A NEW ERA FOR ALKYLATION:

IONIC LIQUID ALKYLATION– ISOALKY™ PROCESS TECHNOLOGY

Enabling the Refinery of the Future
with Next Generation Alkylation Technology

Chevron

Honeywell UOP

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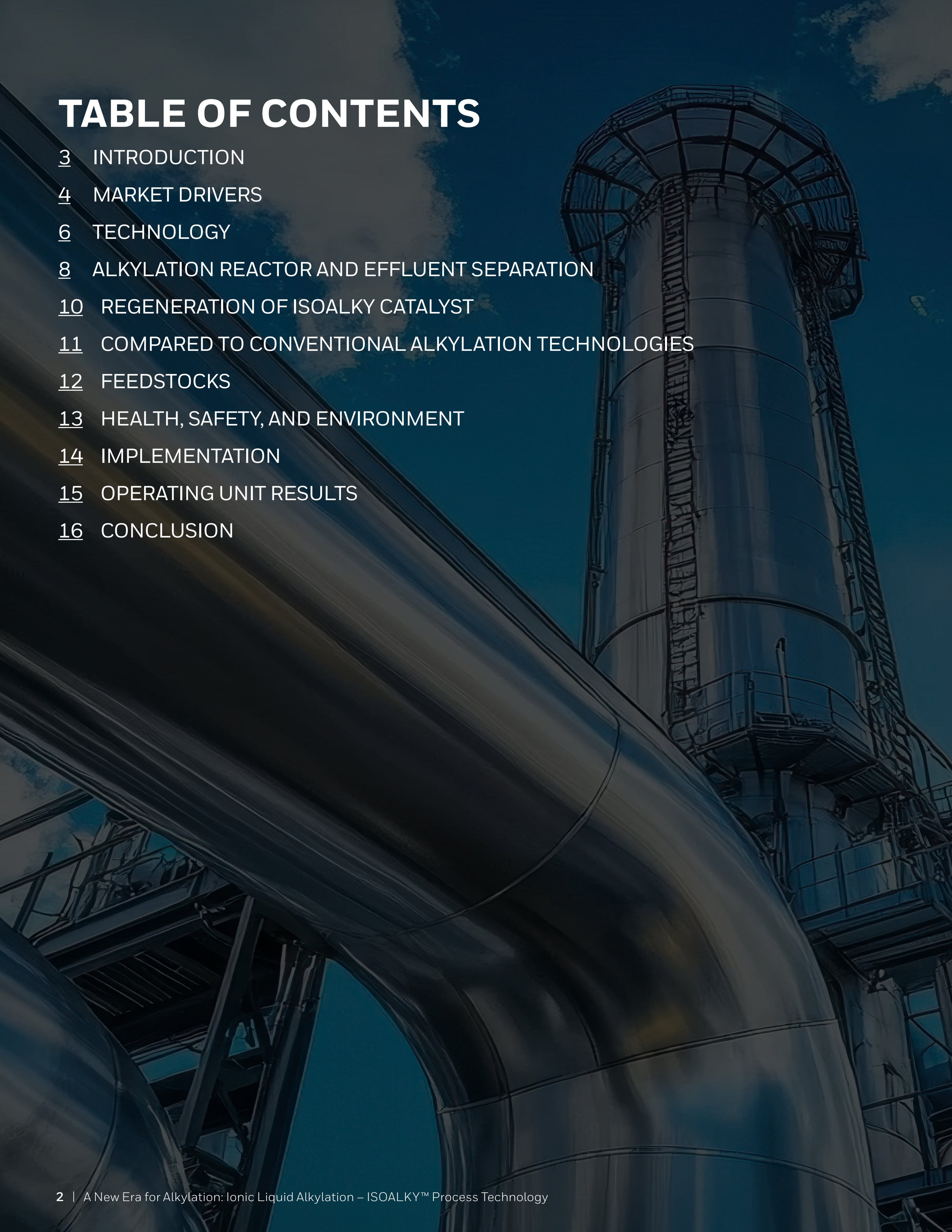

Existing technologies have allowed refiners to successfully produce alkylate for decades, providing a gasoline blend stock that is often ideal due to its high octane and low sulfur properties.

Even with the growth of electric vehicles in the marketplace, demand for alkylate also continues to grow with increasingly stringent fuel standards implemented across the globe. The refinery of the future will not only be able to make fuels that meet the standards of the future, but it will also be able to do so with a greater level of efficiency — making every molecule of raw materials count toward the optimal combination of valuable products while also minimizing emissions. The alkylation technologies based on hydrofluoric acid and sulfuric acid have served these purposes well. However, technological advances have brought about the next generation of alkylation technology, the ISOALKY Process, which enables still more efficient production of alkylate with higher yields, wider range of feedstock options, and reduced emissions, while utilizing a catalyst that is easier to handle.

The ISOALKY process has been commercialized and has over 4 years of operating experience showing the overall value of this new alkylation technology. This operating unit has consistently been able to produce high quality alkylate at design rates, meeting or exceeding initial projections.

