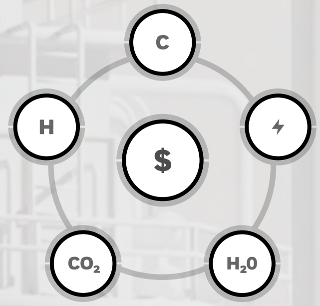
A New Era for Alkylation:



IONIC LIQUID ALKYLATION – ISOALKY™ PROCESS TECHNOLOGY

Enabling the Refinery of the Future with Next Generation Alkylation Technology

Chevron

Honeywell UOP

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INTRODUCTION

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

Demand for alkylate is as strong as ever 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, it will 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, that 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.

In order to provide clear insight to inform better decisions for the refineries of the future, UOP has developed the six efficiencies (UOP E6) framework. This methodology determines the carbon, hydrogen, utilities, emissions, water and capital efficiencies to enable better investment decisions.[1] The ISOALKY Process is inherently more efficient than previous generations of alkylation technology, and those efficiencies are highlighted throughout this paper.

AUTHORS

Hye-Kyung Timken, Principal Scientist, Chevron Fellow, Chevron

Rajeswar Gattupalli, Senior Business Leader, Alkylation & Treating, Honeywell UOP

Jonathan A. Tertel, Senior Product Line Manager, Honeywell UOP

Dominic Weber, Lead Engineer and Alkylation Subject Matter Expert, Honeywell UOP

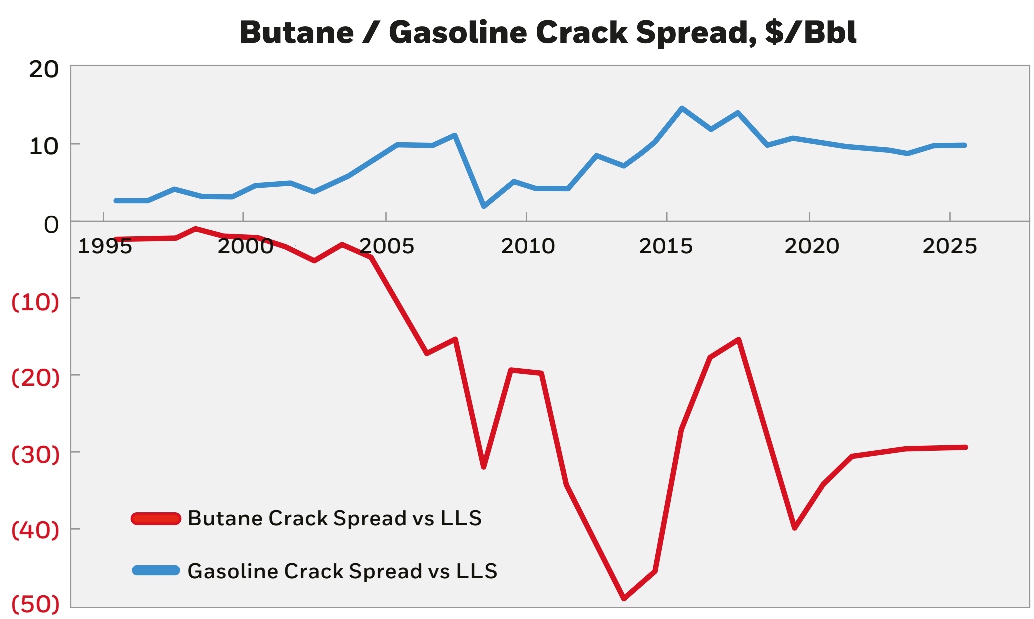
MARKET DRIVERS

Whether refineries move into the future with fuels only, petrochemical driven or a combined product slate, higher octane blendstocks 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.[2] 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 convert them to high-value gasoline product. Alkylate is the 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 blendstocks and compared to international specifications for gasoline.



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.

