Talent that spans the globe with operations in over 40 countries, knowledgeable R&D teams and industry leading tech service.

Technology leadership:
- #1 in FCC catalysts
- #1 in resid hydroprocessing catalysts (ART)
- #1 in independent polyethylene catalysts
- #1 in independent polypropylene catalysts

Leading supplier of hydrocracking catalysts and polypropylene technology licensing

Trust built through long term partnerships over a 150 year history.

Choose Grace Catalysts Technologies, the global leader in specialty inorganic catalysts.
What are the most significant trends impacting the petroleum refining and chemical processing industries?

Several short- and longer-term trends are likely to cause important shifts in how our customers plan and operate. Lower feedstock costs, including lower crude oil prices, are good for transportation fuel demand, but markedly change the economics of the business. Over the next several years, refining capacity will increase primarily in Asia and the Middle East. We see growing demand for low-sulfur diesel, tightening environmental regulations, and increasing use of heavy crudes. Additionally, continuing personal income growth in emerging economies will drive increased consumer consumption of plastics.

Grace has a very positive outlook for the industry. We expect to increase R&D investment and expand our manufacturing capacity to help our customers address these changing market dynamics.

Can you be more specific about the FCC, hydroprocessing, and polyolefins segments?

Within the Refining Technologies market, we expect a continued need for deep conversion and highly metals tolerant catalysts as refiners process opportunity crudes. To meet the growing demand for FCC catalysts, Grace has announced new investments in both capacity and technology innovation. Most of the announced refinery FCC projects are resid-focused, requiring catalysts designed to upgrade the bottom of the barrel while maintaining activity and selectivity in high severity environments.

Within hydroprocessing, we continue to see new units start up around the world. Most of these are fixed-bed resid processing or hydrocracking units. Resid upgrading continues to show strong growth, particularly in Asia as refiners install new fixed-bed resid processing units in front of FCC units to meet the demands for gasoline and propylene. In hydrocracking, refiners are looking for higher conversion and selectivity, especially for the production of diesel.

With growth in consumer products, polypropylene and polyethylene demand is expected to grow faster than GDP.

How is Grace meeting these new needs with technology or innovation?

When our customers see shifts in their business they expect us to find catalytic solutions to their challenges. A prime example is the current expansion of our portfolio of FCC catalysts within the ACHIEVE® catalyst series. This new platform offers a slate of tailor-made technical solutions at multiple price points to help refiners maximize operating flexibility. In commercial application, the economic benefit of ACHIEVE® catalysts has been averaging between $0.40-0.95/bbl which will drive significant improvement to the refiner's bottom line.

For refiners processing resid in their FCC, we have launched MIDAS® Gold FCC catalyst. In this issue, we highlight the commercial benefits observed at Placid Refining Company LLC that have resulted in economic uplift on the order of $7MM/yr.

Our hydroprocessing product portfolio has evolved with a focus on resid conversion as refiners run heavier crudes. ART is launching new products within our ICR® catalyst systems for hydrocracking and fixed-bed resid hydrotreating, as well as in our SmART Catalyst System® for ultra-low sulfur diesel production.

Nearly half of the newly licensed polypropylene capacity will use gas phase UNIPOL® Polypropylene Process Technology. This is the only technology currently employing sixth-generation non-phthalate catalysts, which
Al Beninati Q&A continued...

are sold under Grace’s CONSISTA® catalyst brand. This new family of catalysts expands product range while improving physical properties such as strength, clarity, and processability. They also support our customers’ sustainability efforts, as they are environmentally friendly and fully comply with new REACH regulations.

Grace recently announced plans to separate into two independent public companies. What does this mean for customers of Grace Catalysts Technologies?

Grace Catalysts Technologies customers won’t notice anything in the short run. Over time, the organization will be better focused and will enjoy greater flexibility to allocate resources in order to grow and serve our customers better. Grace will remain No. 1 in FCC catalysts, No. 1 in resid hydroprocessing catalysts, No. 1 in independent polyethylene catalysts, and No. 1 in both independent polypropylene catalysts as well as independent polypropylene process technology licensing.

Right now our global catalysts teams will continue to help our customers capture the opportunities that change creates. The most important way this happens is through innovation. We look forward to seeing many of you at the AFPM Annual Meeting and at our own FCC Technology Conference in Barcelona in April.

Turning the Gears of Innovation in a Fast-Changing Market

IN THIS ISSUE of the Catalagram® we examine some of the key changes and trends that are facing the industry today and Grace’s approach to satisfying the needs created by these changing market dynamics. The best approach for success is to innovate. Grace Catalysts Technologies is turning the gears of innovation by harnessing the power of its superior zeolite technology for new product development, catalyst and process technology for polyolefin production, hydroprocessing catalyst design for heavy feeds, and deep customer collaboration with refiners like Placid Refining.

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Lighter, faster, cleaner, and clearer with CONSISTA® catalysts

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OSHA Voluntary Protection Program Recertifies Lake Charles Facility with its Highest Rating

Louisiana Location is World's Largest Refining Catalyst Plant

The Grace facility in Lake Charles, LA has been recertified with the highest level (Star) for its exemplary safety standards by the Occupational Safety and Health Administration (OSHA) Voluntary Protection Program (VPP).

The VPP is designed to identify and eliminate workplace hazards and recertification represents continuous improvement as well as a commitment to Grace’s longstanding goal of no one hurt.

The largest refining catalyst plant in the world, Lake Charles has been certified with the Star rating for every OSHA inspection since 2005. Less than 1 percent of the worksites in the United States receive this distinction.

One of the criteria for VPP Star status is that a facility achieves average injury rates that are 50 percent lower than other worksites in their industries. Because of a safety-first atmosphere and outstanding health and safety programs, the Lake Charles injury and illness rate has been more than 75 percent below the national average for the chemical industry.

Lee Gauthier, Vice President, Global Operations, said, “I’m proud of our Lake Charles team for their focus, their hard work, their passion, and of course their results, which have earned us this certification once again.”

Gauthier also said, “VPP recertification is evidence that Grace employees and company leadership are committed to the highest level of safety. It requires engagement beyond written rules and management systems. It confirms that we have committed the necessary resources. It demands that everyday activities of every employee reflect an internalized safety culture. That means we don’t just talk about it. We believe it and we do it.”

The VPP certification is a rigorous process managed by OSHA experts and inspectors. It is based on data and performance, not just plans and procedures. The audit includes a review of documents and safety manuals, accident reports, safety meeting minutes, training records, and interviews with employees. One core requirement is employee involvement, and Lake Charles has proven time and again that safety is truly everyone’s responsibility.

Lake Charles represents approximately half of Grace’s catalyst manufacturing capacity and supplies a significant portion of the world’s catalyst market. Operating in Southwest Louisiana since 1953, the Lake Charles facility supplies major refiners worldwide. The 120-acre site consists of four major production areas: sodium silicate, additive plants, fluid cracking catalysts, and hydrotreating catalysts.
Generating Value with FCC Catalyst Innovation at Placid Refining

Jessica Smith, Sr. Technical Sales Manager, Grace

Fuels Demand Continues to Grow
Transportation fuels demand is forecasted to grow by 1% through 2030 (Figure 1). Population growth and economic advancement will drive 2-3% demand growth in emerging regions, offset by flat to declining demand in mature regions.

Global refinery capacity will be increased to meet demand, with the majority of new FCC capacity designed to process heavy feedstocks. Most recently, regulations like Marpol VI, have driven the decline in fuel oil demand, as lower sulfur marine distillates replace fuel oil to limit pollution-causing emissions from ocean transport. Over the same time period considered in Figure 1, fuel oil demand is flat to declining by (0.5%). Hence, refiners must continue to drive bottoms upgrading to align with the global fuel demand mix. The fluid catalytic cracking unit (FCCU) is one of the principal bottoms upgrading units in the refinery. And, specifically, processing high amounts of resid in an FCCU requires a catalyst with a high level of matrix mesoporosity and best-in-class coke selectivity to achieve the deepest conversion of the bottom of the barrel.

Managing Dynamic FCC Feed Quality
The international press continues to highlight the surge in light tight oil production from horizontal fracking in the United States and its impact on global crude markets. Since 2011, 96% of the growth in US crude production came from the development of tight oil formations, prompting refiners to invest in additional crude topping capacity to increase lighter feedstocks processing capability. On the surface, light can suggest “easier to convert,” and studies show that light tight oils and condensates contain less resid than conventional crudes, therefore implying a less technically challenged operation. However, the reality is that light tight oils and condensates are often contaminated with conventional metals, such as nickel and vanadium, as well as unconventional metals such as iron and calcium. These contaminant metals reduce the conversion potential across the entire refinery. Conventional metals can be managed through

Eric Lowenthal has worked in FCC for 15 years in the areas of design, synthesis, and scale-up of new catalysts and additives. He has in extensive experience in bottoms upgrading, the development of catalysts and additives to produce light olefins, and overcoming engineering challenges associated with processing powder and bulk materials.

Kent Turner is an FCC Technical Service Representative for North America with responsibility for the Gulf Coast region. He has over 14 years of refinery and catalyst experience in FCC, hydrotreating, hydrocracking and reforming. He also has experience in refinery economics and crude planning.

Angela Jones works as a Senior Technical Sales Manager in the Gulf Coast region. Angela has held the roles of North American Demand Manager and North America Marketing Manager, Global Marketing Specialist, Process and Quality Assurance Engineer, Production Supervisor, and Controls Systems Engineer during her 22 years at Grace.

incorporation of trapping functionality into the fluid catalytic cracking (FCC) catalyst particle, while high-mesoporosity FCC catalyst mitigates the unfavorable impacts of the unconventional metals in the FCCU.

Refiners are continually faced with the challenge of transforming an ever changing crude slate into a desired mix of valuable products. To maximize the value derived from each barrel of feed, refiners must drive the upgrading of heavy bottoms into LPG, gasoline and LCO. Also, the refining process must be tolerant of changes in the metals content of feedstocks. Advances in FCC catalyst technology have enabled refiners to process feeds and achieve selectivities undreamed of when the FCC process was first developed in the 1940s. Recent advances in catalyst manufacturing and formulation technology at Grace have resulted in the development of high-activity MIDAS® Gold FCC catalyst, a new member of the MIDAS® family of FCC catalysts. In addition to increased activity, MIDAS® Gold FCC catalyst delivers enhanced tolerance against metals contamination and deeper bottoms upgrading in the most severe FCC operating environments.

Placid Refining Overview
Placid Refining Company LLC is an independent, privately held petroleum refining company located in Port Allen, LA, directly across the Mississippi River from Baton Rouge. The refinery produces a full range of transportation fuels that are distributed across the southeastern United States, from Louisiana to Virginia. Placid strives to be an efficient, reliable, and profitable supplier of high-quality transportation fuels at competitive prices.

The refinery processes approximately 60,000 barrels per day (BPD) of crude oil and typically refines crude oils ranging from 28° to 45° API gravity, containing up to 2.0 wt% sulfur. The Port Allen refinery purchases a variety of crude oil types, including Louisiana Light Sweet, Eugene Island, Bonito Sour, Mars Sour, Poseidon Sour, Bakken, West Texas Intermediate as well as Eagle Ford Shale. These crudes vary in quality, composition, and the level of contaminant metals.

The Port Allen facility operates a single 20-22 kBPD FCC unit that processes a blended feed stream containing vacuum gas oils (VGO) and deasphalted oil (DAO) from the operation of a ROSE (Residuum Oil Supercritical Extraction) process that constitutes between 22-35% of the FCC feed diet.

Placid’s FCCU was modified by ABB Lummus from Exxon’s Model IV short contact time reactor with LCO quench to an external folded riser. The feed preheat temperature ranges from 460 to 580°F. The reactor temperature ranges from 960 to 980°F with a catalyst–to-oil ratio between 6.0 and 7.0. The unit operates in full burn with a wet gas scrubber. Wet and dry gas limitations as well as upper regenerator temperature constraints are the typical drivers of the FCC operation along with unit economics.

Catalyst Optimization Nets Opportunities
Placid planned a major debottlenecking project in late 2014, increasing capacity by about 25%. Ahead of the turnaround in September 2014, Placid’s engineering and technical modelers forecasted the rate increase would cause a constraint at the wet gas compressor. Wet gas compressibility was a typical restriction at the pre-turnaround FCC feed rates of 20-22 kBPD.

