

The background of the cover is a dramatic, low-angle photograph of a road at night, illuminated by a bright yellow light source on the right, creating a strong lens flare and illuminating the road surface. A teal-colored geometric shape is overlaid on the top left and bottom right corners.

 **ALBEMARLE**<sup>®</sup>  
Catalyst Courier

ISSUE 80 \ AUTUMN 2011

**THE STORY OF THE BEST-SELLING HYDROTREATING  
CATALYST OF ALL TIME**

**CATILIN ACQUISITION: HOW ALBEMARLE PLANS TO  
EXPAND IN THE BIOFUELS MARKET**

**FCC CATALYSTS: UNDERSTANDING HOW TO MAXIMIZE  
PROPYLENE**

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## EVENTS DIARY 2011

### October

- 10–12 NPRA Q&A and Technology Forum, San Antonio, USA
- 11–13 6th Annual Biofuels International Meeting, Amsterdam, the Netherlands
- 12–14 Albemarle HPC course, Amsterdam, the Netherlands
- 25 From Crude Oils to Biofuels – Trends Impacting Global Fuels Rio de Janeiro, Brazil

### November/December

- 1–3 Downstream Asia 2011, Singapore
- 5–8 Latin American Petrochemical Annual Meeting, Buenos Aires, Argentina
- 8–10 Advanced Biofuels Markets Congress, San Francisco, USA
- 16–17 Biofuels International Expo & Conference, Antwerp, Belgium
- 29 Nov–1 Dec ERTC 16th Annual Meeting, Barcelona, Spain

### December

- 13–15 Sixth Annual Gulf Petrochemicals and Chemicals Association (GPCA) Forum, Dubai, UAE

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JOHN NICOLS  
VICE PRESIDENT, CATALYSTS

In today's challenging refining sector, operators are increasingly focusing on low-cost improvements: the emphasis is on investing a little to gain a lot. Major changes to an established process will generally come with corresponding costs and risks. Furthermore, any investments or modifications being made now are likely to be judged on the period required to achieve payback. As a result of this, it is adjustments that offer quick, tangible economic benefits for relatively small investments that are more likely to be adopted.

This means that refineries are more likely to adjust feedstocks and catalysts than to invest in new process hardware. It is not surprising, therefore, that many refiners are looking at options such as optimizing the catalysts they use in hydroprocessing applications. For example, if operators find a suitable catalyst, they might consider switching to lower-cost feeds that will enable them to capture the increased margin without reducing throughput or cycle length.

In this issue of *Catalyst Courier*, we consider how the refinery sector is seeking high-impact improvements on a tight budget. Our first article (page 6) traces the evolution of the world's best-selling hydrotreating catalyst and examines the varied ways refiners have applied it in their plants. The article on page 12 looks at some of the issues refiners face in challenging hydroprocessing applications and reveals how specialty catalysts can push unit limitations to deliver higher economic returns. We also examine the operational benefits that are offered by quadralobal catalysts and show how selecting existing catalyst products with an optimized shape can help to reduce fill costs (page 14).

As in most industries, refiners have traditionally looked to introduce new methods or technologies when business is booming. When the market is tight, many prefer to hold on to the systems they know and to achieve predictable results. However, experience of previous downturns shows there is always scope for a shrewd investment. Those who make a success of new opportunities now could well be securing a winning advantage for when the market recovers.

A handwritten signature in black ink, appearing to read 'J. Nicols', with a stylized flourish at the end.

## CATILIN ACQUISITION EXPANDS BIOFUELS CATALYST PORTFOLIO

As part of its commitment to expanding its presence in the biofuels market and to offering global customers a broader portfolio of biofuel catalysts, Albemarle has acquired Catilin Inc.

Based in Ames, Iowa, USA, Catilin is a technology leader in developing and applying heterogeneous biodiesel catalysis. Its technology and products will strengthen Albemarle's offerings in this market. The organization will also benefit from research and development and distribution synergies.

"We are excited to offer Catilin technology alongside our existing GoBio™ portfolio to customers in the fast-growing renewable fuels market," said John Nicols, vice president, Catalysts, Albemarle.



## BREAKTHROUGH IN ACTIVITY STUDIES FOR FCC CATALYSTS

Collaboration between catalyst researchers from Albemarle and the University of Utrecht, the Netherlands, has led to an innovative method that uses selective staining to improve the visualization of catalyst components. This research shows that it is possible to pinpoint the active sites in FCC catalysts without destroying the catalysts.

Until now, research was limited to activity measurements, model studies and analyses of spent catalysts. The new spectroscopic tools and staining methods enable researchers to study the accessibility of active sites and view 3D maps of the active sites inside the actual catalysts.

supplied catalyst performance and bulk characterization data. "Our collaboration with the group at the University of Utrecht has led to new insights benefiting both hydroprocessing and FCC catalysts," says Eelco Vogt, research and development director at Albemarle. "The new tools allow us to study active sites in commercial catalysts, rather than the models normally described in literature. This enables us to translate developments into real catalysts much faster and maintain our technology leadership in this highly competitive field."

For more information, see *Nature Chemistry* magazine at [www.nature.com/nchem/journal/vaop/ncurrent/abs/nchem.1148.html](http://www.nature.com/nchem/journal/vaop/ncurrent/abs/nchem.1148.html)

In addition to providing catalyst materials, Albemarle



## RARE EARTHS' CONTINUING MARKET UNPREDICTABILITY

Volatility and unpredictability continue to plague the world's rare earth market and its impact on the prices of FCC catalysts and additives. Two leading price indices recently highlighted the unpredictability of the market: the Asian Metals lanthanum oxide price index dropped to \$90/kg from a high of about \$140/kg, and the Metal-Pages lanthanum oxide index concurrently rose to \$150/kg and lagged the Asian metals decline by two months before dropping to \$80/kg. During this same period, the Asian Metals cerium oxide price index surged to \$140/kg before falling to the current price of \$72/kg.

To keep up with market conditions, Albemarle continues to develop contracts and relationships for FCC catalyst and additive components with rare earth suppliers. Our new low rare earth technology (LRT™) FCC catalyst family will help refineries to maintain activity, stability and selectivity while reducing the impact of the costs of rare earths on those for catalysts and additives.



## KISSAM TAKES THE HELM AS CEO



Having demonstrated broad leadership abilities in various senior roles within Albemarle Corporation since he joined in 2003, Luther (Luke) C. Kissam IV has been promoted to the position of chief executive officer (CEO).

Kissam said of his new role: "I am honored to take on the role of CEO at Albemarle and to

lead our 4000 plus employees around the globe as we work hard to build on our successes of the last decade and continue to deliver sustainable value to our stakeholders.

"We have an exceptional leadership team in place, and I look forward to continuing our mission of delivering Albemarle's Vision 2015."

## ALUMINUM ALKYL FACILITY CONSTRUCTION UNDER WAY

Saudi Organometallic Chemicals Company (SOCC), an Albemarle Nederland BV and Saudi Specialty Chemical Company (Specialty Chem.) joint venture, held a groundbreaking ceremony on 18 September to initiate the construction of a new aluminum alkyls manufacturing facility in Jubail, Saudi Arabia.

The ceremony was attended by representatives from Albemarle, Samsung Engineering, SABIC, SOCC, Specialty Chem. and several regional customers. During the celebration, executives from each company discussed the regional economic benefits that are expected to result from the project.

The construction phase of the new project, which is the first of its kind in Saudi Arabia, is scheduled for completion in the third quarter of 2012. The facility will manufacture 6000 t/y of triethylaluminum, a Ziegler-Natta co-catalyst used in the plastics industry. The plant is being built in this location to meet growing regional demand, which is currently supplied by facilities in Europe, Asia and North America.

## SHIP AHOY!

Albemarle was a proud sponsor of the 2011 voyage of the *Odyssey*, a scientific research vessel owned and operated by Ocean Alliance and staffed by marine researchers from the University of Southern Maine, USA.

