

New solid acid alkylation process for motor gasoline production

Vincent J. D'Amico

Almost everywhere we turn, the talk is about new, stricter environmental regulations being introduced to reduce emissions of ozone precursors and toxics from motor fuels. There are two perspectives on this in the production of motor gasoline: that the fuels used to run our vehicles need to be improved, and that the processes used to make the fuels need to be made more environmentally friendly – ie, 'green' technologies. ABB is working to develop a new gasoline process that will meet both these challenges.

Gasoline is a combination of several refinery-produced components – reformer aromatics, FCC gasoline, alkylate, ethers, etc – that are blended to meet required specifications for octane, oxygen, sulfur, Reid vapor pressure (RVP), end boiling point, aromatics, olefins and benzene. The new regulations will require reduced levels of sulfur, aromatics and benzene while still maintaining high octane and low RVP. The question to ask is, how do we improve the quality of gasoline in the future?

With its high octane number, low vapor pressure and absence of aromatic and olefinic compounds, alkylate is an ideal

clean fuel component because it is low polluting and has low toxicity. In response to the new environmental regulations being legislated on an expanding worldwide basis, we would expect the demand for alkylate to increase. However, the conventional methods used to produce alkylate require large volumes of corrosive liquid hydrofluoric acid (HF) or sulfuric (H_2SO_4) acid. Both can inflict serious injury via skin contact or inhalation and thus pose a perceived hazard to refinery workers and the surrounding community alike. These perceived dangers may actually inhibit the supply growth of alkylate as the process

for obtaining permits for new units can be difficult and time-consuming, and can increase project costs. Further, there are issues of community pressure and the threat that one safety related incident, anywhere in the world, may result in regulatory action affecting all refiners.

ABB Lummus Global, in partnership with Akzo Nobel, has developed a new, environmentally superior process to make alkylate. It uses a solid acid catalyst (SAC) that is environmentally benign and it eliminates the risks associated with liquid acids while producing alkylate of comparable quality at similar cost. Other benefits include higher product yields and

enhanced feedstock processing flexibility with respect to both composition variation and tolerance to impurities.

Background

Motor gasoline alkylate is the product of the acid-catalyzed reaction of an iso-paraffin with an olefin to form a longer chain iso-paraffinic compound. The predominant reactants are iso-butane and butenes, which form primarily iso-octane isomers (eqn 1). Undesirable byproducts include high molecular weight polymers (heavy hydrocarbons) that are the result of olefinic molecules (eg, butenes) reacting with either each other or alkylate (eqn 2). Polymeric byproduct formation is minimized by selecting an optimum reactor operating temperature and utilizing an excess of iso-paraffin in the reaction zone. The higher the iso-paraffin to olefin molar ratio (I/O) in the reactor, the higher the selectivity to alkylate and the less likely the polymerization reaction.

The two conventional technologies, employing either liquid H_2SO_4 or HF as

catalyst, were first commercialized in the 1940s and commercial operations have been generally successful. However in 1988, a well-publicized incident involving the release of HF at a US refinery resulted in renewed focus on the potential environmental and safety hazards of these liquid acid technologies. Most of the concerns are related to the impact of a large-scale release. At ambient conditions, HF vaporizes into the air while H_2SO_4 is a viscous, wetting liquid. In the process, these acids exist as emulsions comprised of the acid and liquefied light hydrocarbon gases (eg, butane). If a vessel or pipe ruptures, the escaping light hydrocarbons vaporize and disperse the acid into a cloud. With HF, the effect is to form an aerosol cloud of volatile acid that will drift downwind; with the less volatile H_2SO_4 , a froth of small bubbles of acid film enclosing hydrocarbon gases and H_2SO_4 globules will drift downwind, wetting its path before eventually settling to the ground.

In response to the 1988 HF release

incident, the US Environmental Protection Agency (EPA) considered banning the operation of HF alkylation units. Instead, a study of the hazards and associated risks concluded that these units could continue to operate if appropriate process safety procedures were adopted and plant modifications were implemented to mitigate the likelihood, magnitude and consequences of an HF release. For existing plants, these modifications can be expensive: the cost to mitigate a plant producing 10,000 barrels per day of alkylate has been estimated to be between US\$ 10MM and US\$ 20MM. [1]

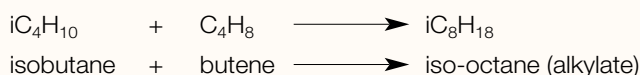
The development of a solid acid catalyst alkylation process was undertaken in response to the above regulatory environment. The new technology addresses the refining industry's need for a reliable, high performance, cost effective alternative to liquid acid technologies for the production of alkylate.

