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Advanced Recycling 2.0: Introducing CirFlex™ Technology

PAGE 6

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GRACE

Turning Complexity into Advantage



Brian Kimberley
Vice President, Marketing,
Performance Catalyst Solutions,
W. R. Grace & Co.

Dear Reader,

In an environment where conditions can change more quickly than ever, staying connected to your customers, your data, and the partners you rely on is essential. That's one reason our focus at Grace remains clear: to help you navigate change, manage complexity, and respond to the unexpected so you can continue delivering the performance your business depends on, day after day.

Turning Complexity into Performance

For refiners, the operating environment is not getting simpler. Feedstock variability continues to increase. Margins remain tight. And external forces from geopolitical shifts to sudden changes in supply and demand can disrupt even the best run operations in the blink of an eye.

Against that backdrop, performance depends on the fundamentals: unit reliability, constraint management, and consistent value delivery.

That is where Grace adds value — and where we continue to invest: FCC, hydroprocessing, and catalyst performance that help refiners improve yields, maintain reliability, and get more from the assets they already operate.

Our acquisition and integration of ART Hydroprocessing™ strengthens that commitment. With Grace now owning 100% of ART (our former joint venture with Chevron), we have integrated hydroprocessing into our portfolio, positioning us to better support the refining system — from pretreatment through upgrading — with aligned teams, consistent technical standards, and clear operational priorities.

Driving Precision and Flexibility

For polypropylene and polyethylene producers, the pressures show up differently but are no less demanding. Feedstock and co-product economics shift quickly. Product specifications continue to tighten. Customers expect consistent performance across an expanding range of applications, including new ways to recycle plastics and incorporate recycled feedstocks.

Units are expected to run reliably while adjusting product slates, targeting different resin properties while responding to changing market demand. Introducing new feedstocks or recycled streams adds another layer of variability — and complexity — within existing assets.

Performance in this environment depends on aligning catalyst systems and operating conditions to control properties, maintain throughput, and manage variability — even as feedstocks and targets continue to shift.

Practical Innovation in Today's Operations

The articles in this issue reflect those realities with real-world examples and data-driven case studies.

Read on and see how refiners are adapting FCC units to process renewable feedstocks, improving propylene yields, and optimizing bottoms upgrading economics. Learn how catalyst design and operating strategy are being developed together to deliver incremental gains, and how digital tools are helping teams make faster, more confident decisions. And in our feature article in this edition, take a look at Grace's new CirFlex™ technology, our innovative approach to Advanced Recycling 2.0 that addresses many of the shortcomings of earlier attempts at recycling plastics.

These are practical applications, developed with customers, to solve the kinds of problems facing the refining and petrochemicals industries today.

> "Our focus at Grace remains clear: to help you navigate change, manage complexity, and respond to the unexpected."

Partnership That Delivers Results

As the environment becomes less predictable, our focus stays the same: helping our customers run better, adapt more quickly, and deliver consistent performance across your operations.

We hope you find this edition of *CATALAGRAM®* magazine useful — a reflection of the experience, technical expertise, and practical solutions Grace can deliver to help you solve today's challenges while preparing for tomorrow's.



Brian Kimberley

What's Inside

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Catalagram®

Welcome to the 2026 edition of *CATALAGRAM*® magazine, the definitive industry magazine for refining and petrochemical professionals, delivering practical technical insight, case studies, and learnings from decades of catalyst innovation and close collaboration with customers.

IN THIS ISSUE, learn how integrated FCC and hydroprocessing technologies, digital solutions, and circular innovations can help you maximize value and flexibility in a changing industry.

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Shown on the cover

The CirFlex™ Circularity Research Unit in operation at Grace's Columbia, MD, USA headquarters.

SPOTLIGHT



REFOLUTION: Advancing FCC Based Pathways for Renewable Fuels

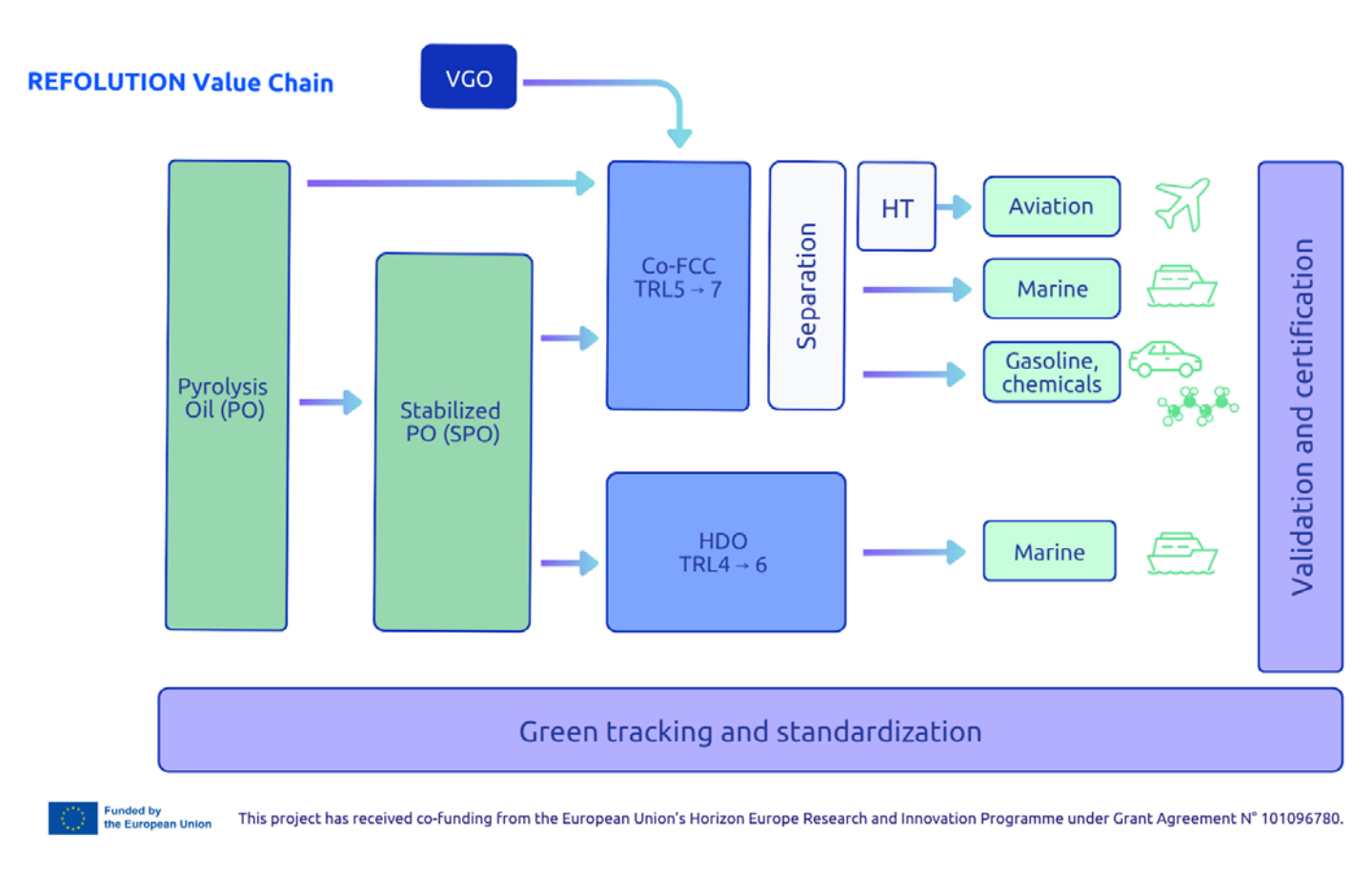
Grace contributes catalytic expertise to an EU initiative exploring FCC based routes for sustainable aviation and marine fuels

As refiners work to reduce the fossil-carbon intensity of transportation fuels, W. R. Grace & Co. (Grace) is contributing its catalytic expertise to help the industry evaluate how existing refinery assets can support emerging renewable fuel pathways. Through participation in initiatives such as REFOLUTION, Grace is engaging as a technical and consulting partner — providing catalyst samples, supporting testing activities, and contributing insight that helps inform how established technologies, particularly fluid catalytic cracking (FCC) and hydrotreating, may be applied to renewable feedstocks while maintaining unit reliability and asset value.

REFOLUTION brings together 14 partners from across Europe, including industrial partners OMV, Neste, Moeve, and Grace; technology companies BTG Biomass Technology Group, BTG NeXT, and BTL; universities such as the University of Groningen and the University of Rostock; research organizations SINTEF, VTT, DLR, and CNRS; and consulting partner ETA Florence.

One of the project's objectives is the application of FCC and hydrotreatment processes to enable the introduction of renewable feedstocks by leveraging existing refinery units, helping reduce investment requirements and accelerate the deployment of advanced biofuels.

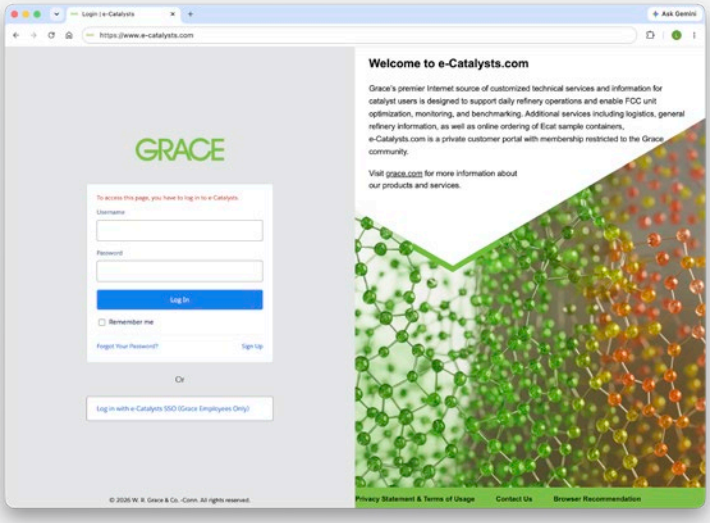
In addition to integrating renewable feedstocks into existing infrastructure, REFOLUTION addresses enablers for industrial adoption, including fuel certification and standardization, the development of digital tools to



track carbon emissions across the process chain, and the assessment of sustainability and economic feasibility. By demonstrating these solutions in real refining environments and developing models and roadmaps for replication, the project aims to reduce technical and economic barriers and provide refiners with practical tools to integrate advanced biofuel production into existing systems.

As the project enters its final phase, with expected completion in December 2026, REFOLUTION reinforces a broader industry insight: that meaningful progress toward lower fossil-carbon fuels will depend not only on new technologies, but on the ability to maximize the value of assets already operated by refiners.

Enhancing Refinery Operations with Digital Solutions



Digital transformation is no longer optional for refiners; it is necessary to stay efficient and competitive. FCC units are complex, margins are tight, and decisions need to be made faster than ever. The real value comes from turning data into action.

Access to FCC operational data is no longer enough. Today's refiners are shifting how teams manage performance, moving away from periodic, manual review toward earlier insight that fits into day to day operating routines. Grace supports refiners with digital solutions that improve visibility, enable better decision making, and deliver measurable results.

At the core is e-Catalysts.com, a secure workspace built specifically for Grace customers. It brings sample data, analysis, and operational insight into one place so FCC teams can easily track samples, access results without delays, and see trends over time. Instead of sorting through scattered data, operators get a clear, organized view that supports how they actually work.

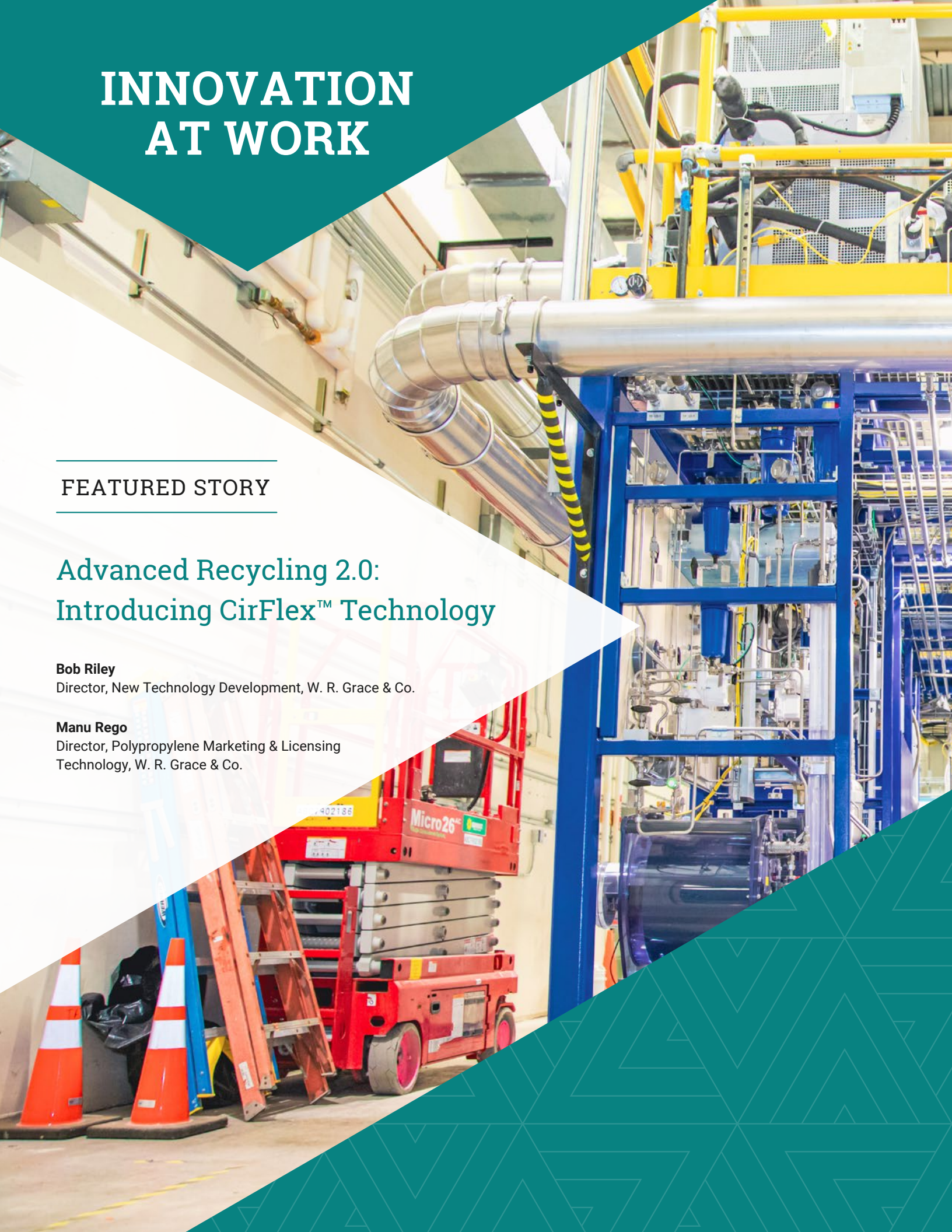
Building on this, e-Catalysts.com Alerts add a proactive layer to FCC monitoring. These automated alerts track catalyst properties and notify teams when something changes, such as unexpected highs, lows, or values outside set limits. This helps customers identify issues earlier and act before they affect performance or economics. In ongoing customer discussions and field experience, Grace has seen growing interest in this type of signal based monitoring, where meaningful changes surface automatically and expert teams can spend less time reviewing data and more time responding to it.