The research team studied the effects of recent oil spills and natural disasters on the Gulf of Mexico's ecosystem, one of the world's most important ocean habitats. They collected and examined samples of fish, squid, krill, Bryde's and sperm whales, and water from depths to 900 m.

Albemarle chairman Mark Rohr said, "Albemarle is dedicated to using scientific research to find safe, sustainable solutions to environmental challenges. We are proud to have supported the voyage of the *Odyssey* as its team seeks to better understand the impacts of society on our important ecosystems."

To learn about this mission, please visit the *Odyssey* crew's blog via our website: <http://albemarle.com/sustainability/sustainability-overview-178.html>.



# STILL SHINING BRIGHT AFTER 14 YEARS

THE STORY OF STARS® Ketjenfine® 757, AS TOLD BY  
SCOTT MARTIN, DIVISION VICE PRESIDENT, HPC, ALBEMARLE



It was 1998, long before ultra-low-sulfur diesel (ULSD) regulations were on the radar screens of most refiners, when Albemarle unveiled a new hydroprocessing catalyst technology platform to the refining industry. Super Type II Active Reaction Sites, known as STARS, technology was the first commercial hydroprocessing catalyst to deliver 100% Type II active sites to activity-challenged reactors throughout the world.

Ketjenfine 757, the first catalyst in the STARS series, came at a key time in the history of hydroprocessing: just before the introduction of clean fuels regulations in Japan, Europe and North America. The step change in desulfurization performance offered by STARS Ketjenfine 757 saved refiners substantial money through reduced capital expenditure and increased revenues from early adoption incentives for clean fuels. This catalyst was truly a game changer for hydroprocessing.

Since 1998, STARS has remained the preeminent Type II catalyst technology, and STARS Ketjenfine 757 has become the best selling hydrotreating catalyst of all time. STARS technology has continued to evolve through the introduction of many new catalysts over the past decade. Yet, even after almost 14 years on the market, STARS Ketjenfine 757 remains a top-performing

catalyst and an excellent choice for many hydrotreating applications. After a surge in market demand in 2005/6 for ULSD implementation, its use has remained fairly constant.

High activity, robust performance in challenging services, rejuvenation to near fresh activity, and attractive fill costs are among the main reasons that STARS Ketjenfine 757 continues to be a leading catalyst in the hydroprocessing market: in 2009, it topped 1000 hydrotreater installations. Now, as STARS Ketjenfine 757 approaches its 14th anniversary, yet another milestone looms, as it will cross the 100,000-t mark for fresh and rejuvenated product.

Type II catalysts are ubiquitous in today's hydrotreating landscape, so it is easy to forget just how novel and pioneering STARS technology was in 1998. Here was a catalyst technology that offered step-out performance but required special start-up procedures and unusual manufacturing techniques compared with the catalysts of the day. Nonetheless, the first applications were overwhelming successes. The performance of STARS Ketjenfine 757 in those first units met all expectations, and those earlier adopters, almost universally, reordered the catalyst for subsequent catalyst changes.

Initial applications of STARS Ketjenfine 757 were primarily in distillate applications for low sulfur (350–500 ppm). The operating severity of those units was, by today's standards,

# “ STARS KETJENFINE 757 HAS BECOME THE BEST SELLING HYDROTREATING CATALYST OF ALL TIME. ”

not high, but then the units were not very capable. Even though the product sulfur level seems trivial today, the extra desulfurization activity of STARS Ketjenfine 757 was used to generate economic return through processing more LCO or operating at higher throughput or extended cycle length.

Compared with the conventional catalysts of the day, STARS Ketjenfine 757 offered many opportunities for refiners to capture additional operating income or to save operating costs. Before the implementation of ULSD regulations, many governments offered incentives for refiners to produce diesel with 50-ppm or lower sulfur content. In many cases, the unmatched desulfurization activity of STARS Ketjenfine 757 made it possible to capture these incentives with existing hardware and relatively minor changes to feedstock and operating conditions.

In addition to distillate hydrotreating, quite a few refiners began to use STARS Ketjenfine 757 in their FCC feed pretreatment units. Low sulfur gasoline specifications were in the process of being implemented and there was an economic incentive to build up sulfur credits to use or sell. As in distillate hydrotreating, the unmatched desulfurization activity of STARS Ketjenfine 757 enabled refiners to use their existing assets with only a catalyst change to capture these tangible benefits.

Even though most refineries have FCC gasoline post-treatment units today, removing sulfur in the FCC feed pretreatment unit remains a viable economic choice. Less octane loss from lower post-treatment operating severity is just one advantage from maximizing sulfur removal in the FCC pretreatment unit: an incentive that will only become stronger if 10-ppm gasoline sulfur regulations are implemented.

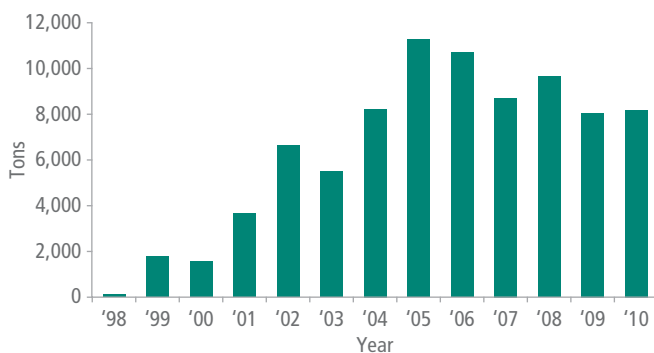
Despite the numerous benefits of STARS technology, there was one aspect, compared with Type I catalysts, that needed

a solution: the large reduction in activity after regeneration. The reason for this was simple enough: the morphology of Type II active sites converted to Type I during regeneration. Consequently, most of the performance benefits of Type II sites were lost. To overcome this limitation, Albemarle developed the first Type II catalyst rejuvenation process: REACT™.

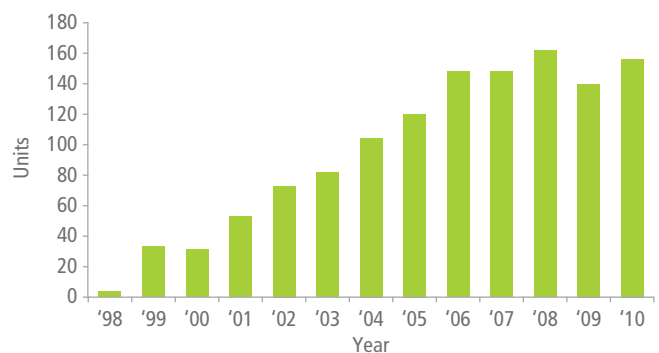
Applying the REACT process to regenerated STARS catalyst completely restores Type II morphology to the active sites and activity levels to near that of fresh catalyst. Shortly after the introduction of REACT in 2003, the cost of molybdenum, nickel and cobalt began to skyrocket, which made REACT a very cost-effective solution for reusing catalyst. In subsequent years, a large proportion of STARS catalysts was REACTivated, in many cases multiple times. On a life-cycle comparison of desulfurization benefit per monetary unit, STARS and REACT are clear leaders.

It is clear that STARS Ketjenfine 757 has aged very well, but it has recently undergone a face-lift to expand its applicability to less severe services. Albemarle has introduced a new quadralobal version of STARS Ketjenfine 757, which can reduce loading density by about 8%. In many cases, the reduced diffusion resistance resulting from the new shape compensates for the reduced density to yield equivalent performance at a lower fill cost. In addition, with the development of STAX® technology, Albemarle can design catalyst systems that utilize the performance benefits of STARS Ketjenfine 757 and simultaneously optimize the overall fill cost.

It has been a long and active life for STARS Ketjenfine 757 and there remains much more in this seasoned veteran. It is the ideal choice for many of today's hydrotreating applications for performance, predictability and value.



STARS Ketjenfine 757 sales are still going strong.



STARS Ketjenfine 757 has a broad range of applications.

# THE CATALYST DESIGN CHALLENGE

## Albemarle AFX™ catalyst: Understanding the mechanisms for maximizing propylene in FCC

Achieving record-high propylene and conversion from wide ranges of feed qualities offers considerable challenges to catalyst design. Key to this is good understanding of the mechanisms involved and then responding with the proper catalyst technology and design to meet a unit's objectives.