The SAC alkylation process

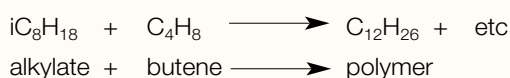
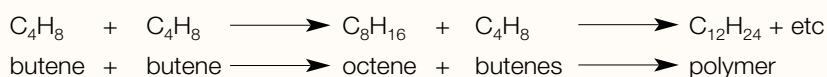
The SAC alkylation process developed by ABB and Akzo Nobel employs a true solid acid catalyst, ie the catalytic acid function is intrinsic to the solid itself rather than being a separate species, such as an immobilized liquid deposited on a solid substrate. As a result, there is no migration or leaching of any potentially corrosive acid from the SAC reactor system into any process or product stream. This new catalyst is similar to others widely used in the refining industry; it is non-toxic and does not require the use of any promoter or activation agent.

1 is a simplified block flow diagram

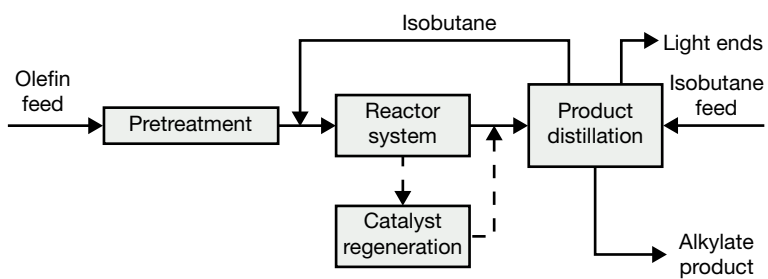
Equation 1: alkylation



Equation 2: polymerization



1 Flow diagram of the SAC alkylation process



of the SAC alkylation process, which consists of four main sections: feedstock pretreatment, reactor system 2, catalyst regeneration, and product distillation for the recovery of alkylate product and recycling of excess iso-butane.

The heart of the process is the reactor system. The SAC reactors operate in the liquid phase in the temperature range of





Table 1: Operating conditions comparison

	SAC	H ₂ SO ₄	HF
Operating temperature	40 – 90 °C	4 – 10 °C	32 – 38 °C
Isoparaffin/olefin (I/O)	8 – 10/1	8 – 10/1	12 – 15/1

40 °C – 90 °C (Table 1), so there is no need for the costly refrigeration systems required for H₂SO₄ reactors. The operating temperature of the alkylation reactors is interrelated to the requirement for excess isoparaffin (eg, isobutane) in the reaction section. At higher temperatures and with lower excess isoparaffin, alkylate octane decreases. To achieve a high octane alkylate and limit heavy hydrocarbon byproduct production, H₂SO₄ units typically utilize a total reaction section feed I/O of between 8/1 and 10/1, while HF units run at an I/O of about 12/1 to 15/1. In comparison, without any alkylate octane debit, the I/O for the SAC process is in the range of 8/1 to 10/1, comparable with the H₂SO₄ process that operates at a significantly lower temperature. In addition, the SAC process does not produce a heavy polymeric byproduct stream, while both HF and H₂SO₄ form acid-soluble oils (ASOs) with this material, which must be further treated for recovery of the dissolved and complexed acids.

Key to the SAC technology's superior performance is the coupling of a robust, stable catalyst with a novel alkylation reactor system that minimizes the peak olefin concentration (ie, maximizes I/O) in the reaction zone. This is accomplished by utilizing serial reaction stages that allow for distributed olefin feed injection, and a reactor type that greatly reduces the olefin concentration gradient across the reactor. As a result, the I/O of each

reaction stage (internal I/O) is increased by an order of magnitude relative to the total feed basis (external) I/O of 8/1 to 10/1 provided into the reaction section.

The high internal I/O also greatly reduces the rate at which the catalyst deactivates. Catalyst deactivation occurs when heavy hydrocarbons build up on the catalyst and block the access of alkylation reactants to the catalyst's active sites. In operation, catalyst deactivation is exhibited by olefin (the limiting reactant) breakthrough into the reactor effluent stream, indicating that it is no longer being fully converted. At this point, the catalyst must be taken off-line and regenerated to restore its activity. The SAC alkylation technology avoids the rapid catalyst deactivation that would necessitate a very high regeneration frequency and result in a short ultimate catalyst life.

In the SAC process, the catalyst may be operated for up to several hours before olefin breakthrough. In practice, a reactor is designed to be taken off-line safely before the expected olefin breakthrough time. Multiple reactors are used and

individual reactors cycle back and forth between on-line alkylation and regeneration to allow for continuous production of alkylate. Catalyst is regenerated *in-situ* (ie, without removal from its reactor) at mild conditions similar to those required for alkylation itself.