Customers using e-Catalysts.com Alerts have seen tangible benefits. Instead of manually reviewing full data sets, they receive focused notifications that highlight what matters most. Many teams now rely on alerts as part of their daily monitoring routines, reporting faster awareness and greater confidence in decisions. Alerts can be tailored to each unit's operating conditions, ensuring they remain relevant rather than generic. They are also delivered through the digital platform and email, making them easy to incorporate into existing workflows.

To further simplify data use, an API allows refiners to pull e-Catalysts.com data directly into their own systems. This removes manual steps, supports near real time analysis, and allows catalyst performance to be evaluated alongside broader plant data. Integrating trusted FCC data into refinery systems reflects a broader operational priority to make catalyst insight easier to access and act on without adding complexity.

e-Catalysts.com helps refiners move from reactive troubleshooting to proactive performance management. Bringing data, operational context, and experience into a single workflow enables FCC teams to respond sooner, make more confident decisions, and capture value more consistently in an increasingly demanding operating environment. This shift toward practical, signal driven decision support is becoming central to how refiners define effective performance management.

INNOVATION AT WORK



FEATURED STORY

Advanced Recycling 2.0: Introducing CirFlex™ Technology

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Advanced recycling has expanded rapidly, but first-generation routes like thermal pyrolysis face persistent limits in yield, product quality, and downstream integration. These first-generation constraints affect both economics and recycled content claims. This article introduces CirFlex™ technology as a next step, using catalytic chemical conversion to produce higher-value, more stable outputs with significantly improved yields. Designed to integrate with existing petrochemical assets, CirFlex™ can reduce process losses, simplify upgrading, and improve compatibility across the value chain. The result is Advanced Recycling 2.0, a more efficient path to plastics circularity that addresses the practical challenges that have held back broader adoption of advanced recycling solutions.

Introduction

Recycling value chains have seen significant growth and development over recent years, driven by regulatory support and an increasing ambition to address plastic waste effectively. At the same time, the first generation of advanced recycling routes — especially thermal pyrolysis — has encountered practical limits in yield, selectivity, product quality, and downstream integration. Those limits directly influence plastics-to-plastics yield, the complexity of downstream upgrading, and the ability to make robust recycled content claims under increasingly restrictive mass balance frameworks.

Grace's CirFlex™ technology represents a major step forward in advanced recycling, offering a new process technology that integrates with existing assets while delivering high yields of high-quality products. In contrast to thermal pyrolysis routes that primarily produce unstable intermediate oils, CirFlex™ technology uses catalytic chemical conversion to deliver higher-value products with higher overall yields, lower contaminant carryover, and improved compatibility with petrochemical value chains. For these reasons, CirFlex™ technology can reasonably be described as Advanced Recycling 2.0. This paper details the fundamentals of CirFlex™ technology, the limitations of first-generation routes, and the role CirFlex™ technology can play in enabling more efficient plastics circularity.

Next Generation Advanced Recycling

Grace holds leading positions in catalyst, process, and polymer technology areas that have direct and indirect connections with advanced recycling. Bringing together our capabilities across these markets, we invented a process technology that is poised to overcome many of the shortcomings experienced in first generation routes. CirFlex™ technology combines the advantages of catalytic chemistry, a proprietary reactor design, and integration with existing petrochemical assets to establish a new benchmark for plastics circularity.

The differentiators are straightforward:

- CirFlex™ technology has demonstrated process yields in excess of 90 wt% across the reactor;
- It can directly produce liquid products and, alternatively, mixtures of light olefins and aromatic monomers in a single reactor step;
- It produces a product slate that is more stable and more compatible with downstream petrochemical use than typical thermal pyrolysis oils; and
- In integrated configurations it can bypass a major downstream loss point by reducing dependence on a separate steam cracking/FCC step.

These differences directly affect economics, carbon intensity, and recycled content claims under restrictive mass balance systems, addressing many of the shortcomings of first-generation advanced recycling processes.

First Generation Advanced Recycling: Progress and Constraints

Among advanced recycling processes, thermal pyrolysis processes are popular choices, based on their ability to handle a wide variety of often otherwise unusable feedstock. Along with that flexibility come some challenges. Metal levels, such as those exemplified in Table 1, along with other impurities, are often generated as part of the advanced recycling process, complicating performance and downstream upgrading.

In thermal pyrolysis, heat is applied to a plastic stream to encourage chemical breakdown of the components. This type of process often produces liquid or wax products as a primary output, which are then sent for further cracking in a steam cracking operation or a petroleum refinery. Based on commercial scale differences, these pyrolysis oils represent a small minority component of the overall feed to the steam cracker or fluid catalytic cracking (FCC) unit. Figure 1 shows the steps in this value chain.

While thermal pyrolysis can be an attractive option to consider based on its relative simplicity and its tolerance to impurities, it is not without challenges. Impurities are often carried through the process, requiring significant cleaning steps prior to steam cracking or refining. Additionally, thermal pyrolysis processes are non-selective, energy intensive, and can have pyrolysis liquid yields in the low 70% range, which creates challenges for successful value chain economics [3].

In addition to impurities, plastic-to-plastic yields are a critical component of the value chain. In 2022, CE Delft studied various types of advanced recycling processes and their surrounding value chains to determine "plastic-to-plastic yields" of chemical recycling technologies. Their approach considered the estimated process losses during recycling and during subsequent processes. This study found that value chains based on thermal pyrolysis processes had an average plastic-to-plastic yield of 49%, due in part to losses in the pyrolysis process itself and subsequently in steam cracking [6]. This yield level puts considerable pressure on the value chain, as less than 50% of the collected plastic can become recycled plastic through these routes.

Regulatory Pressure and the Emergence of Mass Balance Frameworks

Incorporation of recycled content, especially in packaging, has long been an ambition of the plastic industry, driven by the public's interest in sustainable practices. In recent times, we have seen a swell in the corporate commitment to adapting packaging materials to incorporate recycled content, with many fast-moving consumer goods companies establishing meaningful targets for recycled content over the coming decade.

The growth in recycling ambition has been bolstered by regulatory support. Overarching laws such as Europe's Single Use Plastic Directive (SUPD) and Packaging and Packaging Waste Regulation (PPWR), together with the rise of Extended Producer Responsibility (EPR) systems at the country and state level, are expected to drive innovation and investment in the recycling space. These frameworks reward recycled content and reduced packaging footprints, but they also introduce complexity due to differing requirements across jurisdictions.

One of the most important regulatory challenges for the industry is how to account for what can be considered "recyclable," a characterization that has a tremendous impact on the economics of the solutions proposed for plastic recycling. In many jurisdictions, regulators and industry are aligning on using a mass balance approach. Mass balance is a ledger-based system that allows flexibility in the management of recycled-content claims and can be practiced with minimal changes across existing assets.

Across mass balance frameworks, three concepts are especially relevant. Here's how they differ:

- **Free Attribution** systems provide the greatest flexibility to allocate recycled claims across outputs, as long as total claims do not exceed the qualifying recycled input minus losses.
- **Fuels Exempt** systems are more restrictive, limiting the amount of the possible recycled claim based on the disposition of certain process outputs. Any part of the output of a process that becomes a fuel is not eligible for reallocation of its recycled credit.
- **Polymer Only** systems are more restrictive still, allowing recycled claims only on materials that can be traceably confirmed to be converted back into polymers.

Ultimately, the choice of mass balance framework directly affects advanced recycling viability because what can be counted as "recycled" drives both the economic calculus and the circularity claims. As regulations tighten and restrict how content can be allocated, recycling processes that lose material to fuels or inefficient conversion steps will struggle to deliver real value and viability.

With these constraints in mind, Grace developed CirFlex™ technology to produce high yields of stable, petrochemical-compatible outputs in a single step, reducing downstream losses and maximizing the share of product that can credibly qualify for recycled content claims.

End-of-life Treatment of Plastics

End-of-life treatment for plastics varies significantly across different regions of the world. In some regions, plastic is incinerated to recover the chemical energy in the material, producing energy while also producing CO_2 emissions. In other regions, plastics are landfilled, causing the potential for further degradation and containment issues. Recycling of plastics aims to recapture materials before they enter incineration or landfill routes, and reincorporate them into the value chain, achieving carbon circularity.

Feedstock Variability Drives Recycling Process Performance

The primary goal of all plastic recycling processes is to reincorporate plastic content into the value chain, paired with, or in substitution for, virgin materials. The most widely practiced process for plastic recycling today is mechanical recycling, wherein post-consumer and post-industrial plastics are sorted, shredded, washed, and may be further treated, before being melted and usually mixed with virgin resins at a certain percentage. These processes are relatively simple, with high yields and relatively low energy requirements. Mechanical recycling falls short, however, in practicability on all plastics [5]. The limitations of mechanical recycling include:

- **Incompatible Materials –** different plastics have incompatible melting points and chemical structures. When melted together, the resultant composites demonstrate poor mechanical and optical properties that make them unsuitable for reuse.
- **Multilayer Structures –** complex packaging consists of multi-layer flexible films that are either co-extruded or laminated, making layers inseparable and hard to sort and mechanically recycle.
- **Contamination –** food or product residues on packaging substrates present significant challenges for mechanical recycling.

- **Lack of Infrastructure –** most municipal recycling systems are designed for single polymer systems such as PET bottles or HDPE rigid containers.

Additionally, mechanical recycling leads to significant degradation in material properties. Because of this, many companies have suggested that there are practical upper limits to the amount of mechanical recycling that the world can accomplish.

Advanced recycling, also referred to as chemical recycling, is another class of processes that can be applied to certain types of plastics. Examples include solvolysis, gasification, pyrolysis, and catalytic conversions. Some advanced recycling processes can accept a wide range of plastics as feedstocks, and others are much more sensitive to plastic type. Feedstock sorting, quality, and impurity levels must be carefully managed when matching a process technology to an available recyclable feedstock.

Recycling infrastructure remains uneven across regions. In the United States, plastics of all types are often collected in a combined stream with paper/fiber, glass, recyclable metals, and other content, making sorting significantly complex. In these "Single Stream" collection systems, plastics represent only a fraction of the total collected material by weight, compounding variability and processing challenges.

As a result, recycled plastics supplied as feedstocks for mechanical and advanced recycling processes can vary significantly from batch to batch and as packaging materials change over time. Table 1 shows analytical results for various post-consumer plastics that were sourced from industry for post-consumer recycling.

Table 1: Elemental Analysis by ICP-AES for Multiple Post Consumer Plastics (Polyolefin Rich)

Sample ID	Al (mg/kg)	Ca (mg/kg)	Mg (mg/kg)	Na (mg/kg)	P (mg/kg)	Si (mg/kg)	Ti (mg/kg)	Zn (mg/kg)	Ash (mg/kg)
Sample 1	201	2580	354	90	27	532	1300	46	1.4
Sample 2	138	3590	174	66	26	201	750	32	1.4
Sample 3	58	31	6	<5	<5	<5	1.8	<1	<0.1
Sample 4	37	34	11	<5	42	<5	0.6	<1	<0.1
Reference nucleated	<50	<50	<5	<15	<10	5	0.5-1	8	<0.1

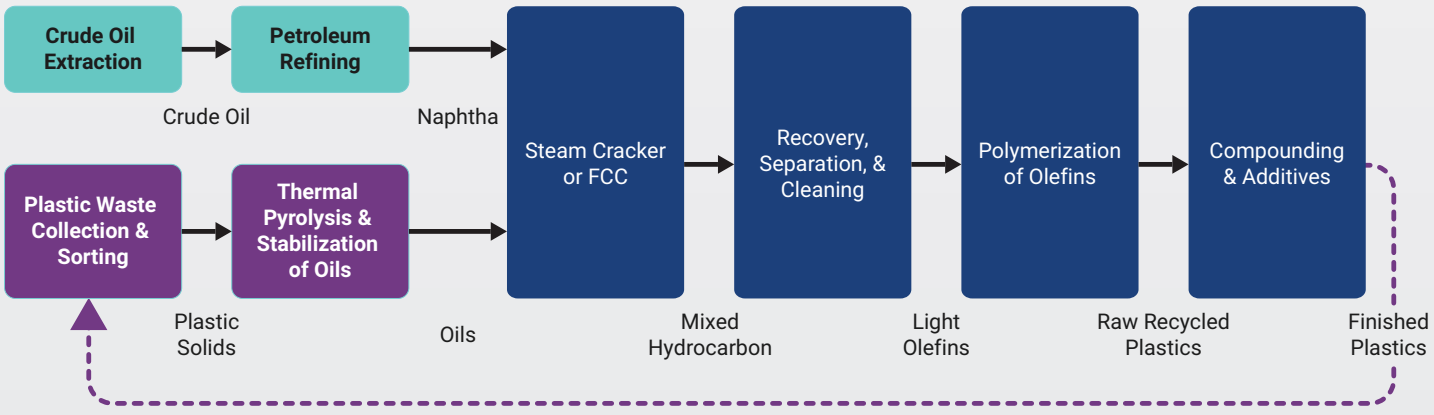


Figure 1: Steps in the Thermal Pyrolysis Value Chain

CirFlex™ Technology: A Different Approach to Conversion

The limitations of first-generation advanced recycling routes highlight the need for a new approach to plastic conversion that improves yields, reduces downstream losses, and produces outputs that are more compatible with existing petrochemical value chains. This is why Grace developed CirFlex™ technology. The name combines "circular" and "flexible," representing its role in plastics circularity and its ability to process a range of feedstocks to produce multiple product streams.