In refining, several cracking processes are applied to break carbon-carbon bonds: hydrocracking, FCC and thermal cracking. Hydrocracking is of little importance for propylene production and is not considered in this article. Thermal cracking processes, such as coking, also play a small role in propylene production. FCC, however, is critical for propylene production. It is predominantly an acid catalyzed cracking process; however, some thermal reactions do take place.

Thermal cracking is a free radical process involving three steps: initiation, propagation and termination. At high temperatures, radicals form during the initiation step. These radicals react further to form ethylene and new radicals, which lead predominantly to ethylene, along with methane and C3s.

FCC, however, makes use of the acid sites in the catalysts and involves

carbocation intermediates. Moreover, in FCC, a higher degree of branching is found, which indicates isomerization reactions. In thermal cracking, very low levels of branched products are found.

In FCC, a remarkable change occurred when zeolite-based catalysts replaced amorphous cracking catalysts. This led to a dramatic increase in gasoline yield accompanied by lower coke and gas: both improvements highly desirable in FCC. However, the gasoline RON dropped drastically. This was attributed to the lower olefins content of the gasoline (Table 1).

These changes in selectivity were attributed to hydrogen transfer reactions whereby the olefins formed initially were converted to more stable paraffins. In addition, the light olefin levels decreased.

Hydrogen transfer is a bimolecular reaction whereby hydrogen is, for example, transferred from naphthenes to olefins to produce paraffins and aromatics. The Brønsted acid sites of the Y-zeolite play a crucial role in these reactions. Catalyst manufacturers have several tools for optimizing the characteristics and functionality of the Y-zeolite, for example, unit cell size

(UCS), silica-to-alumina ratio (SAR), and the sodium and rare earth content.

For propylene generation, other shape-selective zeolites exist; ZSM-5 is most commonly known and applied. The invention of ZSM-5 provided another step change in FCC applications. This zeolite has pore entrances smaller than those of Y-zeolite and drives different catalytic reactions. The smaller pores restrict the access of branched and cyclic hydrocarbons to the catalyst's interior, yet allow straight-chain and monomethyl paraffins and olefins to enter, thereby generating predominantly propylene with some butylenes and ethylene. The reactants are mostly in the C6 and C7 range, but gasoline molecules with carbon numbers between 5 and 10 can also be converted by ZSM-5 to some extent. Figure 1 shows clear evidence of the increased production of C3, C2 and C4, and the strong reduction in C6 and C7 components.

FCC gasoline can be typically classified into five types of hydrocarbon: paraffins (P), iso-paraffins (iP), olefins (O), naphthenes (N) and aromatics (A). Taking a closer look at the different types shows that iso-paraffins and olefins with six or seven carbon atoms are mostly cracked by ZSM-5 (Figure 2). When an olefin is cracked by

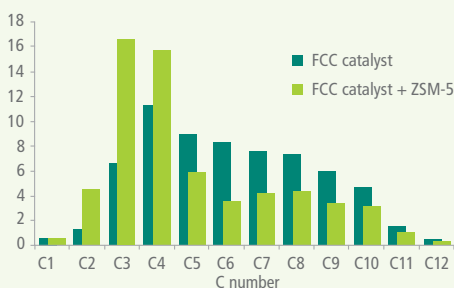


Figure 1: The effect of ZSM-5 on products shown by carbon number.

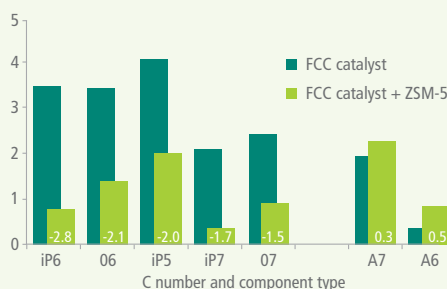


Figure 2 The gasoline components that are most and least affected by ZSM-5.

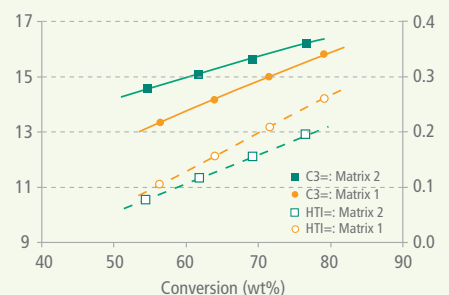


Figure 3: Comparing the effects of different matrices on hydrogen transfer and propylene yield.

	CONVERSION	GASOLINE, VOL%	PROPYLENE, VOL%
Silica-alumina gel	75.5	47.5	8.5
REHY zeolite	85.5	61.0	5.9

Table 1: The change from amorphous cracking catalysts to zeolite-based catalysts led to lower olefin levels.

	ACIDITY	CRACKING	HYDROGEN TRANSFER	ISOMERIZATION
ZSM-5	Very high	High*	–	High
Y-zeolite	High	High	High	Moderate
Matrices	Low to moderate	Low to high	Low to moderate	Low

Table 2: Comparison of key FCC components.

\*Molecular shape and size determine the cracking rate.

ZSM-5, two smaller olefins are produced. The generation of C6 and C7 olefins in the primary cracking steps of FCC is therefore a valuable mechanism that needs managing.

The numbers on the bars in Figure 2 show a reduction in the specific hydrocarbon type. The decrease in light isoparaffins is the largest, but this is speculated to be due to reduced formation of light isoparaffins in the presence of ZSM-5 and other reactions, including cracking to light olefins. The light olefins, however, contribute the most to propylene make, as olefins are more reactive and crack to form two smaller olefin molecules. In general, gasoline-range olefins are the primary reactants for propylene.

The molecules that can be readily cracked by ZSM-5 are in the gasoline boiling range and often referred to as light olefin precursors. Though iso-paraffins are good light olefin precursors, the small pores of ZSM-5 restrict access to only those paraffins with a methyl branch. Longer branches or multiple branches are consequently undesirable. As Y-zeolite catalyses isomerization reactions, these reactions should be carefully controlled.

The right-hand end of the x-axis in Figure 2 shows benzene and methylbenzene, which are two of the few gasoline components to increase slightly with the use of ZSM-5.

## Tools for catalyst design

FCC catalyst manufacturers have a variety of tools available for designing the optimal catalyst for maximum propylene applications (Table 2), as the various catalyst components affect cracking, hydrogen transfer and isomerization in different ways.

Y-zeolite has high acidity and contributes to a high level of cracking. Though Y-zeolites can be varied in terms of UCS, rare earth content and SAR, their hydrogen transfer activity is relatively high and they also possess some isomerization activity.

ZSM-5 has very high acidity and thus high cracking activity, though the cracking rate is determined by the size and shape of the reactants. Its high SAR is also responsible for isomerization. However, ZSM-5 has oligomerization activity, which consumes small amounts of propylene.

Matrices also play a crucial role in FCC catalysis. These are the components

predominantly responsible for pre-cracking large molecules before they enter the zeolites. Albemarle applies a wide range of matrices to its catalysts, as they vary in functionality, for example, bottoms conversion and metals capturing. Their differing functionalities mean their acidity can be rated as low to moderate when compared with Y-zeolite. Their cracking activity varies from low to high, whereas the hydrogen transfer is typically lower than for Y-zeolite, as is the isomerization rate. Figure 3 compares two different matrices having differing hydrogen transfer power. The one with lowest hydrogen transfer leads to the highest level of propylene.

As well as hydrogen transfer, several other secondary reactions, such as cyclization and aromatization, take place, and propylene molecules can also undergo oligomerization. At a certain point, propylene is consumed and its yield decreases.<sup>1</sup> Longer residence times are, therefore, detrimental to maximum propylene yields.

In summary, the following are necessary for maximum propylene yield and are the drivers for the development of Albemarle's AFX catalyst:

- maximize generation of gasoline precursors; these are predominantly C6 and C7 olefins and iso-paraffins.
- minimize hydrogen transfer, which consumes valuable olefins
- control isomerization reactions to form methyl branches
- minimize unwanted secondary reactions as cyclization, aromatization and oligomerization.

