

# Alkylation

## A Key to Cleaner Gasoline & Better Vehicle Mileage

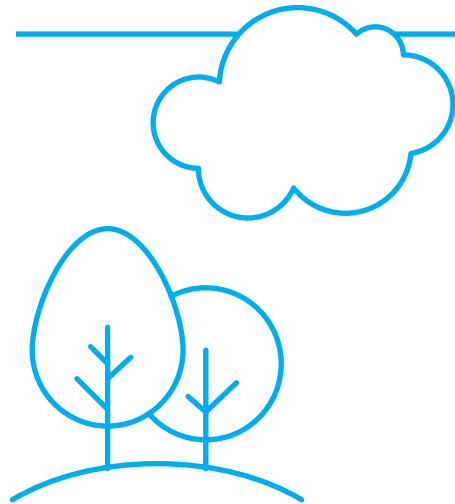
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*American Fuel & Petrochemical Manufacturers (AFPM) is the leading trade association representing the majority of U.S. refining and petrochemical manufacturing capacity. Our members produce the fuels that power the U.S. economy and the chemical building blocks integral to millions of products that make modern life possible.*

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*Alkylation is a refinery process essential to the production of cleaner fuels that satisfy the world's toughest air quality, carbon emissions and auto efficiency standards. Fuel alkylation is part of the American success story of doubling fuel economy, reducing vehicle carbon emissions by half and cutting national air pollutant emissions nearly 80% since the 1970s.*



### U.S. gasoline needs alkylate for its octane and environmental properties

America's fuel refiners use a chemical process called alkylation to produce alkylate, a component of the cleaner gasoline required by today's higher-efficiency automobiles. Nearly 90 U.S. refineries — representing 90% of total U.S. refining capacity — have alkylation units.

Alongside varying combinations of ethanol, reformate and other products, alkylate increases the octane rating of gasoline which works to reduce premature combustion and "engine knock" that can damage a vehicle and downgrade engine efficiency. In optimized engines, higher-octane gasoline supports better vehicle performance and fuel economy, and lower overall greenhouse gas emissions. Beyond contributing octane, alkylate also brings to the table other unique environmental attributes that help vehicles run cleaner, namely low measures of fuel volatility and evaporative emissions —represented by low Reid Vapor Pressure (RVP) —that are essential in parts of the country where smog is a concern. Additionally, because alkylate has no aromatic content and low sulfur, it helps lower vehicle emissions and tailpipe pollution.

IHS Markit trends suggest global demand for alkylate will rise nearly 10% by 2030 as more countries motorize. Investments to expand alkylate production capacity worldwide will be needed to supply this larger market.

### Two alkylation technologies support cleaner fuel

The alkylation process requires a catalyst to enable a chemical reaction that safely converts feedstocks into alkylate. **Sulfuric acid** and **hydrofluoric acid** (HF) are the two commercially proven alkylation catalysts used today, each accounting for about half of U.S. alkylate production.

Both catalysts are used safely by fuel refineries around the country and in a wide range of other industrial settings. They are thoroughly regulated by state and federal workplace and community safety programs, including the Occupational Safety and Health Administration's

(OSHA) Process Safety Management program and the Environmental Protection Agency's (EPA) Risk Management Program. But refineries that use HF go even further. Because nothing is more important to the refining industry than the safety of our people and communities, facilities with HF alkylation units also adhere to exacting industry policies — that go above and beyond what is required by law — to manage risk and keep refining employees, contractors and neighbors safe.

*Once an alkylation unit has been designed and built to use a specific catalyst, it cannot be switched to operate on the other without major equipment modifications that would be infeasible for most facilities to execute. The two catalyst technologies are not interchangeable and require completely different reactor systems.*

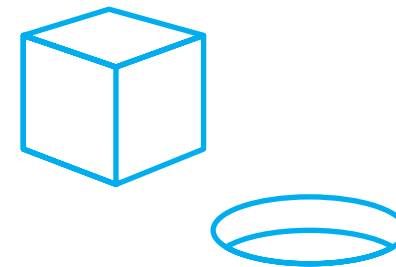
While HF alkylation and sulfuric acid alkylation both accomplish the same thing — producing alkylate for the manufacture of high-octane, low RVP gasoline and aviation fuel — there are significant differences in their processing configurations, equipment and risk mitigation strategies, though neither technology is inherently safer.