How CirFlex™ Technology Works

CirFlex™ technology involves three fundamental steps:

- **Feed Handling/Pretreatment:** The process can receive plastics in various forms, including bales, flakes, or pellets. Specific process steps are designed to intake feedstocks in the form most available and prepare them for the reactor conditions. Of note, the pre-treatment steps designed in the CirFlex™ process are intended for a minimal treatment of the feedstock and presume little to no chemical treatment, solvent use, or high energy consuming steps.
- **Conversion:** The core of the CirFlex™ technology is the catalytic reactor system, which breaks down the large plastic polymers into smaller molecules. CirFlex™ technology is capable of directly producing liquid yields and is alternatively also capable of producing a mixture of light olefins and aromatic monomers (also referred to as High Value Chemicals or HVC), directly in a single reactor step.
- **Products:** This final step separates the products into the appropriate fractions for downstream processing, ensuring the purity and quality of the output. Levels of separation and cleanup necessary will depend on the feedstock quality, the requirements of the downstream processes, and the type of product CirFlex™ technology is targeted to produce.

At its core, CirFlex™ technology is enabled by a unique combination of capabilities that have been practiced with success in other applications for many decades. These include a specific, novel catalyst system along with a proprietary reactor design that was specifically chosen for its ability to overcome some of the processing challenges encountered in first generation thermal pyrolysis and other "Advanced Recycling 1.0" processes.

Using a model feedstock designed to replicate the expected types of plastic available from commercial municipal recycling facilities, CirFlex™ has demonstrated process yields in excess of 90 wt% across the reactor. This yield profile alone boosts the economic potential of this route to recycling far beyond the levels expected in thermal pyrolysis.

Integration without Downstream Penalty

One advantage of CirFlex™ technology is its ability to integrate with existing assets. Figure 2 shows a CirFlex™ unit, focused on max HVC production, integrated in a value chain. Comparing to Figure 1, we note the ability to skip the critical step of steam cracking/FCC. Skipping this step enables significant value to be generated by avoiding the processing losses noted in the steam cracking operation, for example. This integration boosts the plastics to plastics yields significantly while also reducing the carbon intensity of the produced monomers markedly. Additionally, when a restrictive allocation method, such as "mass balance – fuels exempt" is applied to this value chain, CirFlex™ technology enables even greater amounts of recycled claims than traditional technologies, as the yields produced by CirFlex™ technology in HVC mode are primarily chemical monomers.

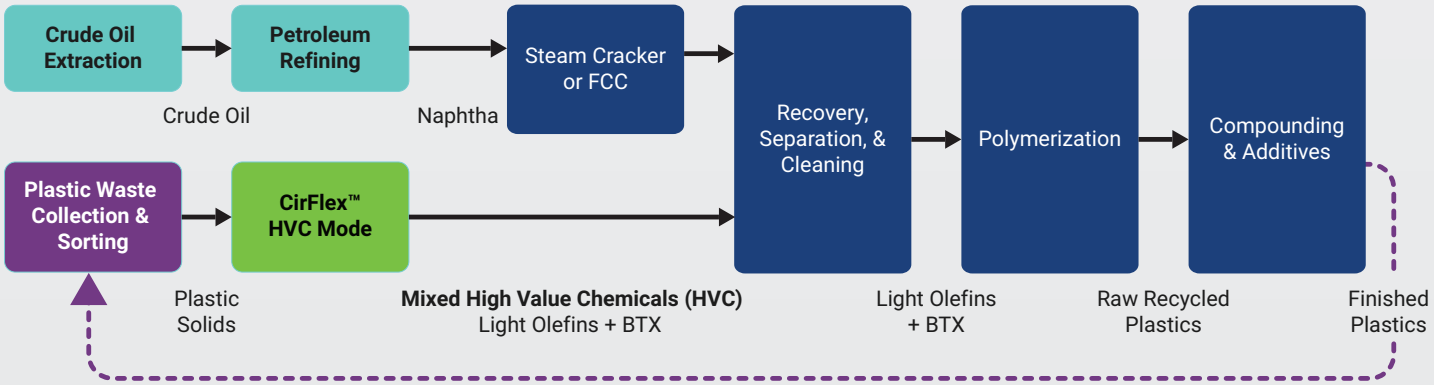


Figure 2: Value Chain for CirFlex™, Max HVC Mode, Integrated with Steam Cracking Recovery

Designed for Real-World Feedstock Variability

CirFlex™ technology accommodates a wide feedstock composition window, including various types of polymer chemistries and forms. While the technology has been initially designed to address hard-to-recycle plastics, Grace has generated laboratory data demonstrating its potential across a wide range of plastic chemistries and mixtures. This is especially important when considering the composition variation expected in commercially available post-consumer plastics. The process has specific design elements that have been incorporated to address this variation to ensure consistent and smooth operation.

Producing Stable, Petrochemical-Ready Outputs

CirFlex™ technology achieves the yields of products using catalytic technology, which creates notably different reactions than those that occur in thermal pyrolysis. In thermal pyrolysis, free radical mechanisms drive non-selective chemical conversion, and reaction selectivities are hard to manage. Additionally, thermal pyrolysis products can continue to react, or even re-polymerize, after the pyrolysis process, leading to unstable liquids requiring immediate treatment.

Unlike thermal pyrolysis processes, CirFlex™ technology produces stable liquid and gas outputs chemically identical to the hydrocarbons produced in traditional petroleum refining and petrochemical processes. These materials are also relatively low in contaminants. Table 2 shows a comparison of attributes in thermal pyrolysis processes compared to CirFlex™ technology.

Table 2: General Comparison of CirFlex™ Technology and Thermal Pyrolysis Processes for Advanced Recycling

Attribute	CirFlex™ Technology (Catalytic Chemical Conversion Process)	Thermal Pyrolysis of Polyolefins	Implication
Overall yield (wt% of plastic feed)	High (as high as 90 wt%+); majority converted to hydrocarbons with high chemical value, including light olefins and aromatics	Moderate yield (typically in the low 70 wt% range), primarily in liquid form; often distributed across light, middle, and heavy cuts	Both overall yields, and the product slate, are key differentiators
Primary yield composition	Olefins, aromatics, and paraffins consistent with catalytic products	High fraction of mono and diolefins (≈50–60%), with aromatics ~10–15%	Pyrolysis oils are highly unsaturated [1]
Diolefin content	Low (controlled by catalytic cracking and hydrogen transfer)	Elevated; diolefins are common pyrolysis products	Diolefins drive product instability and coke formation [1]
Heteroatoms (Cl, O, N, metals)	Very low; catalyst and process reject most contaminants	Present due to additives, residues, and feed contamination	Heteroatoms limit direct refinery use [7, 9]
Product stability (storage/thermal)	Stable hydrocarbon mixture comparable to refinery streams	Thermally unstable; prone to polymerization and viscosity increase	Instability documented across multiple studies [8]
Need for hydrotreating	Minimal or none for chemical use cases	Typically required (often multi stage)	Hydrotreating is standard practice for thermal pyrolysis routes [4, 7]
Hydrogen consumption	Inherent hydrogen balance via cracking chemistry	External hydrogen required for saturation and cleanup	Adds cost and carbon intensity [4]
Refinery/ petrochemical compatibility	Designed for integration with FCC / petrochemical assets	Requires pretreatment, guard beds, hydrotreating	Integration complexity favors CirFlex™ technology [2, 7]

Operating Implications for Energy Efficiency and Cost Structure

The same design elements that differentiate CirFlex™ technology, including catalytic conversion, integrated processing, and reduced downstream steps, also shape its energy and cost profile. The primary energy consumed in the process is derived from the feedstock. By leveraging modern reactor design concepts, the process is able to approach the minimum possible level of energy needed to drive the conversion of plastics to monomers. Additionally, the use of the catalyst system reduces overall energy demand compared to non-selective thermal routes.

These efficiencies extend across the value chain. Early life cycle assessments performed by Grace and by third parties indicate meaningful improvements in global warming potential and non-renewable energy demand, with further validation underway.

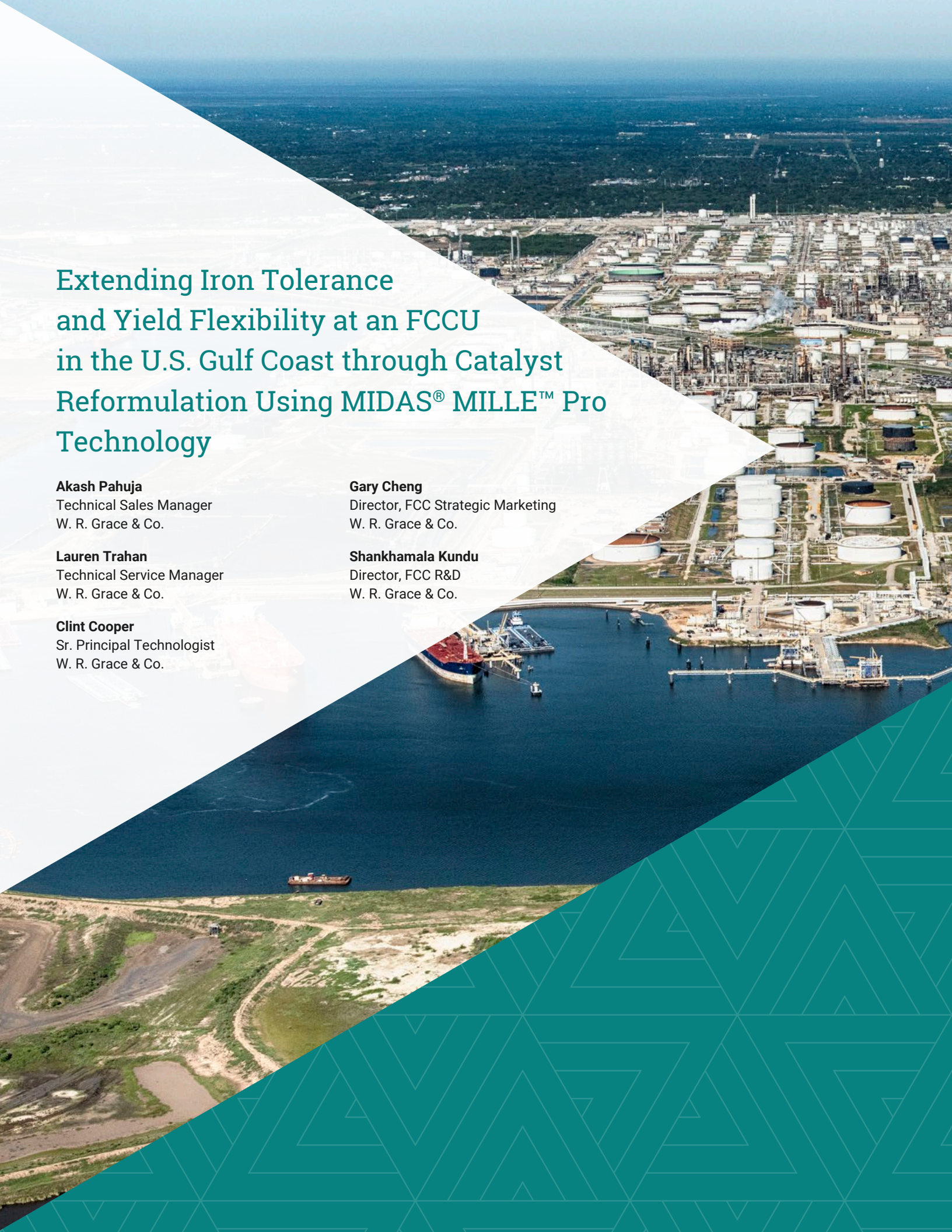
From a cost perspective, capital and operational requirements for CirFlex™ technology have been evaluated under several modes of operation, including against various product goals and integrations with existing assets. Not surprisingly, capital requirements for CirFlex™ vary depending on the feedstock form and composition, type of output (liquids or HVC), and the type of plant (integrated or standalone). However, the process also avoids some of the high costs associated with multi-step upgrading; for instance, it does not require high pressures (which minimizes reactor costs) and is often able to take advantage of existing utility infrastructure at refining and petrochemical operations, thanks to a relatively small footprint. Operating costs align with those in traditional petroleum and petrochemical processes, supporting a more competitive and scalable pathway to advanced recycling.

Conclusion

Grace's CirFlex™ technology represents a significant improvement over other advanced recycling technologies, offering a next-generation solution capable of integrating with existing assets to deliver significantly greater plastic-to-plastic yields, especially under restrictive mass balance accounting methods. With its superior yields, flexibility, and favorable energy profile as measured through life cycle assessment, CirFlex™ technology goes beyond first generation routes to advanced recycling, enabling the world to address the plastic waste problem far more efficiently than was previously possible.

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Extending Iron Tolerance and Yield Flexibility at an FCCU in the U.S. Gulf Coast through Catalyst Reformulation Using MIDAS® MILLE™ Pro Technology

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The processing of heavier feedstocks in fluid catalytic cracking (FCC) units has increased the prevalence of iron poisoning, which can limit catalyst diffusivity, activity, and operational flexibility. At one FCC unit in the U.S. Gulf Coast, increasing Atmospheric Tower Bottoms (ATB) processing resulted in challenging feed qualities, particularly metals like iron and calcium. To address these challenges, a catalyst reformulation incorporating MIDAS® MILLE™ Pro macroporosity technology was implemented. This paper presents a detailed case study of the reformulation, combining unit operating data, Equilibrium Catalyst (Ecat) characterization, kinetic modeling, and advanced diagnostic techniques. The reformulated catalyst extended iron tolerance at elevated added iron levels while maintaining catalyst activity, improving yield flexibility, and enabling a reduction in fresh catalyst addition rate. The reformulation delivered a reduction in catalyst additions of up to three tons per day at constant conditions and enabled the unit to process even more ATB material.