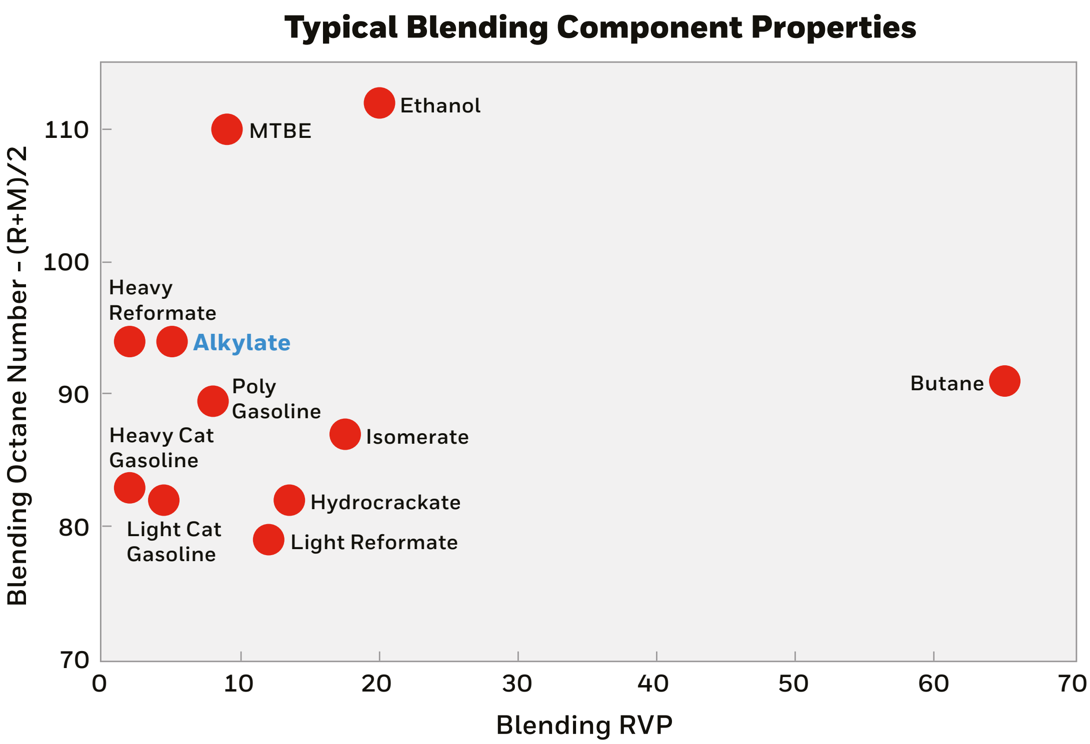


Figure 2: Alkylate stands out as an ideal blending component due to low RVP and high octane.

Specification	RBOB Tier III	CARBOB Phase 3	Euro VI	China V	Alkylate
(R+M)/2, [RON]	87/89/91	87/89/91	[91/95]	[95]	**[95]+**
Sulfur, ppm max	10	20	10	10	**<5**
Benzene, vol-max	0.62	0.8	1.0	1.0	**0**
Aromatics, vol-% max	-	25	35	40	**0**
Oleflns, vol-% max	-	6	18	24	**0**
Oxygen, Wt-% max	2.7	2.2	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 suitable 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 ethylene to amylene.	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.
No hydrogen transfer reaction	Productions of propane and isopentane from the olefin feed during the alkylation step are nearly zero. Also, isobutane consumption is reduced.	ISOALKY Technology is 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:

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

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

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

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 now commercialization of the ISOALKY Alkylation Process.

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. 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.