### Reference

1. Feugnet, F., Echard, M., Gauthier, T.: 2009. Pilot Plant Testing for Resid to Propylene, 8th FCC Forum, 17

# FOCUS ON PARAFFIN ISOMERIZATION

## Boosting yield selectivity and driving down fill costs

**Refinery operators are looking for three key characteristics in the catalyst they choose for their paraffin isomerization process. First, the catalyst has to be highly active so that it maximizes conversion and achieves the highest selectivity at the lowest temperatures; second, the fill cost has to be acceptable; and third, it must tolerate contaminants and resist deactivation.**

Creating a catalyst to deliver outstanding performance in these three areas has required more than a decade of cooperative research and development. ATIS™ catalysts, developed in association with Axens, offer two significant new features: an innovative carrier technology and a novel, patented chloriding technique.

These features deliver outstanding activity on a volume basis, which gives increased octane and yield at lower energy costs; excellent contaminant tolerance, which can help to extend catalyst cycles; and a low-density catalyst that reduces fill costs and offers substantial platinum savings.

The process by which straight paraffins are converted to isoparaffins is limited by the thermodynamic equilibrium, so catalysts that are effective at low

**“ THE LOW DENSITY OF ATIS CATALYSTS, COUPLED WITH THEIR HIGH VOLUMETRIC ACTIVITY, CAN DELIVER PLATINUM SAVINGS. ”**

operating temperatures offer a significant advantage (Figure 1). The carrier technology for ATIS catalysts packs a high number of acidic sites with appropriate strength into each volume element of the isomerization catalyst. This is vital for both high activity and stability.

The high activity of ATIS catalysts enables operators to achieve lower operating temperatures and improved yields of valuable products. When operating temperatures are low, refiners experience substantial gains in C5+ product or, in the case of butane isomerization, higher conversion to isobutane.

For an industry that is still in recovery after the global economic downturn, fill costs remain crucial in catalyst selection. The low density of ATIS catalysts, coupled with their high volumetric activity, can deliver platinum savings of up to 200 g/m<sup>3</sup>. Replacing a standard isomerization catalyst with an ATIS alternative enables refiners to remove significant amounts of platinum from their units and to recover the value of the metal. For a typical 10,000-bbl/d paraffin isomerization unit, replacing

the existing catalyst with ATIS-2L can reduce the platinum requirement by up to 500 troy ounces.

Contamination is a significant problem for refiners using catalysts based on chlorinated alumina. For these catalysts, the main cause of deactivation is the removal of acidic sites by water or water-generating components. When this happens, the sites react to form inactive hydroxylated alumina and hydrogen chloride. The patented chloriding and carrier technologies in ATIS catalysts offer increased tolerance to water deactivation. Tests have shown that ATIS catalyst will robustly tolerate 1 kg of water per 66 kg of catalyst before activity decreases through the poisoning of active acidic sites. This tolerance to water or water-generating components is about 25% better than in other commercially available catalysts.

By choosing ATIS catalysts, which exhibit some of the industry's highest available activities per reactor volume and have improved water tolerance, refiners can take full advantage of high yields and selectivity while minimizing fill costs.

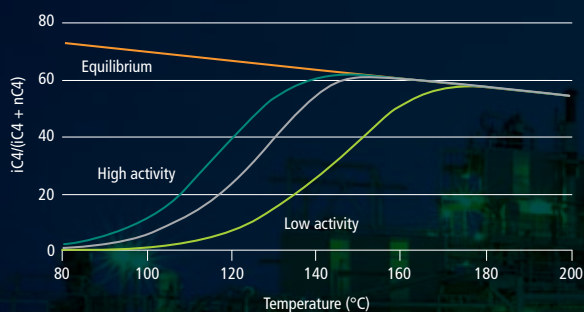


Figure 1: Thermodynamic equilibrium defines the maximum conversion at the operating temperature.



# THE STORY OF ALBEMARLE CATILIN

## Heterogeneous catalysis for cost-effective biodiesel production

**Albemarle's latest acquisition, Catilin Inc., is the brainchild of the late Victor Lin. In 2002, Lin, then professor of chemistry at Iowa State University, Ames, USA, was working on a heterogeneous catalyst that he hoped would dramatically improve the economics of biodiesel production. By 2007, the catalyst's commercial value attracted the attention of investors and Catilin was born.**

Today, most fatty acid methyl ester (FAME) biodiesel is produced from bio-based oils via transesterification, which is usually commercially catalyzed by sodium methylate, though sodium hydroxide and potassium hydroxide are also options. These strong bases generate the kinetics necessary to convert the oils under mild conditions of low temperature and atmospheric pressure.

### Low-temperature operations

Most competing heterogeneous catalysts are acidic and require high temperature and high pressure to work, which makes them less than ideal. The key to what is now called Albemarle Catilin's GoBio™ T300 catalyst is its ability to match the kinetics of some commonly used commercial catalysts, such as sodium methylate, at low temperature. Consequently, economic plant retrofits are possible.

GoBio T300 also tolerates contaminants such as phospholipids, so minimal feedstock pretreatment is necessary. Unlike competing catalysts that are designed for fixed-bed configurations, GoBio T300 is a fine granular solid that is mixed directly into the reactors. It has a relatively low pore volume that contributes to excellent attrition

resistance. Its catalytic activity is due to its alkaline earth composition, which is generally nonhazardous.

In one preferred process that uses GoBio T300, which has many similarities to FCC, the methanol feed and catalyst are mixed in the first reactor. The feed rate is adjusted to maintain a residence time of about an hour with an industry-standard methanol concentration. The reactor effluent flows to a filtration system where the catalyst is captured and returned to the reactor while the biodiesel and glycerin permeate the filter and flow downstream. The immiscible biodiesel and glycerin are collected in a separator as two phases. The biodiesel, unconverted oil and methanol are decanted and routed to the second reactor. The glycerin flows downstream for methanol recovery and storage as a finished co-product.

The flow in and out of the second reactor is similar to the first, except that the methanol concentration is reduced to below 10 vol%. Methanol recovery columns follow a second filtration system and separator. With an eye toward ever-tightening standards, Albemarle Catilin recommends distillation for biodiesel purification.

Because this process does not use water wash, the glycerin is not contaminated with salt or diluted with water, which greatly enhances its value and allows sale to the technical-grade market.

### Cost-effective retrofits

From a marketing perspective, GoBio T300 is attractive because plant retrofits can be completed at relatively low cost. This is important, as the global biodiesel industry has over 170 MMbbl

“ALBEMARLE CATILIN'S SEMI-WORKS PILOT PLANT IN IOWA ADDS TO THE COMPANY'S RESEARCH AND DEVELOPMENT SCALE CAPABILITIES.”



of installed capacity and all are targets for conversion to this preferred process.

A GoBio T300 retrofit typically involves adding a hopper and an injection system to introduce the catalyst, and a filter to separate the catalyst from the biodiesel and glycerin products.

Albemarle Catilin operates a 7000-bbl/y pilot plant near Ames, Iowa, as a demonstration plant. In support of the operation, more than 1500 bench-scale conversions have been completed on a wide variety of feeds, including refined soy bean oil, degummed soy, tallow, corn oil, jatropha and algal oil. In all cases, the catalyst was effective in converting the triglycerides to FAME and glycerol.

GoBio T300 stands alongside GoBio TS-15 to strengthen Albemarle's offerings for the renewable fuels market, and the Albemarle Catilin semi-works pilot plant in Iowa adds to the company's research and development scale capabilities.

# EXCELLING IN CHALLENGING HYDROPROCESSING APPLICATIONS

## NEBULA®: Performance improvement with small volumes

**NEBULA, a specialty catalyst developed jointly by Albemarle and ExxonMobil, consistently demonstrates superior performance in challenging hydroprocessing applications. Compared with conventional catalysts, it is characterized by a much higher hydrogenation activity. Doubling of both hydrodesulfurization and hydrodenitrogenation activity is possible for processes where hydrogenation limits performance.**

Since its introduction, NEBULA has achieved a long track record of successfully pushing unit and process limitations for higher economic returns. In most cases, the higher performance is best exploited by including NEBULA in a STAX® configuration. The different reactions occurring along the flow paths of hydroprocessing reactors often require different functionalities and, therefore, different catalysts.