Introduction

Fluid catalytic cracking (FCC) units remain central to refinery value generation as feedstock quality continues to trend heavier and more contaminated. Increased processing of opportunity crudes, resid-derived streams, and Atmospheric Tower Bottoms (ATB) results in elevated contaminant metals loading in FCC units, particularly iron, calcium, nickel, and vanadium. Among these, iron presents a distinct challenge due to its tendency to deposit on catalyst particle surfaces, form nodules, and block pore mouths. This mechanism can sharply reduce effective diffusivity, restrict access to active sites, and ultimately impair conversion, fluidization, and selectivity.

Traditional mitigation strategies for iron poisoning have relied on higher fresh or purchased Ecat addition rates or reduced feed rates, both of which carry economic penalties. Advances in catalyst design that directly address diffusion limitations offer an alternative approach, allowing FCC units to tolerate higher iron exposure while maintaining performance. This paper documents how Grace scientists implemented a catalyst reformulation in an FCCU, with primary emphasis on extending iron tolerance and secondary emphasis on preserving yield flexibility under increasingly severe operating conditions.

Unit Background and Operating Challenges

This FCCU in the U.S. Gulf Coast operates with objectives that include maximizing liquefied petroleum gas (LPG) and distillate production, maintaining strong bottoms upgrading, and operating within wet gas compressor constraints. To increase refinery flexibility, the site expanded processing of ATB-derived material.

During late 2024, equilibrium catalyst analyses showed significant increases in nickel and vanadium, accompanied by rising total iron, added iron, and calcium oxide (Figure 1). Added iron plus calcium oxide increased from approximately 0.56 wt% to as high as 0.67 wt% during the evaluation period. These trends raised concerns regarding iron nodulation, pore blockage, and loss of effective diffusivity. In parallel, maintaining activity under higher metals required elevated fresh catalyst addition rates, which increased operating expenses and led to an evaluation of a reformulated catalyst solution.

Catalyst Reformulation Strategy

The reformulation strategy focused on incorporating Grace's MILLE™ macroporosity technology into the catalyst blend. The blended MIDAS® MILLE™ Pro technology employs a novel manufacturing step designed to increase macropore volume and optimize pore size distribution, improving internal diffusion and feed vaporization within the catalyst particle. Enhanced macroporosity mitigates the impact of surface iron deposition by preserving internal accessibility even as iron accumulates near pore mouths.

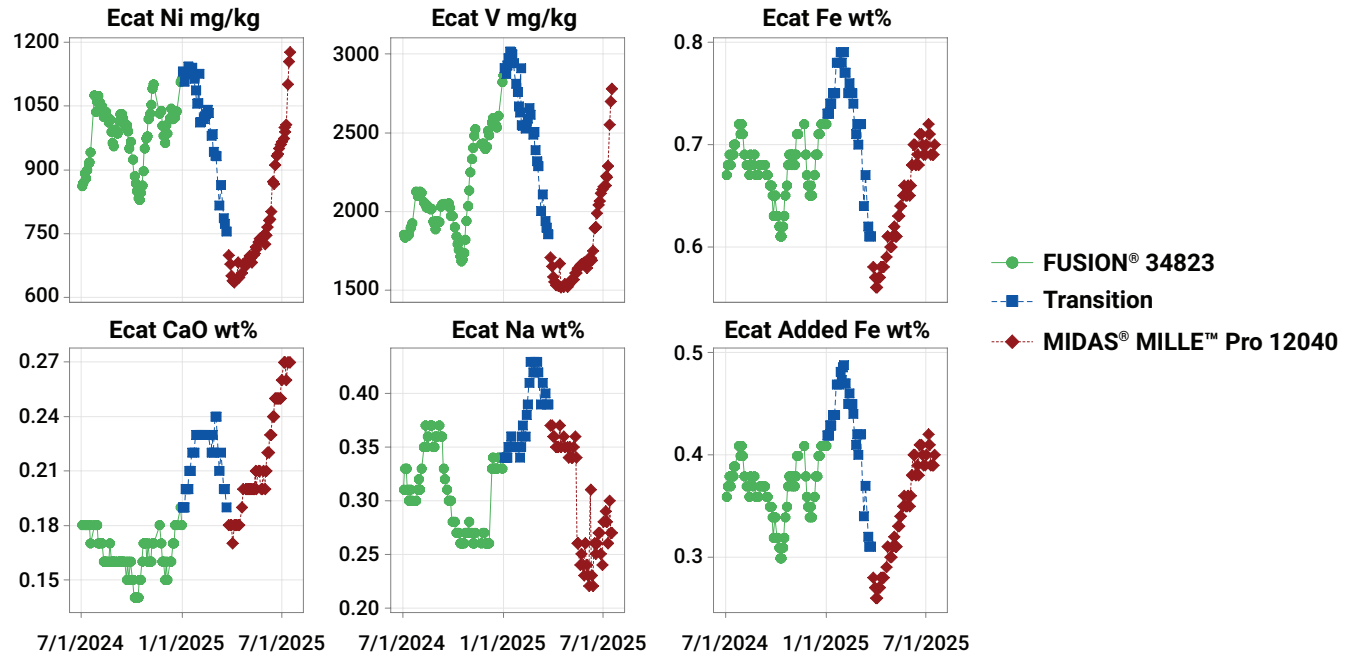


Figure 1: Increased Metals Loading as ATB Processing Severity Increased.

The reformulation was validated using Grace's Iron Deactivation Protocol (Grace-IDP™) method, which is a new iron deactivation method that successfully mimics commercially iron poisoned Ecat, reproducing the expected reduction in diffusivity index across different FCC catalyst systems. The iron deactivated lab catalysts showed the same iron tolerance trends observed in the operating unit, demonstrating that the protocol accurately reflected real unit metals behavior.

Rather than fully replacing the incumbent catalyst, the reformulated system balanced MILLE™ technology-based components with existing catalyst functionality to support activity maintenance, metals trapping, and coke selectivity. Reformulation objectives were explicitly defined as extending tolerance to iron and calcium contamination, maintaining activity and diffusivity at elevated metals, preserving yield flexibility, and enabling reduced fresh catalyst addition rates without sacrificing unit performance.

Evaluation Methodology

Reformulation Implementation

The reformulated catalyst was introduced into the FCCU in early January 2025 and was fully turned over by June 2025. Performance evaluation focused on stabilized operation following this turnover threshold to minimize the influence of legacy catalyst inventory.

Kinetic Modeling

FCC-SIM™ kinetic modeling was used to evaluate catalyst performance independent of short-term operational variability. Multiple steady-state operating periods were selected for both the incumbent and reformulated catalysts, ensuring comparable feed rates, riser outlet temperatures, and catalyst circulation. The incumbent catalyst was calibrated using representative 2024 operating conditions, while the reformulated catalyst was calibrated using 2025 data and back-predicted under 2024 conditions to enable consistent comparison.

Analytical Diagnostics

In addition to routine Ecat measurements, advanced diagnostics were used to assess iron poisoning risk and catalyst health. These included inverse gas chromatography for effective diffusivity, magnetic susceptibility (SuSI) for iron phase characterization, and scanning electron microscopy for surface morphology assessment.

Results and Discussion

Iron Tolerance and Diffusivity Retention

A primary outcome of the reformulation was improved diffusivity retention at elevated added iron levels. Following reformulation, effective diffusivity stabilized at high values and declined gradually as ATB processing increased (Figure 2). Even at added iron plus calcium-oxide levels approaching 0.67 wt%, diffusivity remained well above minimum recommended thresholds associated with iron poisoning (Figure 3).

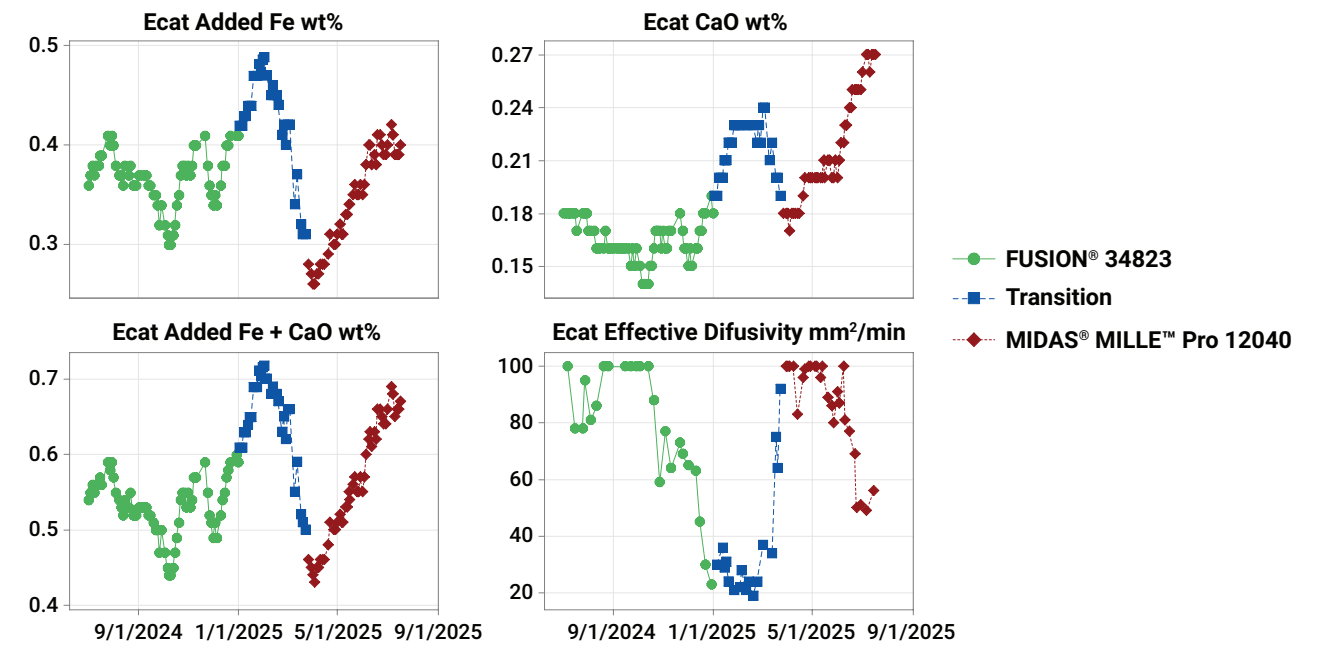


Figure 2: Effective Diffusivity as a Function of Added Iron and Calcium Oxide on Equilibrium Catalyst.

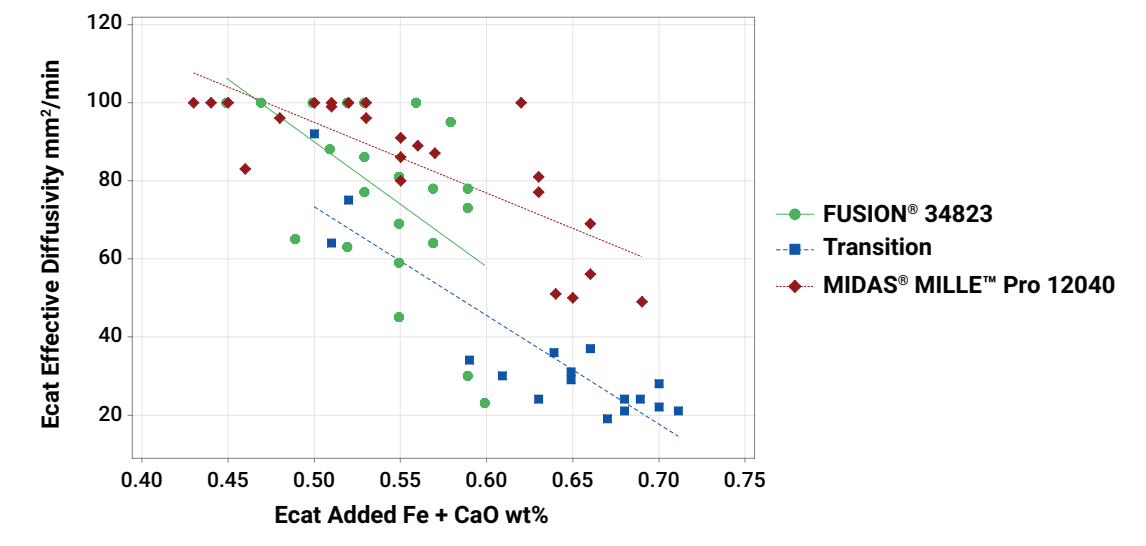


Figure 3: Effective Diffusivity as a Function of Added Iron and Calcium Oxide on Equilibrium Catalyst.

Additionally, magnetic susceptibility measurements returned to baseline values following reformulation, indicating reduced formation of magnetically active iron phases associated with nodulation (Figure 4).