Placid partnered with Grace to evaluate how a modified catalyst solution could provide (i) immediate opportunity and (ii) address the operating changes expected from higher processing rates post-turnaround. Grace’s technical and R&D team evaluated the feed quality, unit operating constraints and desired yield improvements. The base operating conditions and feed properties used for this evaluation are shown in Table 1.

Placid’s FCC feed quality varies depending on crude unit feed composition and upstream unit operating conditions which can be changed based on FCCU bottlenecks. These changes affect the % DAO in the FCC feed as seen in Figure 2 and Figure 3. Also, some opportunity purchased gas oil is periodically charged depending on pricing and FCCU constraints. Placid has seen the amount of fresh metals being deposited on the catalyst increase by nearly 30%. Large, short-term changes in the aromaticity/crackability are occasional problems. These feed quality changes can cause lower catalyst activity and more severe regenerator conditions, resulting in higher dry gas make, higher bottoms and an overall loss of conversion. In order to stabilize performance in the face of feed quality shifts, Grace’s technical service and R&D teams completed catalyst technology screening studies over the range of feed quality experienced in routine operation. This evaluation resulted in the selection of a catalyst system containing MIDAS® Gold FCC catalyst. This investigation into both catalyst technology and feed variability allowed Grace to formulate a solution at Placid that would absorb the shock of high metals feedstocks and mitigate the detrimental effects on unit performance. Grace predicted the catalyst system would reduce
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bottoms production by improving in-unit activity, yield higher conversion to liquid fuels products, reduce dry gas, and improve coke selectivity. Grace formulated a multi-staged approach to allow Placid the opportunity to validate progress and capture the benefit of the new catalyst system as improvements in coke selectivity, bottoms upgrading and conversion were made.

Maximize Deep Conversion in the FCCU with MIDAS® Gold FCC Catalyst
Grace’s R&D and manufacturing organizations have a continuous technical pipeline of improvements in bottoms cracking technology and technologies for processing heavy resid feeds. At Placid, Grace worked together with our refining partner to establish both the need and efficacy of incorporating nickel-trapping functionality into the MIDAS® Gold matrix and enhancing the bottoms conversion activity of the MIDAS® Gold catalyst system.

Nickel-trapping principles from related Grace catalyst technologies have been applied to the MIDAS® Gold catalyst system at Placid. We have previously demonstrated that large-crystal boehmitic aluminas can be incorporated in alumina-sol catalysts to passivate nickel species deposited onto the FCC catalyst, from large, nickel-containing heteroatomic structures in the high-boiling fraction of the resid feed. These boehmitic aluminas combine with the nickel species to form nickel aluminates that limit the oxidation and reduction cycling of nickel oxide that leads to the formation of contaminate coke and gas through dehydrogenation of feed molecules. We can envision the establishment of

<table>
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<tr>
<td>Fresh Catalyst Additions, Short Tons/Day</td>
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<td>DAO, % of Fresh Feed</td>
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<tr>
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Table 1: Placid’s FCCU Base Feed and Operating Conditions

Figure 2: Variation in deasphalted oil content (DAO) in Placid FCCU feed over time

Figure 3: Variation in Placid FCCU feed API over time
stable nickel aluminate species according to the following mechanism:

- Nickel migrates across the matrix surface and encounters boehmitic alumina.
- Nickel by oxidized in the air in the regenerator and reacts with the boehmitic alumina as follows:
  \[ \text{NiO} + \text{Al}_2\text{O}_3 \rightarrow \text{NiAl}_2\text{O}_4 \]
- The nickel aluminate stabilizes the nickel against further reduction and passivates the nickel, preventing it from participating in the oxidation and reduction cycling needed to promote coke and gas formation.

In the MIDAS® Gold catalyst formulation deployed at Placid, Grace overcame previous manufacturing process challenges associated with binding sufficient levels of boehmite alumina, while still producing a mechanically robust, attrition resistant (low DI) FCC catalyst. Furthermore, the introduction of a combination of (i) higher levels of bottoms cracking alumina in the MIDAS® FCC catalysts and (ii) boehmitic, nickel-trapping alumina in the catalyst matrix, produces a material with a modified pore-size distribution. Relative to Grace’s previous MIDAS® catalyst technologies, the resultant matrix has an enhanced pore size distribution in the signature bottoms cracking range of 100 to 600 Å, the desired range required to promote cracking of heavy resid feed molecules, as well as increased porosity above 700 Å (see Figure 4).

The modification of the pore-size distribution in MIDAS® Gold catalyst provides two kinds of benefits that can be better understood in the context of the three types of cracking that take place in the FCCU (see Figure 5).

The higher matrix surface area (MSA) delivered by the MIDAS® Gold catalyst — and increase in the volume of 100 to 300 Å pores — offers more acid sites on the matrix surface for Type III cracking of naphthene-aromatic feed molecules and larger saturated ring structures in the feed, through carbocation activation and cracking. In addition, the increase in pore volume above ~700 Å reduces feed diffusion limitations in the catalyst-feed mixing zone, and offers increased catalyst surface area suitable to enhance resid vaporization and “pre-cracking,” including thermal cracking of the highest-boiling resid molecules and the generation of \(\alpha\)-olefins associated with the initiation of the cracking cycle.

![Figure 4: Mercury pore-size distribution of MIDAS® and MIDAS® Gold catalyst after CPS deactivation with 10,000 ppm total metals. The MIDAS® Gold catalyst sample shows an increase in volume of 100 to 300 Å pores and also an increase in the pore volume of the largest pores above ~700 Å suggesting a more open pore structure, amenable to improved feed vaporization and precracking of heavier feeds after feed atomization at the riser feed nozzle.](image)

![Figure 5: Schematic representation of three types of bottoms cracking that takes place on the solid acid sites of the FCC catalyst (adapted from X. Zhao, et al., 2002).](image)
Placid Refining Company, LLC Realized Benefits with MIDAS® Gold FCC Catalyst

The data presented here cover the FCC unit operation over an 18-month period between January 1, 2013 and June 30, 2014 and compares Competitor A catalyst to Grace’s MIDAS® Gold-containing catalyst system, GENESIS® SA50 catalyst. Data from upset operations, unit shutdowns and test runs have been excluded from this analysis for consistent comparison and improved clarity.

Grace predicted the catalyst system would reduce bottoms production by improving in-unit activity, yielding higher conversion to liquid fuels products, reduce dry gas, and improve coke selectivity. As catalyst turnover increased, a clear 2 lv% increase in conversion was observed (see Figure 6). This conversion represents the highest achieved conversion level since 2009 (Figure 7).

Unit conversion is governed by catalyst coke selectivity. Catalyst activity will only affect the catalyst circulation rate required to meet this conversion. Thus, catalyst coke selectivity is a key variable driving unit conversion. The improved coke selectivity of the MIDAS® Gold catalyst platform alleviated Placid’s regenerator temperature constraint, providing more operational flexibility. MIDAS® Gold catalyst delivered 3-4 lv% higher conversion at the same coke yield compared to the competitive benchmark catalyst (see Figure 8). Conversion improved with Grace’s MIDAS® Gold catalyst technology over the wide range of catalyst-to-oil ratios (C/O) associated with the Placid FCCU operation. The improvement results from the design features of MIDAS® Gold catalyst technology as well as application of a more balanced zeolite-to-matrix ratio, optimized for Placid’s operation.

Another key performance indicator achieved with Grace’s MIDAS® Gold catalyst was a reduction in bottoms yield and bottoms gravity. Figure 9 shows the slurry yield reduction of ~ 1 wt% at constant C/O when compared to the competitive benchmark catalyst. Bottoms reduction can
occur either through increased severity or a more selective catalytic design. Grace’s MIDAS® Gold catalyst represents a more selective design, with an optimized pore structure that delivered on the predicted bottoms improvement, as demonstrated in Figure 10 with a decrease of 1.5 vol % at constant reactor temperature, while the right graphic illustrates the step change that occurred in slurry API: down by 2.5° when MIDAS® Gold catalyst was introduced.

Grace’s MIDAS® Gold catalyst delivered the promised performance at Placid and increased production of higher value products as demonstrated by the increase in liquid volume swell pictured in Figure 11.

The robust stabilization of nickel, due to improvements in the MIDAS® Gold catalyst design, protects against the production of dry gas as shown in Figure 12 illustrating a 20% reduction in hydrogen production.

Grace’s MIDAS® Gold catalyst gave an economic advantage over a competitive benchmark catalyst by delivering on improved coke selectivity that results in volume expansion and slurry upgrades to more valuable products. Gulf Coast product values from June, 2014 were used to estimate the annualized economic improvement of ~ $7MM to Placid from the yield shifts occurring with MIDAS® Gold catalyst shown in Table 2.

Figure 9: The slurry yield dropped ~1 wt% at constant C/O in the Placid FCCU after the shift to Grace MIDAS® Gold catalyst.

Figure 10: After the Placid FCCU shifted to MIDAS® Gold FCC catalyst, slurry yield dropped by ~1.5 vol%. Right shows the significant reduction in slurry API with utilizing MIDAS® Gold FCC catalyst.

Table 2: Improved product yields with MIDAS® Gold catalyst compared to the Competitor Benchmark.
MIDAS® Gold Delivers Deep Bottoms Conversion for Refinery A.
MIDAS® Gold has been applied in several other FCCUs with similar objectives as Placid. Refinery A was processing heavy resid utilizing a competitive resid benchmark FCC catalyst but desired deeper bottoms conversion. A switch to MIDAS® Gold FCC catalyst provided the desired yield improvements without sacrificing coke and gas selectivity. Figure 13 illustrates how under constant feed conditions, the MIDAS® Gold catalyst reduced bottoms by 15%.

Maximize FCC Profit with MIDAS® Gold FCC Catalyst
Grace is pleased to introduce our latest resid conversion innovation, MIDAS® Gold FCC catalyst. MIDAS® Gold FCC catalyst is the highest activity catalyst in the MIDAS® series. The incorporation of industry-leading metals traps and a further optimization of catalyst matrix porosity enables refiners to drive conversion deeper into the bottom of the barrel. Placid’s application of the novel MIDAS® Gold catalyst improved FCCU profitability by reducing production of lower value streams (bottoms and dry gas), and increasing production of liquid fuels. MIDAS® Gold FCC catalyst allowed Placid to increase profitability despite unpredictable feed quality variations and high contaminant metals. The MIDAS® Gold FCC catalyst provides yet another layer in portfolio flexibility by which a refiner can partner with their Grace technical service team to tailor their yield profile and maximize FCCU profitability.

Figure 12: Ecat ACE Testing from Placid FCCU showing a reduction in H2 production across a range of contaminant metals after the unit switched to MIDAS® Gold (top). Commercial operating data from Placid FCCU shows a reduction in H2 production when the unit shifted to MIDAS® Gold catalyst (bottom).

Figure 13: Refinery A realized a 15% reduction in bottoms yield with MIDAS® Gold compared to the competitive benchmark.

Reference:
MIDAS® GOLD
The Gold Standard for Resid Upgrading

MIDAS® FCC catalysts are Grace’s high matrix catalysts with proven success for deep conversion of resid. MIDAS® Gold, the latest member of the family, is a high activity formulation that delivers

▶ Superior coke-selective bottoms upgrading
▶ Stable activity against metals contamination
▶ Formulation flexibility for a customized yield profile

We offer several distinct MIDAS® formulas, suitable for a broad range of feed and operating objectives. Let Grace technical experts show you the best fit for your operation.

grace.com
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Achieving Advantages with State-of-the-Art FCC Catalyst Solutions

Christophe Chau, Grace
Rosann Schiller, Grace

The drop in crude prices affects individual customers in different ways, as refiners reoptimize process and yield objectives based on the availability and cost of crude. In response, Grace is commercializing a slate of new FCC catalysts to provide solutions for refiners’ current needs. The new products will complement the products launched over the last two years that were focused on resid conversion and managing shale or tight oil feedstocks in the FCC.