Using proprietary modeling tools, STAX, Albemarle's catalyst system design technology, places catalysts in an optimum sequence to exploit the particular chemistry and process conditions needed. This is particularly important for using NEBULA, when, as a fraction of the total reactor volume, it can significantly boost a unit's performance.

### Application in naphtha and kerosene hydrotreatment

For naphtha hydrotreating, the preferred way to exploit NEBULA's activity is to increase the feed difficulty, for example, by adding more cracked naphtha while maintaining a strict specification for product nitrogen.

A refiner with a 25-bar naphtha hydrotreater selected a NEBULA–STAX loading (with approximately 60% STARS® Ketjenfine® 848 at the reactor's top) and was able to start processing full-range FCC naphtha. Intakes of this feed up to 20% were achieved while maintaining the product nitrogen within reformer specifications (<0.5-ppm sulfur and nitrogen).

For kerosene hydrotreating, the best results with NEBULA are found in the medium- and high-pressure ranges. The high hydrogenation activity of NEBULA makes it possible to obtain full saturation of diaromatics and noticeably increase the smoke point.

### Application in diesel hydrotreatment

Diesel hydrotreating is the most frequent application of NEBULA–STAX loadings: typically in units with over 50-bar hydrogen partial pressure (ppH<sub>2</sub>). Depending on NEBULA's position in the reactor, a wide variety of targets is achievable.

Several commercial units are loaded with a NiMo catalyst at the top of the reactor, NEBULA in the middle and a CoMo catalyst at the bottom. Such a solution exploits the high hydrodesulfurization and hydrodenitrogenation activity of NEBULA while avoiding commensurate increases in hydrogen consumption. The activity boost provided by NEBULA can lead to two possible benefits. First, it is possible to achieve significant increases in cycle length at the same operating severity. However, a second, more lucrative, benefit is to increase the throughput to the unit or to process

a less-expensive, more-challenging feedstock at equal cycle length.

NEBULA's effect on hydrogen consumption is explained as follows. In the cases mentioned earlier, the NEBULA is in a reactor zone where the nitrogen level is still relatively high. This prevents the excess hydrogenation of monoaromatics that NEBULA might induce in a low-nitrogen environment, so, in terms of aromatic saturation, it behaves like a conventional catalyst. This situation can be reversed when maximum density reduction is targeted. In such a case, a catalyst system with NiMo catalyst in the top and middle of the reactor and NEBULA at the bottom means the NEBULA is in a low-nitrogen environment where it can substantially increase the saturation of monoaromatics.

Figure 1 shows a pilot plant test to illustrate the capabilities of NEBULA–STAX loadings. The evolution of product sulfur is shown as a function of time onstream for a reference catalyst and for the same catalyst with NEBULA in a STAX configuration. The test was carried out at 70-bar ppH<sub>2</sub> with two different intakes of LCO (30 and 60%). Throughout the test, the NEBULA-containing system yielded a substantial improvement in performance, with the overall system activity benefit being about 50%. That benefit was consistently maintained, even with the activity return point condition at the end of the test, which clearly demonstrated the stability of the system.

Commercial experience confirms the benefits that can be obtained through NEBULA–STAX loadings. In one unit running at approximately 70 bar, a



NEBULA–STAX system has been loaded for the third straight time. In that unit, thanks to NEBULA, it has been possible to simultaneously increase both the intake and the cut point of coker gas oil (up to 380°C) while maintaining a 30-month cycle length. Figure 2 shows the evolution of the weighted average bed temperature as a function of time. It can be seen that the catalytic system, besides providing an outstanding initial activity, also achieves great stability. Conventional catalyst systems generally cannot exceed cycle lengths of 18 months.

## Application in hydrocracking pretreatment

For hydrocracking pretreatment, the main goal is typically maximizing hydrodenitrogenation activity. For such an operating target, applying NEBULA is ideal. It is possible to exploit NEBULA's hydrodenitrogenation activity for economic return in many ways. The catalyst could be used to maintain the same performance as conventional catalyst while increasing throughput, or to increase the cycle length at the same

throughput. However, many refineries already run at maximum throughput and have several turnaround constraints that may limit the economic return.

There is an additional way to exploit NEBULA's activity in a hydrocracker: running with lower nitrogen slip to the downstream cracking catalyst. This improves conversion through reduced nitrogen inhibition of cracking sites. The increased cracking activity can increase conversion using the same cracking catalyst, or change the yield structure toward more distillate by using a more distillate-selective catalyst.

Yet another opportunity is to change the feed diet to more-distressed, lower-cost components and capture the increased margin while maintaining throughput and cycle length.

There are several commercial examples with NEBULA in hydrocracking pretreatment operations. In one case, using NEBULA in a 150-bar mild hydrocracker made it possible to reduce the start-of-run weighted average bed temperature by 20°C. This enabled

the refiner to practically double the cycle length. As with ultra-low-sulfur-diesel applications, a STAX catalyst system design is typically used. In a hydrocracker, this strategy protects NEBULA from fouling materials in the feed and tunes the NEBULA intake to control heat release and deliver the best value to the refiner. NEBULA also has been widely applied in LCO hydrocracking, particularly in the North American market.

NEBULA–STAX catalyst systems are used in a wide range of hydroprocessing applications with feedstocks ranging from naphtha to heavy VGO. The unmatched activity of NEBULA opens numerous opportunities to capture economic return. When combined with Albemarle's STAX technology, it is possible to obtain a significant performance enhancement with a relatively small NEBULA content, thereby reducing catalyst system expenditure and often reducing the payback time for the NEBULA investment to a few months.

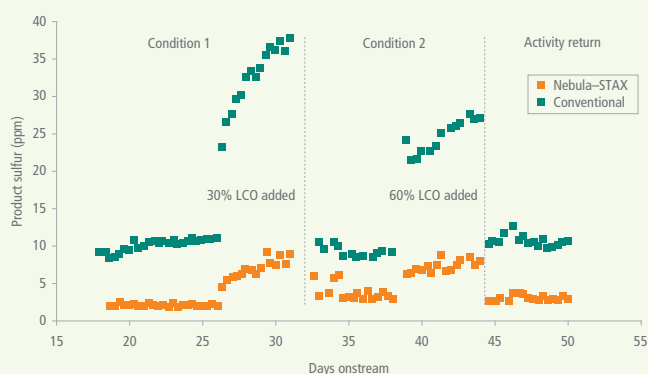


Figure 1: Pilot plant comparison between reference catalyst and a NEBULA–STAX loading.

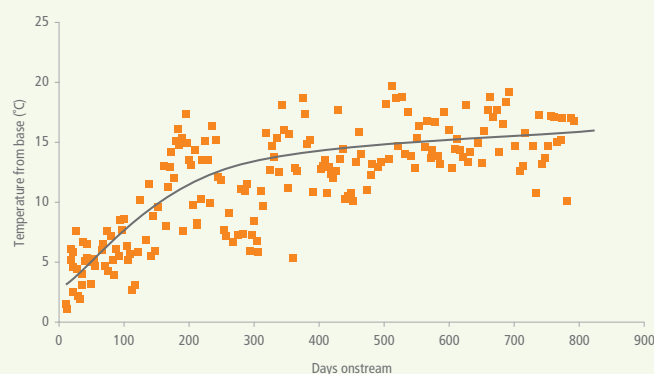


Figure 2: Deactivation rate for a commercial ultra-low-sulfur-diesel unit loaded with a NEBULA–STAX system.

