

2015 CATALYST DEVELOPMENTS: INNOVATION AND VALUE CREATION

Hydrocarbon Processing invited major catalyst companies and industry consultants to share their insights regarding innovations and trends for new catalytic technologies.

Challenges to be solved. “As challenging as things currently appear in Europe, things in North America are markedly more encouraging; the US is better positioned, with the boon of ‘shale oil and gas,’ although it is consuming more time than anticipated to monetize,” said John Murphy, president of The Catalyst Group Resources (TCGR). “This is due to the compositional differences between shale gas, NGLs and tight oil, and the unprepared infrastructure (plants and pipelines) to deal with the phenomena. The logistical challenges are significant (along with the opportunities). For example, with 15+ new crackers announced for construction in the 2015–2018 period, there is not enough EPC capacity for them to all be built within this timeframe.”

A number of refinery, petrochemical and commodity chemical plant closures have occurred, and multinational companies are shifting their investments regionally. These trends are likely to continue. Naphtha feedstock cost disadvantages, relative to inexpensive gas, will force moves to specialty chemicals and value-added enterprises to remain competitive, but this will require the rejuvenation and reinvestment in innovation to be sustainable.

Brittany McGinley, president of The Catalyst Group (TCG), added that it is clear the industry is at a crucial inflex: the rapid and substantial changes that catalyst users and manufacturers have experienced in the last 15 years in both feedstock development and end-product manufacturing location have required successful competitors to have an extremely sophisticated understanding of the entire value chain and to be highly flexible and to continually reposition their product offering to meet market needs. This highly changeable environment has also influenced how market players have developed their near- and medium-term growth strategies.

From an organic perspective, catalyst manufacturers and users alike are following two major trends:

- **Enhancing and influencing market pull** by investigating or developing technology licensing to allow better control of catalyst revenues or by influencing end customer needs by developing catalysts that create unique (and brand-able) product properties
- **Developing customer intimacy** by better understanding end-user (either the product formulator or end consumer) needs and with the offering of highly desirable custom or tolling catalyst business.

From an inorganic perspective, consolidations via mergers and acquisitions are expected to continue through 2015, coupled with investments in adjacent and synergistic markets. This will allow market participants to typically focus on three areas:

- Enhancing regional presence to allow faster regional product delivery or better local market penetration, such as with increased interest in greater ASEAN
- Enhancing product margins by back-integrating into key raw materials such as zeolites and organometallics
- Adding new business models such as technology licensing businesses or technical services.

According to TCGR’s recently completed biannual industry report titled “Intelligence Report: Business Shifts in the Global Catalytic Process Industries, 2013–2019,” the global merchant catalyst market is forecast to grow from \$25.3 B/yr in 2013 to \$33.5 B/yr by 2019, with an AAGR of 5.4%/yr, higher than global GDP. The two largest sectors after environmental, which include mobile and stationary sources, are refining, at over \$7 B, and petrochemicals, at nearly \$5 B, as illustrated in **FIG. 1**.

New developments for the refining industry. “Catalyst and process developments over the last several years have focused on the processing of light tight oil (LTO), increasing distillate selectivity and quality, converting higher amounts of residual oil, and enhancing petrochemical feedstock,” said Murphy. “Dewaxing technology is now receiving more attention, due primarily to LTO processing.”

Specific developments include:

- All three western FCC manufacturers (Albemarle, BASF and Grace) are promoting LTO catalysts designed to handle these paraffinic feeds and to counteract contaminant metals.
- Sinopec China has continued to maintain a minor FCC catalyst presence in the global marketplace, despite no longer having a pricing advantage due to the return of rare-earth prices to near baseline levels.
- New reforming catalyst grades from Axens and UOP have been developed to provide additional reformate yield and hydrogen, as well as greater aromatics for petrochemical feed.
- With lower-cost hydrogen available in North America, vendors are promoting new high-activity hydrotreating catalysts to maximize saturation and volume swell.

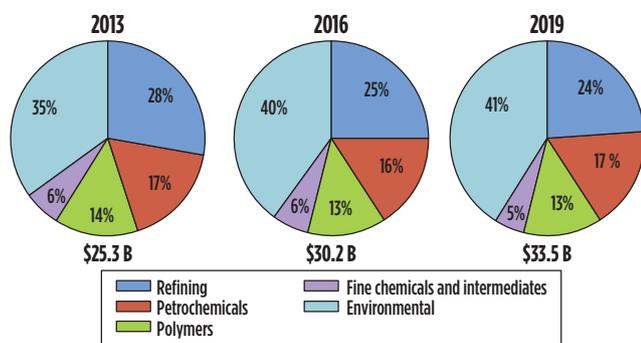


FIG. 1. Global catalyst value, 2013–2019. Source: TCGR’s “Intelligence Report: Business Shifts in the Global Catalytic Process Industries, 2013–2019.”