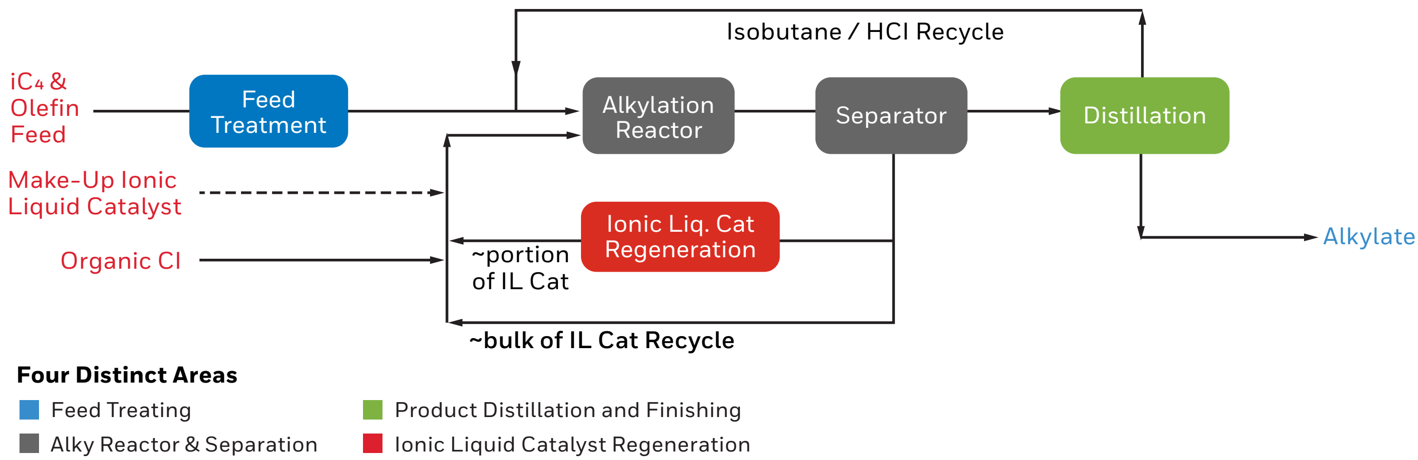


Figure 3: ISOALKY Process flow diagram

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. Typical process conditions are shown in Table 3.

ISOALKY Process Conditions	
Reaction medium	Hydrocarbon continuous phase with droplets of ionic liquid catalyst
Temperature	30-120 ºF (-1 - 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 30 – 120ºF (-1 – 49ºC). The ISOALKY Process can be designed to fit the needs of each refinery according to the desired product quality and the available cooling capability. ISOALKY Technology could produce higher octane number alkylates than other alkylation technologies by operating at ~50ºF (10ºC) reactor temperature or lower. The impact of temperature on alkylate quality is shown in Figure 4.

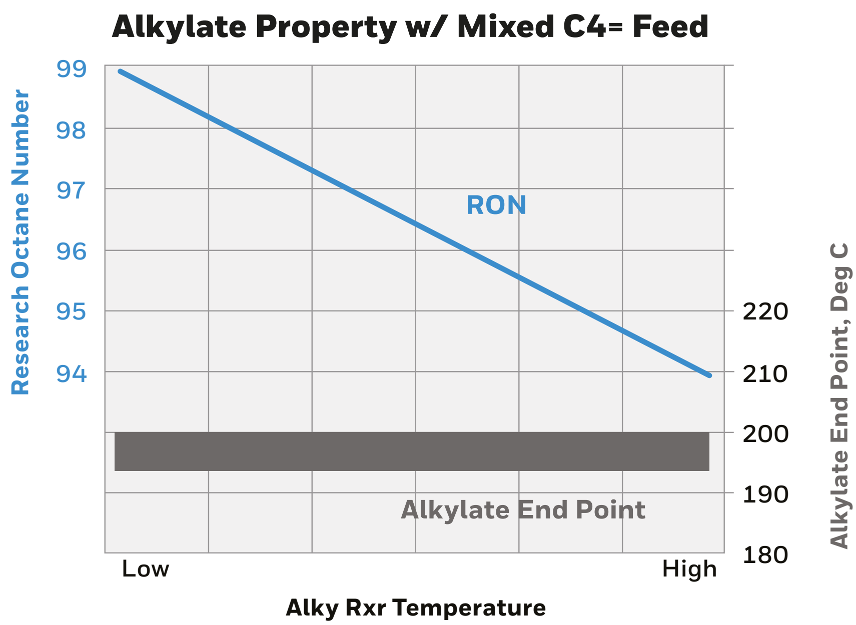


Figure 4: The ISOALKY Process yields high quality alkylate at high and low operating temperatures, with highly consistent alkylate end point and RON generally 2 numbers higher than can be achieved with the sulfuric acid process at the same temperature.

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.