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MARKET DRIVERS

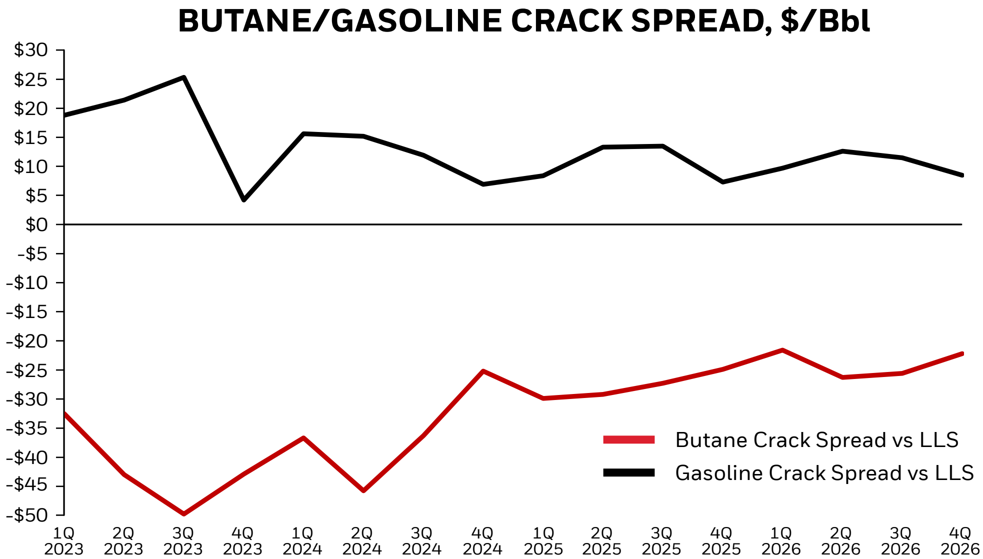
Whether refineries move into the future with fuels only, petrochemical driven or a combined product slate, higher octane blend stocks will be of prime importance.

For refineries staying in fuels, regulations such as Corporate Average Fuel Economy (CAFE) standards impact gasoline production by driving up octane demand.[1] Higher compression gasoline engines are known technology for improving engine efficiency. If gasoline technologies continue to improve and higher compression engines gain in their progress towards becoming the dominant strategy adopted by automakers for meeting CAFE standards, the demand for higher octane fuels will increase. The refining industry faces pressure to adjust its product slate to meet this increased demand.

Refineries that invest in moving to petrochemical production will be especially sensitive to octane constraints in the blending pool. The production of both gasoline and petrochemicals may be a mid-term phase that is only five to ten years long, or the production of both may be the long-term goal. In either case, changing the reformer and FCC units to align with the requirements for petrochemical production leaves the gasoline blending pool in need of more high-octane blending components.

One avenue to address this shift is to increase the use of alkylation technologies, which can take advantage of the relatively inexpensive feed, namely butanes and olefins, and convert them to high-value gasoline product. Alkylate is often an ideal blending component due to its high-octane rating, low RVP, and negligible levels of undesirable components like aromatics, olefins and sulfur. Figure 1 shows the prices and spread between n-butane vs. LLS crude and premium gasoline vs. LLS crude in the U.S. Gulf Coast. This spread represents the opportunity that refineries have to enhance their profit margins. Figure 2 and Table 1 show some of the key qualities of alkylate compared to other gasoline blend stocks and compared to international specifications for gasoline.

MARKET DRIVERS



Note: Butane Spread Vs LLS based on nominal prices of Normal butane in USGC market, with LLS Crude
Gasoline crack spread Vs LLS based on Gasoline Premium prices (nominal) in USGC market with LLS Crude

Figure 1: Price spreads for butane and gasoline compared to LLS crude in the US Gulf Coast.
Source: Wood Mackenzie: Oil Products Price Forecast update July 2025

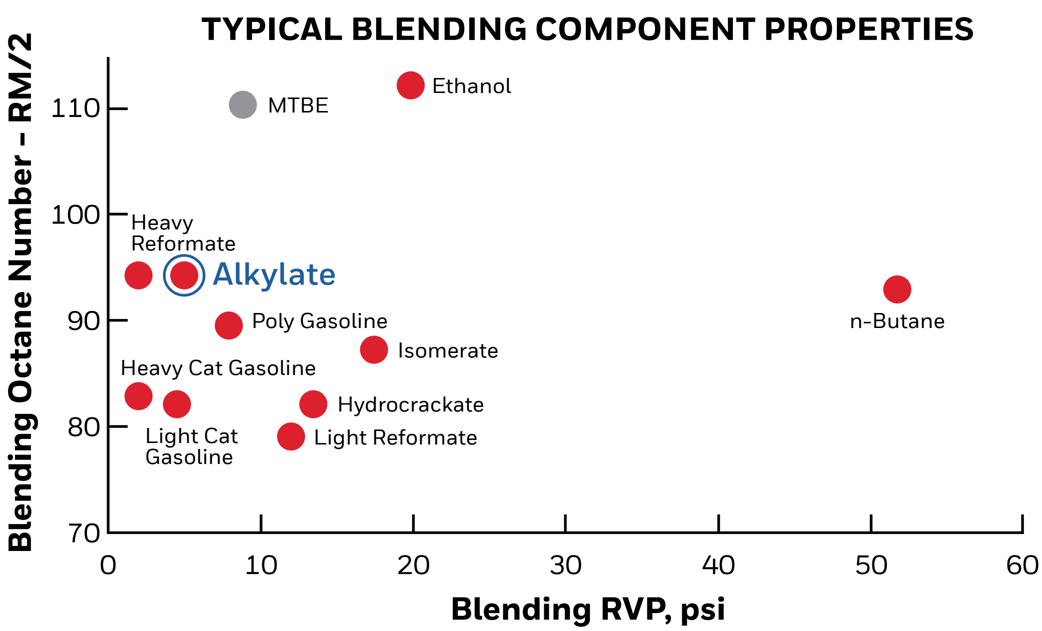


Figure 2: Alkylate stands out as an ideal blending component due to low RVP and high octane.