# GET INTO BETTER SHAPE

## Improving cost-effectiveness with quadralobal catalysts

**In recent years, and largely as a result of the global economic slowdown, refinery operators have seen a substantial drop in their margins. This has resulted in additional financial pressures, and, across the industry, there is a strong and sustained focus on finding more cost-effective solutions to refining issues.**

Optimizing catalyst shape to create one with fewer internal diffusion restrictions is a valuable improvement for refiners because it means that more use is made of the active surface area. Catalyst utilization depends on the external-surface-area-to-volume ratio and the ratio of intrinsic reaction rate ( $k$ ) and diffusion rate ( $D_{eff}$ ), as described by the Thiele modulus.

The particle external-surface-area-to-volume ratio for quadralobal extrudates compares favorably with the ratio for cylindrical extrudates. The main benefit of the quadralobal catalysts is a shorter diffusion path to the core that means that sulfur, nitrogen and aromatic species can access more active sites in the particle, which results in higher catalyst utilization.

A study conducted for ultra-low-sulfur diesel (ULSD) reactions used modeling techniques to simulate simultaneous, steady-state diffusion and  $n^{th}$  order reaction of key sulfur molecules. This model was run over the reactor's length, which was necessary because the reactant concentration affects the local reaction rate and, therefore, the reaction/diffusion ratio. The study indicated that most of the mass transfer limitation occurred at the top of the reactor. It also showed that the reactants penetrated deeper into the quadralobal particles than into the cylindrical particles, and that the quadralobal shape can be used to optimize catalyst utilization.

Taking the Thiele modulus as a starting point, pilot plant data and model calculations have shown that a quadralobal extrudate offers an 8% improvement in catalyst utilization when compared with a cylindrical catalyst form (Figure 1). A 1.3-mm quadralobal extrudate (shown on Figure 1 as 1.3Q) has almost the same catalytic efficiency as a crushed sample: the crushed sample having no diffusion barrier at all. The quadralobal extrudate increases the relative weight activity.

Quadralobal catalysts have a higher interstitial void fraction than cylinders, which results in an 8% lower loading density and a lower bed pressure drop. The resulting relative volume activity of quadralobes compared with cylinders is therefore equal, as the 8% lower density offsets the 8% better utilization. Consequently, there is no net activity loss when a reactor is filled with the same volume of quadralobes compared with the same volume of cylinders.

Albemarle now offers most of its catalysts for hydrodesulfurization, denitrification and aromatic saturation in a shaped catalyst design. The STARS® Ketjenfine® 757, 767, 770, 771 (CoMo) and Ketjenfine 905 (NiCoMo) catalysts are all available in quadralobal form.

NiMo catalysts for VGO and residue applications were already being supplied as quadralobes because diffusion restrictions are even more critical in these heavy applications. For STARS Ketjenfine 905, volumetric activities of more than 100% have been achieved by switching from cylindrical to quadralobal particles.

For ULSD production, performance testing on a range of straight-run and cracked feed blends demonstrated that the volume activity of quadralobal (1.3Q) CoMo catalysts was equal to their cylindrical (1.5E) counterparts. For refinery operators, choosing quadralobal catalysts that were originally in cylindrical form means they can achieve the same performance with a reduced catalyst tonnage, which results in lower fill costs.

“ALBEMARLE NOW OFFERS MOST OF ITS CATALYSTS FOR HYDRODESULFURIZATION, DENITRIFICATION AND AROMATIC SATURATION IN A SHAPED CATALYST DESIGN.”

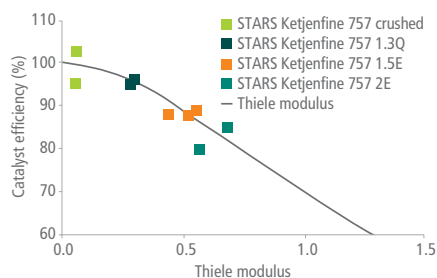


Figure 1: The 1.3-mm quadralobal extrudate (1.3Q) has almost the same catalytic efficiency as a crushed sample.

# SPECIALTY ZEOLITES

## Fast-track development at Albemarle

**Synthetic zeolites are very important in refining and petrochemicals. Zeolites have created breakthrough technologies, for example, FCC, and incremental process improvements, for example, isomerization. Currently, new and emerging businesses such as automotive emission control and alternative fuel technologies are utilizing their versatile nature.**

Finished zeolite-based catalysts represent about 6% of all used catalysts, although growth is forecast for the near future. Zeolite manufacturers must be capable of developing such high-performance materials on a research and development (R&D) scale; realizing a short time to market; producing these zeolites in commercial volumes; and delivering either zeolite powder or finished catalyst to the end-user.

The discovery and development of zeolites in the 1940s stimulated many novel and selective catalytic processes. The industrial laboratories of oil companies made major discoveries in hydrocarbon conversion, while academic and industrial research institutes investigated new zeolite types and uses. This work resulted in more than 200 different structures with different properties, some of which form the basis of modern zeolite catalysts.

Despite their versatile chemical and physical properties, potential end-uses and market outlook, only about 15 structures are commercialized. This results from the expensive, hazardous and/or environmentally undesirable ingredients that may be necessary to create the zeolite structure; the multiple post-treatments for optimizing performance; and the final shaping of the finished product.

Such technical challenges may hamper some zeolite producers from entering new and emerging markets that require newly developed specialty zeolite materials or zeolite-related materials such as silicoaluminophosphates (SAPO). For Albemarle, the step into the specialty arena was logical. We have decades of experience in researching and developing zeolite catalysts, and a significant annual commercial capacity. The specialty market fits with our core competences in zeolite expertise and manufacturing, and shaping of the finished catalysts.

SAPOs have some very interesting properties, and have recently had much commercial interest: for example, SAPO-34 has commercial use in the methanol-to-olefins process.

The development trajectory of an Albemarle SAPO-type molecular sieve exemplifies our approach and capabilities for scaling up from research to commercial-scale production: a short time-to-market approach. Our research laboratories use high-throughput experimental tools that enable us to quickly optimize the use of specific raw materials, recipe variables, crystallization conditions, etc.

After the basic zeolite properties, optimizing the zeolite or SAPO product moves to performance targets that correlate to the customer's application. Such targets include catalytic activity and/or selectivities, deactivation rate, sulfur uptake and thermal and hydrothermal stability. By applying a design-of-experiments approach in a high-throughput laboratory environment, we can synthesize several hundred SAPO batches within months to obtain an optimal product formulation



at specific crystallization and post-treatment conditions.

Scaling up to commercial-scale volumes requires well-designed equipment and know-how, especially for manufacturing issues. However, the complexity and diversity of such specialty zeolite products often require additional empirical information and ideas. Typically, we establish all the scaling up parameters; qualify the raw materials; check all the quality, health, safety and environmental aspects; perform a post-treatment analysis, and draft a preliminary certificate of analysis during the pilot and semi-commercial stages. Commercial production often starts after six months' development, but this also depends on our customer's product evaluation procedures.

Albemarle's continuing R&D in the specialty zeolites field will generate additional knowledge and closer relationships with customers, and result in high-performance products. Thereby, our products will help our customers to quickly develop, commercialize or upgrade their processes while realizing maximum performance targets.

# UP AND RUNNING

## Hyundai Oilbank starts up residue FCC unit in Korea

**Hyundai Oilbank (HDO), an independent petroleum refiner located in Daesan, Korea, has recently commissioned a grassroots residue FCC unit at its Daesan facility to maximize transportation fuel or propylene production, as dictated by the market.**

The residue FCC unit is designed to process 52,000 bbl/d of hydrotreated atmospheric tower bottoms from a variety of crude oils, primarily Middle Eastern. It is a state-of-the-art UOP design incorporating the latest reactor technology and two-stage regenerator configuration. Hyundai Oilbank selected a catalyst system from Albemarle's UPGRADER™/OPAL™ family of catalysts to meet the stringent yield requirements while processing the heavy, contaminated feed. If the market value of propylene increases sufficiently, DuraZOOM™ additive, which maximizes LPG yield and olefinicity, will augment the fresh catalyst addition to the unit.

Albemarle's UPGRADER catalysts are accepted worldwide as some of the premier residue cracking catalysts for upgrading heavily contaminated residue feedstocks to valuable transportation

fuel products while minimizing the yield of heavy fuel oil components.