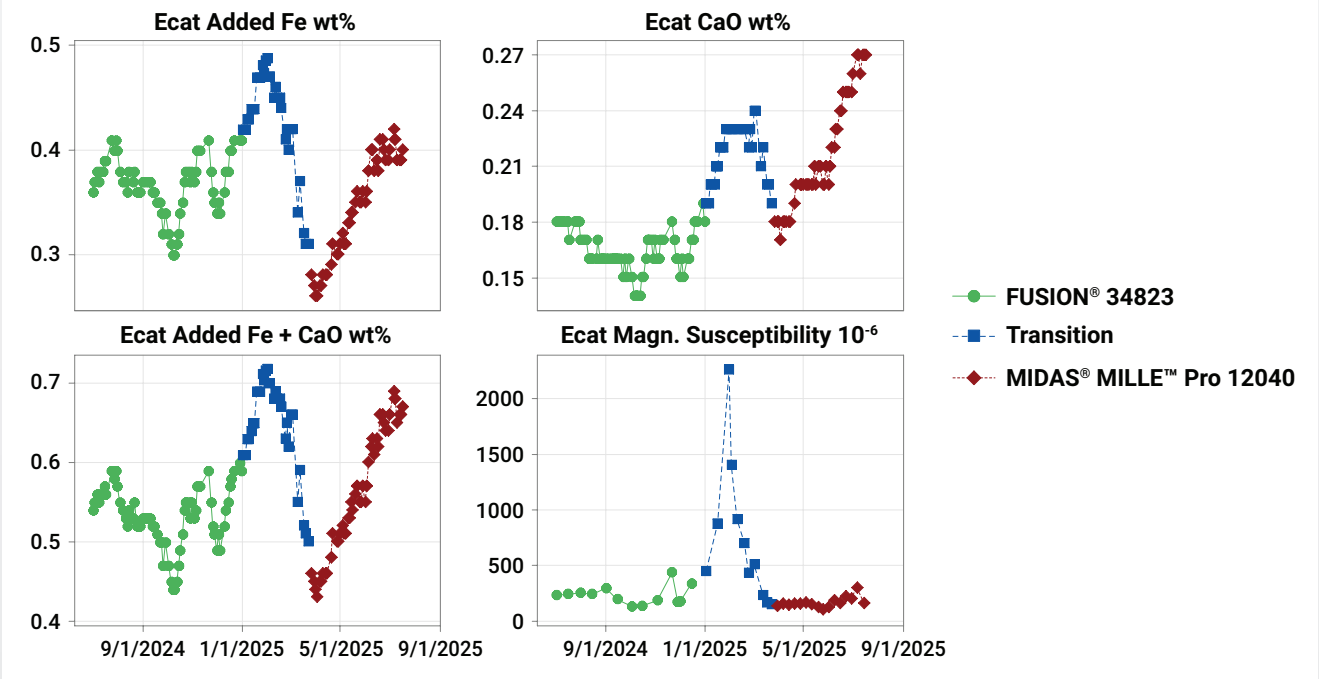


Figure 4: Magnetic Susceptibility Response with Increasing Added Iron.

Activity Maintenance

Despite rising contaminant metals, equilibrium catalyst microactivity (MAT) values remained stable throughout the evaluation period (Figure 5). Activity retention was notably improved at higher metals loading, consistent with reduced diffusional limitation and preserved access to active sites.

Yield Flexibility

The reformulated catalyst delivered favorable yield shifts aligned with unit objectives. Dry gas yield decreased modestly, providing incremental wet gas compressor relief. Distillate yield increased, and slurry yield decreased, consistent with improved bottoms upgrading. In the ACE® Technology (Advanced Cracking Evaluation) testing data, LPG yield appears to have declined while gasoline yield increased; however, this was attributable to ZSM-5 decaying from the unit inventory during late 2024 and early 2025 (Figures 6 and 7). Figure 8 provides a more detailed view of the uplift under baseline conditions.

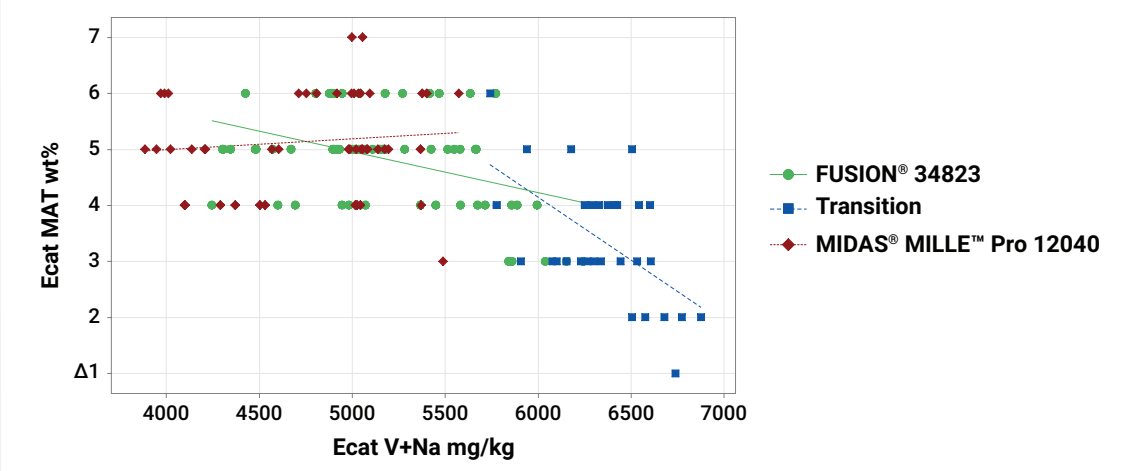


Figure 5: MAT Retention as a Function of Contaminant Metals.

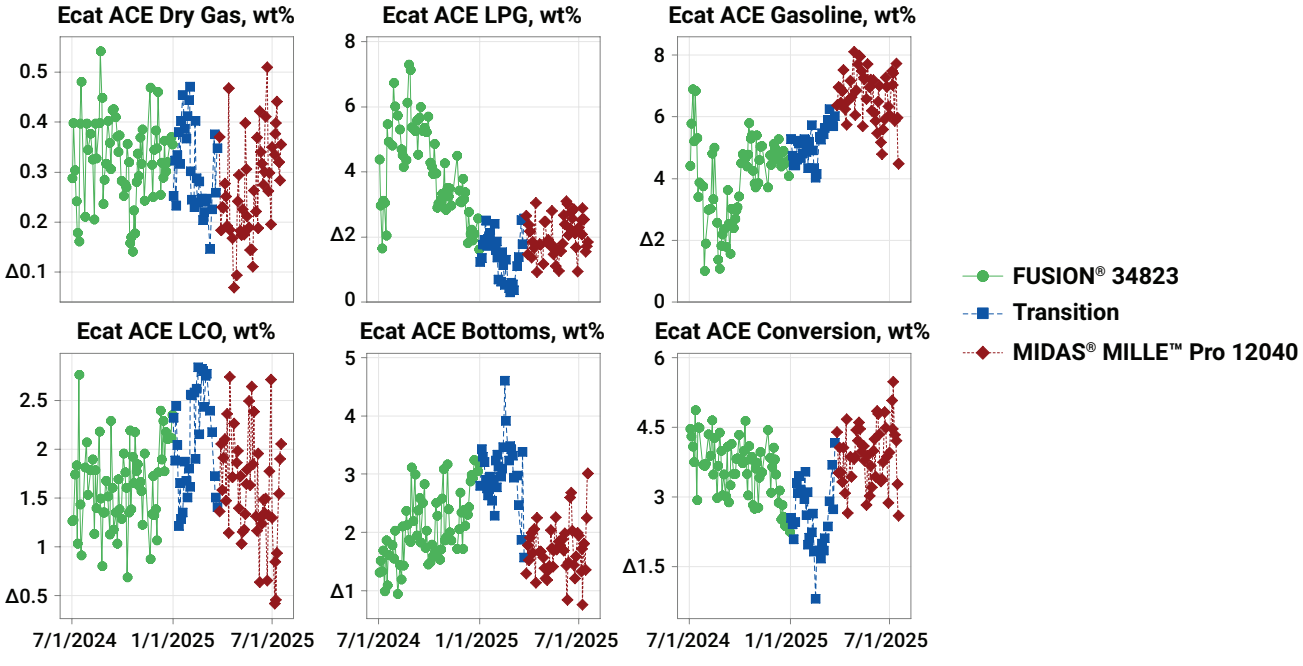


Figure 6: ACE Yield Selectivity Shifts Observed with the Reformulated Catalyst.

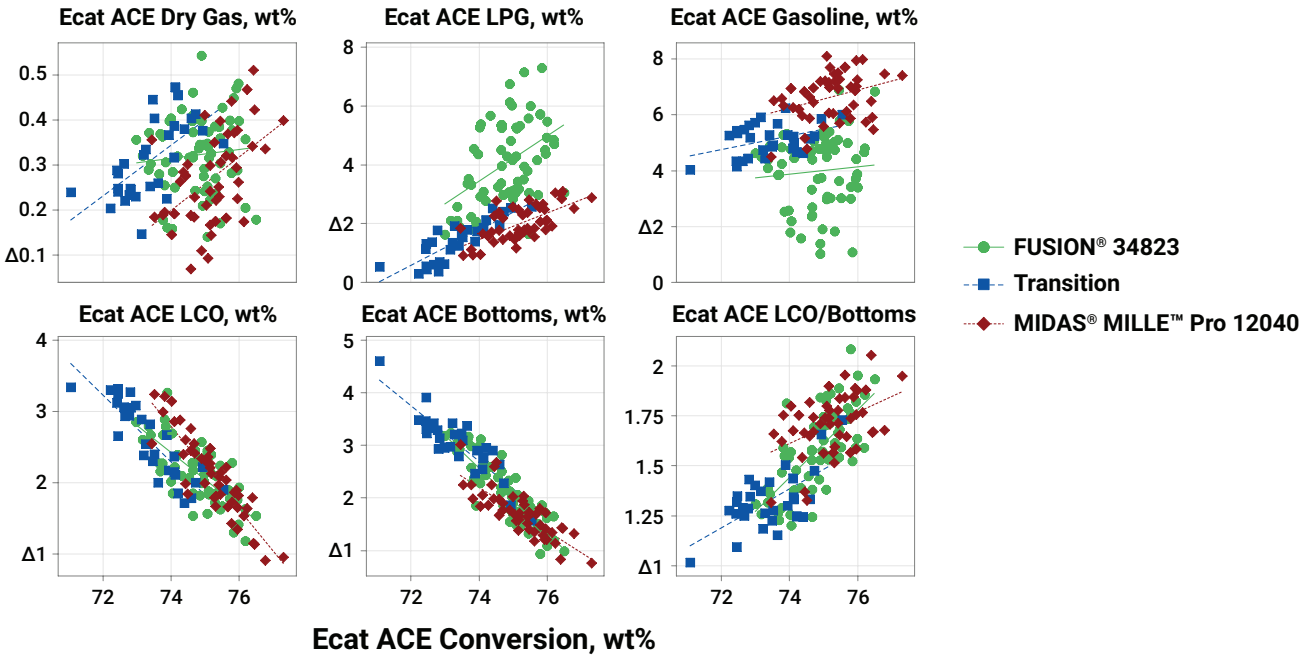


Figure 7: ACE Yields as a Function of ACE Conversion.

Unlock a New Standard for Iron Challenged FCC Units.

MIDAS® MILLE™ Pro technology preserves yield flexibility under elevated iron conditions enabling improved unit economics and optimized catalyst addition rates.

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Economic Impact

Improved metals tolerance and activity maintenance enabled a sustained reduction in fresh catalyst addition rate up to three tons per day at constant conditions. Grace FCC-SIM™ kinetic modeling indicated uplift under baseline operating conditions, reflecting a combination of improved product slate and reduced catalyst consumption (Figure 8).

Advanced Diagnostics and Iron Monitoring

Advanced analytical tools played a critical role in managing iron poisoning risk. Effective diffusivity provided a sensitive indicator of pore blockage, while magnetic susceptibility offered insight into iron oxide phase behavior. Using the scanning electron microscope (SEM) diagnostic tool, Grace scientists visually tracked how iron accumulates on catalyst particles during a high-iron feed trial. As iron loading increased, the SEM showed a transition from small, scattered nodules to larger, coalesced surface patches that were controlled by the catalyst reformulation. As shown in Figure 9, comparing SEM images across time points and catalyst grades verified that the trial stayed within expected iron growth profiles and assessed how well the catalyst design tolerated iron under the elevated iron conditions.

Conclusion

The catalyst reformulation implemented at the FCCU demonstrates that advanced macroporosity design can effectively extend iron tolerance while preserving yield flexibility and economic performance. Under increasing ATB processing severity, the reformulated catalyst maintained activity, diffusivity, and fluidization while enabling reduced catalyst addition rates and favorable yield shifts. The reformulated catalyst continues to be used in the FCCU. This case study illustrates a practical pathway for FCC units to accommodate higher iron exposure without sacrificing operational stability or economics.

	FUSION® vs MIDAS® MILLE™ Pro Delta Constant Conditions	
Operating Conditions		
Regenerator Bed T, F	-6	
C/O	0.33	
Catalyst Circulation Rate, TPM	3.7	
Wet Air Rate, KSCFM	4	
WGC Rate, KSCFM	-0.3	
Ecat Properties		
Ecat MAT, wt%	-0.7	
Standard Cut Yields (430/650F)	**wt%**	**vol%**
Total Dry Gas	-0.05	-
C3	0.08	0.15
C3=	0.15	0.26
nC4	0.06	0.09
iC4	0.18	0.29
C4=	0.38	0.56
Gasoline	-0.18	-0.26
LCO	0.20	0.37
Slurry	-0.95	-0.70
Coke	0.13	-
Total	0.00	0.76
Conversion	0.8	0.3
C3 Olefinicity	-1.0	
C4 Olefinicity	0.2	
Total C3=, BPD	264	
Total C4=, BPD	564	
LCO/Slurry	0.3	

Figure 8: FCC-SIM™ Modeled Economic Comparison Between Incumbent and Reformulated Catalyst.