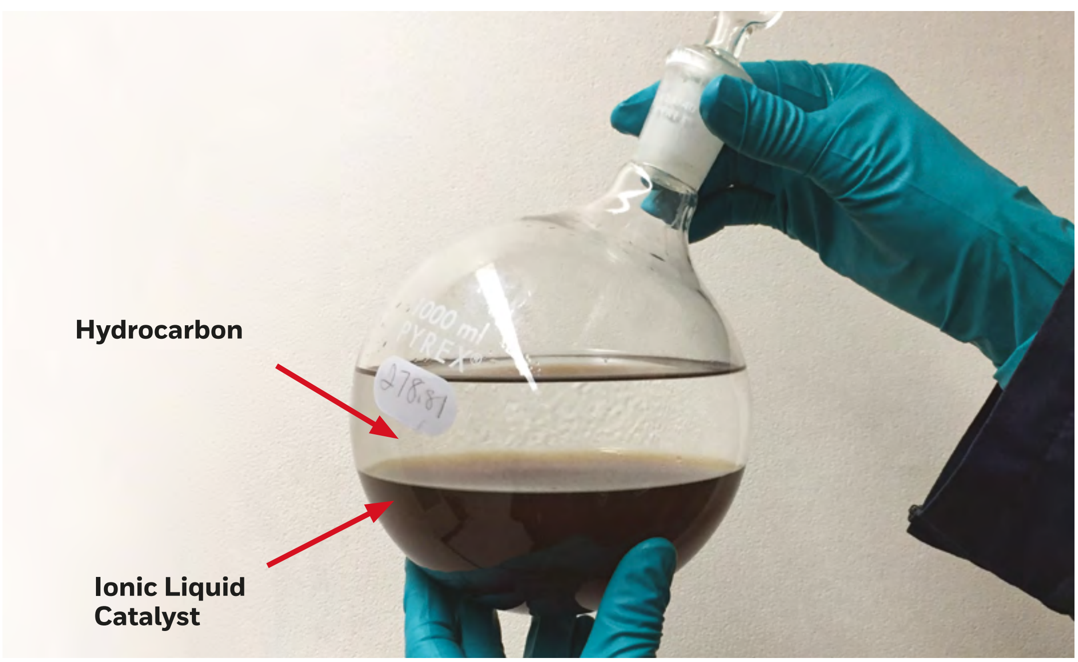


Figure 5: Hydrocarbon product separation from the ionic liquid is easy due to negligible solubility of ionic liquid in hydrocarbon.

Efficient separation and recovery of the ionic liquid catalyst minimize 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.

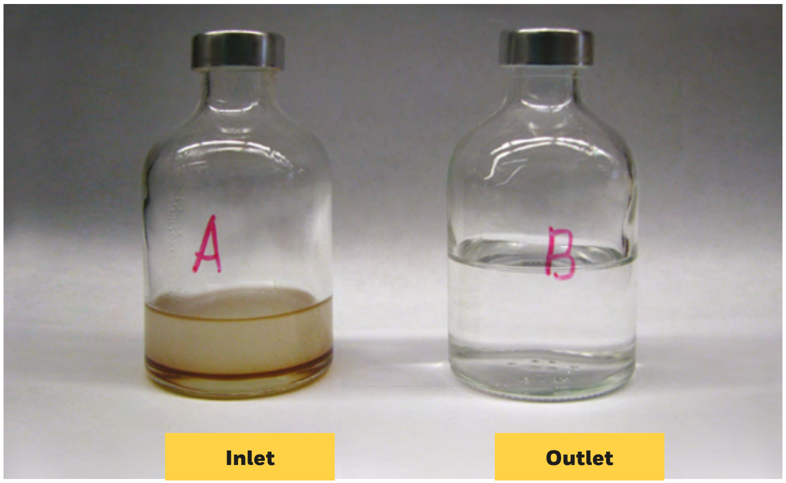


Figure 6: Alkylate reactor effluent containing ionic liquid catalyst (inlet) and hydrocarbon stream after coalescer (outlet). Efficient separation system generates water clear reactor effluent to the distillation column.

The effective separation of the ionic catalyst from the reactor effluent is also important for protection of downstream equipment. After five years of operation at the demonstration 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.

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 unique 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.

Reuse of the ISOALKY Catalyst with on-line regeneration enables very low ionic liquid catalyst consumption.

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.