- For low-pressure ULSD units, higher hydrodesulfurization (HDS) activity or more cost-effective catalysts have been introduced. New specialty hydrotreating guard-bed catalysts have been brought to market to handle contaminants such as arsenic, iron and silicon.

Other refining developments. Grace has developed solutions to help refiners lower slurry yield, take advantage of distillate crack spreads and to address the trend toward increased residue and opportunity crude processing.

Rosann Schiller, director of marketing for Grace Catalysts Technologies, said, "Processing opportunity crudes, along with upgrading the bottom of the barrel into light cycle oil (LCO) and lighter products, are some of the challenges facing refiners looking to maximize the value from their FCCUs. Grace is now expanding its portfolio of catalysts under the ACHIEVE series to address market challenges."

According to Schiller, the ACHIEVE series (100, 200, 300, 400, 800) comprises state-of-the-art catalyst technologies designed to maximize refiners' profitability. In response to the tight-oil revolution in the US, Grace successfully launched the ACHIEVE 400 FCC catalyst to address the octane debits that were being encountered by refiners. During this research and development (R&D) program, five key catalytic functionalities were developed:

- Higher-diffusivity matrices
- Dual zeolite technology
- Flexible hydrogen transfer
- Advanced metals tolerance
- Higher activity.

Meeting new challenges. Designing the best catalyst systems from these functionalities encompasses the Grace approach to FCC catalyst design. The ACHIEVE formula contains high-diffusivity matrices for deep conversion of the bottom of the barrel and resistance to poisoning from unconventional metals. The latest generation of integral metals traps are used to protect active components from deactivation while preserving coke selectivity and minimizing dry gas production. Additionally, the dual-zeolite feature delivers increased naphtha octane, higher LPG olefins yield, as well as ultra-high activity to help maintain unit heat balance.

"The ACHIEVE series was developed as a tailor-made solution and optimized to meet specific refinery opportunities while not exceeding the refinery's constraints," said Schiller. "We are proud of our close customer partnerships and a broad product portfolio built on talent, technology and trust. We are ready to work with refiners to select the catalysts with the right balance of operational flexibility, product capability and overall value to meet their requirements."

Advances in hydroprocessing. Criterion Catalysts and Technologies is launching a series of new hydroprocessing catalysts based on its ASCENT technology platform. The results of an extensive high-throughput experimental program indicate that refiners can expect a 10%–20% increase in activity. Significantly, the gains come without compromising other key features of the catalysts: notably, their limited hydrogen consumption, good physical properties, lower density and ease of regeneration—all of which make ASCENT technology an outstanding

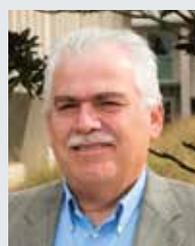
THE AUTHORS

RIVE TECHNOLOGY, INC



DAVID C. ALDOUS joined Rive Technology, Inc., as CEO in 2012. He brings over 30 years of diverse experience in the refining, chemicals and catalyst industries, including over 20 years at Royal Dutch Shell, where he was executive vice president of strategy and portfolio. Mr. Aldous also served as president of Shell Canada Products. He brings deep experience in the catalyst industry from his six years as president and CEO at CRI/Criterion. Prior to joining Rive, he was CEO of Range Fuels. Mr. Aldous holds a BS degree in fuels engineering from the University of Utah and an MBA with distinction from Northwestern University.

CRITERION CATALYSTS AND TECHNOLOGIES



SAFA GEORGE is vice president of catalysts technology for Shell and CRI/Criterion. In 1980, he joined Shell Canada's research group and was appointed section head of refining projects in Shell Canada's Montreal East refinery. In 1990, Dr. George joined Criterion Catalyst as the technical service coordinator and he became vice president of technical services in 2000. Dr. George was appointed vice president of catalyst technology for Shell and CRI/Criterion in 2009. He holds a BS degree and PhD both in chemical engineering from Imperial College of the University of London, and McGill University, Canada, respectively.