SPECIFICATION	RBOB TIER III	CARBOB PHASE 3	EURO VI	CHINA VI	BS VI	ALKYLATE
(R+M)/2, [RON]	87/89/91	87/89/91	[91/95]	[98]	[91/95]	[95]+
Sulfur, ppm max	10	10	10	10	10	< 5
Benzene, vol-max	0.62	0.82	1.0	0.8	1.0	0
Aromatics, vol- max	-	35	35	35	35	0
Olefins, vol- max	-	10	18	15	18	0
Oxygen, wt- max	2.7	2.7	2.7	2.7	2.7	0

Table 1: Alkylate is a blending component that meets or exceeds gasoline specifications worldwide.

TECHNOLOGY

ISOALKY Technology is a next-generation alkylate gasoline manufacturing process.

From one end of the process to the other, ISOALKY Technology offers performance improvements over conventional acid-catalyzed alkylation process technology. Capital and operating expenses associated with ISOALKY Technology are comparable to existing technologies, and the technology is slate in the future both for greenfield construction as well as retrofit of existing alkylation process units. Some of the most notable advantages are summarized in Table 2.

ADVANTAGES OF ISOALKY TECHNOLOGY		
ADVANTAGE	**QUANTIFIED**	**BENEFIT**
ISOALKY Catalyst is highly active; low catalyst inventory needed	Catalyst volume in reactor of 3% to 6% is all that is needed for alkylation.	Refiners can produce the same or more volume of alkylate with less catalyst, smaller reactor.
Higher octane alkylate	ISOALKY Technology is able to achieve up to 99 RON with mixed C_4 feed.	Refiners are enabled to make higher octane gasoline or to maintain octane in the gasoline pool while redirecting usual gasoline blend stocks like reformate to other uses such as petrochemicals.
Feed Flexibility	The same ISOALKY Reactor can accept feedstocks ranging from propylene to amylene as well as being able to use iC5 along with iC4.	One ISOALKY Unit will give a refinery the option to utilize whichever feedstock is most profitable right now and in the future, even if a different feedstock becomes more advantaged in the coming years.
Product Flexibility	Operating parameters can be adjusted to enable production of jet fuel along with alkylate.	One ISOALKY Unit will allow the refinery the ability to adjust the product is often ideal.
No hydrogen transfer reaction	Productions of propane and isopentane from the olefin feed by hydrogen transfer during the alkylation step are nearly zero. Also, isobutane consumption is reduced.	ISOALKY Technology is often ideal for upgrading of C_3= through C_5= with maximum feed efficiency.
Low polymer make and no polymer disposal - creates yield advantage	Low polymer make and the conversion of polymer to naphtha enables +3 vol% yield advantage.	With low polymer make, all olefins are utilized to make alkylate gasoline. Thus, ISOALKY Technology gives higher alkylate yield. Polymer is converted to regen naphtha and blended back into alkylate gasoline and provides additional yield.
Reduced environmental impact	No SOx emission; Lower CO_2 generation; Significantly reduced caustic waste generation.	On-line regeneration eliminates polymer incineration or spent catalyst incineration. No washing of product streams and generation of much smaller volume of spent catalyst reduce the caustic use significantly.

Table 2: ISOALKY Technology shows performance advantages, operational flexibility and reduced environmental impact.

The predominant chemistry for alkylation can be represented as:

$iC_4 + C_4{=} \rightarrow C_8$ alkylate

$iC_4 + C_3{=} \rightarrow C_7$ alkylate

$iC_4 + C_5{=} \rightarrow C_9$ alkylate

TECHNOLOGY

A strong acid is required to catalyze the reaction and refineries currently use technologies with either hydrofluoric acid (HF) or concentrated sulfuric acid (H_2SO_4) catalyzing the reaction. Research and development in ionic liquids led to the discovery that certain ionic liquids are very effective at alkylation of olefins and subsequent efforts over many years led to scale-up, development and commercialization of the ISOALKY Alkylation Process in 2021.

The ionic liquid catalyst used in the ISOALKY Process is a state-of-the-art chloroaluminate-based ionic liquid catalyst. The ionic liquid alkylation catalyst can be characterized by the general formula Q^+A^-, wherein Q^+ is an ammonium or phosphonium cation and A^- is a negatively charged ion such as $AlCl_4^-$ or $Al_2Cl_7^-$. The specific ionic liquid selected for use as the ISOALKY Catalyst was chosen for its activity and selectivity for alkylation process and long-term stability.

A trace amount of anhydrous hydrogen chloride (HCl) co-catalyst is needed to maintain the alkylation reactivity for extended periods of operation, and this is generated in-situ by organic chloride promoter addition.

The process, depicted in Figure 3, consists of feed treating, alkylation reaction with effluent separation, product distillation, and ionic liquid catalyst regeneration. Product distillation is the same for ISOALKY Technology as for existing alkylation units, so units that will be retrofit with ISOALKY Technology are able to use existing distillation equipment. In fact, many revamp units are able to see a 30+% increase in alkylate production with no change in the distillation equipment due to the lower iso-paraffin/olefin (i/o) ratio requirements. The actual increase in alkylate production will depend upon additional feed availability and current i/o ratio. The feed treatment for the ISOALKY Process is the same as what is currently used in hydrofluoric acid alkylation units, allowing for reuse of feed treatment equipment from HF alkylation units in an ISOALKY Technology retrofit. The remaining steps in an ISOALKY Process unit are unique and require specific equipment.

