no modifications. In several tests, butanol consumption is similar to that of gasoline, and when blended with gasoline, provides better performance and corrosion resistance than that of ethanol or E85. Anyway, converting the algal oil into bio-gasoline can be done by using various processes, such as:
 - Aqueous phase reforming (APR), which uses water and catalysts to convert the oil into a mixture of hydrocarbons that match the properties of gasoline
 - Pyrolysis, which uses high temperatures and low oxygen to decompose the oil into a bio-oil that can be further refined into gasoline
 - Gasification, which uses high temperatures and steam to convert the oil into a synthesis gas that can be further processed into gasoline
 - Anaerobic digestion, which uses microorganisms to ferment the oil into biogas (mostly methane) that can be used as a fuel or upgraded into gasoline
- **Algal Aviation Bio-Jet fuel:** Trials of using algae as biofuel were carried out by Lufthansa and Virgin Atlantic as early as 2008, although there is little evidence that using algae is a reasonable source for jet biofuels. By 2015, cultivation of fatty acid methyl esters and alkenones from the algae, *Isochrysis*, was under research as a possible jet biofuel feedstock. There are different ways to do this, depending on the type and composition of the algal oils. One common way is called transesterification, which involves reacting the triglycerides with an alcohol (such as methanol or ethanol) and a catalyst (such as sodium hydroxide or potassium hydroxide) to produce biodiesel and glycerol. Another way is called hydroprocessing, which involves treating the triglycerides with hydrogen and a catalyst (such as nickel or cobalt) under high temperature and pressure to produce jet fuel and propane. A third way is called hydrothermal liquefaction, which involves heating the whole algae biomass with water under high temperature and pressure to produce a mixture of fuels including jet fuel, gasoline, and diesel. (Photo 5)



Photo 5 - A conical flask of "green" jet fuel made from algae.

Environmental aspect of algal biofuel

In comparison with terrestrial-based biofuel crops such as corn or soybeans, micro algal production results in a much less significant land footprint due to the higher oil productivity from the microalgae than all other oil crops. Algae can also be grown on marginal lands useless for ordinary crops and with low conservation value and can use water from salt aquifers that is not useful for agriculture or drinking. Algae can also grow on the surface of the ocean in bags or floating screens. Thus, microalgae could provide a source of clean energy with little impact on the provisioning of adequate food and water or the conservation of biodiversity. Algae cultivation also requires no external subsidies of insecticides or herbicides, removing any risk of generating associated pesticide waste streams.

In addition, algal biofuels are much less toxic, and degrade far more readily than petroleum-based fuels. However, due to the flammable nature of any combustible fuel, there is potential for some environmental hazards if ignited or spilled, as may occur in a train derailment or a pipeline leak. This hazard is reduced compared to fossil fuels, due to the ability for algal biofuels to be produced in a much more localized manner, and due to the lower toxicity overall, but the hazard is still there, nonetheless. Therefore, algal biofuels should be treated in a similar manner to petroleum fuels in transportation and use, with sufficient safety measures in place always.

Studies have determined that replacing fossil fuels with renewable energy sources, such as biofuels, have the capability of reducing CO₂ emissions by up to 80%. An algae-based system could capture approximately 80% of the CO₂ emitted from a power plant when sunlight is available. Although this CO₂ will later be released into the atmosphere when the fuel is burned, this gas CO₂ would have entered the atmosphere regardless. The possibility of reducing total CO₂ emissions therefore lies in the prevention of the release of CO₂ from fossil fuels.

Furthermore, compared to fuels like diesel and petroleum, and even compared to other sources of biofuels, the production and combustion of algal biofuel does not produce any sulfur oxides or nitrous oxides, and produces a reduced amount of carbon monoxide, unburned hydrocarbons, and reduced emission of other harmful pollutants. Since terrestrial plant sources of biofuel production simply do not have the production capacity to meet current energy requirements, microalgae may be one of the only options to approach complete replacement of fossil oil products.