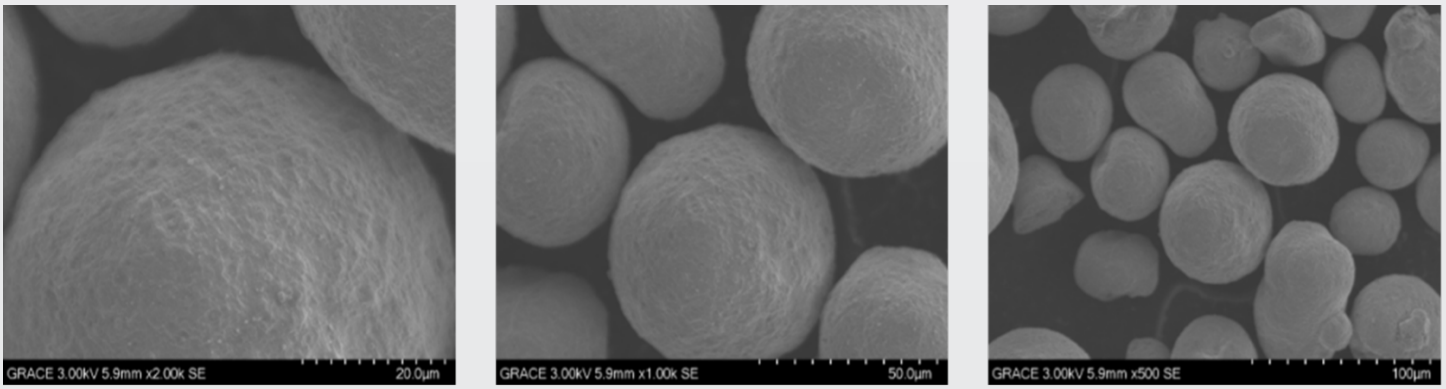


Figure 9: SEM Images Illustrate Catalyst Surface Morphology Under Increasing Iron Exposure.



Compounding Value: Run-Over-Run RDS Catalyst Optimization Drives Increased RFCC Profitability

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This article explores how ART Hydroprocessing™ (ART), a Grace company, collaborates with its fixed-bed resid desulfurization (RDS) customers across successive operating cycles to drive sustained, long-term performance improvement. Through an integrated approach combining product innovation, catalyst system optimization, and data driven modeling, customers continue to raise the performance bar from run-to-run. As demonstrated in two case studies, these capabilities have enabled customers to successfully process higher metal opportunity crudes in their RDS units while simultaneously delivering improved Resid Fluid Catalytic Cracking (RFCC) feed quality.

The case studies that follow illustrate how ART applies state of the art catalyst technology and optimized system design to address specific customer objectives, delivering run-over-run improvements in both RDS feed flexibility and downstream RFCC feed quality.

In Case Study 1, the application of this integrated approach over seven operating runs enabled an RDS unit to process feeds containing 14% higher nickel + vanadium (Ni+V) metals while still achieving improved RDS product quality. The resulting reductions in RFCC feed Ni+V, Micro Carbon Residue (MCR), and sulfur translated to a profitability uplift of $1.21/bbl.

In Case Study 2, ART partnered with a customer over five operating runs to accommodate increased RDS feed metals while delivering lower MCR to the RFCC unit, resulting in an incremental uplift of $0.38/lb.

Together, these case studies demonstrate the value of combining advanced RDS catalyst technology with data driven system designs to expand opportunity crude processing while improving downstream RFCC performance and overall refinery economics.

Foundations of Continuous Improvement

ART has a long track record of helping fixed-bed residue hydrotreating customers enhance downstream RFCC economics and improve low sulfur fuel oil production through tailored catalyst solutions. Over the past 25 years, ART has continually advanced its catalyst portfolio to enable RDS units to maintain target cycle lengths and improve RFCC feed quality while processing increasingly challenging feeds.

For customers operating ART catalysts across multiple cycles, performance gains are compounded through a run-over-run optimization approach, in which operating experience and performance data are leveraged to implement targeted system adjustments from one cycle to the next. Continuous improvements in kinetics and metals capacity, coupled with a deep understanding of catalyst layer interactions, allow customers to experience cumulative gains in feed flexibility and RFCC feed quality. These improvements translate directly into increasing economic value over successive operating cycles.

Product Innovation

Building on decades of R&D investment and long-term customer feedback, ART develops catalyst technologies tailored to specific operating objectives. A primary objective for many fixed-bed residue hydrotreating units is to maximize profitability by processing opportunity crudes with very high metals content (primarily Ni and V) without sacrificing run length.

To address this challenge, ART developed the ICR 800 demetallation (demet) catalyst incorporating learnings from previous-generation catalysts such as HOP 606H and ICR 187. ICR 800 features an engineered pore structure and balanced catalyst metals function that enhances access of large metals containing resid molecules to the active sites, resulting in higher hydrodemetalation (HDM) reaction rates and end of run (EOR) metals capacity.

As shown in Figure 1, ICR 800 maintains high HDM activity throughout the cycle while delivering increased EOR metals capacity compared to ICR 187. This improved demetallation performance protects downstream conversion catalysts and enables higher hydrodesulfurization (HDS) and carbon residue reduction (HDMCR) activity across the system at EOR.

To maximize overall HDM performance, conversion catalysts with enhanced metals tolerance are required. Even with the improved upstream HDM performance provided by ICR 800, some Ni and V will inevitably slip through the demetallation layers and deposit on the conversion catalyst. In these catalyst layers, smaller pores are more susceptible to plugging, leading to accelerated catalyst deactivation over the course of the run.

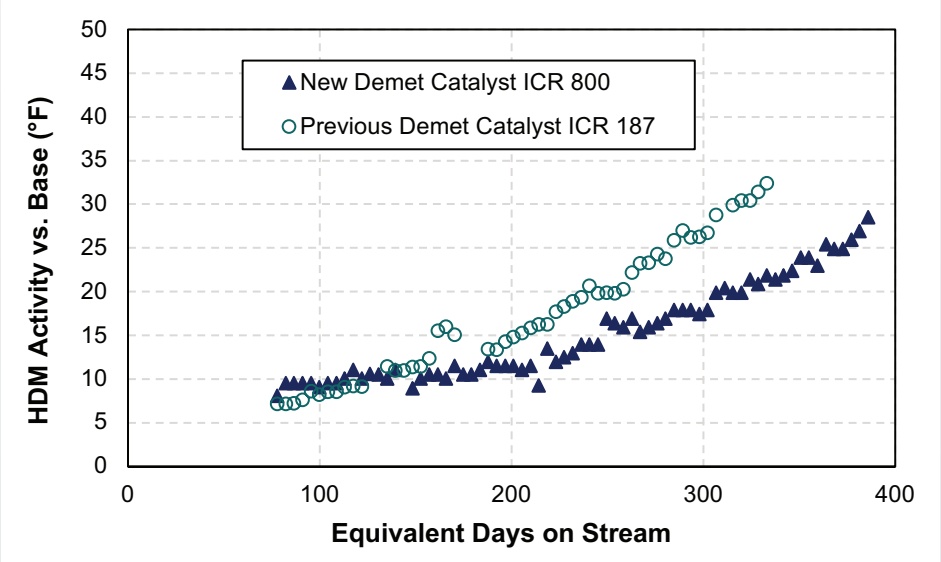


Figure 1: HDM Performance Comparison of ICR 800 with ICR 187

To improve conversion bed stability and sustain HDS and HDMCR activity through EOR, ART developed ICR 196, an advanced conversion catalyst. Targeted modifications to the pore structure enable ICR 196 to tolerate higher levels of metals deposition with reduced deactivation, resulting in higher EOR HDS and HDMCR activity compared to prior-generation conversion catalysts such as ICR 186. Figure 2 shows the middle of run (MOR) to EOR improvement in HDMCR activity.

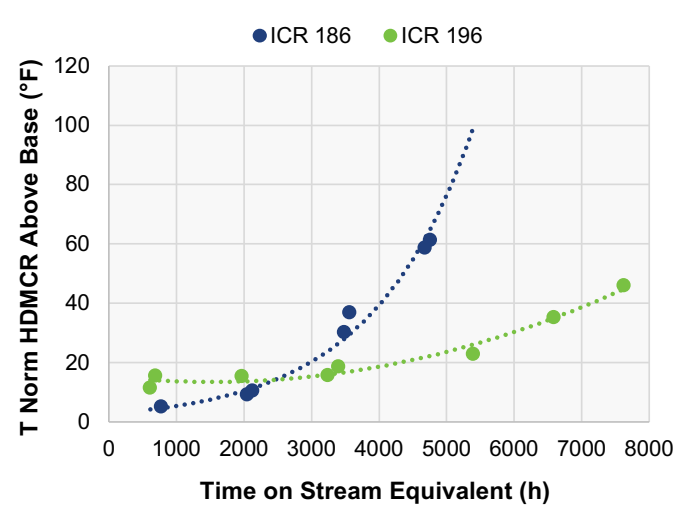


Figure 2: HDMCR Performance Comparison of ICR 196 with ICR 186

Another way ART helps RDS customers produce higher quality RFCC feed is by delivering improved MCR reduction. Recognizing the importance of catalysts with increased MCR activity, ART prioritized the development of two next generation conversion catalysts.

The first is ART's latest deep conversion catalyst, ICR 192, which demonstrates significant improvements in HDS and HDMCR activity compared to prior generation catalysts such as ICR 171, as shown in Figure 3. ICR 192 is specifically designed to target the most difficult to remove sulfur containing molecules and exhibits enhanced hydrogenation functionality, enabled by a higher density of active sites and a modified pore structure.

The second conversion catalyst development is ICR 199, which bridges the high stability of ICR 196 with the high activity of ICR 192. ICR 199 delivers enhanced sulfur, nitrogen, and MCR conversion while providing increased tolerance to Ni and V deposition. Its optimized metals formulation and tailored alumina support maximize active site availability, enabling sustained reaction rates and the maintenance of low product MCR throughout the run, as shown in Figure 4.

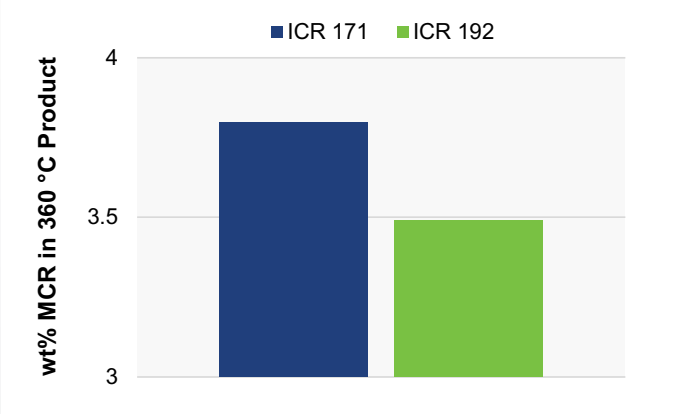


Figure 3: MCR Levels for ICR 192 Versus ICR 171

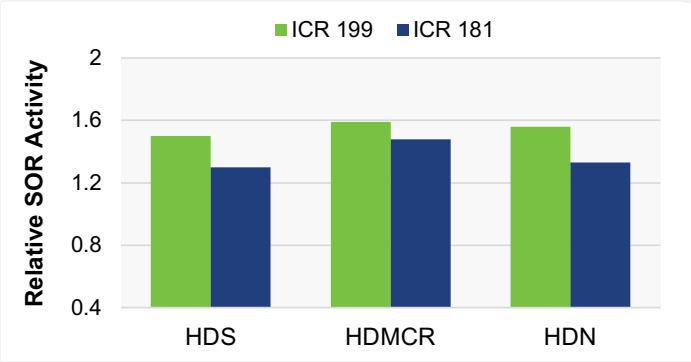


Figure 4: HDS, HDMCR, and HDN Activity Comparison for ICR 199 Versus ICR 181

These four improved catalysts summarized in Table 1 were implemented in the following two case studies over a period of operating cycles to deliver cumulative gains in RFCC feed quality through higher metals capacity and HDMCR activity.

Table 1: ART's Latest Generation RDS Catalysts

Catalyst Development	Primary Attribute
ICR 800	Improved Metals Capture in the Demetallation Layer
ICR 196	Improved Metals Capture in the Conversion Layer
ICR 192	Higher Activity Deep Conversion Catalyst
ICR 199	Hybrid for Improved Metals Capture and Conversion

Run-Over-Run Proprietary Modeling

Catalyst innovation is only one component of ART's value proposition in fixed-bed resid hydrotreating. Successfully processing opportunity crudes while improving RFCC feed quality also requires deep expertise in severe resid feeds, along with a detailed understanding of catalyst system design tailored to the specific RDS unit and operating cycle. ART applies a proprietary kinetic modelling platform to design customized catalyst systems, supported by an extensive feedstock and performance database developed from pilot plant testing and commercial operating data across a broad global base of fixed-bed resid hydrotreaters.

For customers running ART catalysts over multiple cycles, operating data from each run is systematically incorporated to recalibrate the model and refine performance predictions for subsequent cycles. Crude specific activity data and bulk feed properties are then used to optimize the next catalyst loading and system configuration. This iterative, data-driven approach enables run-over-run improvements in RFCC feed quality while enabling customers to progressively increase feed severity and expand crude slate flexibility in their resid hydrotreating units.

Continuous Improvement in Action

RDS Case Study 1

Changing refining market conditions have increased the importance of RDS-RFCC configurations that can capitalize on opportunity crudes while consistently delivering high-quality RFCC feed. In this environment, one customer sought an optimized catalyst system capable of processing feeds with more than a 10% increase in feed metals. To maintain profitability, the solution had to preserve run length and throughput, while maintaining or improving RFCC feed quality relative to the base case.

Over multiple cycles, ART partnered with the customer to develop and implement the ICR 800 demetallation catalyst and ICR 196 conversion catalyst, improving metals capacity and HDMCR activity throughout the entire run. Figure 5 summarizes the changes in volume of the optimized catalyst system compared to the base system.

Leveraging ART's proprietary kinetic model, extensive feedstock database, and deep understanding of the customer's specific operating conditions, the catalyst system was further refined on a run-by-run basis to improve HDMCR stability. The resulting optimized system featured a larger proportion of demetallation catalyst and reduced volume of deep-conversion catalyst, as summarized in Table 2.

Optimizing the catalyst system over seven operating cycles enabled the RDS unit to process feeds with a 14% increase in metals content. Over the same period, RDS feed MCR and sulfur also increased. Despite the increased feed severity, the optimized catalyst system demonstrated improved stability, as illustrated in Figure 6. The normalized catalyst average temperature (CAT) for the most recent run remained approximately 17 °C lower at EOR compared to the base case. In addition, the optimized system achieved a 22% increase in metals on catalyst at EOR relative to the base case, confirming the enhanced metals capacity of the optimized catalyst loading.