Decommissioning one type of alkylation unit to rebuild around the other technology would be a massive undertaking for a facility, and many would find it impossible given other considerations at their sites. In fact, there is no proven commercial pathway for refineries to switch from one alkylation catalyst to the other. No refinery has ever converted an HF unit over to sulfuric acid alkylation,

and projects to transition from HF to even newer alkylation technologies are still in early phases. Eliminating the use of either HF or sulfuric acid technology would severely diminish U.S. capacity to manufacture cleaner gasoline in line with consumer demand.

### The myth of interchangeable alkylation technology

Multiple factors dictate which alkylation technology a refinery will use, including feedstocks, space constraints, transportation logistics and refinery location. The selection of an alkylation catalyst impacts configuration of the entire refinery operation and its other process units. Once a technology is chosen and the alkylation unit is designed and built to use a specific catalyst, refineries cannot flip a switch and swap to the other. HF and sulfuric acid technologies are not interchangeable.



### Square footage and feedstock volume

Sulfuric units require more energy and space than HF units. Sulfuric alkylation requires more acid catalyst, which means there must be additional feedstock deliveries and a larger overall reactor. Additionally, sulfuric acid units require a refrigeration system and access to acid regeneration units, either onsite or nearby. These are not considerations for facilities with HF units.

### Location and waste reduction

Alkylation technology is often a reflection of other feedstocks produces onsite. That means other refinery processes and proximity to petrochemical plants factor into the decision around alkylation catalysts.

Refineries do not waste product, and complex refineries with fluid catalytic cracking units (FCC units) need to have a system in place to utilize their propylene and butylene byproducts.

Refineries that are close to chemical facilities may have the option of selling their propylene and butylene as feedstocks to manufacture plastics and sanitizers. For refineries without this option, HF alkylation technology provides an answer where sulfuric acid technology does not. HF units can co-process both propylene and butylene to make alkylate.

### Alkylation optionality

Research into alternative alkylation technologies is ongoing, but HF and sulfuric acid are still the only commercially proven catalysts available to refiners today. Part of the reason for this is the refining industry's exacting commitment to safety and reliability. Engineers and scientific researchers follow a multi-year, multi-step process to test new fuel alkylation technologies, which includes:

- Bench-scale testing to demonstrate feasibility of chemistry
- Pilot plant testing to verify process viability
- Demonstration unit testing to determine scalability and evaluate process, components and material compatibility
- Commercial unit testing to confirm scalability and ongoing reliability
- At least one or two turnaround cycles (three – five years each) to evaluate safety and reliability over time, and to monitor equipment and unit components for the effects of corrosion and other potential wear

Both solid acid catalyst (e.g., AlkyClean, K-SAAT) and ionic liquid alkylation technologies (e.g., ISOALKY, Ionikylation) are being explored and show considerable promise. As of January 2021, ISOALKY is the only other technology in operation in the United States apart from HF and sulfuric acid. More time and testing are needed to ensure these newer technologies can safely and efficiently produce the components of cleaner gasoline in a range of differently sized and configured refineries.

Recent progress suggests that new unit builds and conversions may become economically feasible. But we still have a lot to learn. We don't yet know what total costs are associated with the adoption of newer catalysts or the reliability of these technologies over time.

*Refinery alkylation is subject to layers of regulation and accountability, including strict oversight from:*



- ✓ Industry and auditors, per comprehensive API RP-751 policies
- ✓ OSHA
- ✓ EPA
- ✓ Department of Homeland Security
- ✓ Department of Defense
- ✓ Chemical Safety Board
- ✓ State and local authorities



## Other refinery processes support alkylation & the production of cleaner fuels

America is home to some of the most sophisticated and advanced refineries in the world. Our complex refineries feature several interconnected processes that each play a part in turning crude oil — even the toughest-to-refine heavy sour types — into fuels clean enough for today's high-performance engines and stringent U.S. air quality and auto emissions standards.