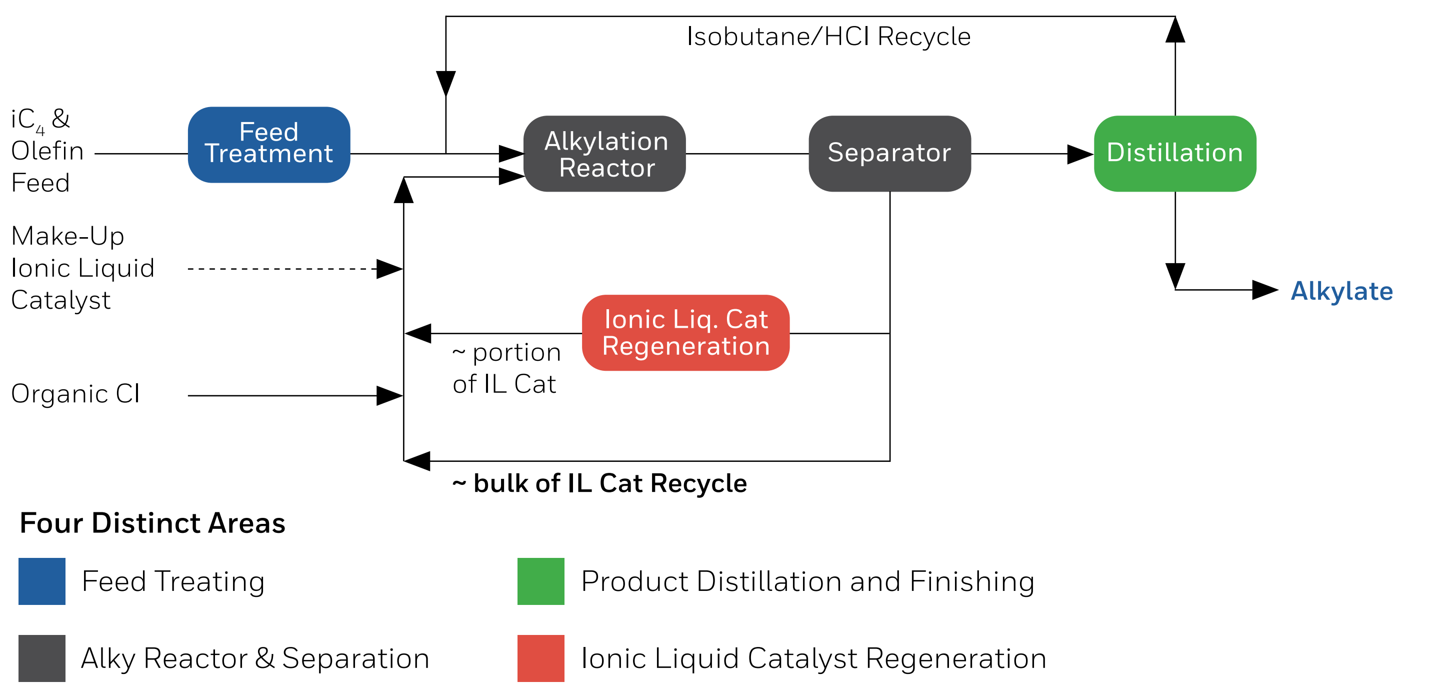


Figure 3: ISOALKY Process flow diagram

ALKYLATION REACTOR AND EFFLUENT SEPARATION

The alkylation reaction occurs at the interface of the ionic liquid catalyst droplets and the hydrocarbon phase, making the reactor a biphasic reaction system.

Due to a significantly higher activity of the ISOALKY Catalyst compared to the conventional acid catalysts, a much smaller catalyst volume and a shorter residence time are used in the ISOALKY Reactor. The ionic liquid catalyst is estimated to be 60 times more active than the H_2SO_4 catalyst.[2] Typical process conditions are shown in Table 3.

ISOALKY PROCESS CONDITIONS	
Reaction medium	Hydrocarbon continuous phase with droplets of ionic liquid catalyst
Temperature	50-120 ºF (10 - 49ºC) operable window
Pressure	60-250 psig (5.2 - 18.6 kg/cm^2) operable window
Isobutane/ Olefin molar ratio	6 -10 external I/O
Ionic liquid catalyst volume	3 – 6 vol% of ionic liquid catalyst
Olefins conversion	> 99.9%
Conjunct polymer formation	~0.3% to 0.5 wt% of olefins

Table 3: ISOALKY Technology has a wide operating window where the process can operate reliably.

The ionic liquid catalyst has a very wide operable temperature window of 50 – 120ºF (10 – 49ºC). The ISOALKY Process can be customized for each refinery, keeping in mind the the desired product quality and the available cooling capabilities. ISOALKY Technology could produce higher octane number alkylates than other alkylation technologies by operating at ~50ºF (10ºC) reactor temperature.

The reactor design includes injection nozzles for efficient dispersion of the ionic liquid catalyst and an external heat exchanger. There are no moving parts, such as impellers, in the reactor which ensures reliable operation. The reactor can operate in a wide range of olefin feed rates and 50% turn down is feasible.