A History of Innovation
Grace has a history of providing value to its customers with new products through innovation. A recent example is the product innovation resulting from the rare-earth supply crisis in 2010. Eight (8) new low- or no-rare-earth FCC catalysts and additives were commercialized, reducing the risk posed by limited rare-earth supply for most of our customers. The ACHIEVE® series (100, 200, 300, 400, 800) comprises state-of-the-art catalysts technologies designed to increase refinery profitability. To maximize the value from their fluid catalytic cracking (FCC) units, refiners seek to increase processing of opportunity crudes as well as capture economic opportunities as crack spreads fluctuate. As refiners adjust their operating conditions and yield objectives in response to the current market environments, Grace’s newest FCC catalytic solutions will help them maximize profit and manage the uncertainties of increased opportunity crude processing.

The ACHIEVE® series of FCC catalysts
In response to the tight oil revolution in the United States, Grace launched the first product in the series, ACHIEVE® 400 FCC catalyst, addressing the octane debits that were being encountered by North American refiners. This breakthrough technology has delivered an economic uplift on the order of $3-7M/yr in multiple commercial applications due to the boost in slurry conversion, FCC naphtha octane, and butylene yield.

During this research and development program, five key catalytic functionalities were developed to provide the yield flexibility desired by refiners.

- Increase distillate yields with high diffusivity matrices
- Reduce dry gas with advanced metals traps
- Drive conversion with ultra-high activity zeolites
- Maximize resid processing with leading coke selectivity
- Boost refinery octane with dual-zeolite technology

Designing the best catalyst systems from these functionalities encompasses the Grace approach to customized FCC catalyst design. Every ACHIEVE® formula contains high diffusivity matrices to maximize distillate yield from the bottom of the barrel and provide resistance to poisoning from unconventional metals. ACHIEVE® catalyst can be formulated over a range of activity, rare-earth exchange, and isomerization activities. Grace’s capability to modulate hydrogen transfer activity in our self-manufactured zeolites, affords each refiner the optimal LPG to gasoline ratio for their operation.

The individual ACHIEVE® catalyst series are differentiated by the incorporation of varied functionality, specifically chosen to meet the desired yield and process objectives of the individual refiner. Inclusion of Grace’s latest generation of integral metals traps protects active components from deactivation while preserving coke selectivity and minimizing dry gas production. Improvements in coke selectivity enable the refiner to maximize processing of resid or other opportunity feed stocks. Refiners wishing to drive to high conversion benefit from ultra-high activity zeolites. Additionally, the dual-zeolite option delivers increased naphtha octane as well as increased LPG olefinicity: butylene, propylene, or both.

Christophe Chau has over 20 years of experience in refining catalysts. This experience includes new catalyst development, catalyst evaluation and scale-up, and technical service. He joined Grace in 2014 and is currently Marketing Manager for Refining Technologies in EMEA and CIS. He holds a Chemical Engineering degree and a PhD in heterogeneous catalysis.

Rosann Schiller is Marketing Director, Refining Technologies. Rosann joined Grace in 1998 and has held roles in Technical Service, Technical Sales, and Marketing. She most recently served as Marketing Director, FCC Commercial Strategy. She earned her Master’s Degree in Chemical Engineering from Johns Hopkins University.
The following examples illustrate how the flexibility of the ACHIEVE® catalyst family have been applied commercially to improve FCCU yield and profitability.

**Figure 1: The critical functions of ACHIEVE® technology platform promote five core catalytic opportunities.**

### Commercial Case Studies

**Maximize Conversion with ACHIEVE® 100 Catalyst**

When processing lighter feedstocks, insufficient catalytic activity requires that the catalyst circulation rate increase so that conversion, and thus the coke yield from the catalyst, increases to satisfy the FCC heat balance. If the FCCU cannot physically circulate enough catalyst, it will be necessary to either reduce the unit charge rate or the reaction severity to stay within the FCC catalyst circulation limit. Use of a high activity catalyst can counter the effects of low delta coke, but it is important to select a catalyst with the proper coke selectivity (coke to conversion relationship). ACHIEVE® 100 catalysts are formulated with ultra-high activity zeolite to counter the effects of low delta coke, while delivering the proper coke. In commercial application, ACHIEVE® 100 catalyst delivered enhanced activity over a competitive catalyst. At constant coke, the switch to ACHIEVE® 100 catalyst resulted in higher activity, higher gasoline and lower bottoms and an economic uplift of ~$0.40/bbl (Table 1).

**Increase Fuels Yields with ACHIEVE® 200 Catalyst**

Grace has been highly successful incorporating both nickel and vanadium metals trapping into FCC catalyst, mitigating the negative impacts of the metals. Currently 65+% of our worldwide customers are taking advantage of these innovations in their catalyst formulations.

<table>
<thead>
<tr>
<th>Competitive Base</th>
<th>ACHIEVE® 100</th>
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<tbody>
<tr>
<td>C/O Ratio</td>
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<tr>
<td>Conversion, wt%</td>
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<tr>
<td>Dry Gas, wt%</td>
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<td>LPG, wt%</td>
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<td>LCO, wt%</td>
<td>17.2</td>
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<tr>
<td>Bottoms, wt%</td>
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</table>

**Table 1: ACHIEVE® 100 catalyst outperforms competitive technology in a light feed application at constant coke.**

An example of excellent metals trapping performance is evident in ACHIEVE® 200 catalyst system as shown in Figure 2. Refinery operating data after the reformulation to ACHIEVE® 200 catalyst resulted in higher gasoline yields and lower hydrogen, delta coke and slurry yield. The superior metals tolerance of the ACHIEVE® catalyst allowed the refiner to increase conversion without increasing catalyst addition rate. The changes in operating conditions and yields after moving to ACHIEVE® catalyst are summarized in Table 2, and the increase in gasoline yield and drop in slurry resulted in a benefit of ~$0.70/bbl for the refinery.

**Boost Refinery Octane with ACHIEVE® 400 Catalyst**

A common challenge reported by refiners operating on unconventional feeds, such as shale or tight oil, is a loss of gasoline pool octane, caused by reduced volume of alkylation feedstock. ACHIEVE® 400 catalyst is formulated with multiple zeolites with tailored acidity, to deliver an optimum level of butylenes to keep the alkylation unit full and maintain refinery pool octane. Incorporation of isomerization activity into the catalyst particle itself results in a more desirable yield pattern than would be realized by use of a traditional octane boosting FCC additive. In addition, ACHIEVE® 400 has been shown to increase the octane of FCC naphtha. In multiple commercial trials, ACHIEVE® 400 is delivering incremental octane and butylene, worth on average $0.60/bbl.

**Manage Unconventional Metals with ACHIEVE® 800 Catalyst**

A resid unit experienced deteriorating performance as a result of processing high-carbon, high-iron opportunity feedstock and experienced iron poisoning. The symptoms of iron poisoning include a loss of bottoms cracking, as feed particles are blocked from entering the catalyst
particle, and a drop in conversion. Catalyst design can be optimized to resist the effects of contaminant iron (and calcium) found in many opportunity feedstocks. The high diffusivity matrices in ACHIEVE® an optimum distribution of mesoporosity, maintaining performance at high-contaminant metals loading, because diffusion to active sites remains unhindered. Commercial data demonstrate an improvement in gasoline and distillate yield, and a reduction in both dry gas and bottoms yields due to improved coke selectivity. The shift to ACHIEVE® in an annualized yield improvement of $0.95/bbl over the base catalyst formulation.

ACHIEVE® the Advantage™
Processing additional opportunity crudes, as well as upgrading the bottom of the barrel into light cycle oil (LCO) and lighter products, are two ways refiners can maximize the value from their FCCU. The ACHIEVE® (100, 200, 300, 400, 800) comprises state-of-the-art catalysts technologies that are in multiple commercial applications today. The new technologies are enabling refiners around the globe to capture opportunities in a dynamic market.

The ACHIEVE® series is a suite of tailor-made catalytic solutions, optimized to meet specific refinery opportunities while not exceeding operating constraints. Grace is proud of our close customer partnerships and broad product portfolio built on talent, technology and trust. Our commercial and technical service teams are ready to work with each refiner to select the catalysts with the right balance of operational flexibility, product capability and overall value to meet the individual requirements for each FCC.

Please visit grace.com or contact your local Grace representative to learn more about the ACHIEVE® catalyst series.
Case Studies Prove Value of EnhanceR™ Platform

Dan McQueen, Grace  Christophe Chau, Grace

Grace’s EnhanceR™ platform is the leading FCC catalyst technology in EMEA. Over 70% of all residue processing FCCUs in EMEA (Ecat Ni+V > 5000 ppm) use EnhanceR™ technology. The EnhanceR™ series is the No. 1 selling technology in EMEA and includes NEKTOR™ 4G, a catalyst featuring advanced metals tolerance and flexible hydrogen transfer, and ResidCrackeR™ 4G, a catalyst which delivers improved slurry conversion to distillate via high diffusivity matrix.

The following case studies illustrate the commercial benefits of these latest generation technologies.

Improving Refiner Profitability
NEKTOR™ 4G was successfully used in a coke-burn limited FCC unit at Refinery A. Refinery A operates a 50 kBPD FCCU of UOP design. Due to regenerator temperature constraints, the amount of residue is limited. The switch to NEKTOR™ 4G catalyst resulted in lower delta coke. This led to a cat/oil increase of +0.5 and an increase in unit conversion of +0.7 wt%, NEKTOR™ 4G’s lower delta coke, as illustrated in Figure 1, relieved the regenerator bed temperature constraint. The refinery was able to use the improved delta coke to process heavier feeds which in turn boosted profitability by approximately $5 per ton of feed (see Table 1).

NEKTOR™ 4G catalysts bring the following performance benefits to unit operations:

- lowest delta coke for heavy metal feeds
- excellent coke to bottoms performance
- high intrinsic activity and stability
- excellent attrition resistance

In another case study ResidCrackeR™ 4G was successfully used in Refinery B. Refinery B operates a 30 kBPD FCCU and was seeking to improve bottoms upgrading into max LCO, within the regenerator temperatures and air blower limitations. ResidCrackeR™ 4G provided a 1-2 wt% boost in LCO yield through enhanced bottoms upgrading, as illustrated in Figure 2, without compromising the excellent coke selectivity of the base catalyst.

The use of ResidCrackeR™ 4G resulted in better bottoms upgrading into LCO while maintaining excellent coke selectivity. The FCC unit at Refinery B was able to increase its operating window and process more residue.

ResidCrackeR™ 4G catalysts bring the following performance benefits to unit operations:

- premium bottoms upgrading
- selective cracking towards LCO
- excellent coke selectivity
- excellent attrition resistance

The success of the EnhanceR™ technology platform which resulted in the NEKTOR™ 4G and ResidCrackeR™ 4G catalysts has been proven in EMEA. Additional trials are in progress.

Normalized shifts vs. base

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Shifts vs. Base</th>
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<tr>
<td>Conversion</td>
<td>+0.7 wt%</td>
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<tr>
<td>C1+C2</td>
<td>-0.5 wt%</td>
</tr>
<tr>
<td>C3+C4</td>
<td>+1.3 wt%</td>
</tr>
<tr>
<td>Gasoline</td>
<td>-0.1 wt%</td>
</tr>
<tr>
<td>LCO (wt%)</td>
<td>-0.5 wt%</td>
</tr>
<tr>
<td>Slurry</td>
<td>-0.2 wt%</td>
</tr>
<tr>
<td>Regenerator T(°C)</td>
<td>-16°C</td>
</tr>
<tr>
<td>Cat/Oil</td>
<td>+0.5</td>
</tr>
<tr>
<td>Unit profitability</td>
<td>+ $5/MT feed</td>
</tr>
</tbody>
</table>

Table 1. NEKTOR™ 4G improved unit profitability by $5 per ton of feed processed by allowing greater flexibility to process heavier feed in Refinery A.

Figure 1. NEKTOR™ 4G enabled heavier feed processing through lower delta coke at Refinery A.

Figure 2. ResidCrackeR™ 4G technology improved bottoms upgrading into LCO while maintaining coke selectivity at Refinery B.
Leading the Way with Fixed Bed Resid Hydroprocessing Technologies

Helping Refiners Take Advantage of Heavier Feeds

Refiners today are challenged to produce transportation fuels containing near-zero levels of contaminants. At the same time, high crude oil prices rationalize capital projects to produce cleaner products from heavier feeds. There has been significant growth in worldwide Resid Desulfurization/Vacuum Resid Desulfurization (RDS/VRDS) capacity in the past 20 years to meet the growing global demand for cleaner fuels and petrochemicals, and to enable processing of heavier crudes. Refiners are challenged to maximize profitability by running poorer quality, opportunity feeds that simultaneously impact many of the operating units. RDS and particularly the integrated RDS/RFCC unit complex are refinery processes in which properly designed catalyst systems can enable refiners to take advantage of heavier feeds.