Microalgae production also includes the ability to use saline waste or waste CO₂ streams as an energy source. This opens a new strategy to produce biofuel in conjunction with wastewater treatment, while being able to produce clean water as a byproduct. When used in a micro algal bioreactor, harvested microalgae will capture significant quantities of organic compounds as well as heavy metal contaminants absorbed from wastewater streams that would otherwise be directly discharged into surface and groundwater. Another possibility is the use of algae production systems to clean up non-point source pollution, in a system known as an algal turf scrubber (ATS).

This has been demonstrated to reduce nitrogen and phosphorus levels in rivers and other large bodies of water affected by eutrophication, and systems are being built that will be

capable of processing up to 110 million liters of water per day. ATS can also be used for treating point source pollution, such as the wastewater mentioned above, or in treating livestock effluent.

- Carbon dioxide: Bubbling CO₂ through algal cultivation systems can greatly increase productivity and yield (up to a saturation point). Typically, about 1.8 tons of CO₂ will be utilized per ton of algal biomass (dry) produced, though this varies with algae species. Each ton of microalgae absorbs two tons of CO₂. The algae residues could produce renewable energy biogas through anaerobic digestion too.
- Wastewater: A possible nutrient source is wastewater from the treatment of sewage, agricultural, or flood plain run-off, all currently major pollutants and health risks. However, this waste water cannot feed algae directly and must first be processed by bacteria, through anaerobic digestion. If wastewater is not processed before it reaches the algae, it will contaminate the algae in the reactor, and at the very least, kill much of the desired algae strain. In biogas facilities, organic waste is often converted to a mixture of carbon dioxide, methane, and organic fertilizer.

Organic fertilizer that comes out of the digester is liquid, and nearly suitable for algae growth, but it must first be cleaned and sterilized. The utilization of wastewater and ocean water instead of freshwater is strongly advocated due to the continuing depletion of freshwater resources. However, heavy metals, trace metals, and other contaminants in wastewater can decrease the ability of cells to produce lipids biosynthetically and impact various other workings in the machinery of cells. The same is true for ocean water, but the contaminants are found in different concentrations.

Thus, agricultural-grade fertilizer is the preferred source of nutrients, but heavy metals are again a problem, especially for strains of algae that are susceptible to these metals. In open pond systems the use of strains of algae that can deal with high concentrations of heavy metals could prevent other organisms from infesting these systems. In some instances, it has even been shown that strains of algae can remove over 90% of nickel and zinc from industrial wastewater in relatively short periods of time.

Economic viability of algal oil

There is clearly a demand for sustainable biofuel production, but whether a particular biofuel will be used ultimately depends not on sustainability but cost efficiency. Therefore, research is focusing on cutting the cost of algal biofuel production to the point where it can compete with conventional petroleum. The production of several products from algae has been mentioned as the most important factor for making algae production economically viable. Other factors are the improving of the solar energy to biomass conversion efficiency (currently 3%, but 5 to 7% is theoretically attainable) and making the oil extraction from the algae easier.

In a 2007 report a formula was derived estimating the cost of algal oil for it to be a viable substitute to petroleum diesel:

$$C_{(\text{algal oil})} = 25.9 \times 10^{-3} C_{(\text{petroleum})}$$

Where: $C_{(\text{algal oil})}$ is the price of micro algal oil in dollars per gallon and $C_{(\text{petroleum})}$ is the price of crude oil in dollars per barrel. This equation assumes that algal oil has roughly 80% of the caloric energy value of crude petroleum.

The IEA estimates that algal biomass can be produced for a little as \$0.54/kg in open pond in a warm climate to \$10.20/kg in photo bioreactors in cooler climates. If the biomass contains 30% oil by weight, the cost of biomass for providing a liter of oil would be approximately \$1.40 (\$5.30/gal) and \$1.81 (\$6.85/gal) for photo bioreactors and raceways, respectively. Oil recovered from the lower cost biomass produced in photo bioreactors is estimated to cost \$2.80/L, assuming the recovery process contributes 50% to the cost of the final recovered oil. If existing algae projects can achieve biodiesel production price targets of less than \$1 per gallon, the United States has realized its goal of replacing up to 20% of transport fuels by 2020 by using environmentally and economically sustainable fuels from algae production.

Which countries do have algal fuel technologies?