ISOALKY PROCESS

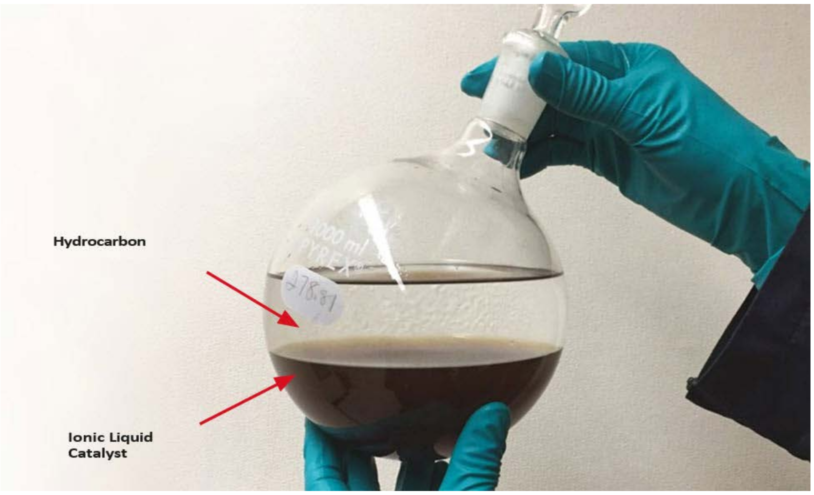


Figure 5: Hydrocarbon product separation from the ionic liquid is easy due to negligible solubility of ionic liquid in hydrocarbon.

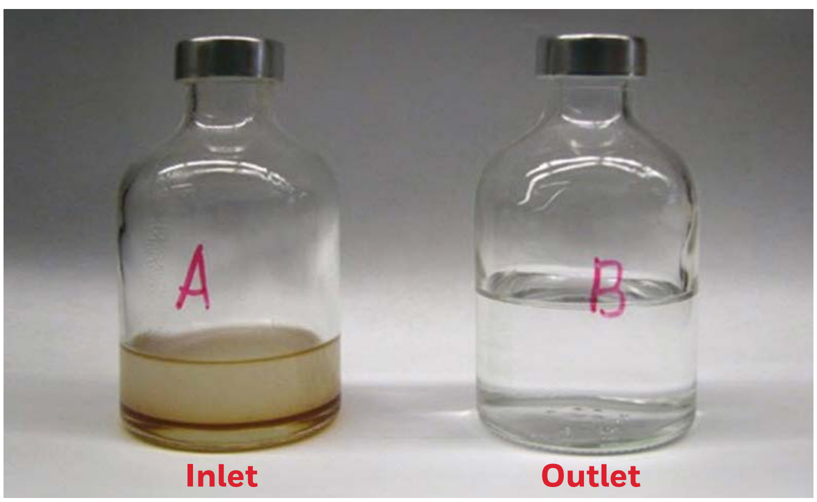


Figure 6: Alkylate reactor effluent containing ionic liquid catalyst (inlet) and hydrocarbon stream after coalescer (outlet). Efficient separation system generates water clear reactor effluent to the distillation column.

Efficient separation and recovery of the ionic liquid catalyst minimizes the loss of the ionic liquid catalyst via carry-over to the distillation section. This separation is achieved with a proprietary liquid-liquid coalescing technology that allows full separation of the ionic liquid catalyst from hydrocarbons.[3] The separated, water-clear (Figure 6) effluent stream is fractionated into product streams in the distillation unit.

The effective separation of the ionic catalyst from the reactor effluent is also important for protection of downstream equipment. After ~four years of operation at the ISOALKY Process unit in the Chevron Salt Lake City refinery, inspection did not uncover any corrosion of the downstream fractionation equipment. The material of construction for the distillation section was killed carbon steel. Refiners considering retrofit of an existing alkylation unit will be able to utilize the existing downstream equipment without corrosion concerns because the efficient separation of the ionic liquid catalyst enables very high purity of the effluent hydrocarbon stream.