Albemarle's FCC technical service and applications technology groups assisted Hyundai Oilbank with pre-start-up and unit commissioning activities. Pre-start-up activities included inspection of the unit, the fresh and equilibrium catalyst loading systems, and the DuraZOOM additive system; and hands-on training for the unit's operators on catalyst loading and unloading from the storage hoppers. Both Hyundai Oilbank and UOP also reviewed the start-up procedures and the critical path to ensure seamless start-up.

Shortly after charging the feed, fresh UPGRADER catalyst was added to replace the start-up inventory of equilibrium catalyst. Turning over the 915-t inventory with fresh catalyst was expected to take a couple of months at an addition rate of 18 t/d.

Initially, Hyundai Oilbank intends to maximize transportation fuel yields. Later this year, the UPGRADER catalyst system will be replaced with fresh Albemarle AFX™ catalyst to maximize propylene yield while maintaining

exceptional gasoline selectivity and minimum heavy fuel oil production. DuraZOOM additive will also augment the AFX catalyst to tune and further increase the propylene yield, as economics dictate.

Albemarle has established an operating data transfer mechanism with Hyundai Oilbank that provides direct access to Hyundai's data retrieval system for the residue FCC unit. This data will be the basis for input to and management of KBC's CATOP® FCC simulation model for the unit. This enables Albemarle to continuously monitor the unit's operation and advise on catalyst performance, process optimization and feed quality impact for maximizing unit profitability.

In summary, fresh feed was introduced to the residue FCC unit in May 2011, and raised to the desired 52,000-bbl/d throughput very quickly. The unit was promptly lined out and has experienced no operating difficulties to date. Extremely thorough preparations, including unit construction and checkout, and operator training by Hyundai Oilbank, UOP and Albemarle contributed to the successful start-up of this new unit.

“ALBEMARLE UPGRADER CATALYSTS ARE ACCEPTED WORLDWIDE AS SOME OF THE PREMIER RESIDUE CRACKING CATALYSTS FOR UPGRADING HEAVILY CONTAMINATED RESIDUE FEEDSTOCKS TO VALUABLE TRANSPORTATION FUEL PRODUCTS WHILE MINIMIZING THE YIELD OF HEAVY FUEL OIL COMPONENTS.”



# ANOTHER GO-ULTRA™ SUCCESS

## Refiner increases FCC unit throughput and profits

**Improving performance is a major goal of all refiners and choosing the most suitable catalyst can make a significant difference to the bottom line. Some Albemarle customers have selected GO-ULTRA catalyst to improve the economics of their FCC units.**

The main economic objectives of one refinery were gasoline maximization, slurry cracking and reduced delta coke. The refinery had been using a catalyst based on Albemarle's proven JADE™ manufacturing technology, but Albemarle's FCC technical consultants suggested that GO-ULTRA would be a better fit to achieve these objectives, as this catalyst family was developed for this purpose. GO-ULTRA has shown in the laboratory and in commercial operation that it will improve coke selectivity and gasoline production, and reduce mass transfer limitations.

Given the potential benefits, the refinery agreed to a trial with GO-ULTRA. Albemarle development work has shown that the novel ADM-25 matrix in GO-ULTRA results in improved yield selectivities and optimized mesoporosity, which contributes to faster diffusion reactants and products. This helps to minimize unwanted secondary reactions, such as those made by coke and gas. GO-ULTRA also results in higher equilibrium activity owing to the acidity of its active sites.

The GO-ULTRA catalyst family is well received in the global refining market, and uptake has risen steadily since its introduction in 2009. A wide variety of FCC units currently use GO-ULTRA, including designs from six licensors on three continents with nickel plus vanadium contents on equilibrium catalyst ranging between 600 and 6500 ppm. Owing

to its improved pore size distribution, GO-ULTRA is a versatile product used in units processing feeds with wide boiling point ranges, from highly hydrotreated to heavy VGO.

### Laboratory results

Albemarle's fluidized standard test is very useful for separating operating condition effects from catalyst selectivities because it is undertaken at constant feed and operating parameters on a laboratory scale. Using this technique on the refinery's equilibrium catalyst confirmed that coke yield at constant conversion improved by 5% on a relative basis during the change-out to GO-ULTRA. The improved coke selectivity contributed to lower FCC unit delta coke, higher catalyst-to-oil ratios, increased circulation rates and enhanced conversion. In addition, the gasoline selectivity improved by 4%, which is consistent with the trends expected from GO-ULTRA.

### Commercial results

During the change-out to GO-ULTRA, the refinery increased its throughput, used a feed with less favorable properties and changed the operating conditions. Therefore, some adjustments had to be made before comparing the performance of the base catalyst with GO-ULTRA. The FCC unit data was normalized to a constant set of feed properties and operating conditions using Albemarle's rigorous kinetic model.

Table 1 shows that, under constant conditions, GO-ULTRA reduced FCC unit delta coke and contributed toward a more attractive yield slate, including higher gasoline yield, lower slurry and higher conversion. Although the new yield slate was economically attractive in itself, increasing the feed rate improved FCC unit profitability by nearly \$1/bbl of fresh


	BASE	CHANGE WITH GO-ULTRA
<b>FEEDSTOCK PROPERTIES</b>		
API gravity 	Base	0
Sulfur	Base	0
Conradson carbon, wt%	Base	0
<b>OPERATING CONDITIONS</b>		
Volume flow, bbl/d	Base	0
Reactor temperature, °C	Base	0
CO, vol%	Base	0
Delta coke, wt%	Base	-0.01
Regenerator temperature, °C	Base	-5
Air flow rate, MMscf/d	Base	0
Catalyst-to-oil ratio	Base	0.2
<b>CATALYST DATA</b>		
Addition rate, st/d	Base	0
Activity, wt%	Base	0
Ni, ppm	Base	0
V, ppm	Base	0
<b>YIELDS</b>		Relative % change
Dry gas, wt%	Base	0
LPG, LV%	Base	0.8
Gasoline, LV%	Base	1.0
LCO, LV%	Base	0.4
Slurry, LV%	Base	-7.5
Coke, wt%	Base	0
Conversion, LV%	Base	0.9

Table 1: Under constant conditions, GO-ULTRA reduced FCC unit delta coke and contributed toward a more attractive yield slate.

feed. It is also important to realize that the financial benefits were aided by the lower level of rare earth oxide in the GO-ULTRA catalyst, which reduced catalyst costs at a time of soaring rare earth prices.

# THE ZIEGLER CONNECTION

## How two paths crossing helped to shape the company Albemarle has grown into today

Organometallics, primarily aluminum alkyls, are critical for converting refinery olefin streams into value-added products such as polyethylene, polypropylene and synthetic rubber. Since the late 1950s, when Ethyl Corporation (Albemarle's progenitor) secured a licence from Professor Karl Ziegler to manufacture tetraethyllead (TEL) using triethylaluminum (TEA), Albemarle has been a manufacturer and supplier of aluminum alkyls and related organometallics.

This article provides a historical perspective on how the separate pursuits of Ethyl/Albemarle and Ziegler ultimately led to their crossing paths, and what the legacy of that connection means for Albemarle today.

### Ziegler discoveries

The advanced processes currently used to make polyolefins, such as high-density polyethylene and isotactic polypropylene, began with two profound discoveries in Ziegler's laboratory at the Max Planck Institute at Mülheim, Germany. These both had aluminum alkyls at their core.

The first discovery was that ethylene chain growth (the Aufbau reaction) to higher  $\alpha$  olefins occurred on aluminum, specifically aluminum alkyls such as TEA. The second, even more remarkable, discovery in late 1953 showed that when TEA was combined with other metals, such as titanium, high-molecular-weight polyethylene was easily produced under remarkably mild conditions. Giulio Natta later showed that, by using Ziegler's mixed-metal catalysts, isotactic polypropylene could also be produced. For their discoveries, Ziegler and Natta jointly received the Nobel Prize for

Chemistry in 1963.<sup>1</sup> The inventions spawned new fields of research in polymer science and organometallic chemistry that have led to very large global industries for the production and the application of the new polyolefins.

