

# AlkyClean® Solid Acid Catalyst Alkylation Technology

**MCDERMOTT**  
TECHNOLOGY

**ALBEMARLE®**

## Overview

McDermott and Albemarle have jointly developed the AlkyClean® process, an inherently safer, environmentally friendly and sustainable solid acid alkylation technology.

The AlkyClean process employs Albemarle's zeolite-based AlkyStar™ catalyst coupled with Lummus Technology's innovative reactor processing scheme to yield a high quality alkylate product with consistently high octane values, low vapor pressure, limited heavy ends and no olefins, aromatics or sulfur.

The world's first solid acid catalyst alkylation unit applying the AlkyClean technology was started up in August 2015 in Shandong, China, by Shandong Wonfull Petrochemical Group Co., Ltd. It has operated successfully since that time.

The AlkyClean process received the 2016 Presidential Green Chemistry Challenge Award from the U.S. Environmental Protection Agency (EPA). The EPA's Presidential Green Chemistry Challenge program promotes the environmental and economic benefits of developing and using novel green chemistry,

while recognizing individuals and organizations on a national level for successfully researching, developing and implementing such technologies.

The total installed cost of a facility utilizing the AlkyClean process, including OSBL (regeneration facilities, safety installations, etc.), is comparable to current liquid-acid processes, particularly HF units. With no liquid acids or chlorides in the system, no product treatment or disposal of hazardous material is required. Carbon steel construction is suitable due to the lack of corrosive acids in the system and the mild operating conditions employed in the process.



First commercial AlkyClean unit in China

## Advantages

Process Features	Process Benefits
Robust, true-solid-acid catalyst	<ul style="list-style-type: none"> <li>Eliminates corrosive liquid acid use and associated safety concerns</li> <li>Tolerant to feedstock impurities, changes in feedstock olefin composition and process upsets (e.g., water spikes)</li> </ul>
Removes safety risks associated with liquid acids	<ul style="list-style-type: none"> <li>Lower maintenance and monitoring requirements</li> <li>Eliminates costs associated with mitigation (acid dump and water spray systems), disposal of acids or chlorides, and vapor suppression additives</li> </ul>
Low pressure, liquid phase operation in the temperature range of 50°C - 90°C	<ul style="list-style-type: none"> <li>Eliminates costly refrigeration requirements associated with H<sub>2</sub>SO<sub>4</sub> units</li> <li>Carbon steel construction material results in lower costs</li> </ul>
Does not produce acid soluble oil by-product	<ul style="list-style-type: none"> <li>Improves alkylate yield; no by-product disposal</li> </ul>
No emissions to air, water or ground	<ul style="list-style-type: none"> <li>Environmentally friendly process</li> </ul>

### Performance Characteristics

The solid acid catalyst used in the AlkyClean process contains no halogens and is very robust with regard to water and other feed impurities such as oxygenates, sulfur compounds and butadiene. Any deactivation of the catalyst from these impurities is restored via high temperature (250°C) gas phase regeneration with hydrogen.

The product quality and alkylate yield from the AlkyClean process are comparable to that of liquid acid processes; however, no acid-soluble oils are formed. This results in reduced olefin feed consumption per unit of alkylate production (higher yield) and eliminates the need for by-product disposal. High quality product can be obtained with various feeds, including raffinate containing butene-1 (an octane debit for HF alkylation units).

The AlkyClean process produces an alkylate that has:

- High octane number (RON / MON)
- Low vapor pressure
- Comparable end point
- No olefins, aromatics and sulfur

Alkylate quality matches or exceeds that of products from liquid acid processes. Operating conditions, alkylate yields and properties are all comparable for the various processes. However, the AlkyClean process does not require refrigeration or extensive cooling because the reactor temperatures are higher than those used in liquid acid units.