Catalyst	Volume %
Demet (ICR 187)	A
Transition	B
Conversion (ICR 186)	C
Conversion	D
Deep Conversion	E



Catalyst	Volume %
Demet (HOP-606H)	+6.4
Demet (ICR 800)	+6.3
Demet (ICR 187)	A -3.1
Transition	B -2.5
Conversion (ICR 196)	C +20.2
Conversion	D -10.3
Deep Conversion	E -17

Figure 5: Evolution of Catalyst Selection over Seven Cycles

Table 2: Evolution of Catalyst System Optimization

	Change from Base System, Vol%
Demet	+9.6
Transition	-2.5
Conversion	+9.9
Deep Conversion	-17.0

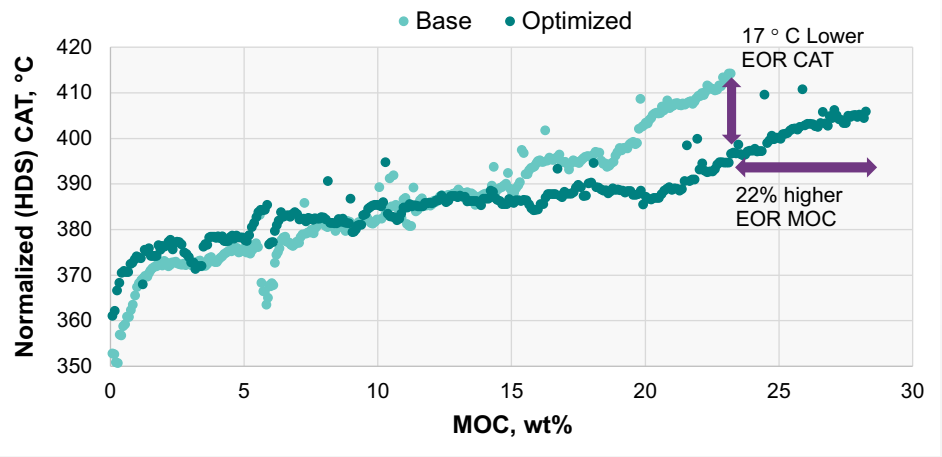


Figure 6: Normalized HDS Performance for the Optimized System

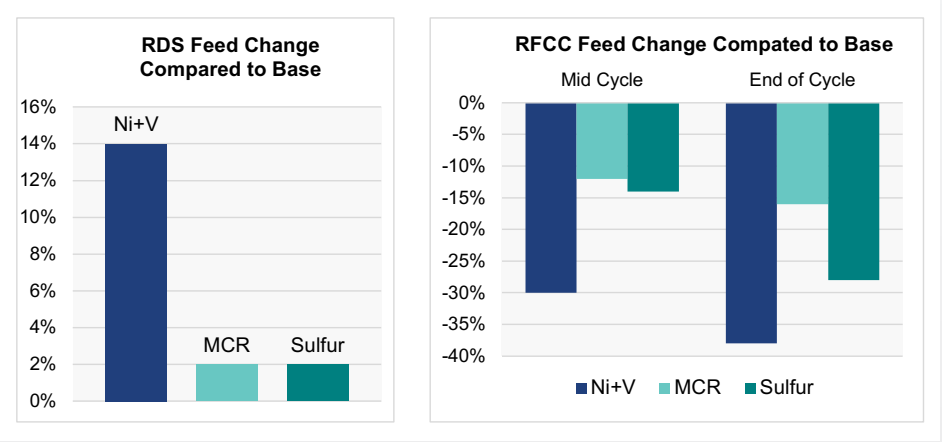


Figure 7: Change in RDS Feed and Resulting RFCC Feed Using the Optimized Catalyst System

Catalyst	Volume %
Demet (ICR 187)	A
Transition	B
Conversion (ICR 186)	C
Conversion (ICR 181)	D
Deep Conversion	E

Catalyst	Volume %
Demet (ICR 800)	+21.2
Demet (ICR 187)	A -22.1
Transition	B +1
Conversion (ICR 196)	C +1.4
Conversion (ICR 199)	D +1.2
Deep Conversion	E -11.3
Deep Converion (ICR 192)	+8.6

Figure 8: Comparison of the Base Catalyst System (left) to the Optimized Catalyst System (right) after Five Cycles.

The ability to process significantly more severe feeds allowed the customer to process opportunity crudes without compromising downstream RFCC performance. In fact, despite the increased severity of the RDS feed, the resulting RFCC feed quality was improved. Figure 7 shows the percentage increase in RDS feed metals, MCR, and sulfur from the base case to the optimized catalyst system, along with the corresponding improvements in RFCC feed quality at both middle and end of run.

RDS Case Study 2

At a second resid hydrotreater, the customer's primary objective was to reduce MCR in the RFCC feed. Over five operating cycles, ART optimized the catalyst system by utilizing the newly developed ICR 199 and ICR 192 to improve HDMCR activity. Leveraging insights gained from Case Study 1, ICR 800 and ICR 196 were also incorporated to increase overall metals capacity and improve system stability.

Figure 8 details the evolution of the catalyst layering from the base catalyst to the optimized system. The use of these higher metals capacity catalysts enabled a slight decrease in total demetallation catalyst volume, accompanied by a corresponding increase in the transition catalyst volume, to further maximize system activity (Table 3).

Table 3: Evolution of Catalyst System Optimization

	Change from Base System, Vol%
Demet	-0.9
Transition	+1.0
Conversion	+2.5
Deep Conversion	-2.7

The catalyst activity of the optimized case subsequently increased, which can be seen in the normalized CAT of the optimized catalyst system being approximately 10 °C lower than the base case (Figure 9).

Despite the more severe RDS feed containing higher metals, MCR, sulfur, and asphaltenes, the optimized catalyst system delivered a 12% reduction in MCR for the RFCC feed. Sulfur and nitrogen were also reduced. The change in RDS and RFCC feed properties in the optimized catalyst system compared to the base case catalyst system are summarized in Figure 10.

Modeling the Impact on RFCC Profitability

Together, these two case studies demonstrate that incremental, run-over-run optimization of RDS catalyst systems can deliver substantial improvements in downstream RFCC feed quality. Table 4 summarizes the primary RFCC feed property shifts with the optimized catalyst profiles for each of the two case studies discussed.

Established models were used to quantify the operational and economic impact of the improved RFCC feed properties (Table 5).

In Case Study 1, RFCC feed quality improved substantially. The reduction in feed V lowered Ecat V by approximately 2,000 mg/kg, resulting in higher activity as measured by microactivity (MAT). While an increase in MAT would typically be expected to increase regenerator temperature, the concurrent improvement in delta coke (driven by lower MCR and lower Ni) more than offset this effect. The net effect was a reduction in regenerator temperature by 11 °C. The combined benefits of higher MAT and lower delta coke lead to a significant increase in conversion, which based on representative economics from early 2026, corresponded to an estimated profitability uplift of $1.21/bbl.

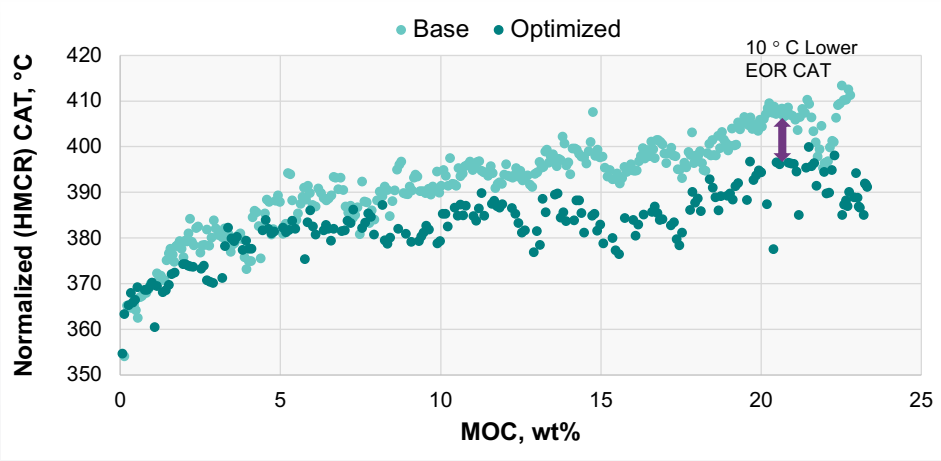


Figure 9: Normalized HDMCR Performance for the Optimized System

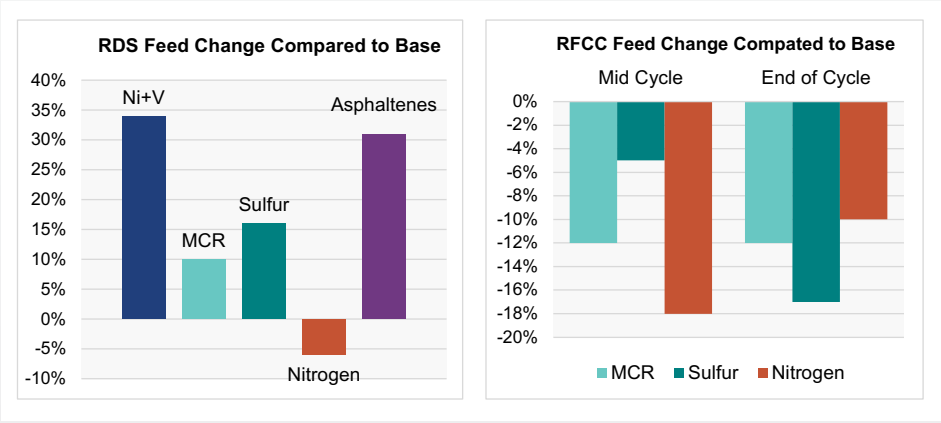


Figure 10: Change in RDS Feed and Resulting RFCC Feed Using the Optimized Catalyst System

Table 4: Impact of Catalyst System Optimization on RFCC Feed Properties at EOR for Case Studies 1 and 2

RFCC Feed Property Shifts	Case 1 End of Run	Case 2 End of Run
API	-	0.4
Specific Gravity	-	-0.002
S, wt%	-0.13	-0.07
Nitrogen, mg/kg	-	-129
MCR, wt%	-0.77	-0.55
Ni, mg/kg	-2.6	0.7
V, mg/kg	-5.4	1.7

Table 5: Impact of Improved RFCC Feed Quality on RFCC Operating Conditions and Product Yields

RFCC Operational Shifts	Case 1 End of Run	Case 2 End of Run
Regenerator Temperature, °C	-10.5	-10.7
Circulation Rate, t/min	2.7	1.7
Ecat MAT, wt% FF	6.0	-1.0
Conversion, wt% FF	9.3	0.5
Dry Gas, wt% FF	0.0	-0.2
LPG, wt% FF	4.0	0.3
Gasoline Yield, wt% FF	5.2	0.5
LCO Yield, wt% FF	-3.1	-0.1
Slurry Yield, wt% FF	-6.2	-0.4
Profit Improvement, $/bbl	1.21	0.38

In Case Study 2, the RFCC feed quality shifts were more mixed. Improvements were observed in API, nitrogen, and MCR, even though metals increased. The higher feed V resulted in a slight drop in MAT. However, the model still indicates a net conversion gain driven by the improvements in API, nitrogen, and MCR. The predicted regenerator temperature also declined by 11 °C. Using the same economics as above, these performance changes correspond to a profitability uplift of $0.38/bbl.

Conclusion

Collectively, these case studies demonstrate how ART's customer-driven catalyst development, combined with proprietary modeling and run-over-run optimization, enables refiners to process higher severity opportunity crudes while still allowing for an improvement of RFCC feed quality.

In Case Study 1, seven cycles of continual optimization increased EOR metals on catalyst by 22% while delivering more stable HDMCR and HDS activity throughout the run. This resulted in lower RFCC feed metals, MCR, and sulfur relative to the base case. RFCC modeling showed that these changes to the RFCC feed quality increased MAT and improved delta coke, driving higher conversion while reducing regenerator temperature. Under representative early 2026 economics, this translated to an estimated $1.21/bbl uplift.

In Case Study 2, five cycles of catalyst system refinement and deployment of next-generation conversion catalysts reduced RFCC feed MCR by 12% while also improving sulfur and nitrogen, despite processing a significantly more challenging RDS feed. Although higher RFCC feed metals resulted in a slight drop in MAT, modeling still predicted a net conversion gain and a $0.38/bbl profitability uplift.

Taken together, the results highlight a critical insight into RDS–RFCC integration. Maximizing RFCC profitability requires improvement in metals removal, as well as in MCR reduction. Minimizing RFCC feed metals protects catalyst activity, while lowering MCR reduces delta coke and regenerator temperature, together capturing the full economic benefit of improved feed quality.

In both cases, customers were able to process opportunity feedstocks, adding significant levels of incremental value across the RDS-RFCC configuration.

Continued collaboration with ART across multiple operating cycles can deliver compounding performance gains and economic returns.

Reference

Foster, A.; Tsai, Y.; He, R.; Cooper, C.; Amalraj, S.; *Designing Improved Resid Hydrotreating Catalyst Systems for Higher RFCC Profitability*, Grace Catalagram 130 (2025).



Maximizing Propylene Production through Operational Excellence, Innovative Catalysts, and Hardware Design

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Global demand for propylene is rising sharply, driven by expanding use in plastics, chemicals, and everyday goods. Refiners are under increasing pressure to respond — maximizing output while managing cost and emissions. This article explores how one refiner unlocked higher propylene yields in FCC operations. Through a real-world case study, it shows how a holistic approach to catalyst design helped deliver measurable gains in desired yields and profitability.

Propylene plays a vital role in the petrochemical industry, with approximately 70% of propylene production going into the manufacture of polypropylene, a widely used polymer in durable goods, automobiles, construction, and packaging, among a variety of other uses. Propylene is also used in the manufacture of propylene oxide, acrylonitrile, cumene, and more, with end applications in polyurethanes, solvents, and pharmaceuticals. The demand for propylene is expected to grow significantly in the coming decades (Figure 1), driven by rising demand from population growth and improved standard of living, particularly in the Asia-Pacific region.