RDS Operation

RDS/VRDS units operate in two primary modes: low sulfur fuel oil (LSFO) or resid FCC feed mode (RFCC). In LSFO mode the product from the unit goes to the refinery fuel pool, and the key product specification is sulfur. In RFCC mode, the product from the RDS unit needs to meet more stringent requirements of low MCR, metals, sulfur, and nitrogen before it goes to the downstream resid FCC unit (see Figure 1). Globally 73% of existing resid desulfurization units produce feed for RFCC units. RFCC unit objectives could be to maximize transportation fuels, or the desired FCC products could be petrochemical feedstocks, as is often the case for the Asia Pacific region. There is operating flexibility for an FCC unit that is derived from the daily catalyst replacement rate (on the order of 0.2 to 0.4 lb catalyst/BBL of feed). Catalyst additions can be increased to compensate for poorer feed quality; however this negatively impacts the refiner’s profitability. Therefore, RDS/VRDS product specifications for RFCC mode can encompass a broad potential range of concarbon (MCR), metals [nickel (Ni), vanadium (V), iron (Fe)], and sulfur contents as shown in Figure 1.

To achieve this wide range of potential RDS product objectives, the design of RDS/VRDS catalyst systems is a methodical process that incorporates products from four functional groups: Demetallization, Transition, HDS/HDMCR, and Deep HDS/HDMCR/HDN. Each RDS/VRDS catalyst system is unique in terms of the quantity of each functional group used, the specific products selected within a group, and the location of these products. Proper catalyst system design can 1) significantly improve the yield and product quality of the RDS/VRDS unit, 2) enable the refiner to process poorer quality feeds, or 3) extend run length of the unit. ART has been extremely successful in continually improving RDS operations through focused R&D efforts to develop and commercialize catalysts across the functional groups that extend the capability of the RDS/VRDS unit (Figure 2).

Dr. Babu Patrose is Director of Sales for Advanced Refining Technologies. Dr. Patrose’s career of 33 years in Refining Catalysts includes 15 years in Resid Hydroprocessing R&D, followed by assignments in Technical Sales and Marketing for FCC and RDS catalysts. Prior to his current role Babu served as ART’s Global Product Segment Director for RDS catalysts. He received his B.S. from the Indian Institute of Technology and his M.S. and Ph.D in Chemical Engineering from Lehigh University.
Strong customer involvement in ART’s product development process insures that new catalysts continue to support key industry trends and meet evolving customer needs. As a result, ART supplies 60% of the RFCC feed units and 57% of the LSFO units that are currently operating worldwide. Customers have been pleased with the results. More than three-quarters (76%) of the RDS units that ART supplies continue to retain ART as their supplier for more than five years, and roughly half of them have multi-year supply contracts with ART. Refiners extend their supply relationships with ART due to continuous improvements in catalyst system performance as shown in Figure 3. This refiner, located in Asia Pacific, processed significantly poorer quality feed over the course of six sequential runs while maintaining their target one-year run length and producing product to specifications.

This was possible due to continuously evolving catalyst system designs that created the capacity needed to process poorer quality feed without sacrificing other run objectives. The refiner processed cheaper, heavier crudes and greater amounts of low value opportunity crudes which resulted in the declining feed quality to the RDS, but increased their profitability by more than $60 million over five years.

**RDS CATALYST SYSTEM DESIGN**

Improved catalyst system design is possible due to constant development of new products within each of the four catalyst functional groups. While overall catalyst system performance typically achieves 85-95% removal of feed sulfur, 70-98% removal of feed metals, and 30-65% removal of MCR, the ultimate performance of a catalyst system for a given feed is dependent upon the functional group components. The functional groups are arranged in order according to Figure 4.

The ability to customize base alumina structure to tailor pore sizes, and also control metals dispersion and activity is critical to creating a portfolio of catalysts that when combined provide the required overall system performance. Beginning at the top of the reactor, demet catalysts with open pores to capture particulates and metals are the essential leading component to insure protection of downstream conversion catalysts. Transition catalysts pickup where demet catalysts left off, removing remaining feed metals while shifting performance focus to sulfur removal. Catalyst pore structure becomes more tailored and moderate metals loadings are incorporated to accomplish both tasks. Conversion and deep conversion catalysts perform the bulk of feed treatment, and catalyst structure shifts to create high amounts of surface area and accommodate maximum levels of active metals necessary to reduce sulfur, nitrogen, and MCR.
Improved RDS Catalysts

Two examples of new products in different functional groups resulting from ART’s significant catalyst development efforts are ICR 187 and ICR 192.

ICR 187 is an enhanced demet catalyst that was developed to provide higher metals capacity than ICR 161, providing greater protection of downstream conversion catalysts. Improved metals removal is achieved through design of a tailored catalyst structure, shown in Figure 6, which enables feed molecules to access mesopores residing in the structure.

Greater access of feed to mesopores improves HDM activity and increases metals capacity, which is necessary for processing more challenging feeds with higher metals content.

Figure 7 shows the improved metals removal capacity for ICR 187 compared to ICR 161. Refiners could alternatively take advantage of the higher metals removal capability to increase RDS/VRDS unit run length.

Poorer quality feeds with higher metals content also require higher capacity for MCR, sulfur and nitrogen removal. Catalyst systems incorporating improved conversion catalysts create even greater capacity for processing challenging feeds, thereby boosting profitability.

Figure 8 shows how ART has continuously extended the performance of its deep conversion catalyst portfolio over the last decade.

Better performing conversion catalysts need enhanced hydrogenation to maintain product specifications in the face of increasing customer feed contaminant levels. Diffusion becomes more rate limiting for sulfur removal (HDS), MCR conversion (HDMCR), and for nitrogen removal (HDN) as metals and coke that are present in increasing concentrations in poorer quality feeds deposits in catalyst pores, as shown in Figure 9.

ICR 192 is ART’s latest deep conversion catalyst with significant improvement in HDS, HDMCR and HDN over ICR 171, the prior conversion catalyst incorporated into ART RDS/VRDS catalyst systems (see Figures 10 through 12).

Figures 11 and 12 show extended aging results for ICR 192 tested with atmospheric resid where the performance advantages in HDMCR and HDS are all maintained over the base ICR 171 catalyst for the duration of the deactivation period.
Figure 13 shows that ICR 192 has 20% higher initial HDN activity, and the advantage remains consistent from start of run to end of run.

Additionally, ICR 192 diesel cut (350-680°F) contains 18% lower sulfur and nitrogen, which can potentially alleviate diesel pool blending constraints.

The performance enhancement for ICR 192 is derived from higher metals levels in the catalysts but with modified pore structures to insure active participation by the metals present.

RDS/RFCC Improves Refinery Economics
The combination of new products in ART’s portfolio and the knowledge of how to incorporate the best combination of products for each unique customer application into ART’s RDS/VRDS catalyst systems enable our customers to process tougher feedstocks and extended operations as they progress from run to run. ART catalyst systems also create opportunity beyond the RDS/VRDS unit, particularly when the unit is upstream of an RFCC unit.

An example follows in Table 1 where improved RDS performance is used to drive economics to more lucrative RFCC operation. In Case 1 RDS/VRDS catalyst improvements reduce MCR, metals, and nitrogen levels in RFCC feed by 10%. The lower metals in feed results in higher RFCC catalyst activity, and the combination of lower metals with reduced MCR content produces less coke. Higher activity and lower coke yield results in greater yields of more profitable products at the expense of less profitable products. Key RFCC operating variables are held constant (catalyst addition rate, feed rate, feed temperature, riser temperature) for the example.

Typical Asia Pacific region economics for both feed and products indicate that the Improved RDS (Case 1) results in $1.20/BBL higher margin than the base case. For a refiner processing 50,000 barrels per day in the RFCC unit, incremental profit of over $21.5 million dollars annually is achieved by improving the upstream RDS unit performance. In an alternate scenario to Case 1, the refiner could opt to
reduce expenses by using the improvement in RDS/VRDS unit performance to reduce RFCC catalyst addition rate by an estimated 10% (Table 1, Case 2). This brings Ecato metals up and Ecato MAT activity back to base levels, reducing RFCC bed temperature and resulting in higher catalyst circulation rate that slightly offsets yield losses from the higher metals on catalyst.

Applying the same Asia Pacific region economics to Case 2 results in slightly lower margin than Case 1. The RFCC operation in Case 2 still results in $0.97/BBL higher margin than the base case, but the margin has declined due to poorer yields with lower RFCC catalyst additions. For a refiner processing 50,000 barrels per day, incremental profit of over $17.4 million dollars annually is achieved by this operation with improved upstream RDS unit performance.

More important than reduced RFCC catalyst expenses, the refiner could process cheaper, heavier crudes and/or incorporate an estimated 5-10% additional atmospheric resid (AR) into the RFCC feed at similar product yields. The AR could be purchased on the open market, or incrementally produced from the upstream crude unit. It is estimated that the profit generated by introducing incremental AR into RFCC feed could be worth about $28.8 million per year to the example Asia Pacific refiner with a 50,000 barrel per day RFCC unit.

Alternatively, 5-10% low value vacuum resid (VR) could be processed through the RDS unit without negative impact on downstream RFCC unit yields. It is estimated that this incremental VR case would be worth $36 million per year to the example refiner in the Asia Pacific region.

It is understood that individual refinery economics likely differ from those provided in the examples, as feedstock availability and regional product demands can shift pricing significantly. However, the opportunity provided by improved RDS catalyst system performance is significant for any refiner desiring to process more resid through their refinery process units.

Catalyst System Optimization
ART works with each customer to understand the best use of our continuing RDS catalyst developments. Technical service personnel design catalyst systems to provide RDS/VRDS unit performance improvements aligned with each refiner’s capability and objectives. Our catalyst development pipeline incorporates industry trends, regionally specific feed/product attributes and an understanding of upstream/downstream economics to establish step-out targets for each of the four functional groups. As soon as new products are commercialized that meet targets, subsequent targets are established for R&D, enabling ART to continue providing catalyst systems that exceed prior system performance. Refiners can benefit from the resulting RDS unit operation improvements in a variety of ways, and ART works with customers to attain the optimal mode of operation.

<table>
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<tr>
<th>Catalyst System Optimization</th>
<th>Base Case</th>
<th>Improved RDS</th>
<th>Improved RDS + Lower RFCC Catalyst Additions</th>
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Table 1: Improved RDS Performance Enhances RFCC Yields and Refining Profitability
Global leader in hydroprocessing catalysts offering the complete range of catalysts and services
Understanding the Potential for FCC Feed to Generate Valuable Products

Abstract
In this work, over 100 FCC feed samples, originating from diverse geographic locations and consisting of assorted FCC refinery streams, were assembled. To assure applicability to industrial processes, the following refinery streams, which are frequently part of the riser feed blend, were included in this study: Atmospheric and Vacuum Gas Oil, Light and Heavy Coker Gas Oil, Hydrocracked Residue, Atmospheric Residue, and Deasphalted Oil. All of these feeds were characterized for the following physicochemical properties: density, boiling point temperature distribution by SIMDIS, Refractive Index, Conradson Carbon, total and basic nitrogen, Sulfur, and Metal content. Hydrogen content was assessed by H-NMR. Other specialized techniques, such as SARA, UV-vis, and Mass Spectrometry for selected samples characterization were also employed to study the hydrocarbons types and the chemical composition. At the end, all feeds were evaluated in the ACE pilot plant using two different commercial FCC catalysts. These catalysts were laboratory-deactivated using CPS metal-free deactivation protocol. The rationale for using metal-free lab-deactivated catalysts, besides simplifying the analysis, was to focus on the interactions between catalyst active sites (zeolite and matrix) and hydrocarbon feed components during the cracking process.