Capital Efficiency

Capital efficiency is especially good with ISOALKY Technology because of the smaller volume of catalyst and resulting smaller size of the reactor and regeneration sections. 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.

Comparison of ISOALKY Technology to Conventional Alkylation Technologies

	H_2SO_4	HF	ISOALKY
Alkylation temperature, ºF	30-60	95	30-120
Alkylation pressure, psi	60	200	60 - 200
Catalyst volume in reactor	50%	50 - 80%	3-6%
Alkylate quality w/ mixed $C_4^=$	95 RON	95 RON	95 -99 RON
Alkylate yield	Base	Base	Base +3 vol%
Conjunct polymer formation rate, wt% Olefin	1- 1.5%	~0.5%	0.3 -0.5%
Handling of conjunct polymer	Incineration	Incineration	Converted to naphtha & LPG
Catalyst make-up rate, lb IL/ bbl alkylate	400-1400 x Base Off-plot regen	~3 x Base On-line regen	Base On-line regen
Safety and Environmental Impact	Large acid inventory, sAcid transport for off-plot regen facility, SOx emission during regeneration	Smaller acid inventory, Volatile HF requires engineering controls and special PPE	Smallest catalyst inventory, Non-volatile catalyst, Integrated regeneration, Reduction of caustic solution waste

Table 4: ISOALKY Technology has 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.

A higher RON of 99 can be achieved with the ISOALKY Technology at 30ºF (-1ºC) alkylation reactor temperature with a typical, mixed C_4 olefin feed from a refinery FCC unit. 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 high-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 ideal for upgrading of C_5= to predominantly C_9 alkylate gasoline or jet fuel.

Ethylene alkylation is of interest to some refiners, and ISOALKY Technology can make an excellent alkylate product from ethylene. With methane and light gas (H_2, N_2) removed, a 50%-50% mix of ethane/ ethylene from an FCC unit can be alkylated to make 2,3-dimethly butane selectively.

Carbon Efficiency
This ability to upgrade more material, combined with the 3 vol% overall yield improvement, makes ISOALKY Technology very carbon efficient. An important factor in ISOALKY Technology's carbon efficiency is that the occurrence of the hydrogen transfer reaction is negligible; virtually eliminating 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 an unprecedented 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 the 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 brought 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.

HS&E Comparison: ISOALKY vs HF and Sulfuric

Issue	H_2SO_4	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 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.

Water Efficiency

ISOALKY Technology does not require any wash water for product streams, making it much more water efficient than conventional alkylation processes. Clean water is a scarce resource that is becoming increasingly important in water-stressed areas around the globe. Regardless of the status of clean water in any given location, the ability to avoid additional steps involved with wash water and to produce excellent alkylate more efficiently is a benefit.

Emissions Efficiency

Due to the nature of the unique online regeneration system, the ISOALKY Process offers significant reduction in air emissions compared to regen processes that include combustion. The emissions efficiency of the ISOALKY Process is a notable improvement, 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.

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.

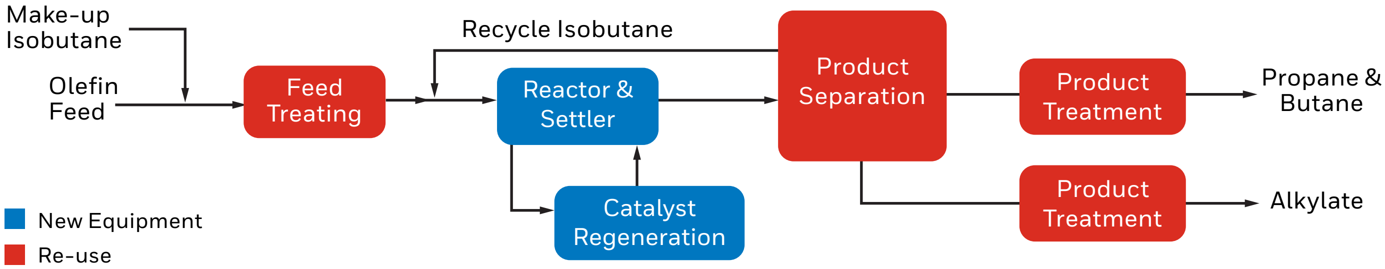


Figure 7: Retrofit of HF plant with ISOALKY Technology - many existing equipment can be reused

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.