SAC activity is restored during the cyclic regeneration by a low temperature 'washing' step with isoparaffin (ie, isobutane) in the absence of reactant olefins (ie, butenes). Long term testing with commercial feedstocks over hundreds of operating cycles has demonstrated the stability of the catalyst's performance under this mode of operation. Based on this work, the ultimate solid acid catalyst life is projected to be at least two years. At the end of its useful life, the SAC is returned to its manufacturer, Akzo Nobel, eliminating any potential catalyst disposal problem for the refiner.

Significant test work has also been carried out to determine the impact of different impurities and olefin compositional variation (eg, butene isomer) on process performance and product quality. The general conclusions are that the major feedstock impurities are well tolerated by the robust SAC and that the

2 SAC alkylation process reactor

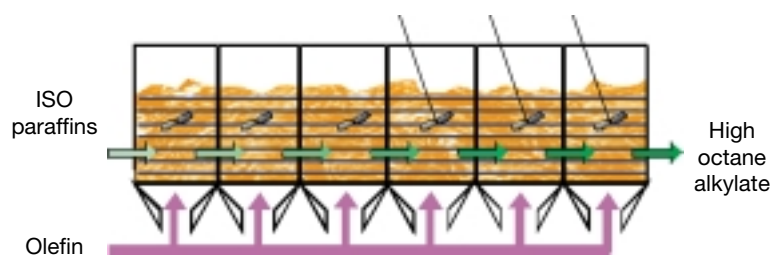


Table 2: Impact of feed olefin on alkylate product octane

Feed olefin	SAC	HF	H ₂ SO ₄
100% 2-butene	x	x	x
100% 1-butene	x	x – 6	x
35% isobutene	x – 0.5	x – 2	x – 7

feedstock butene distribution has only a minor impact on product octane. It is projected that the SAC process, in comparison with the liquid acid technologies, will be able to run with less stringent feedstock pretreatment requirements, eliminating the need for expensive removal equipment.

As *Table 2* shows, the SAC technology appears to be less sensitive to feed olefin compositional variation than both liquid acids. Of the butene isomers, 2-butene generates the highest octane alkylate. For SAC and H₂SO₄, increasing 1-butene relative to 2-butene had no measurable impact on product octane, indicating that 1-butene is isomerized to 2-butene. HF does so also, but only to a limited extent. The table also shows the relative impact on octane of a feed olefin stream containing 35% isobutene.

Based on a prototype process design, capital investment requirements for the new SAC process were developed. The results indicate that the total installed cost (TIC) for a SAC alkylation unit is 10% – 15% lower than an equivalent capacity H₂SO₄ unit, which puts the investment cost for the SAC unit about on par with the cost for a HF unit. With respect to cost of production, it is estimated that costs for the SAC and H₂SO₄ technologies are comparable, and while production costs

for HF units are judged somewhat lower, higher maintenance costs can offset this advantage. Existing liquid acid alkylation units may be revamped to SAC operation and the existing feedstock pretreatment and product distillation/recycle facilities would normally be reused.

To judge performance as measured by product octane, projections were made for a feedstock blend consisting of 10% 1-butene, 60% 2-butene and 30% isobutene. For the SAC process, the expected alkylate octane is 96 RON, which is essentially the same value expected for the H₂SO₄ process and slightly higher (by up to 0.5 RON) than estimated for the HF technology. The alkylate product from the SAC process meets all other specifications (eg, vapor pressure and end boiling point) for reformulated gasoline blendstock.

To summarize, the SAC alkylation process provides the following benefits to the refiner:

- Eliminates the use of corrosive liquid acids and associated safety concerns
- Eliminates the production of a heavy hydrocarbon byproduct stream
- Eliminates the need for process refrigeration and associated operating and maintenance costs
- Has an increased tolerance to feedstock impurities and requires less stringent pretreatment

- Has a reduced sensitivity to changes in feedstock C4 olefin composition
- Has a higher yield of alkylate product per unit of olefin consumption
- Alkylate octane is equivalent to that obtained by liquid acid catalysts
- Plant investment for a new plant is 10% – 15% lower than for an H₂SO₄ unit
- Has the potential to be retrofitted into an existing liquid acid unit

This new 'green' technology is now entering its commercial demonstration unit phase, with the expectation of being fully proven in time to meet regulatory-driven demand for a less toxic and more environmentally friendly motor gasoline. With all of these very positive projected benefits, we anticipate the SAC technology will fill a crucial niche in the refinery processing portfolio.

Author

Vincent J. D'Amico

ABB Lummus Global
1515 Broad Street
Bloomfield NJ 07003
USA
vincent.j.d'amico@us.abb.com

References

- [1] **Geren P.M. et. al.:** Fixed-Bed Alkylation – Commercialization of the Topsoe Process, Solid Acid '95 Conference, (1995) pp. 4-5.