Detailed statistical analysis of feed samples properties produced correlations that would allow FCC refinery engineers to infer other unknown feed properties when only limited feed characterization information is available. Another aspect of this research resulted in the development of the tools for prediction of hydrocarbon type distribution in the feed simply based on just feed density and boiling temperature distribution data. However, the most useful finding is a set of correlations between different feed properties and products yield obtained from pilot plant experiments. Reliable predictions were obtained for different FCC products, Dry Gas, C3 and C4 Olefins, Gasoline and its quality expressed by RON and MON, LCO, Bottoms, and Delta Coke. Because the pilot plant data is frequently used to evaluate the feed and catalyst interactions under standard conditions, the tools developed here would help refinery engineers understand the effect of each feed component on the heat balance, product yields, and gasoline quality. Knowing the feed quality and its theoretical cracking capabilities would allow FCC operators to make appropriate changes in operating conditions, such as catalyst addition rate and riser and feed preheat temperature, to maximize feed potential and useful product yields. Some practical examples were provided for applying such statistical models to aide field operations.

How To Estimate Product Yields
FCC unit feed is the most important variable of the process, because it has the greatest impact on operating conditions, yield and product quality. A feed for any FCC unit basically consists of the following hydrocarbon families: paraffins and cycloparaffins, which are the saturates;
aromatic hydrocarbons with a different number of aromatic rings; and resins and asphaltenes, in cases where residue is processed. Feed behavior in the riser also depends on the mechanical and operational conditions of the unit, and the concentration and distribution of these hydrocarbon families.

Therefore, the feed quality depends on the following factors: quality and type of crude processed by the distillation units and the refining systems existing in the refinery. The products of these alternate processes, such as the thermal conversion units like delayed coking, flexicoking and visbreaking, the hydrogen adding units like gas oil and residue hydrotreatment, and the hydrocracking of gas oil, liquid-liquid deasphalting units like the DEMEX process, and streams from lubricant production are sent to the FCC unit.

One of the biggest advantages of the FCC process is the flexibility to process all kinds of streams that are normally sent as complex mixtures, where the mixing processes are not always efficient enough to ensure a completely homogeneous blend. In general terms, the FCC unit feeds worldwide are blends of the following streams: atmospheric and vacuum gas oils as the major components, atmospheric residues, coker and visbreaking gas oils, hydrocracking residues, hydrotreated gas oils and residues, furfural extracts, demetallized oil (DMO), etc. However, one of the greatest weaknesses and problems in refineries is the lack of physical-chemical analyses for proper feed characterization and, what is more important for engineers, supervisors, and operators, the ability to predict the impact of the feed on yield, operating conditions (heat balance), and product quality.

The purpose of this paper is precisely to provide the staff of FCC units with useful tools to quantify the potential yield of the feed determined by chemical composition, i.e. by the different hydrocarbon families. However, the most important thing is that these potential yields are calculated using properties typically analyzed in any refinery laboratory in the world, such as specific gravity, distillation, sulfur content, and refractive index.

To conduct this study, Grace selected more than 100 types of FCC feeds from all over the world with different compositions. These feeds contain all the streams mentioned earlier, which are normally used in the patterns to feed these units. °API was used as selection criterion, considering feeds between 11 °API and 32 °API.

Feeds were fully characterized by all the physical-chemical analyses mentioned herein. The types of hydrocarbons in the feeds were determined by SARA analysis, mass spectrometry, UV-Vis and 1H-NMR, to quantify hydrogen content, which is an important property of FCC feeds.

Potential feed yields were analyzed in an ACE (1) unit under the following operating conditions: Reaction temperature 527°C (980°F), reaction time of 30 sec., feed flow 3 g/min., catalyst/oil ratio of 4.0, 6.0, and 8.0, adjusted by varying the amount of catalyst in the reactor. Two Grace commercial catalysts were used, deactivated by the CPS unit at 793°C (1460°F) (2); the properties of the deactivated catalysts are reported in (3,4). It is important to mention that the catalysts were deactivated in the absence of metals, since the purpose of the study was to study the interaction of the active sites of the catalyst (matrix and zeolite) with the different types of hydrocarbons in the selected feeds; and the metal contaminants (Ni and V) interfere with the reactions of hydrogen transfer, dehydrogenation and catalytic activity, which was not in the interest of this research.

Feed Classification
In order to understand FCC feed composition, they have to be classified by hydrocarbon type. There are many methods to do so in literature (5, 6, 7). In this paper, we used Correlation Index (CI) and hydrogen content. Correlation Index (6) is a property developed to classify crudes and petroleum fractions by the US Bureau of Mines, according to the following equation:

\[ \text{Correlation Index} = 473.7*d + \frac{48640}{(K+273)} - 456.8 \]

Equation 1

Where K is the mid-boiling point in °C and d is specific gravity. The meaning of this property is very similar to the K characterization factor. However, unlike the K factor that ranges between 11.0 and 13.0, CI ranges from 0 to 100. In this wide range, n-heptane = 0, cyclohexane = 50, while benzene = 100, which leads to the conclusion that low values correspond to paraffinic feeds, values close to 50 are typical of naphthenic feeds and higher values are of feeds that have a larger proportion of aromatic hydrocarbons.

Studies conducted with gas oils from different crudes (8) established that paraffinic feeds have a CI of less than 42. CI between 42 and 55 are cycloparaffinic, so as CI reaches about 50, the proportion of paraffinic hydrocarbon decreases and naphthenic hydrocarbons increases.
In values between 50 and 55, the proportion of aromatic hydrocarbons begins to increase. Feeds with values over 55 can be classified as aromatic (Fig. 1).

The hydrogen content of all the feeds was measured using hydrogen nuclear magnetic resonance (1H-NMR) (3,4). In accordance with this property, the hydrogen content in paraffinic feeds (K factor > 12.0) is greater than 12.8[%,], while naphthenic feeds (K factor between 11.5 and 11.8) have a hydrogen concentration ranging from 12.0 to 12.8[%]. Finally, the hydrogen content of aromatic feeds is less than 12.0[%]. Hydrogen content is an important property of FCC feeds, because it defines, as will later be demonstrated, the yield distribution of valuable products, because the higher the hydrogen content in the feed, the more hydrogen will be distributed in the valuable FCC products (7).

The feeds studied in this project were selected with a wide ⁶API range: between 11.4 and 32.4⁶ API, which is equivalent to hydrogen content between 9.5 and 14.25[%] and a correlation index ranging from 24 to 88. This wide range comprises virtually all the combine feeds and the different components used in the different FCC units in the world.

**Chemical Composition of FCC Feeds**

Since one of the purposes of the study was to demonstrate that the behavior of FCC feeds was due to the types of hydrocarbons present, hydrocarbon distribution was analyzed using different methods: SARA analysis, mass spectrometry, and UV-Vis. This information was used to develop correlations for refinery staff to calculate certain important properties of the feed and get a better idea of feed quality and its influence on unit operation.

The first property to be calculated is feed hydrogen content. In this case, the hydrogen content measured by 1H-NMR and Correlation Index was used. As mentioned earlier, CI is a property calculated based on feed density and distillation, which are two properties that are typically measured in all refinery laboratories. Figure 1 concludes that the correlation between these two properties is quite good and is represented by Equation 2, with a correlation coefficient of 0.966 and a standard error of 0.204.

\[
\text{Hydrogen Content, } [\%] = 15.724 - 0.06798\times\text{CI} \\
\text{Eq. 2}
\]

Another important property that defines feed quality is saturate content, defined by the sum of paraffinic and cycloparaffinic (naphthenic) hydrocarbons. Due to the chemistry of cracking reactions, the interactions with the active sites of the catalyst, the catalyst morphology to allow diffusion through the pore system, and the mechanical and operating conditions of the unit, these hydrocarbons must be converted into valuable products, mainly gasoline and LPG at an efficiency of at least 90%. This is why it is important to determine and be able to quantify saturated hydrocarbon content in FCC feeds (Fig. 2).

\[
\text{Saturate Content; } [\%] = \frac{1}{0.15498 - 0.05378\times\ln(\text{H})} \\
\text{Eq. 3}
\]

In this graph, the lowest hydrogen and saturate value belongs to heavy cycle oil, which in some FCC units is sent to the riser as recycled. In addition, the highest values belong to combined feeds of excellent quality and hydrocracking residues.
Other important hydrocarbon families in FCC feeds are aromatics, which cannot be cracked due to the difficulty in accessing the active sites of the catalyst. These hydrocarbons are normally dealkylated, i.e. the lateral paraffinic chains are broken along with the cycloparaffinic rings attached to the aromatic ring. In these hydrocarbons, monoaromatics tend to be dealkylated and the monoaromatic ring with minor lateral groups goes to the naphtha fraction, providing good octane rating. Figure 3 shows the correlation between the hydrogen content and aromatic concentration of the FCC feeds, represented by Equation 4, with a Correlation Coefficient of 0.950 and Standard Error of 2.88.

Aromatic Content; [%] = -95.1947 + 33.86928*(%H) - 1.82886*(%H)^2

Equation 4

In order to validate the calculations of saturate and aromatic content, several feeds were analyzed by Mass Spectrometry (MS). This analytical technique shows the full distribution of the hydrocarbons in the crude oil fractions.

Table 1 shows the comparative distribution of the type of hydrocarbons in Hydrocracking (HCK) residue and vacuum coker gas oil. In addition, it lists certain properties such as H2 content, °API and sulfur content.

Table 1. Hydrocarbon Distribution by Mass Spectrometry

<table>
<thead>
<tr>
<th>Feed</th>
<th>Saturates</th>
<th>Aromatics</th>
<th>Saturates</th>
<th>Aromatics</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>46.00</td>
<td>49.83</td>
<td>46.86</td>
<td>47.88</td>
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<tr>
<td>2</td>
<td>53.47</td>
<td>43.10</td>
<td>57.30</td>
<td>37.38</td>
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<td>3</td>
<td>47.90</td>
<td>42.83</td>
<td>47.50</td>
<td>47.22</td>
</tr>
<tr>
<td>4</td>
<td>54.73</td>
<td>41.90</td>
<td>57.11</td>
<td>37.56</td>
</tr>
<tr>
<td>5</td>
<td>66.17</td>
<td>32.73</td>
<td>66.63</td>
<td>28.73</td>
</tr>
<tr>
<td>6</td>
<td>53.00</td>
<td>39.93</td>
<td>52.44</td>
<td>42.20</td>
</tr>
<tr>
<td>7</td>
<td>58.80</td>
<td>40.33</td>
<td>62.66</td>
<td>32.31</td>
</tr>
<tr>
<td>8</td>
<td>84.50</td>
<td>15.07</td>
<td>77.55</td>
<td>19.81</td>
</tr>
<tr>
<td>9</td>
<td>41.17</td>
<td>50.97</td>
<td>45.01</td>
<td>49.76</td>
</tr>
<tr>
<td>10</td>
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<tr>
<td>11</td>
<td>50.97</td>
<td>43.60</td>
<td>52.73</td>
<td>41.91</td>
</tr>
</tbody>
</table>

Table 2. Hydrocarbon Distribution by MS and Calculated

On the other hand, due to its high diaromatic content, the coker gas oil tends to increase LCO yield, while triaromatics and tetraaromatics are slurry and coke precursors. In addition, the high content of sulfured compounds in coker gas oil explains its high sulfur content.
Analysis by MS was used to corroborate and validate the equations developed to calculate the saturate and aromatic content of the feeds. Table 2 compares the total aromatic and saturate contents reported by MS and those calculated using the correlations presented (Eq. 3 and 4). These results led to the conclusion that the correlations developed are chemically valid because, although the techniques used are completely different, the values obtained were very similar to those reported by MS.

**Calculation of Potential Yields of FCC Feeds**

As mentioned earlier, the main purpose of this paper was to predict the potential yields of FCC feeds and find the determinant variables of this behavior. In order to do so, all the feeds were run through the ACE unit under standard conditions. The following is a brief explanation of the methodology used.

Gasoline yields and the conversion obtained for each feed at the three severities, i.e. the three C/O (catalyst/oil) ratios were linearized building a graph of gasoline selectivity (gasoline yield/conversion) as a function of kinetic conversion (C/100-C), where C is the conversion obtained in the ACE unit (Fig. 4). Once the equation, intercept and slope were obtained, the maximum conversion was calculated, where the maximum gasoline yields is obtained. Figure 5 illustrates the form of a graph of this type, which shows the experimental values obtained in the ACE unit with two catalysts and the theoretic values calculated based on the straight-line equation.