ISOALKY™ CATALYST

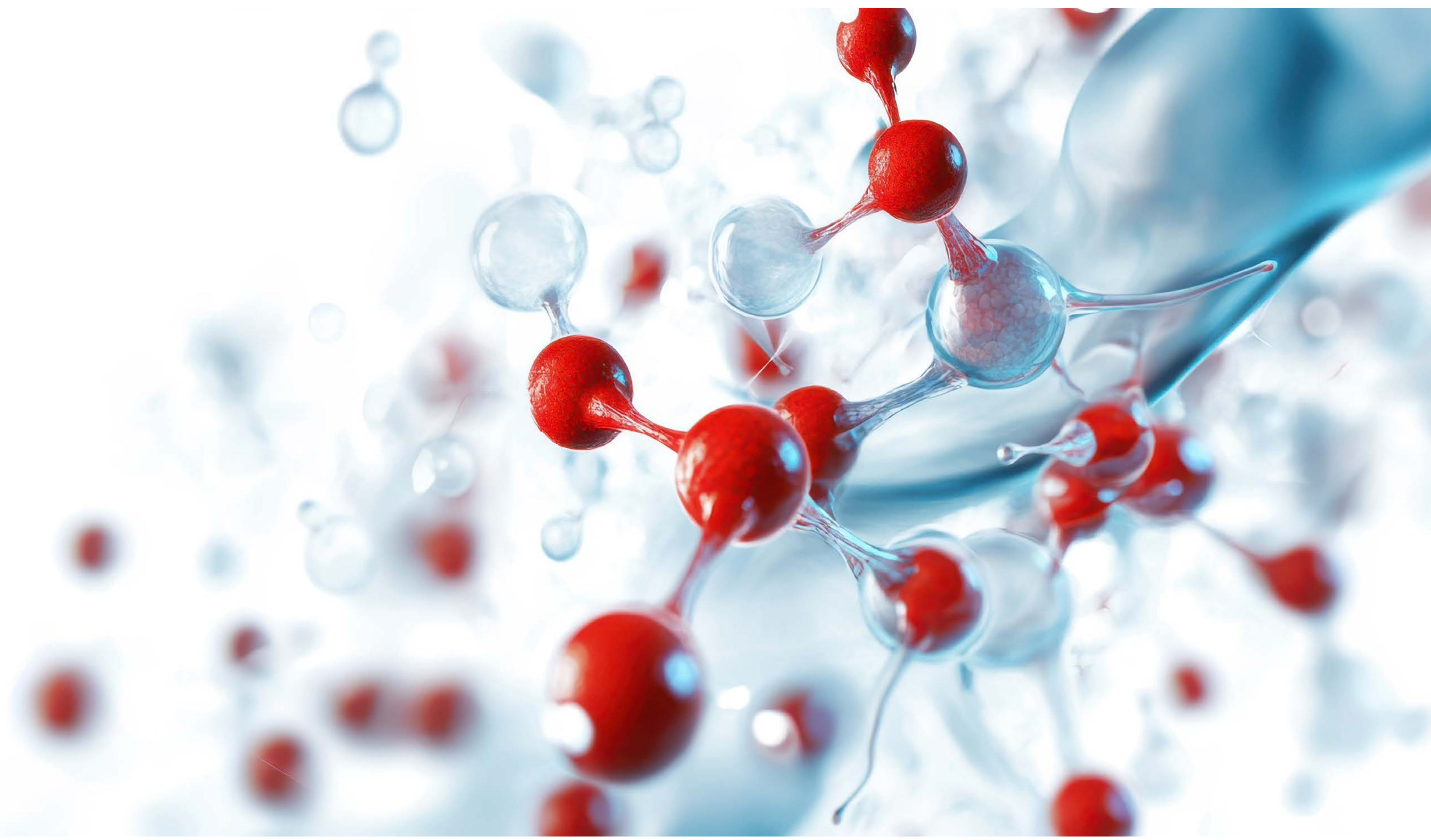
REGENERATION OF ISOALKY CATALYST

All alkylation processes generate “conjunct polymer” also known as “acid soluble oil,” or simply called “polymer”.

Conjunct polymer is formed by undesirable side reactions of olefin and alkylation catalyst. Since it deactivates the catalyst, removal of conjunct polymer is required in order to maintain catalyst activity.

A portion of used ionic liquid catalyst is sent to the regeneration unit to remove an amount of the conjunct polymer equal to the amount formed during the alkylation reaction. The on-line regeneration converts conjunct polymer into saturated hydrocarbons with gasoline boiling range called “regen naphtha” and lighter hydrocarbons classified as LPG. The regeneration unit effluent is sent to the alkylation reactor section where the regen naphtha and LPG are transferred to the hydrocarbon stream and then sent to the distillation section.

Four years of operating experience have demonstrated the regeneration of the catalyst operating better than originally designed, enabling the very low catalyst consumption. The process also allows it to handle any upset in upstream operations easily.



COMPARED TO CONVENTIONAL ALKYLATION TECHNOLOGIES

Table 4 compares key features of conventional alkylation technologies with ISOALKY Technology.

ISOALKY Technology will have an estimated 3 vol% alkylate yield-advantage compared to the sulfuric acid processes due to the lower conjunct polymer formation, on-line regeneration, and conversion of conjunct polymer back to regen naphtha.

Significantly higher activity of the ISOALKY Catalyst coupled with efficient on-line regeneration results in a significantly lower catalyst inventory requirement. The inventory volume requirement for the ionic liquid catalyst is an order of magnitude less than that of the sulfuric acid process. This allows refiners to make more alkylate with less capital investment.

	ISOALKY™	SULFURIC ACID	SOLID ACID*
Catalyst Inventory, MT	**Base**	**20 x Base**	**10 x Base**
Acid Consumption, lb/bbl	**<0.03**	**12 - 42**	**Catalyst change out every 2-3 yrs**
Polymer Make, wt%	<0.3	1 – 2	0.5 - 1 (Coke on catalyst make)
Spent Caustic, lb/bbl	0.07	3	Info Not Available
Alkylate Yield (bbl/bbl olefin)	>1.8	1.7 – 1.8	>1.8
I/O ratio (fractionation size)	**8**	**8**	**10 – 15**
Alkylate Quality w/ Mixed C4= (30% iC4=)	~96-98 RON	95-96 RON	96-97 RON
Commercial Experience	C3/C4 Feeds	C3/C4 Feeds	C4 MTBE Raffinate (Easiest feed to process)
Alkylate Sulfur, wtppm	<1	<5	<5

Table 4: ISOALKY Technology has a wider operating window, better RON, better yield via efficient operation. The properties of the catalyst and efficient operation allow better safety and lower environmental impact.

*Solid catalyst comparison based on public data and UOP's experience developing solid acid alkylation technology for 10+ years

With the wide operating temperature window, ISOALKY Technology customers may select their reactor temperature based on their octane number requirements. For the ISOALKY Technology, a selective hydroisomerization of C_4 olefin feed, which converts 1-butene to 2-butene, is necessary to achieve the highest-octane number.

FEEDSTOCKS

The ISOALKY Process makes better use of a wider range of feedstocks, allowing refiners to upgrade more material into high value alkylate.

ISOALKY Technology performs optimally with a wide range of olefin feedstocks. Alkylation of 100% pure propylene feed, 100% pure isobutylene feed, 50/50 mol% mix of C_3=/C_4= feed from a refinery and 20/80 mol% mix of C_4=/C_5= feed from a refinery were tested and all showed comparably optimal performance. The performance and alkylate quality of 100% isobutylene feed is similar to those of mixed C_4 olefins.

Additionally, production of propane, n-butane or n-pentane from the olefin feed during the alkylation step are nearly zero. Formation of isopentane from a mixed C_5= feed during the alkylation step is low and the C_9 selectivity is high, suggesting that the ISOALKY Technology is often ideal for upgrading of C_5= to predominantly C_9 alkylate gasoline or jet fuel. For refiners looking to find a seasonal home for iC5, the ISOALKY unit is a great option. While slightly lowering octane, the low RVP of the alkylate product makes it a good choice during the summer months.