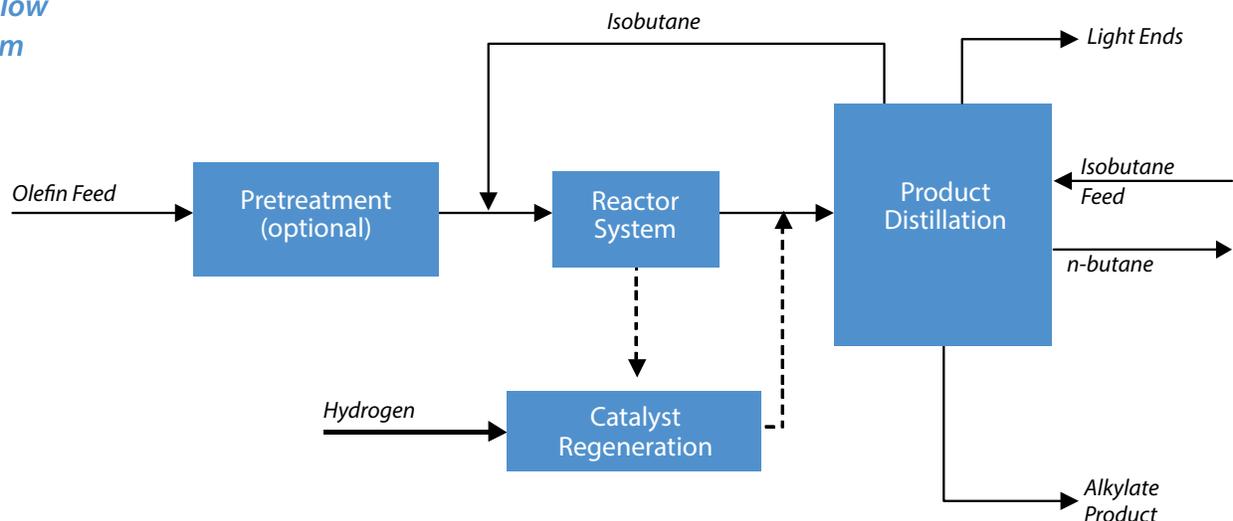
### Value to the Refiner

A true solid acid alkylation process gives the refiner a real choice for the first time.

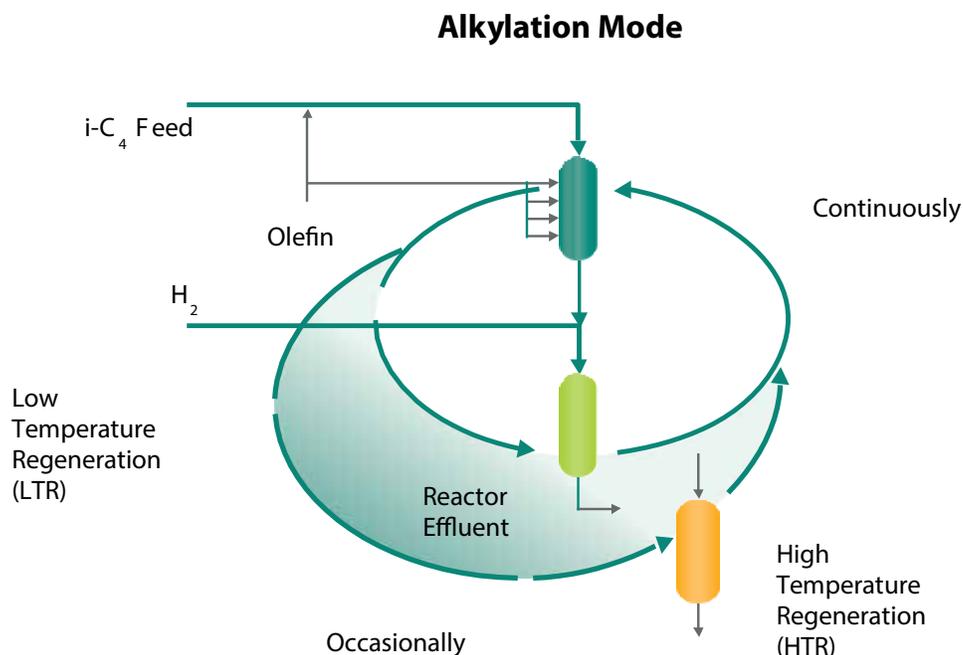
The AlkyClean process delivers value to the refiner:

- Commercially proven package of process design, catalyst and operating procedures
- Capital and operating costs competitive with liquid acid processes
- High alkylate product quality and yields
- Flexible operation with a high on-stream factor under mild operating conditions
- Suitable for new units or revamping or debottlenecking liquid acid units, particularly HF units

### Block Flow Diagram



## Reactor Schematic



## Process Description

The process consists of four main sections: feedstock pretreatment (depending on contaminant level), reaction, catalyst regeneration and product distillation. Olefin feed is pretreated if necessary and, together with isobutane recycle, enters the reactor. The reactor operates in the liquid phase in the temperature range of 50°C - 90°C and at a pressure between 20-30 barg (290-440 psig). Multiple reactors are used to allow for continuous alkylate production, as individual reactors cycle between on-line alkylation and low temperature regeneration, and are occasionally taken off-line for high temperature regeneration.

During low temperature regeneration, olefin addition is stopped and hydrogen is added to achieve a low reactor concentration of dissolved hydrogen, while maintaining liquid-phase alkylation reaction conditions. This allows for a seamless switchover between operations and minimizes energy consumption. Over time, there is still a gradual loss of catalyst activity, which is recovered by taking a reactor off-line for a high temperature regeneration that fully restores catalyst activity. The swing reactor, coupled with long catalyst life, allows the refiner to tailor turnarounds in line with FCC requirements.

## AlkyStar: An Advanced Catalyst Technology

Albemarle's AlkyStar catalyst has taken solid acid technology a major step forward. The strength, type and number of the zeolite's acid sites on the AlkyStar catalyst are optimized to enhance hydrogen transfer reactions over multiple alkylation reactions. The catalyst's particle size and porosity are tailored for optimal diffusion control of molecular traffic within the zeolite structure. High I/O ratios at the catalyst active sites are obtained and conditions favorable for high octane numbers and yields of desired products are achieved at low deactivation rates.

## Design and Operational Features

The general process scheme, isobutane circulation rates and other conditions are similar to those of liquid acid alkylation processes. The main difference for the AlkyClean process is the use of multiple fixed-bed reactors operating in cyclical mode, which permits continuous operation while one reactor is being regenerated or undergoing routine maintenance.

With this innovative continuous regeneration scheme, the performance is maintained without inconvenience to the plant operator.

Low temperature regeneration of the catalyst is carried out by switching from olefin feedstock to a small amount of hydrogen. There is no change to the reactor conditions, and the switch is programmed automatically. During the low temperature regeneration, the dissolved hydrogen cleans the catalyst, thereby delaying the build-up of longer-chain hydrocarbon molecules. However, a high temperature regeneration, with hydrogen in the gas phase at temperatures of about 250°C (480°F), is eventually required to completely restore catalyst performance, once every one or two weeks.

## Retrofitting

Liquid acid units, particularly HF units, can be revamped to use solid acid AlkyClean technology while retaining their existing feedstock preparation and distillation/recycling facilities. Additionally, product post-treatment is eliminated from the revamped plant. The solid acid process uses fixed-bed reactors without the special metallurgical requirements of liquid acids.

## Safety and Environmental Benefits: A Shared Value Creation

AlkyClean technology is a true solid acid catalyst process. The hazards associated with liquid acid use are absent, as are the measures necessary to mitigate these hazards. This gives economic benefits but above all confidence that the interests of refinery personnel and the general public are being served through the high standards of safety and environmental protection.

- Liquid and solid wastes are minimal
- Catalyst consumption is the lowest of any alkylation process
- The in-situ regeneration procedure ensures a long catalyst life; the hydrogen off-gas stream from the regeneration is suitable for other refinery applications
- As the alkylate produced is free of acids and halogen compounds, it requires no further treatment
- The AlkyClean process does not produce acid-soluble oil, a by-product of the liquid acid processes that needs to be incinerated

- Downstream treatment and waste disposal aspects are eliminated because there is no need for washing and neutralization procedures to remove acids
- Emissions to the atmosphere from the unit are nonexistent because there is no need for flaring or fired heaters
- Active component in spent catalyst is reclaimed for re-use



Green Chemistry Challenge Award

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