In addition, it shows the maximum gasoline yield and the maximum conversion value at that point. This value is known as the feed crackability factor. Once the maximum conversion (crackability factor) is obtained for each feed, this value is used to calculate the other yields of the FCC products at that point of maximum gasoline yield, i.e. to calculate the yields for dry gas, C3, C3=, C4, C4=, total LPG, gasoline, LCO, slurry and coke. Gasoline is defined by the cut C5-221°C (430°F), LCO was defined by the cut 221-371°C (430-700°F) and slurry or bottoms were defined by the cut 371°C+ (700°F+). In addition, other properties such as FCC naphtha octane RON and MON were calculated at that point and delta coke. In the latter cases, the equation for linearization is based on kinetic conversion.

To calculate these yields, each of the FCC products has to be linearized, for which the ratios listed in Table 3 were used. In this table, the value of C is conversion at maximum gasoline yield. For the purposes of this paper, only the results obtained from the product yields of each of the feeds with Catalyst 2 are shown. The product yields of Catalyst 1, which has higher zeolite content, i.e. greater activity and better selectivity are different.

<table>
<thead>
<tr>
<th>Ratios</th>
<th>X</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Gas (DG)</td>
<td>C/(100-C)</td>
<td>DG Yield</td>
</tr>
<tr>
<td>C3</td>
<td>C/(100-C)</td>
<td>Yield C3</td>
</tr>
<tr>
<td>C3=</td>
<td>C/(100-C)</td>
<td>Yield C3=</td>
</tr>
<tr>
<td>C4=</td>
<td>C/(100-C)</td>
<td>Yield C4=</td>
</tr>
<tr>
<td>LPG</td>
<td>C/(100-C)</td>
<td>LPG Yield</td>
</tr>
<tr>
<td>Gasoline</td>
<td>C/(100-C)</td>
<td>%Gasoline/C</td>
</tr>
<tr>
<td>Coke</td>
<td>C/(100-C)</td>
<td>Coke Yield</td>
</tr>
<tr>
<td>LCO</td>
<td>C</td>
<td>% ALC/(100-C)</td>
</tr>
<tr>
<td>Slurry</td>
<td>1-C/100</td>
<td>Slurry Yield</td>
</tr>
</tbody>
</table>

*Table 3. Ratios to Linearize Yields*
Calculation of Maximum Conversion - Crackability Factor

In order to predict the crackability factor (CF) of the feed, all the physical and chemical properties of the feeds were used; finally, the maximum conversion was defined by the multivariable model of Eq. 5 and Fig. 6.

\[
\text{Crackability Factor} = 450.7 - 1.296 \times \text{API} + 1.53901 \times \text{H}_2 - 0.562 \times \text{CI} - 224.28 \times \text{Ref.Ind} + 10.51 \times \text{N}
\]

Eq. 5

Where: API is the feed °API, H2 is Hydrogen Content, CI is the Correlation Index, Ref. Ind. is the Refractive Index and N is the feed’s total nitrogen. The correlation coefficient was 0.938 with a standard deviation of 1.55.

It is interesting to see how the refractive index, which is a simple property that is easy to measure in refinery laboratories, becomes an important property in predicting the crackability factor of FCC feeds. The refractive index is a property that responds to the type of hydrocarbon in the feeds. If this property is increased, saturate content decreases and aromatics begin to increase, so the crackability of the feed decreases.

Figure 7 shows that the crackability factor can also be calculated directly based on the hydrogen content of the feed using the following equation. Figures 6 and 7 lead to the conclusion that the vast majority of the feeds used in the FCC units have a maximum conversion of more than 70%, where lower values are related to coker gas oils and heavy cycle oils.

\[
\text{Crackability Factor} = \frac{85.87257}{(1 + 399.7161 \times e^{-0.6393 \times \%\text{H}})}
\]

Eq. 6

Calculation of Maximum Gasoline Yield

The potential maximum yield of gasoline is defined as the yield at the maximum conversion point, which is guided by the chemical composition of the feed and the distribution of the hydrocarbon families present. It is important for the refiner to know this value in order to optimize and adjust the unit to obtain this potential yield. The mechanical and operating conditions as well as the type of catalyst are important variables to bear in mind.

To predict the maximum potential gasoline yield of the feeds, the main physical and chemical properties of the feeds were used once again. Figure 8 shows a very good correlation, based on the following model (Eq. 7):

\[
\text{Maximum Gasoline} = 89.6285 + 0.3403 \times \text{Aromatics} + 0.7511 \times \text{CF} - 0.3476 \times \text{Cl} - 61.2848 \times \text{Ref.Ind}
\]

Eq. 7
In this equation, in addition to the properties explained in Equation 5, the multivariable model included aromatic content and crackability factor (CF). The model shows a correlation coefficient of 0.962 and a standard deviation of 1.3. Like in the case of maximum conversion, maximum gasoline yield can be predicted directly based on hydrogen content, saturate content and correlation index. Since it is considered to be applied the most in refineries and in order to simplify the calculation, the equation is included to calculate maximum gasoline yield based on the correlation index (Figure 9 and Eq. 8):

\[
\text{Maximum Gasoline; } [\%] = 46.457 + 0.6382 \times \text{CI} - 0.011 \times \text{CI}^2
\]

Eq. 8

In this case, the correlation coefficient is 0.959 and standard deviation is 1.88. According to these results, most FCC feeds have a correlation index between 35 and 60 for a maximum gasoline yield that can range from 45 to 56[\%], where the higher values are for highly paraffinic, hydrotreated gas oils, and hydrocracking residues.

**Calculation of the Yields of Other Products**

Below are the equations developed by the multivariable model for the different FCC products based on the main feed properties:

**Calculation of LPG Yield**

In many countries, LPG (C3, C3=, Total C4 and C4=) is a very important product, particularly in refineries where there are alkylation and polymerization units for high-octane gasoline production. Therefore, knowing the impact of the feed on the yield of this product is important information when it comes to adjusting the respective operating conditions for the best economic value and where the use of ZSM-5 based olefin additives is a variable to increase the production of these important FCC streams. Equation 9 defines the calculation of LPG yield at the maximum gasoline conversion point. Beyond this point (overcracking), LPG yield is increased by second order reactions and that of gasoline is reduced. The correlation coefficient was 0.91 and standard deviation was 0.64.

\[
\text{LPG Yield; } [\%] = -54.456 + 0.838 \times \text{API} + 0.099 \times \text{Aromatics} + 0.311 \times \text{CF} + 0.317 \times \text{CI} + 7.190 \times \text{N} + 0.455 \times \text{S} + 0.1765 \times \text{Saturates}
\]

Eq. 9

In this equation, S is the sulfur content of the feed. According to the results obtained with the ACE unit and the evaluation conditions of the different feeds, LPG yield ranged from 11 to 23[\%], where the highest values belonged to more paraffinic gas oils, hydrotreated feeds and hydrocracking residues.

In this study, correlations were developed for each of the products that make up the LPG. Below are those of C4 olefins and iC4 only, because they are considered the most important ones for refineries with alkylation units:

\[
C4= \text{ yield } = -26.778 + 0.175 \times \text{API} + 0.0401 \times \text{Aromatics} + 0.073 \times \text{CF} + 12.255 \times \text{Ref. Ind} + 6.770 \times \text{N Basic} + 0.343 \times \text{S} + 0.0591 \times \text{Saturates}
\]

Eq. 10

\[
iC4 \text{ yield } = 14.044 + 0.317 \times \text{API} + 0.095 \times \text{CF} + 0.453 \times (\% \text{H}) + 0.170 \times \text{CI} - 24.943 \times \text{Ref. Ind}
\]

Eq. 11

The correlation coefficient for C4 olefin yield was 0.925 with a standard deviation of 0.26, while for iC4 (isobutane), the coefficient was 0.934 with a standard deviation of 0.20.

**Calculation of LCO Yield**

Light cycle oil (LCO) is another important FCC product, considering the increase in diesel fuel consumption in many countries around the world where, in some FCC units, LCO is one of the main products because it allows the addition of this stream to hydrotreated diesel streams and the increase in the volume thereof in the refinery. Equation 12 and Figure 10 show the results for the calculation of LCO yield.

\[
\text{LCO yield; } [\%] = 114.604 + 0.314 \times \text{API} - 0.618 \times \text{CF} + 0.182 \times \text{CI} - 42.695 \times \text{Ref. Ind} + 6.023 \times \text{N}
\]

Eq. 12

![Figure 10. Calculation of LCO Yield](image-url)
The correlation coefficient obtained was 0.962, with a standard deviation of 0.88. The data in Fig. 10 lead to the conclusion that for most FCC feeds, LCO yield ranges from 15 to 27\%\%. The highest values in Fig. 10 belong to heavy cycle oil and heavy coker gas oils. These results confirm the advantage of recycling heavy cycle oil (HCO) to the riser when one of the unit’s objectives is LCO production.

It is important to point out that the lowest values are from Hydrocracking residues where, despite the low LCO precursor content, identified as all the diaromatic hydrocarbons and sulfured aromatics (<3\%, see Table 1), LCO yield is relatively high. This suggests that LCO in the hydrotreated feeds is produced by dehydrogenation of cycloparaffinic rings and structures as a result of hydro-treatment, which had already been found in previous studies (9 and 10).

**Calculation of Bottoms Yield**

As mentioned earlier, for the purposes of this study, bottoms are the hydrocarbon fractions with boiling points above 371\°C (700\°F). This fraction includes HCO and slurry. The results presented in this paper are those obtained with Catalyst 2 in Figure 5, whose technology is to increase bottoms conversion, mainly focused on LCO.

\[
\text{Bottoms yield, } [\%] = 44.647 - 0.662 \times \text{API} - 0.20 \times \text{Aromatics} - 0.466 \times \text{CF} + 1.541 \times (\% \text{H}) - 9.162 \times \text{N Basic} - 0.405 \times \text{S}
\]

Eq. 13

Equation 13 had a correlation coefficient of 0.924 and a standard deviation of 0.72. These results lead to the conclusion that bottoms yield in the ACE unit for the vast majority of the feeds and a catalyst with an active and selective matrix technology can range from 3\% to 8\%\%, where the lowest values belong to paraffinic feeds and hydrocracking residues.

**Calculation of Dry Gas and Coke Yield**

Dry Gas Yield; [\%] = \(-1.445 + 0.044 \times \text{Cl} + 2.716 \times \text{N Basic} + 0.038 \times \text{CRR} + 0.062 \times \text{S} + 0.020 \times \text{Saturates}\)

Eq. 14

Coke Yield; [\%] = \(-181.786 + 0.384 \times \text{API} + 0.106 \times \text{Cl} + 113.35 \times \text{Ref. Ind} + 0.518 \times \text{CRR}\)

Eq. 15

In Equations 14 and 15, CRR is the Conradson Carbon Residue (\%). The correlation coefficient to calculate dry gas was 0.914 with a standard deviation of 0.13, while for coke, the correlation coefficient was 0.939 with a standard deviation of 0.48.

**Calculation of Delta Coke**

Delta coke is perhaps one of the most important variables in the FCC process, because it governs heat balance. Delta coke is defined as the quantity of carbon that is burned in the regenerator. This value includes the following types of coke:

- Catalytic Coke: produced in the active sites of the matrix and the zeolite
- Contaminant Coke: produced by metals (Ni and V)
- Circulation Coke: the coke absorbed by the catalyst pores and is not stripped
- Coke Additive of the Feed: the heavy fraction of the feed that is not vaporized at the conditions of contact with the hot catalyst from the regenerator.