Ethylene alkylation is of interest to some refiners, and ISOALKY Technology can make an excellent alkylate product from ethylene. Whether the ethylene is polymer grade ethylene or even dehydrated ethanol, this olefin feed can be processed to deliver ~100 RON without needing an additional dimerization step, increasing alkylate yield by ~50% over those processes that do.[4]

This ability to upgrade more material, combined with the 3 vol% overall yield improvement, makes ISOALKY Technology as the alkylation technology with a higher yield per barrel of olefin processed. Hydrogen transfer reaction is also negligible: minimizing the loss of carbon to less valuable isopentane and propane by-products as well as minimizing isobutane consumption. The ISOALKY Technology truly offers unparalleled flexibility, enabling refiners to produce higher quality alkylate with a wide range of feedstock options and high level of efficiency.

HEALTH, SAFETY, AND ENVIRONMENT

The ISOALKY Process is one that can be operated with the standard refinery protocols for protecting people, property and the environment, eliminating the need for additional personal protective equipment, safety systems, and training associated with the use of hydrofluoric and sulfuric acids.

The ionic liquid catalyst is a liquid salt (consisting of positive and negative ions only) at ambient temperature. It has the typical properties of a salt such as no measurable vapor pressure, stability for long term storage, and low solubility in hydrocarbon. These properties allow for easier handling of the catalyst in a refinery. Ionic liquid catalyst spills can be contained and managed easily since the catalyst does not vaporize. The ionic liquid catalyst has a low vapor pressure and has low toxicity and corrosivity properties, allowing it to be handled with the same standard protocols used for many of the other liquids present in refineries. Furthermore, the quantity of ionic liquid catalyst required in the ISOALKY Process is one third of the amount required for hydrofluoric acid alkylation and hundreds of times smaller than the amount required for sulfuric acid alkylation. Thus, a refiner using the ISOALKY Process for alkylation will benefit from easier operations, both because the level of work required to safely handle the ISOALKY Catalyst is in line with standard refinery procedures, and because the quantity of work hours, supplies, and equipment needed for handling this catalyst are reduced due to the smaller volume.

ISSUE	H2S04	HF	ISOALKY	COMMENTS
Human toxicity: Risk to personnel	M	H	L	• H_2SO_4: highly corrosive • HF is highly corrosive to tissues & bones • ISOALKY Catalyst is less corrosive and less acutely toxic than H_2SO_4
Catalyst release: Risk to public	L	H	L	• H_2SO_4: non-volatile, but can form mist • HF: volatile, forms aerosol/ vapor cloud • ISOALKY Catalyst reacts with H_2O to form HCl, but reaction limited by moisture in air
Acid tanker truck accident: Risk to public	H	H	L	• H_2SO_4: Lower consequence of incident but many truck trips • HF: Severe consequence, but lower volumes transported • ISOALKY Catalyst: <1% of volume transported versus H_2SO_4
Catalyst regeneration (Environmental impact)	H	M	L	• H_2SO_4: SO_2 and CO_2 emissions from regeneration • HF: incineration of conjunct polymer • ISOALKY Process converts polymer to naphtha then blends to alkylate product

H = Highest potential impact **M** = Intermediate potential impact **L** = Lowest potential impact

Table 5: ISOALKY Catalyst is less corrosive than sulfuric acid and HF and has the least impact on environment.

Unlike conventional, mineral acid-based alkylation processes, ISOALKY Technology has no risk of acid run-away due to the low volume of the ionic liquid catalyst in the process and the limited solubility of hydrocarbon in the ionic liquid catalyst. Impacts of severe process upsets and continuous build-up of conjunct polymer in the ionic liquid are simply alleviated by reducing the olefin feed and continuing on-line regeneration of the ionic liquid catalyst.

Emissions Reduction

Due to the nature of the online regeneration system, the ISOALKY Process offers significant reduction in air emissions compared to regeneration processes that include combustion, especially when compared to the sulfuric acid process. Not only does the ISOALKY Process avoid the emissions associated with combustion when regenerating catalyst, the conjunct polymer does not have to be discarded because it is recovered in such a way that it can be added to the alkylate product.[5]

ISOALKY™ TECHNOLOGY

IMPLEMENTATION

As mentioned above, an existing alkylation unit can be converted to use ISOALKY Technology.

In the case of such a retrofit, the feed treatment equipment, product separation (distillation) equipment, and butane and propane product treatment equipment may be reused. The new technology will require new equipment for the reactor and settler (effluent separation), catalyst regeneration, and alkylate product treatment. See Figure 7.