For 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.

EFFICIENCY

All considered, the ISOALKY Technology is an appealing investment for both new and existing alkylation units due in large part to its efficiency across categories.

Demonstrating the viability of an investment is becoming more involved as technologies advance, and as refining and petrochemical facilities become more integrated. While current industry benchmarks provide metrics to track the relative performance of existing operating facilities, these metrics may not tell the full story. They are valuable for comparing the performance of a facility relative to its peers, but they do not provide the critical information required to make informed decisions on future investments.

UOP identified six critical factors mentioned at the start of this paper for measuring the performance of a refining and petrochemical facility investment, and these six factors form the UOP Six Efficiency (E6) framework. These factors were derived from the critical drivers common across all major refining and petrochemical projects.

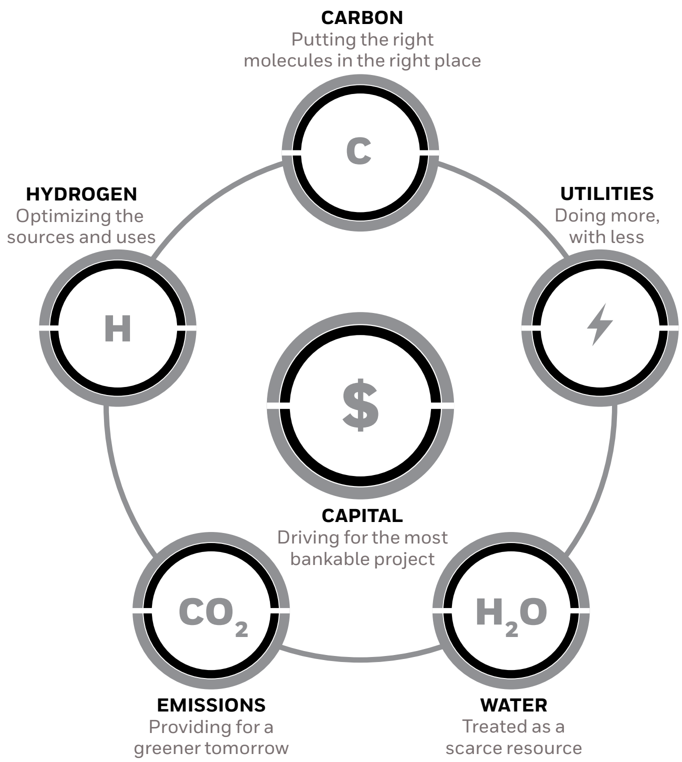


Figure 8: The six efficiencies are Carbon, Hydrogen, Emissions, Water, Utilities, and Capital

The UOP E6 model shapes the Refinery of the Future by driving efficiency improvements for the following categories:

- **Carbon:** the goal is to maximize the transformation of crude oil and other inputs into high-value products. This means putting the right molecules in the right processes while doing the minimum amount of work needed to convert them into high-value products.
- **Hydrogen:** the goal is to optimize integration between sources and uses of hydrogen. This means putting it on and taking it off as few times as possible – using hydrogen as sparingly as possible.
- **Utilities**: the goal is to minimize net usage, ensuring the best use of energy to convert feedstocks into high-value products.
- **Emissions**: the resource involved with emissions is really the environment, but what is measurable are releases such as greenhouse gasses. The goal is to minimize the carbon footprint and have the lowest possible impact on the environment.
- **Water**: water is a scarce resource worldwide. The goal is to minimize usage and ultimately aspire towards zero discharge.
- **Capital**: the goal with capital is always to maximize return on investment while meeting all of the project goals.

For a given refining and petrochemical configuration or process, such as alkylation technology, the effectiveness of each category is measured as an efficiency by quantifying and comparing against an annual benchmark. By quantifying the efficiency of each of the six factors, the UOP E6 model provides fundamental insight into an investment’s feasibility, thus enabling better business decisions.

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 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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For More Information

For more information, please contact your UOP representative or visit us online at www.uop.com.

UOP LLC, A Honeywell Company
25 East Algonquin Road
Des Plaines, IL 60017-5017, U.S.A.
www.uop.com

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