As mentioned earlier, two metal-free catalysts that were deactivated in the CPS unit were used, so contaminant coke has not been taken into consideration. Furthermore, the desorption process in the ACE unit is very efficient, as it is carried out for at least seven minutes. With these two explanations, it can be concluded that the delta coke under evaluation is the catalytic coke and the coke additive of the feed, which is directly related to the Conradson Carbon Content, as demonstrated in Equation 16, which resulted in a correlation coefficient of 0.956 and a standard deviation of 0.04. Figure 11 shows that the coke (catalytic and feed) transported by the catalyst to the regenerator at the operating conditions of this study ranges for most feeds between 0.2 and 0.7%. Values above 0.8 are blends of feeds with residual components that have high Conradson carbon contents and feeds such as heavy cycle oil and coker gas oils with high coke precursor aromatic contents (triaromatics and heavier).

\[
\text{Calculation of Delta Coke, } [\%] = -26.77 + 0.0294 \times \text{CRR} + 0.037 \times \text{API} + 0.0664 \times (\% \text{H}) + 16.821 \times \text{Ref. Ind} + 0.446 \times \text{N}
\]

Eq. 16

![Figure 11. Calculation of Delta Coke](image.png)
According to the equations to calculate heat balance in the reactor and regenerator, neither the catalyst nor the feed have an impact on coke yield, expressed as %FF at constant operating conditions. Both catalyst and feed have an impact on delta coke, because the difference between regenerator and reactor temperature is governed by delta coke. In other words, for a given reaction temperature, higher delta coke corresponds to higher regenerator temperature. Therefore, the catalyst circulation will be reduced, and the conversion will tend to decrease. This is why delta coke is so important character in characterizing coke selectivity of the catalyst.

Figure 12 illustrates the concept of coke selectivity between the two catalysts used, expressed by the calculation of delta coke. As mentioned earlier, all the feeds were evaluated in the ACE unit with two different metal-free catalysts. Catalyst 1, following deactivation, has a zeolite/matrix ratio of 3.9, while in Catalyst 2, it is 1.1. These differences are due to the fact that the two catalysts were designed for different purposes. Catalyst 2 is for high conversion of bottoms to LCO with good coke and gas selectivity. Notice that although the matrix content between the two catalysts is very different, the delta coke difference is relatively small. However, it is clear that Catalyst 1 has a better coke selectivity factor that can range between 5 and 10% less. This difference will translate into a better heat balance in the unit, i.e. lower reaction temperature and higher circulation. Therefore, Catalyst 1 is better for operations that require improved flexibility in regenerator temperatures, to process, for instance, a large amount of heavy feed.

This shows that the evaluation and selection of the catalyst for an FCC unit is a very important process because it can lead to major economic benefits for the refiner.

Calculation of Octane RON in Naphtha
Research Octane Number (RON) is perhaps the main property to identify FCC naphtha quality. Naphtha RON depends on catalyst properties (type of zeolite), the presence of additives (ZSM-5), operating conditions (reaction temperature) and type of feed.

\[
\text{Calculation of RON} = 177.864 - 0.192 \times \text{CRR} - 0.234 \times \text{API} + 0.0328 \times \text{Aromatics} - 54.942 \times \text{Ref. Ind} + 7.90 \times N \text{ Basic} + 0.229 \times S
\]

Equation 17 shows that naphtha RON is directly related to aromatic content because, as mentioned earlier, if the aromatic content of the feed is increased, gasoline yield decreases, but RON increases due to the presence of monoaromatic hydrocarbons that, upon breaking the lateral chains caused by cracking reactions, become part of the FCC naphtha range. The Correlation Coefficient of Eq. 17 was 0.904 with a standard deviation of 0.30. It is important to point out that the method of the RON (machine) has 0.2-octane repeatability. For the purpose of this study, the RON of the gasoline fraction of syncrude from the ACE unit reactor was measured by gas chromatography and calculated using Grace software. According to the results, the RON of most of the feeds studied ranged from 89.0 to 93.5 octanes.

Application of the Results at the Commercial Plant
To conclude, some examples are presented below to illustrate the application of this paper in the real world, that is to say, at a commercial plant, and how this knowledge can benefit the FCC unit operator.

Procurement of Gas Oils
One of the applications of calculating the chemical properties of the feed and knowing potential yield is in the procurement of gas oils or combined feeds for FCC units. It is a very common practice in many countries, particularly when there are not enough domestic FCC feed components available.

Table 4 provides an exercise carried out for an FCC unit. All the properties reported in the table are calculated using the basic properties measured in the laboratory. It also provides a comparison of the properties calculated for the VGO-Ref and the three bids submitted by the vendors of these products. The VGO-Ref. are the typical properties calculated for the feed that is normally processed in the unit. As you can see, this is very useful additional information for Refinery Management to make better decisions.
According to this information, the best bid that will provide the best economic value more (LPG+Gasoline) for the unit is Bid 2. Bid 2 is very similar to the unit’s typical feed, while Bid 1 is a more aromatic feed with a significant decline in valuable products. In addition, since Bid 1 is more aromatic, the metal and sulfur content is higher than the reference, for instance, the VGO-Ref. has 0.8 ppm of Ni + V, while Bid 1 has 2.1 ppm of Ni+V. The sulfur of the unit’s typical feed is 1.2[%] and that of Bid 2 is 2.3[%], which means the sulfur content of the FCC naphtha would be higher, as well as the addition of fresh catalyst. Bid 1 is probably less expensive than feeds 2 and 3, but if you calculate the loss in valuable products, the increase in naphtha sulfur and the increase in the addition of fresh catalyst, at the end of the day, the unit will most likely be less profitable by procuring this feed. It is important to mention that this is the theoretic yield potential of the feeds, where the deltas presented among the different products herein may be higher in the commercial unit due to the operating conditions and mechanical limitations thereof.

<table>
<thead>
<tr>
<th>Calculated Properties</th>
<th>VGO-Ref.</th>
<th>Bid 1</th>
<th>Bid 2</th>
<th>Bid 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>0.9125</td>
<td>0.9279</td>
<td>0.9042</td>
<td>0.9176</td>
</tr>
<tr>
<td>MeABP, °F</td>
<td>776</td>
<td>831</td>
<td>752.2</td>
<td>834</td>
</tr>
<tr>
<td>MeABP, °C</td>
<td>413</td>
<td>444</td>
<td>400</td>
<td>446</td>
</tr>
<tr>
<td>Correlation index</td>
<td>46.3</td>
<td>50.6</td>
<td>43.8</td>
<td>45.6</td>
</tr>
<tr>
<td>H₂ content, mole%</td>
<td>12.8</td>
<td>12.5</td>
<td>12.9</td>
<td>12.8</td>
</tr>
<tr>
<td>Saturate content, mole%</td>
<td>52.8</td>
<td>49</td>
<td>55.3</td>
<td>53.5</td>
</tr>
<tr>
<td>Aromatic content, mole%</td>
<td>41.8</td>
<td>45.4</td>
<td>39.4</td>
<td>41.1</td>
</tr>
<tr>
<td>Diaromatic content, mole%</td>
<td>13</td>
<td>15.6</td>
<td>11.6</td>
<td>12.6</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.5086</td>
<td>1.5153</td>
<td>1.5082</td>
<td>1.5101</td>
</tr>
<tr>
<td>Maximum conversion, mole%</td>
<td>75.8</td>
<td>74</td>
<td>76.4</td>
<td>76</td>
</tr>
<tr>
<td>Gasoline yield (max. conv.), mole%</td>
<td>51.9</td>
<td>50.5</td>
<td>52.3</td>
<td>52</td>
</tr>
<tr>
<td>LPG yield (max. conv.), mole%</td>
<td>18.7</td>
<td>17.7</td>
<td>18.9</td>
<td>18.8</td>
</tr>
<tr>
<td>Gasoline + LPG, mole%</td>
<td>70.6</td>
<td>68.2</td>
<td>71.3</td>
<td>70.8</td>
</tr>
<tr>
<td>LCO yield (max. conv.), mole%</td>
<td>19.6</td>
<td>20.5</td>
<td>19.1</td>
<td>19.5</td>
</tr>
<tr>
<td>CF</td>
<td>73.5</td>
<td>69.5</td>
<td>75.5</td>
<td>74.1</td>
</tr>
</tbody>
</table>

Table 4. Properties calculated for GO bids

Theoretic Potential Yield and Yield Obtained in the Commercial Unit

Figure 13 provides an example where the unit’s gasoline yields are compared with the theoretic yields calculated at the maximum conversion point.

The data in Figure 13 show that the plant’s gasoline yield tends to decrease from an average value of 50[%] to 47.5[%] at the end of the period. There are many factors that can have an impact here, such as feed quality, operating conditions (reaction temperature, catalyst circulation, C/O ratio, atomization of the feed, addition of fresh catalyst, Ecat activity, etc) and mechanical issues. The maximum conversion calculated from the feed properties also tends to decrease, which explains the decline in the unit’s gasoline yield. Although the calculated maximum gasoline yield potential and unit gasoline yield both tend to decrease, there is a delta of around 2[%] between calculated and achieved yields that could be potentially exploited by adjusting operating conditions. Using this example for an FCC unit of 50,000 BPD, recovering 1% based on feed quality means an increase in gasoline production by 500 BPD i.e. 15,000 barrels/month, which is a significant economic benefit for the refinery and an improvement in its refining margin.

Make Better Decisions to Optimize the FCC Unit

The behavior of feeds and the components thereof in FCC units is governed by chemical composition, type and distribution of the hydrocarbon families contained therein. Hydrogen content of FCC feeds is an important property to define and study their behavior. The most important properties to characterize an FCC feed are: density at 15°C, distillation (D-1160, SimDis), refractive index, nitrogen and sulfur content and Conradson carbon residue. Additionally, the crackability factor (conversion at the maximum gasoline conversion point) is an important property in defining FCC feed quality and delta coke is an important property to define feed impact on heat balance and catalyst coke selectivity.

There are many other cases where the knowledge provided in this paper can be applied to the real world of the commercial units. For instance, this methodology could help in understanding the effects of new feed components, such as coker gas oils, atmospheric residue, hydrocracking residue, and hydrotreated feeds, or changes in component ratios of different streams, such as an increase in the residue or heavy fraction stream in the combined feed, on FCC unit operations. The information provided
herein is useful for the FCC unit engineers to make their calculations and predictions and to review the operating conditions to get the most from the potential volume in the FCC feeds.

Reference:
9. Ian P. Fischer, Uriel Navarro; FCC Feed Characterization for two FCC’s units of the Barrancabermeja refinery (Colombia), Petro Canada project 352-89-53, April, 1989.
Abstract
The CONSISTA® catalyst family for polypropylene (PP) production is a non-phthalate based catalyst that provides outstanding productivity, a broad xylene soluble design window, and very high hydrogen response. This new PP catalyst family has been denoted as 6th Generation (Gen) technology. The phthalate based Z-N catalysts are also known as 4th Gen PP catalysts. This paper focuses on one of Grace’s main PP development themes: clearer materials through catalyst technology. This study specifically compares the properties of multi-axially oriented thermoformed cups produced with PP made with either 6th Gen or 4th Gen catalyst systems. Different CONSISTA® catalyst-based PP materials are tested: homopolymer PP (HPP), low-ethylene-content random copolymer (LER) and random copolymers (RCP). The paper also compares how the nucleator / clarifier package affects the cups’ optical and mechanical properties. A performance map of cup mechanical versus haze properties is provided.

Lighter, Faster, Cleaner, and Clearer with CONSISTA® Catalysts
PP has seen unprecedented growth in thermoforming applications in the last 10 years. This growth has been driven by inter-material inter-process substitution in dairy containers such as bowls for margarine/spreads and the use of PP injection molding for high volume simple symmetrical designs and containers.

These include trays for sandwich meats and other deli items; bakery and produce trays; portion cups (sliced/chopped fruit lunch cups); take-out containers and clear drink cups (fast food, airplane, stadium, cold/coffee applications). In addition to this, the industry is no longer trying to run on polystyrene lines. Instead, machine manufacturers are now building on-purpose PP lines, e.g. OMV lines with improved temperature control, and highly zoned temperature control. Finally, the industry has also seen new resin and clarifier technology that provides better transparency in un-drawn zones, such as the flange around the lip of the trays.

Grace has identified four themes that drive PP product development: lighter materials, faster processing, and cleaner and clearer materials. This study focuses on the fourth theme (clearer materials) and specifically on thermoformed applications for which clarity is a key performance attribute.

Grace commercialized a new family of non-phthalate based PP catalysts in 2011. This new catalyst technology was branded as CONSISTA® catalyst systems and is also known as 6th Gen PP catalysts. The CONSISTA® catalyst family for PP provides outstanding productivity, improved comonomer distribution, a broad xylene soluble design window and very high hydrogen response.