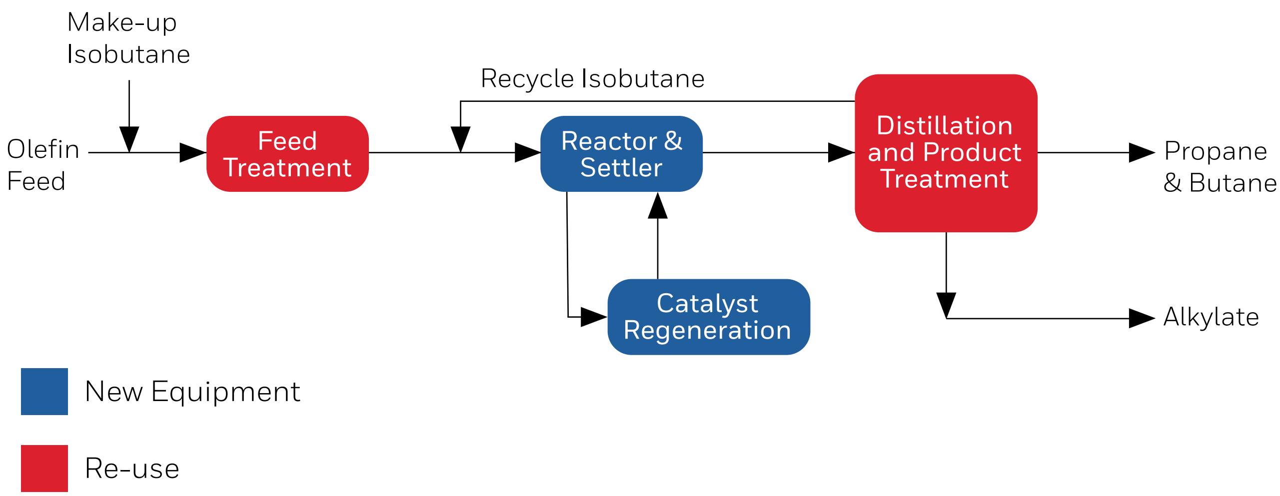


Figure 7: Retrofit of HF plant with ISOALKY Technology - much existing equipment can be reused

There is potential to increase the capacity of an alkylation unit when converting to ISOALKY Technology due to the difference in isoparaffin/olefin ratio. If the existing unit is operating at a ratio higher than 8, converting to an ISOALKY Process could increase capacity without requiring modifications to feed treating or product separation sections, greatly increasing the Return on Investment.

For the new construction of an alkylation unit, ISOALKY Technology is the latest option which presents capital and operating expenses that are similar to conventional technologies, but with all of the additional benefits to yield, product quality, and HSE factors described above.

OPERATING UNIT RESULTS

Chevron – Salt Lake Refinery has been operating their ISOALKY unit since 2021.

Chevron had a successful startup of the first commercial scale ISOALKY unit at their refinery in Salt Lake City, Utah, USA, in January 2021. This unit is designed to process approximately 5,000 barrels per day of alkylate product. The feed to the unit is the full FCC LPG product with roughly a 50:50 ratio of propylene to butylene.

This was a conversion of an existing HF Alkylation unit to the ISOALKY Technology. Major sections of the unit, such as the feed pretreatment, fractionation, and propane and butane product treating sections were reused in the revamp of the unit. With thorough preparation for tie-ins and pre-shake-down of the new section of the plant, the final transition from the HF Plant to the ISOALKY Plant was executed in about 6 weeks.

The initial start-up was smooth and Chevron achieved on-spec alkylate quality within 2 days of olefin feed introduction. Alkylate gasoline production to the full design capacity was demonstrated soon after. The overall performance summary is captured in the table below. The unit operations have been stable and reliable. The regeneration unit performed reliably and no conjunct polymer byproduct stream was generated. The ionic liquid catalyst consumption has been low throughout the operations. The consumption of the organic chloride promoter was higher than our expectation. Currently efforts are in progress to lower the promoter consumption.

Chevron completed the first turnaround of the unit in the 4th quarter of 2024 after nearly 4 years of operation. The turnaround duration was similar to a turnaround of a HF Alkylation unit. Compared to HF units, we saw significant advantages in plant clean-up, and the aspects of health, safety and environment (HSE). Only water or steam were used to clean the unit and equipment, and the resulting wash-water was processed through the refinery waste water treatment plant. Standard refinery personal protective equipment (PPE) was used for the entire turnaround operation. Since this is the first turnaround, extensive inspections were conducted. Consistent with the Demonstration Plant results, the turnaround inspection results were mostly positive and the distillation section (killed carbon steel construction) did not show any corrosion concerns. We have identified a few areas for improvement, which will be implemented in all future designs.

FEED AND PRODUCT PROPERTIES	
Olefin Feed	56% C_3=, 44% C_4=
RON	Met Target
MON	Met Target
Alkylate End Point	Met Target
RVP	Met Target

HRR PERFORMANCE (IL CATALYST REGENERATION)	
CP (Conjunct Polymer) Formation	Better than Target
CP Conversion in HRR	Better than Target

THROUGHPUT	
Alkylate Production, BPD (demonstrated)	Per Design
Olefin flow, BPD	Per Design

IL CATALYST AND CO-CATALYST CONSUMPTION	
IL Catalyst Target Consumption, lb/bbl alkylate	Met Target
Co-catalyst Target consumption, lb/bbl alky alkylate	Higher Than Target**

**Modification in place for new designs

ISOALKY™ ALKYLATION

CONCLUSION

ISOALKY Alkylation Technology is a commercially viable alternative and offers a compelling economic solution compared to conventional liquid acid technologies.

It is a revolutionary new commercially proven technology which offers refiners the ability to upgrade low-value refinery butanes and olefins to high-value alkylate and to improve the quality of their gasoline pool. This ability to improve the gasoline pool is important to all refiners as product specifications change, but it is especially beneficial to refiners that are adding petrochemical production capacity in order to keep up with the changing global market.

ISOALKY Technology can be used for new alkylation plants as well as for retrofitting existing facilities to improve their performance. The ISOALKY Catalyst exhibits superior performance with a wide range of olefin feeds compared to conventional acid catalysts. The ionic liquid catalyst has negligible vapor pressure and can be regenerated on-site, resulting in a lower environmental impact compared to conventional liquid acid technologies.

The ISOALKY Process is expected to make a significant impact on global production of clean fuels in the years to come.

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