According to the web search results, there are several countries that have algal fuel technologies or are developing them. Some of them are:

- United States: The US Department of Energy initiated the Aquatic Species Program in 1978 to explore the potential of algae as a source of liquid transportation fuels. The program was

discontinued in 1996, but research on algae biofuels continued in various academic and industrial settings. In 2009, the US Department of Energy announced a \$600 million funding for algae biofuel projects. Some of the companies involved in algae biofuel production in the US are Sapphire Energy, Solazyme, Algenol, and Synthetic Genomics.

- China: China is one of the largest producers of algae biomass in the world, mainly for food and feed applications. China has also invested in algae biofuel research and development, with several pilot plants and demonstration projects across the country. Some of the institutions and companies involved in algae biofuel production in China are the Chinese Academy of Sciences, Qingdao Institute of Bioenergy and Bioprocess Technology, ENN Group, and Sinopec.
- India: India has a large potential for algae cultivation due to its favorable climate, abundant sunlight, and availability of land and water resources. India has also initiated several research and development programs on algae biofuels, such as the National Algal Biofuel Technology Mission, the Indo-US Joint Clean Energy Research and Development Center, and the Indo-UK Algal Bioenergy Consortium. Some of the institutions and companies involved in algae biofuel production in India are the Indian Institute of Technology Kharagpur, Reliance Industries, Bharat Petroleum, and Oil and Natural Gas Corporation.
- European Union: The European Union has supported several research and innovation projects on algae biofuels under its Framework Programmes for Research and Technological Development. Some of the projects are ALGADISK, BIOFAT, DEMMA, FUEL4ME, MIRACLES, PUFACHAIN, and SPLASH. Some of the institutions and companies involved in algae biofuel production in the EU are Wageningen University & Research, University of Bielefeld, Evonik Industries, AlgaEnergy, and Algae-Tec.
- These are some examples of countries that have algal fuel technologies or are developing them. There may be other countries that are not mentioned here. You can find more information by search results.

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Rock Bottom: Commodity Tariffs....Friend or Foe?

Ron Cormier

Welcome to the November installment of “The View from Rock Bottom”. EPM utilizes my pen, research, and professional insights to reflect on and evaluate current issues and trends important to our common interests within the hydrocarbons industry. Hopefully these topics are global in nature and certainly affect most of our readership base, either directly or at least somewhat noticeably close to home.

This month, we look backward at ongoing experience, effects, and outcomes driven by mandated commercial tariffs’ application through value chains. Across many strategic product chains, these surcharges are levied by governments on our hydrocarbon and renewables industry’s commodity performance materials and services; offerings meant to improve our daily existence around the world.

While Donald Trump and President Joe Biden differ starkly on many policy issues, they are remarkably similar on trade policy. Notably, President Biden has maintained tariffs on billions of dollars of Chinese imports dating to the Trump administration, all while maintaining a flawed process of granting tariff exclusions to select industries.

Trump wanted to expose unfair Chinese trade practices. For years, American businesses had complained that China was trading unfairly – subsidizing domestic industries, disrespecting intellectual property rights, and even forcing American companies to turn over their tech secrets in exchange for the right to operate in China. Trump wanted to use the tariffs to force China to change its ways, said Robert Lighthizer, who was the U.S. Trade Representative in the Trump administration. “[It] was part of an overall strategy of taking on China for the first time and really ringing the alarm for the world that China is a predator,” Lighthizer told to NPR.

Biden’s trade adviser has been reviewing the China tariff. Biden hardly ever mentions the China tariffs. Yet, he has kept them. After he took office, Biden’s top trade official – U.S. Trade Representative Katherine Tai –

launched a review of the Trump tariffs. That process is expected to wrap up later this year. In an interview, Tai sought to separate the rationale for the tariffs from the way they were imposed. “[It] was done in a pretty provocative way with a lot of confrontational chest thumping, which I think drew some concerns both internationally and domestically – and I’m putting it diplomatically,” Tai told NPR.

Instead of working through the World Trade Organization, Trump used U.S. domestic laws to launch an investigation and then unilaterally impose tariffs. The strategy was widely denounced. “Everyone in town, in Washington, was against us,” Lighthizer said. Those tariffs, put in place when Trump invoked Section 301 of the Trade Act of 1974 (“Section 301 Tariffs”), have not only failed to achieve their objectives, but have hurt U.S. businesses and consumers along the way. As part of its ongoing review of the Section 301 tariffs, the U.S. Trade Representative (USTR) should listen to many comments calling for the end of this failed trade war.