### Ethyl history

Ethyl originated in 1924 as a joint venture between Standard Oil of New Jersey (now ExxonMobil) and General Motors to develop one of the first industrially relevant organometallics, TEL, a gasoline anti-knock agent. During the late 1940s and early 1950s, TEL and anti-knock agent development continued to be primary focuses for Ethyl. However, when Ethyl's proprietary position for both the use and manufacture of TEL began to expire in the late 1940s, the company anticipated increased competition. Consequently, it looked for ways to diversify away from being what was essentially a one-product company.

When Albemarle Paper Company purchased Ethyl in 1962, diversification began in earnest, primarily into the specialty chemicals area. This area of the company grew enormously over subsequent years. Diversification was ultimately so successful that the decision was made in 1994 to spin off this part of Ethyl into a new stand-alone company, what is now Albemarle. (Ethyl, a part of NewMarket Corporation, still continues to market fuel and lubricant additives.)<sup>2</sup>

### Ziegler and Ethyl

As a result of the seminal discoveries in his laboratories, Ziegler expanded his research in organoaluminum chemistry. One invention, which was greatly relevant to Ethyl's business at the time, was a new synthesis of TEL using

TEA. Because of the clear threat this development posed to its business, Ethyl licensed the Ziegler TEL process and the requisite TEA process in the 1950s.

An extract (Figure 1) from a letter in 1959 between Esso-Standard Oil Development Company (one of Ethyl's joint-venture owners) and Ethyl research and development in Baton Rouge, USA, captures one such interaction with Ziegler at the time. The letter details the discussion with Ziegler on his insights for pilot-scale production using his direct TEA process.

Ultimately, Ethyl never used the TEA-based process to produce TEL. However, because of its move toward diversification, research in the area of aluminum alkyls led to new classes of commercially relevant chemicals and a significant position in ortho-alkylated amines and phenols, which found applications as intermediates for herbicides, antioxidants, fungicides and pharmaceuticals. This technology is still used by Albemarle today.

However, the most significant aluminum alkyl-based work was the huge effort that began in the late 1950s/early 1960s to develop the Ziegler Aufbau chemistry for the production of both synthetic alcohols and olefins. This work became a large part of Ethyl/Albemarle for many years until the business was sold to Amoco (now Ineos) in 1995.

With the ever-expanding growth in the applications of Ziegler-Natta polyolefin technology, aluminum alkyls became commercially important in their own right as co-catalysts. Because of the development and scale of the alcohols and olefins business, Ethyl

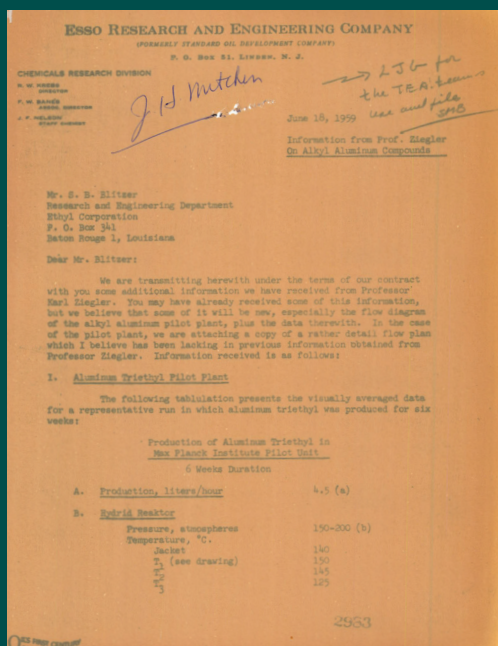


Figure 1: Extract from a letter between Esso and Ethyl research and development in 1959 concerning discussions with Karl Ziegler on the TEA process.

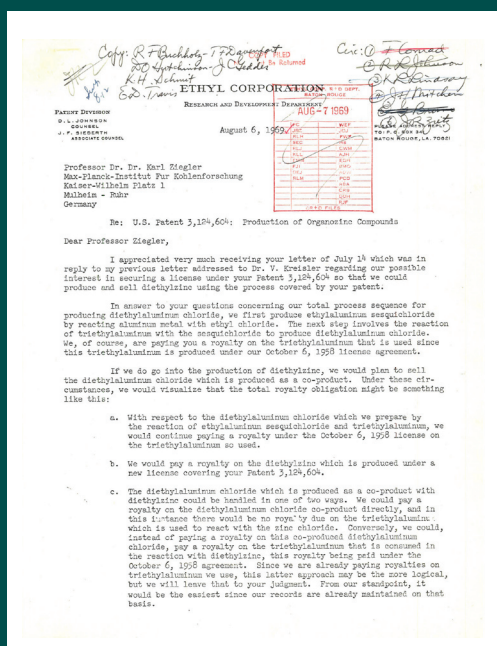


Figure 2. Extract from a letter to Ziegler from Ethyl on securing a DEZ license.

was ideally positioned to become a commercial supplier of TEA and other organometallics, and began to do so in 1962. Albemarle is now one of the world's largest producers of organometallics and has manufacturing plants in Pasadena, Orangeburg and Baton Rouge, USA; Osaka, Japan (Nippon Aluminum Alkyls, a joint venture with Mitsui); Feluy, Belgium (through a contract with Ineos); and at a new grassroots facility in the Middle East due to come on line in 2012, the Saudi Organometallic Chemicals Company, a joint venture with Saudi Specialty Chemicals Company, a SABIC subsidiary.

Other organometallics also became commercially important. One of these was diethylzinc (DEZ). In the late 1960s, Ethyl approached Ziegler about securing a license for the manufacture of DEZ. An extract from a letter outlining this interaction is shown in Figure 2. Albemarle continues to manufacture DEZ in the USA and in Japan through Nippon Aluminum Alkyls.

## Legacy of the Ziegler–Ethyl/Albemarle connection

Although applications of organometallics are still primarily in the polyolefin area, expansion into other areas has occurred. Albemarle now supplies high-purity metal organics such as trimethylgallium, triethylgallium and trimethylaluminum, key components in the manufacture of high-brightness LEDs, from its facility in Baton Rouge. A new facility producing high-purity metal organics will come online in early 2012 in Yeosu, South Korea.

In the late 1980s and early 1990s, Ethyl/Albemarle became involved in the single-site polyolefin catalyst revolution, a new generation of Ziegler–Natta type catalysts. Today, Albemarle is not only a supplier of the components that go into these catalyst systems, but also of the finished catalysts themselves. Finally, with Albemarle taking a position as a merchant supplier of Ziegler–Natta polyethylene catalysts in 2008, the Ziegler connection has come full circle.

“ THE ADVANCED PROCESSES CURRENTLY USED TO MAKE POLYOLEFINS, SUCH AS HIGH-DENSITY POLYETHYLENE AND ISOTACTIC POLYPROPYLENE, BEGAN WITH TWO PROFOUND DISCOVERIES IN ZIEGLER'S LABORATORY AT THE MAX PLANCK INSTITUTE AT MÜLHEIM, GERMANY. ”

### References

<sup>1</sup>For a historical perspective by Günter Wilke, see *Angew. Chem. Int. Ed.*, 2003, 42, pp5000–5008

<sup>2</sup>For a history of Ethyl/Albemarle through 1983, see Robert, J. C., *Ethyl: A History of the Corporation and the People Who Made It*, University Press, Virginia, 1983



# Pure STARS™ power.

Albemarle's robust, reliable, high-activity  
NiMo catalysts deliver world-class performance.

Albemarle's high-quality NiMo catalysts are reliable, robust performers that provide best-in-class activity, utilizing patented STARS™ technology for optimum performance in USLD and hydrocracking pretreatment services. Their superb long-term dependability is matched by the technical support, knowledge and experience that have made Albemarle the leader in hydroprocessing solutions. For more information on our full line of NiMo-based products, visit [www.albemarle.com/nimo](http://www.albemarle.com/nimo).

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