Alkylation units allow refineries to upgrade lower value feedstocks into high value alkylate. Other refinery units produce the feedstocks required for alkylation, so wherever fuel alkylation units are located you will typically find one of more of the following complementary processes nearby:

### Fluid catalytic cracking (FCC)

A fluid catalytic cracking unit, often called a "cat cracker," "cat unit," or "FCC," makes it possible to convert low value, heavy gas oil (what some might call "the-bottom-of-the-barrel") into higher value products like gasoline. The process also generates **butane, propylene, and butylene** byproducts that serve as building blocks for a wide range of consumer products, and, separately, as feed for a refinery's HF alkylation unit. Without a process like cat cracking to enable product optionality from a range of crude oils, refineries would have a much harder time producing the exact products demanded by the global market.

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*Other refinery units produce byproducts that feed the alkylation process.*

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### Butane Isomerization

Butane isomerization converts butane produced by refineries, including FCC units, to isobutane. While butane is also a source of octane, it needs to be limited in finished gasoline to keep evaporative emissions low, per the Clean Air Act's Reid Vapor Pressure (RVP) rules. Converting excess **butane into isobutane** through isomerization creates a valuable feedstock for refinery alkylation units.

### Catalytic Reformer

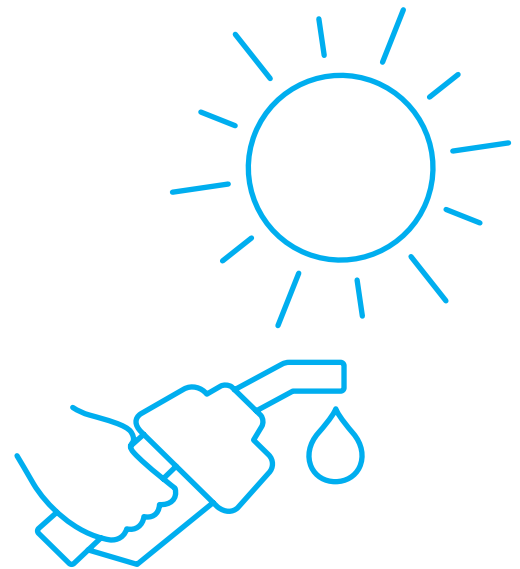
Alkylation and isomerization units aren't the only sources of fuel octane at refineries. Catalytic reformers produce octane too — converting low-octane naphtha (produced during crude distillation) into high-octane reformate to be blended into gasoline. Whether gasoline is regular, midgrade or premium, reformate is likely a source of some of its octane (along with alkylate, butane and ethanol). Like the butane isomerization process, **isobutane is a byproduct** of catalytic reforming that can be used to support alkylation.

### Hydrocracker

Hydrocracking units perform similar functions as FCC units, but tend to help refineries maximize diesel fuel production. Hydrocrackers turn heavier hydrocarbons into lighter products suitable for distillates as well as gasoline and jet fuel. But where the FCC unit produces propylene and butylene olefins, **hydrocracking produces straight isobutane** — ready-made to feed an alkylation unit.

### How it all connects to alkylation

Each of the above processes can be a complement to alkylation. In alkylation units, a concentrated catalyst, such as hydrofluoric acid or sulfuric acid, kicks off a chemical reaction where **alkylate is made from olefins and isobutane** feedstocks produced by other refinery processes. Alkylate is a critical fuel component that is high in octane, low in sulfur and Reid Vapor Pressure and contains zero aromatics or olefins — features of the cleanest gasoline on the market.



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*These highly interrelated and sophisticated processes are used throughout the country to turn a broad range of crude oil and hydrocarbons into the cleaner fuels Americans — and the world — depend on.*

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## Alkylation and the future of liquid fuels

U.S. refiners set the bar globally for process safety, reliability and maximizing the production of cleaner fuels from even the toughest-to-refine crude oils. The alkylation process that yields low-sulfur, high-octane alkylate is core to modern refining and delivers a cleaner future for U.S. auto transportation.

Internal combustion engine vehicles only function at their best when they're running on the right kinds of fuel — the specific fuel prescribed by their manufacturer. Cleaner, higher octane gasoline helps optimized engines reach their maximum efficiency. Alkylate from U.S. refineries is a key component of this gasoline and helps bring to life the benefits of fuel economy and cleaner driving for consumers and the environment.