The “301 Review” Process

Last year, the USTR initiated a statutory four-year review of the Trump administration’s Section 301 tariffs, asking industries that supported the tariffs to weigh in on their efficacy and potential continuation. Since there was at least one comment in support of every tariff, USTR Katherine Tai found the feedback sufficient to justify the maintenance of the tariffs. This decision triggered another review, which invited comments from all interested parties. The second phase of the Section 301 review process, launched in October 2022, allowed the public to submit “comments on the effectiveness of the [tariff] actions in achieving the objectives of the investigation, other actions that could be taken, and the effects of such actions on the United States economy, including consumers.” The comment period concluded in January 2023 and yielded 1,497 submissions, which the USTR is currently in

286 submitted submissions were essentially duplicates, written by the same company, same person, and with the same content. Thirty were completely empty, fully redacted comments, as well as comments containing information irrelevant to the tariffs. Excluding those left them with 1,181 comments that can be broken down as follows: 4 submissions supported tariffs on some products, but not others; 260 submissions supported the continuation of tariffs; and 917 submissions favored removal of the tariffs. Most comments were submitted by firms, with some additional comments from interested individuals, nongovernmental organizations, and academics. Some sectors opposed to the tariffs included outdoor goods, upholstery, and apparel industries. On the other hand, support for the tariffs came from the tungsten, ceramic tile, and forging industries to name a few. In another post, we outline the views of the few, but loud, voices that are still clamoring for protection.

Who Pays the Cost of the Tariffs

Several studies have examined the cost of the Section 301 tariffs on the U.S. economy. For example, economists Mary Amity, Stephen J. Redding, and David Weinstein showed that by the end of the first year that the tariffs were in place, U.S. real income declined by \$1.4 billion per month. More recently, trade analysts Tori Smith and Tom Lee from the American Action Forum found that U.S. consumers largely bore the brunt of the tariffs, paying a total of \$48 billion—with half of this figure paid by U.S. firms that rely on intermediate inputs from China.

A recent report by the United States International Trade Commission agreed that the cost of the tariffs was passed through to U.S. importers. Back in 2019, President Biden also agreed, stating, “Trump doesn’t get the basics. He thinks his tariffs are paid for by China. Any beginning econ student at Iowa or Iowa State could tell you the American people are paying his tariffs.”

The comments submitted to the USTR should then come as no surprise: many firms listed how the tariffs have led to a decrease in wages and employment, as well as less investment in domestic research and development (R&D). Firms have also noted the difficulty in sourcing alternative inputs, the added challenges posed by retaliatory tariffs from China, and the lack of concrete change to China’s behavior since the tariffs’ implementation. The costs are varied but significant. While many respondents acknowledged that COVID-19 and high inflation contributed to layoffs, lower

wages, and fewer hirings, tariffs were identified as an important factor in firms’ decisions to reduce their workforces. Some companies even pointed directly to the Section 301 duties as being the driving force behind such measures.

The U.S. Fashion Industry Association noted a reduction in employment in the apparel production industry by thirteen thousand people since the implementation of the Section 301 tariffs—a 12% reduction in the total workforce. Phillips and Temro Industries Inc., specializing in heating, cooling, and electrification systems, placed responsibility on the tariffs for fewer bonuses, a reduction in their workforce by twenty-five people, and the need to move the manufacturing of a product line to China. Other submissions noted the costs imposed on R&D and competitiveness. iRobot, the company behind the Roomba automated vacuum cleaner, claimed that it “paid tens of millions in tariffs on goods imported from the [Section] 301 tariff lists between Jan. 1, 2021, and Oct. 12, 2021,” the cost of which came out of the R&D budget—in addition to being passed through to consumers.

Water Pik, the tooth flossing manufacturer, stated that the tariffs reduced investment in R&D and marketing, resulting in a diluted market share as foreign companies were able to invest in and launch new low-cost substitutes. These missed opportunities will likely not be recouped. Another consistent issue raised in the submissions was the difficulty, and sometimes impossibility, of finding an alternative for Chinese imports. Such was the case with woven furniture manufacturers that could not find another source of cane webbing.