THE CATALYST GROUP



BRITTANY MCGINLEY is president of The Catalyst Group (TCG), with over 12 years consulting experience, and currently managing TCG's operations, strategic initiatives and relationships for its consulting division. Prior to her appointment to vice president in June 2011, she served TCG in the role of project manager, providing project oversight, analyses and key deliverables for client confidential projects as well as multi-client studies. She has been a member of TCG consulting team since October 2008. Ms. McGinley holds a BS degree in business administration from Babson College.

THE CATALYST GROUP RESOURCES



JOHN J. MURPHY is the president of The Catalyst Group Resources (TCGR), the information services component of The Catalyst Group (TCG). TCGR monitors and analyzes technical and commercial developments in catalysis as applied to global refining, petrochemical, polymer, fine/specialty and environmental industries. Mr. Murphy develops, manages and contributes to member-directed programs and multi-client studies. He graduated from Bowdoin College with an AB degree in chemistry and has an MBA from Lehigh University.

GRACE CATALYSTS TECHNOLOGIES



ROSANN SCHILLER is marketing director for Grace Catalysts Technologies, based in Columbia, Maryland. She has been with Grace for 16 years, and has held a variety of roles in FCC technical service, sales, product management and marketing. Ms. Schiller holds an MSE degree in chemical engineering.

system for many distillate hydrotreating and cracker feed pretreatment applications.

“Although highly active Type II catalysts have taken center stage recently, with Criterion’s class-leading CENTERA technology being a prime example, mixed Type I/II catalysts still have much to offer in terms of all-around performance,” said Safa George, Criterion’s vice president for catalyst R&D. “There are refiners with low- to medium-pressure units or that are short of hydrogen, and they are just as keen to raise conversion, extend run lengths and process tougher feeds. This is why ASCENT has remained a key part of our portfolio for 10 years.”

The new catalysts represent third-generation technology. “We started by optimizing the support’s pore structure and then turned to the balance between the metallic [cobalt (Co) and nickel (Ni)] and non-metallic promoters and the molybdenum (Mo) in the catalysts,” said George. “This latest advance is linked to improved dispersion of the active sites on the support and has borrowed from manufacturing techniques used to make CENTERA catalysts. Over time, we have continually enhanced what ASCENT technology has to offer. These latest products border on the activity normally associated with pure Type II catalysts.”

The first catalysts offered to customers include CoMo (DC-2535) and NiMo (DN-3532) for distillate hydrotreating. The latter is intended for tougher feeds. In a range of tests, NiMo (DN-3532) has shown a sharp increase of about 20% in relative volume desulfurization activity over its predecessor. Criterion is also introducing a new hydrocracker feed pretreatment catalyst, NiMo (DN-3552); it has at least 20% higher desulfurization and denitrogenation activity than the previous benchmark product and does not consume any more hydrogen.

“Hydroprocessing is a complex business: no two units are the same, and refiners’ business drivers also vary widely,” said George. “We have to maintain a strong portfolio of catalysts to add value to individual applications.”

Newcomer to catalyst development. Rive Technology, a developer of innovative materials-based solutions for catalytic and separations processes in the petroleum refining and chemicals industries, is commercializing the molecular highway zeolite technology for FCC in collaboration with Grace Catalysts Technologies. The molecular highway technology improves the mass transfer into and within the zeolite crystals of catalysts and adsorbents through a series of larger mesopores within the zeolite. In FCCUs, the mesopores, or molecular highways, significantly improve diffusion into and out of the zeolite crystals of the FCC catalyst, leading to improved coke selectivity, enhanced bottoms upgrading, decreased dry gas production, and enhanced $C_3=$ and $C_4=$ yields.

Rive Technology is also working with Zeolyst and Criterion to develop and commercialize hydrocracking catalysts incorporating molecular highway technology. Initial work for middle distillate applications has shown significantly enhanced diesel selectivity. The companies anticipate product availability in 2016. Additionally, Rive continues to work with several leading oil and chemical companies, as well as technology providers to those industries, on additional high-value applications of molecular highway technology.

“Rive continues to demonstrate value to refiners through application of molecular highway technology in FCC,” said

David Aldous, CEO of Rive Technology. “With the recent debottlenecking of our supply chain, we expect to see accelerated commercial adoption of our technology within the industry in 2015.”