The CONSISTA® catalyst family was developed with the capability to produce broader molecular weight distribution (MWD) PP. It is well known that broader MWD helps PP stretch ability and enhances strength and stiffness in Bi-axial Oriented Polypropylene (BOPP) film (1-4) as well as in thermoformed articles. Low molecular weight (MW) molecules provide easier processability at fabrication conditions while highly aligned, high MW chains and crystal orientation improve film stiffness and strength. Increasing MWD was also found to correlate with decreasing film thickness distribution (1). Finally, CONSISTA® catalyst-systems-based random copolymers (RCP) show a more random ethylene distribution than RCP based on 4th Gen catalysts. This results in enhanced optical properties for the same ethylene content.
This paper is aimed at establishing how the broader MWD and the more random ethylene incorporation of CONSISTA® catalyst-based PP improve properties of thermoformed cups. The paper also studies how two advanced clarifiers, Milliken MILLAD® NX8000 and HYPERFORM® HPN600ei, modify the optical and mechanical properties of CONSISTA® catalyst-systems-based homopolymer PP (HPP), Low Ethylene Content RCP (LER), and RCPs.

Experimental Methods

The HPP, LER, and RCP used in this study were produced at the UNIPOL® PP pilot plant in South Charleston, WV. All materials were formulated with anti-oxidants (Irganox 1010 and Irgafos 168) and an acid scavenger (DHT-4A) in addition to clarifiers (MILLAD® NX8000 and HYPERFORM® HPN600ei).

Pellet Melt Flow Rate (MFR), Xylene Solubles (XS), Polydispersity Index (PI), and FTIR analyses were performed in Grace labs. MFR was measured according to the ASTM method D1238. Xylene Solubles (XS) were measured with a Viscotek instrument equipped with Flow Injection Polymer Analyzer. Sample preparation of Viscotek XS method is very similar to what is described in the ASTM method D5492. Viscotek calculates XS concentration via a Refractive Index method, instead of the filtration method of ASTM D5492. The PI is a rheological measurement that relates to polymer MWD. The PI was measured via a cone and plate Rheometer at 190°C. Polymer melting behavior was measured at a heating rate 10°C/min with a TA model Q1000 DSC. The instrument is equipped with Thermal Advantage software for data acquisition and analysis. Ethylene content was measured with FTIR using a calibration specific to CONSISTA® catalyst systems.

An in-line sheet-forming and thermoforming process was used to produce deep draw cups. Cast-sheet was produced by feeding PP formulated pellets to a sheet-forming line. The line is composed with three major sections (1) Reifenhauser 80 mm single-screw extruder with L/D 33:1, (2) coat hanger-manifold die and (3) water bath and a set of chill-rolls. The 1.9 mm thick sheet was fed into an Illig RDM-54K solid phase former, which is equipped with upper and lower infrared ceramic heaters. Sheet-forming and thermoforming were set at similar conditions for all samples each time. The molded cup is 139 mm tall and 500 ml in volume. It has a wide mouth (93 mm rim diameter) and the opening is gradually reduced to the bottom (59 mm diameter). Cup wall thickness is thicker at the top and gradually reduced toward the bottom. Wall thickness was measured with a Magna-Mike 8500 and was reported as an average of five readings with standard deviation. Cup optics was measured at the same height where wall thickness is around 275 μm. Wall thickness reduction is about seven-fold at this location. Clarity and haze were measured with a BYK Gardner Plus haze meter according to ASTM D1003-11. Gloss was measured with a BYK Gardner micro-TRI-gloss gloss meter according to ASTM D523. Sheet casting, cup forming, and optical and mechanical cup properties analyses were conducted at the Milliken lab in Spartanburg, SC.

Assessing Performance

Four different PP resins were used for this study: a 4th Gen catalyst-based HPP, a 6th Gen catalyst-based HPP, LER, and RCP. Some of these resins were formulated with clarifiers as stated above. Table 1 contains the resin design and formulation details associated with all samples tested in this study.

Table 2 shows all cup performance property values associated with samples A and D for use throughout the paper.

<table>
<thead>
<tr>
<th>Code</th>
<th>Family</th>
<th>MFR</th>
<th>XS (%)</th>
<th>El. (%)</th>
<th>PI</th>
<th>Catalyst</th>
<th>Clarifier</th>
<th>Clarifier Conc. ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>HPP</td>
<td>2.3</td>
<td>2.2</td>
<td>0</td>
<td>4.0</td>
<td>SHAC®</td>
<td>HPN600ei</td>
<td>400</td>
</tr>
<tr>
<td>B</td>
<td>HPP</td>
<td>2.1</td>
<td>3</td>
<td>0</td>
<td>4.6</td>
<td>CONSISTA®</td>
<td>None</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>HPP</td>
<td>2.1</td>
<td>3</td>
<td>0</td>
<td>4.8</td>
<td>CONSISTA®</td>
<td>NX8000</td>
<td>2000</td>
</tr>
<tr>
<td>D</td>
<td>HPP</td>
<td>2.1</td>
<td>3</td>
<td>0</td>
<td>4.6</td>
<td>CONSISTA®</td>
<td>HPN600ei</td>
<td>400</td>
</tr>
<tr>
<td>E</td>
<td>LER</td>
<td>2.1</td>
<td>2.6</td>
<td>0.7</td>
<td>4.6</td>
<td>CONSISTA®</td>
<td>None</td>
<td>0</td>
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<tr>
<td>F</td>
<td>LER</td>
<td>2.1</td>
<td>2.6</td>
<td>0.7</td>
<td>4.5</td>
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<td>NX8000</td>
<td>2000</td>
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<tr>
<td>G</td>
<td>LER</td>
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<td>2.6</td>
<td>0.7</td>
<td>4.5</td>
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<td>HPN600ei</td>
<td>400</td>
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<tr>
<td>H</td>
<td>RCP</td>
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<td>5.8</td>
<td>3.3</td>
<td>4.4</td>
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<td>NX8000</td>
<td>2000</td>
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<td>4.1</td>
<td>4.2</td>
<td>CONSISTA®</td>
<td>NX8000</td>
<td>2000</td>
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<table>
<thead>
<tr>
<th>Code</th>
<th>Cup Haze %</th>
<th>Cup Clarity %</th>
<th>Cup Ext 20° Gloss %</th>
<th>Cup Int 20° Gloss %</th>
<th>Cup Top-Load N</th>
<th>Cup Side-Wall N</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>5.6</td>
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<td>44</td>
<td>10</td>
<td>254</td>
<td>4.9</td>
</tr>
<tr>
<td>C</td>
<td>3</td>
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<td>92</td>
<td>91</td>
<td>304</td>
<td>4.9</td>
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<tr>
<td>D</td>
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<td>96.9</td>
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<td>77</td>
<td>273</td>
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<td>92</td>
<td>237</td>
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<td>90</td>
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<td>91</td>
<td>81</td>
<td>200</td>
<td>3.7</td>
</tr>
<tr>
<td>I</td>
<td>2.2</td>
<td>97.3</td>
<td>93</td>
<td>92</td>
<td>174</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Table 1: Attributes of the resins used in this thermoforming study.

Table 2: Performance of cups produced with all samples evaluated here.
Catalyst Comparison
Figure 1 shows the cup performance comparison of samples A and D. Performance has been compared using a 0 to 10 scale for which 10 is best and 0 is worst. The higher number is always better in this comparison. Accordingly, higher haze, clarity, or top-load numbers mean improvement.

It is apparent from Figure 1 that cups produced with samples A and D show about the same clarity. However, sample D shows improved haze (about 7% better) and top load (about 9% higher) than sample A. It is interesting to note that gloss inside and outside the cup is lower for sample D than A. Gloss is primarily influenced by surface roughness whereas haze is influenced by both surface roughness and crystal size. Surface smoothness could be affected by the material rheological properties. The broader MWD (reported here as PI) and lower MW of sample D could be responsible for higher resistance to drawing forces during the forming step, potentially resulting in topological roughness. What is interesting is that this increased roughness does not result in poorer haze or clarity.

It is also important to note from Figure 1 and Table 2 that cup top-load is much higher for sample D than sample A. This is to be attributed to the broader MWD of sample D that results in higher modulus under processing conditions. (This is potentially a result of better thickness uniformity associated with broader MWD, as discussed in reference [1]).

PP Design Comparison
The comparison of samples A, D, and G is particularly interesting since they contain the same clarifier (HPN600ei), but differ in catalyst used and molecular design (G is an LER, whereas A and D are HPP samples). Figure 2 shows the property performance comparison for cups produced with samples A, D, and G. It would appear from these results that the broader MWD of CONSISTA® catalyst-based LER enables enhanced cup haze properties and top loads simultaneously resulting in a unique property balance when compared to the 4th Gen based HPP. This is particularly relevant in relation to the top-load value (about 8% higher for sample G compared to sample A).

Figure 1: Spider diagram comparison of cup properties produced with samples A and D.

Figure 2: Spider diagram comparison of cup properties produced with samples A, D, and G.

Figure 3: Top-load as a function of haze for cups produced with samples A, D, and G. The arrow highlights the performance improvement when CONSISTA® catalyst-based resins are used to produce the cups.
It is interesting to note that the haze improvement observed with cups produced with sample G is also accompanied by increased gloss values (see Table 2). As mentioned earlier, gloss is primarily controlled by surface roughness, and this increase would indicate that cups produced with sample G have a smoother surface. This could be the result of slightly lower crystallization and melting points associated with sample G compared to samples A and D given the presence of a small concentration of ethylene. This change in thermal behavior could result in a more homogeneous polymer distribution during the drawing stage.

Influence of Clarifier Type
The influence of the clarifier in thermoformed cups’ performance is also studied. The performance of cups containing HYPERFORM® HPN600ei versus cups containing MILLAD® NX8000 were compared. The influence of ethylene content beyond the LER level is also explored.

Figure 4 shows the change in cup top-load as a function of haze for samples A, C, D, F, G, H, and I. It is noteworthy from this graph that cups made with PP based on NX8000 and CONSISTA® catalyst-based PP show a breakthrough performance. This is most remarkable for samples C (HPP) and F (LER). Cups produced with these samples not only show a breakthrough change in haze, but also in top-load. The change in top-load is more noticeable with cups produced with sample C. It is also important to note that increasing the ethylene content (samples H and I) does not yield an improvement in cup haze (about the same as cups produced with LER in sample G) and has a very detrimental effect on cup top-load.

The performance associated with cups produced with samples C and F deserves further discussion. The cup produced with sample C shows a haze improvement of 42% with respect to cups produced with sample D and a top-load improvement of 11%. When compared to sample A (4th Gen catalyst-based sample), the improvements are 46 and 23%, respectively. Regarding cups produced with sample F, they show a haze improvement of 42% versus those produced with sample G while keeping the top-load at the same level. When cups produced with sample F are compared with sample A, the improvements in haze and top load are 61 and 10%, respectively.

Breakthrough Enhancements
One of Grace’s main PP development themes is clearer materials through catalyst technology. This study compared the properties of multi-axially oriented thermoformed cups produced with 6th Gen and 4th Gen catalyst-systems-based PP. Different CONSISTA® catalyst-based PP materials were tested: homopolymer PP (HPP), low-ethylene-content random copolymer (LER), and random copolymers (RCP). The paper also compared how the nucleator / clarifier package affects the cups’ optical and mechanical properties. A performance map of the cup’s mechanical versus haze properties was provided. The main conclusions derived from this study were: (i) 6th Gen catalyst-based materials enable production of cups with improved top-load and clarity as a result of broader MWD and higher stereo-regularity; (ii) LER samples based on 6th Gen catalyst systems represent a quantum leap in cup performance when formulated with the MILLIKEN HYPERFORM® HPN600ei clarifier; (iii) the combination of Grace’s 6th Gen catalyst technology with MILLIKEN’s most advanced clarifier technology, MILLAD NX8000, produces breakthrough enhancements in top-load and haze for deep-drawn cups.

Reference:
1. Tamura, Satoshi; Kuramoto, Itaru; Kanai, Toshitaka, Polymer Engineering and Science, 52 (6), 1383 – 1393, 2012
2. G. Balbontin, G. Morini, WO 2002030998 A1
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