Chattem Chemicals, a company that uses sarcosine salt sourced from China as an input, wrote that a domestic alternative does not exist in sufficient quantities. Furthermore, the third-party alternative that does exist, Dutch sarcosine salt, is double the price of Chinese sarcosine salt. In the end, they were forced to absorb the cost of the tariff as the former was not a realistic, reasonably priced option. Many other advanced product manufacturers highlighted the lack of competitive domestic or third-country sources for inputs, not only because of higher prices but also a lack of manufacturing knowledge. Ultimately, their production was disadvantaged at home and abroad as they had to compete with foreign companies that did not face the same tariffs. Exporters also felt the pinch from

higher costs, increased competition from unaffected foreign companies, and Chinese retaliatory tariffs, which all contributed to a reduced share in global markets for many industries.

The American Soybean Association claimed that the trade war not only harmed U.S. soybean producers, but also made foreign competitors more appealing. For example, Brazil benefited from Chinese retaliatory tariffs on U.S. soybeans, which saw a 63% drop in exports from January to October 2018.

Chinese retaliatory tariffs also reduced market access and raised prices for Alaskan and Pacific Northwest fishermen who found themselves in a less competitive position compared to other seafood exporters such as Russia and Vietnam. With U.S. seafood exports typically accounting for “two-thirds of Alaska seafood sales value,” the United Fishermen of Alaska urged the removal of the tariffs because “maintaining foreign market access is critical for the livelihoods of Alaska fishermen and other seafood sector participants.”

Finally, several firms also argued that the tariff actions were not effective in eliminating or countering China’s actions, policies, and practices that were the impetus for the tariffs in the first place. In addition, several pointed out that their products’ technologies are not strategically important to China’s “Made in China 2025” industrial program, and others noted that they made low-tech products with little to no intellectual property that would be strategically significant to the U.S. economy.

Furthermore, as Blazer Brand, a Pennsylvania-based small business that makes trash and recycling tools stated, “we’ve used a mixture of Chinese-made and American-made molds for seven years,” and “our compression-type molds are mostly made in the U.S. As patent holders, it is our responsibility to safeguard intellectual property, if it’s unsafe to make in China a tariff won’t be the driving force behind that decision.” Essentially, U.S. companies are perfectly capable of assessing their own risk.

Chad Bown, a senior fellow with the Peterson Institute for International Economics, said there are probably thousands of similar cases. “That’s the sort of perverse nature of these tariffs,” said Bown. “Any time you use a policy tool like tariffs, and you don’t apply them uniformly across all products, you, in essence, create the incentives for economic activity to shift away from the products that are being subject to the tariffs, to the things that are not

being hit with the tariffs; conventions are severely mixed.”

It’s Time to Dump Trump’s Tariffs

The evidence is clear—the Trump tariffs have failed and the costs on the U.S. economy continue to pile up. Examining all the comments submitted to the USTR for the Section 301 review confirms that harm caused by the tariffs is widespread, significant, and counterproductive to U.S. goals to discipline China’s behavior.

Instead of propping up Trump’s failed China policy, the Biden administration has restarted a dialogue with China to directly address the source of trade tensions, and bring formal trade complaints to the World Trade Organization to provide oversight and generate international judicial rulings that China will take more seriously than unilateral U.S. tariffs.

How Secretary of State Blinken is tackling the China relationship (and others in the region) and other tensions with China have changed the debate. When the tariffs were put in place, the focus was on economics and trade policy, said economist Chad Brown. “The conversation has shifted entirely. It’s not about that anymore. It’s all about national security ... the heightened tensions that we’re seeing over Taiwan, military engagements, balloons floating over the United States, things of that nature that we’re really having to grapple with today,” Brown said. And as Biden’s officials complete their review of the tariffs, there’s another factor that makes it hard to have a nuanced approach to changing the policy. Biden is also during the 2024 presidential campaign, where Trump – the father of these tariffs – is the current Republican frontrunner. Wow, about as clear as mud then.....

Until January, we hope our loyal readership enjoys rich, relaxing, and joyous holidays with family and friends. May you all enjoy good tidings and blessings into 2023.

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