More refining news. Dewaxing technology that favors isomerization over cracking to preserve diesel stream volume is available from catalyst/process providers such as Haldor Topsøe, Shell/Criterion and UOP/ExxonMobil. Clariant is also a supplier of dewaxing catalysts. All hydrocracking catalyst companies have focused on distillate selective grades for jet/kerosene and diesel. With the recent agreement between Advanced Refining Technologies (ART) and Chevron Lummus Global (CLG), all competitors have catalyst and process connections either in-house or via agreements and alliances.

Slurry hydrocracking using “nano” catalysts offers a step change upward in resid conversion; in particular, the Eni Slurry Technology (EST) process is operating at an industrial level at this time. Use of refinery-type processes based on FCC and hydrotreating technology to produce second-generation biofuels remains a niche application.

The continuing global shift from gasoline to distillates and petrochemicals will encourage new products for all catalytic processes. Expansion of hydraulic fracturing will result in the application of LTO catalysts and also to process improvements in regions outside the US.

WHAT IS NEW IN PETROCHEMICALS?

According to TCGR’s John Murphy, a number of new process developments have been announced, including:

- **Aromatics.** The main thrust has been to develop new catalysts, adsorbents and process schemes aimed at improving the economics and energy efficiencies of producing primarily p-xylene. Gevo is developing a route to renewable p-xylene.
- **Organic syntheses.** The most significant development in this area is a new BP process to produce acetic acid from syngas that eliminates methanol as an intermediate and avoids the need for corrosive iodides. A novel business/technology development is the production of ethanol from acetic acid, commercialized in China by Celanese, and intended to essentially produce fuel ethanol from coal.
- **Oxidation.** There have been several developments in this category, dealing with productions that are made via oxidation but with processes utilizing different routes. A startup company, Novomer, is developing a route to react carbon monoxide (CO) with ethylene oxide to produce acrylic acid; it is in the early stage of work. Eastman Chemical Co. and Johnson Matthey Davy Technologies have announced a process to produce ethylene glycol from syngas (but not passing through oxalates as an intermediate, as is being practiced in China), starting from coal.
- **Syngas and derivatives.** Haldor-Topsøe A/S has announced several improvements in reforming and low-temperature shift catalysts. For methanol, the news is the resurgence of methanol production in North America, thanks to low-cost shale gas methane,



with plants being moved by Methanex from South America, “mothballed” plants being started up, and new plants being constructed.

- **Hydrogenation.** There have been noteworthy developments in higher-efficiency catalysts for acetylene hydrogenation and the hydrogenation of edible oils and fatty acids.
- **Dehydrogenation and olefins.** Several technologies are now under development in Japan and China to dehydrogenate butenes to butadiene. A novel development by INVISTA and LanzaTech, in New Zealand, is intended to produce butadiene from waste CO via 2,3-butanediol. In ethylene, Braskem, is supporting a demonstration plant by the startup company Siluria, which has announced the development of methane-coupling technology to produce ethylene. Also, ExxonMobil has announced that its new ethylene plant in Singapore can crack crude oil, thus eliminating the need to first produce naphtha for feedstock purposes.
- **Chemicals from biomass.** Many developments are occurring in the area of chemical process technology based on sugars and other biomass feedstocks. The most important developments involve current or planned production plants for bio-ethylene, bio-butadiene, bio-butanol and bio-1,3-butanediol:
 - o Bio-ethylene is being produced by at least two organizations—one based on glycerin, a renewable

feedstock; and the other, a Chinese technology based on corn as a feedstock.

- o Several technologies are being developed, with plants announced to produce bio-butadiene—one via bio-butanol by Cobalt Technologies, and several involving Genomatica via bio-butanediol.
- o In bio-butanol, two organizations are developing technology to produce isobutanol—Gevo, with an operating plant that was converted from ethanol production; and Butamax, a JV between BP and DuPont, with a similar technology and business plan.
- o Several projects are under development, utilizing licenses of Genomatica’s one-step process to convert sugars to bio-1,3-butanediol, with BASF and Novamont both building plants. Other organizations including Myriant and BioAmber, are developing routes to biobutanediol, based on converting renewable feedstocks to succinic acid, which is then hydrogenated using Davy Process Technology, which also produce co-products tetrahydrofuran (THF) and gamma butyrolactone (GBL).

“In 2015, it is important to focus on market and value creation,” said McGinley. “This will require new products, new geographic markets and new processes/technology using cost-advantaged feedstocks. This is not for the faint-hearted; it requires creativity and risk, as well as investment. But some positive signs are finally emerging that justify these changes.” **HP**