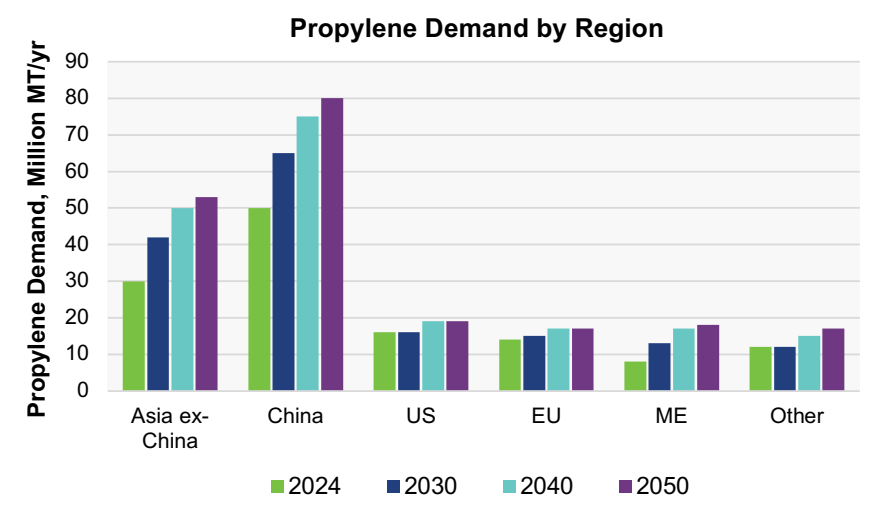


Figure 1: Propylene Demand by Region.

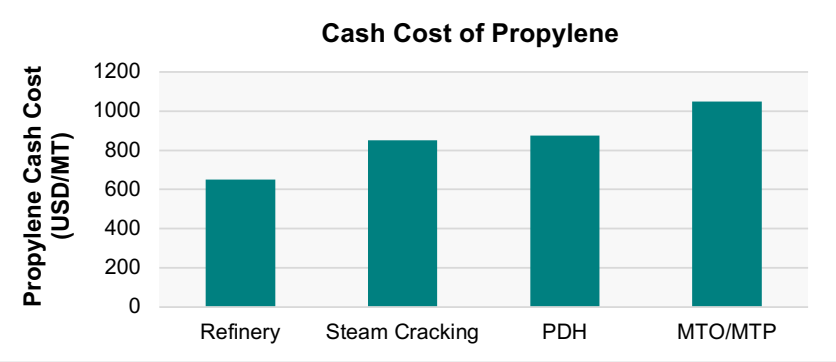


Figure 2: Cash Costs of Propylene.

Propylene from FCCUs

Fluid catalytic cracking units (FCCUs) are not only the most flexible, but also the most cost advantaged, easy to implement, and least carbon intensive of the primary propylene production routes. The flexibility of FCCUs allows refiners to reformulate or revamp existing units with relatively lower investment to adapt the FCCU's propylene production capabilities to evolving market dynamics. This contributes to a lower cash cost of propylene for FCCUs compared to other technologies such as steam cracking, propane dehydrogenation, and other on-purpose propylene production technologies (Figure 2). The use of ZSM-5 additive in FCCUs also enables refiners to increase propylene production at constant or reduced Scope 1 emissions, effectively reducing carbon emissions per unit of propylene produced.

Maximizing Propylene in a Novel Unit Design

The following case study illustrates how one refiner improved propylene yields in a new high-severity (HS) FCC (HS-FCC™) unit.

It includes details on the development, testing and implementation of a customized catalyst solution utilizing a combination of Grace's flagship high-diffusivity, low-Z/M bottoms cracking MIDAS® catalyst family along with the highest activity propylene selective ZSM-5 additive, ZAVANTI™. This catalyst solution boosts cracking of gasoline range olefins into the desired propylene and ethylene yields, all while providing superior activity retention and minimizing thermal cracking and catalyst losses. With the Grace catalyst system for the HS-FCC™, the refiner was able to boost commercial unit propylene yields by > 1.5 wt% ff, ultimately increasing profitability for the customer.

The Licensor's Novel HS-FCC™ Unit Design

The HS-FCC™ unit design was jointly developed by Eneos in Japan, Saudi Aramco and King Fahd University of Petroleum and Minerals, and is licensed by Axens and Technip Energies.

The HS-FCC™ process utilizes a downflow, instead of the typical riser reactor. The unit operates at a very high reactor outlet temperature (580 °C–620 °C [1,076 °F–1,148 °F]). To minimize dry gas formation at this high temperature, it is important to have a short contact time and minimize back-mixing in the downflow reactor and the Tempest™ catalyst/products separator (Figure 3).

Regenerated catalyst flows downward from a withdrawal well. Feed is injected radially and downward using a patented injection system. The downflow reaction system eliminates back-mixing and provides narrow residence time distribution. The typical residence time is less than one second, and the catalyst-to-oil ratio is in the range of 15–30.

Feedstocks can be vacuum gasoil (VGO), de-asphalted oil (DAO), atmospheric residue (AR), vacuum residue (VR), and heavy coker gasoil (HCGO).

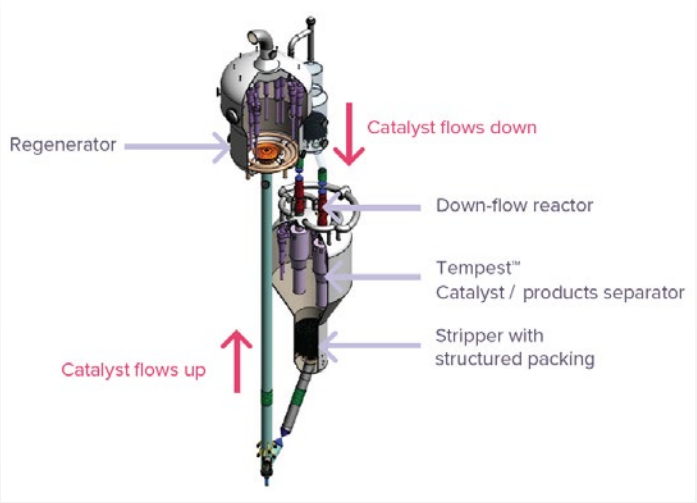


Figure 3: The HS-FCC™ Unit Configuration.

Optimizing a Catalyst System for the HS-FCC™ Unit Design

Since starting up the first commercial HS-FCC™ unit in 2018, the Asian refiner focused on processing resid to propylene and has continually worked with the technology licensor and catalyst suppliers to stabilize operation and optimize catalytic solutions for the HS-FCC™ unit. In May 2020, after experiencing lower than expected propylene yields on the incumbent catalyst, the refiner tasked Grace with the following objectives for a catalyst reformulation:

- Improve olefins yield: propylene and ethylene;
- Improve the catalyst-to-oil ratio to increase light olefins yield; and
- Improve operability and costs with reduced catalysts losses.

Grace's approach was to optimize the entire catalyst system, selecting the best base catalyst and ZSM-5 technology pairing to maximize propylene and ethylene yields (Figure 4).

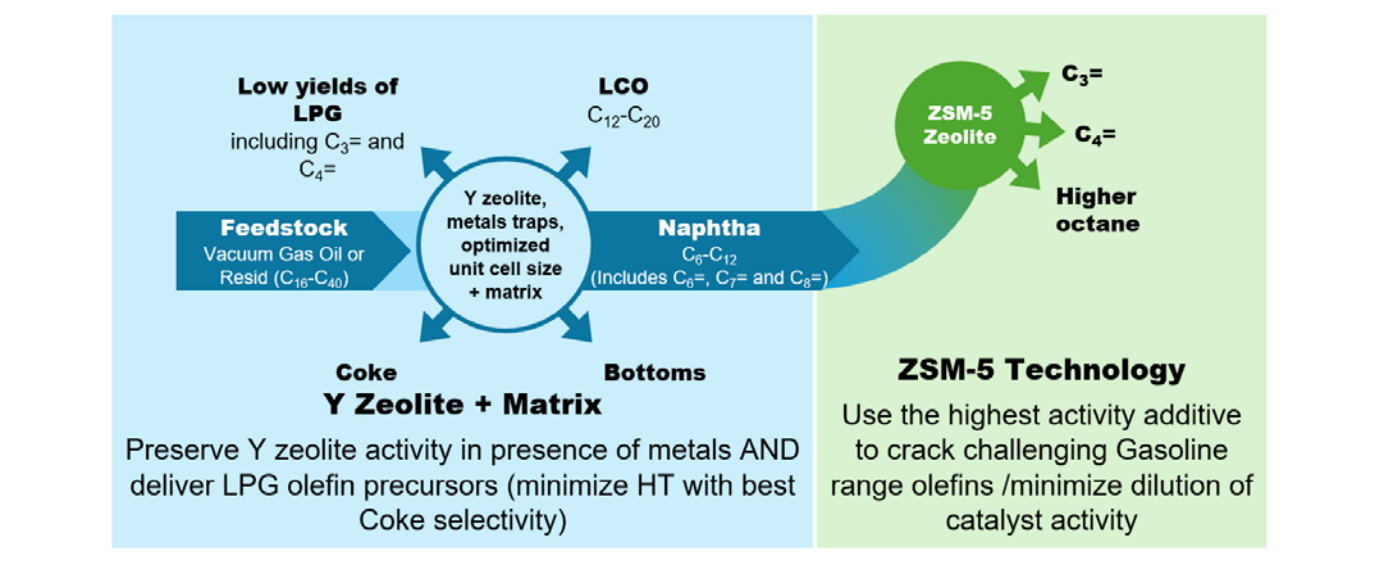


Figure 4: Selecting the Best Base Catalyst (Y-Zeolite/Matrix Component) and ZSM-5 Technology System to Maximize Propylene.

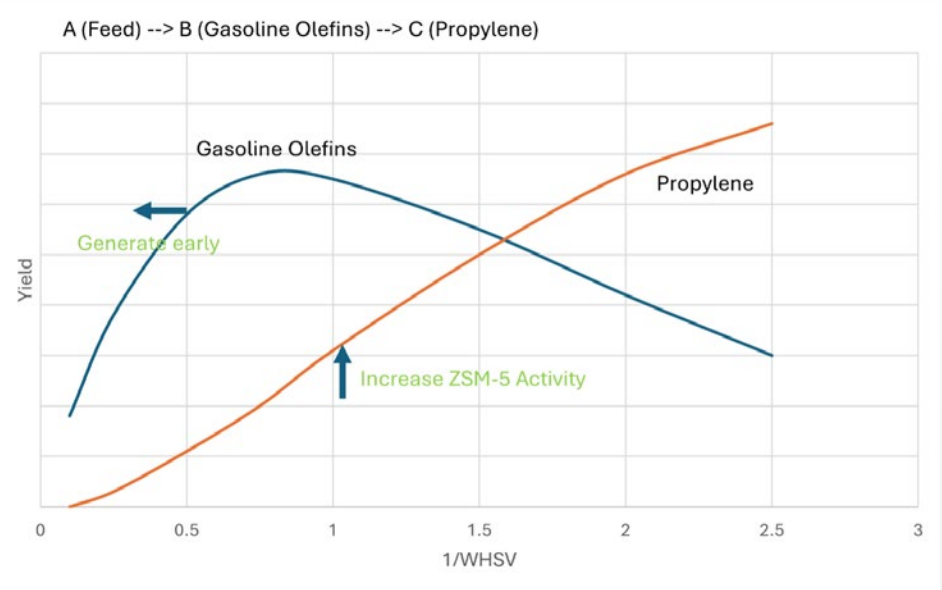


Figure 5: High Catalyst Porosity and Diffusivity to Facilitate Feed Adsorption, Vaporization, and Diffusion, Increasing Unit Conversion

The short residence time in the HS-FCC™ design makes it critical for a catalyst system to facilitate efficient vaporization of heavy feed molecules. Therefore, it is important for the selected catalyst to have optimum pore size distribution to allow the feed molecules to be cracked into desirable products while reducing non-selective secondary reactions that can result in undesirable byproducts like dry gas and coke. In addition, the high weight hour space velocity (WHSV) — or short space time — of a downflow reactor design requires not only faster transport of feed molecules into catalyst to generate gasoline olefins, but also quick transport of gasoline olefins to the ZSM-5 component to be cracked into light olefins (Figure 5). To this end, catalysts with high porosity and diffusivity were tested to facilitate feed adsorption, vaporization, and diffusion, increasing unit conversion.

For the additive component, Grace studied gasoline samples from the unit operating with the incumbent catalyst and found that they still contained large amounts of C5 and C6 olefins, suggesting that the propylene production at the time was limited by the activity of the ZSM-5 additive. To address the deficiency in ZSM-5 activity of the incumbent catalyst, Grace tested its highly propylene selective ZAVANTI™ ZSM-5 additive technology to ensure more of the gasoline range olefins generated by the base catalyst were cracked into the desired propylene and ethylene products.

With the criteria laid out for the base catalyst and ZSM-5 additive system, Grace selected several of its most suitable technologies for pilot scale Davison Circulating Riser (DCR™) testing.

DCR™ Testing and Selection of the Optimized Catalyst System

Due to the unique operation of the HS-FCC™, Grace made several adjustments to its DCR™ pilot plant to better simulate HS-FCC™ conditions and allow for proper testing of catalyst candidates. First, the riser outlet temperature was increased to the temperatures used in the HS-FCC™ (580 °C–600 °C [1,076 °F–1,112 °F]). Next, the unit pressure was reduced, and the reactor steam and lift nitrogen were increased to shorten catalyst and vapor residence time in the riser. Ultimately, a vapor contact time of less than one second was achieved, leading to DCR™ yield patterns in line with those found in literature for pilot studies on HS-FCC™ unit design.

With DCR™ calibration studies completed to match HS-FCC™ unit yields, the modified DCR™ operating parameters were used to test multiple catalyst families and formulations, along with various ZSM-5 additive levels, to select an optimized catalyst system to meet the refiner's yield objectives. From the DCR™ results in Figures 6-8, catalyst option 3 exhibited the best balance of yields in terms of propylene, ethylene, and conversion.

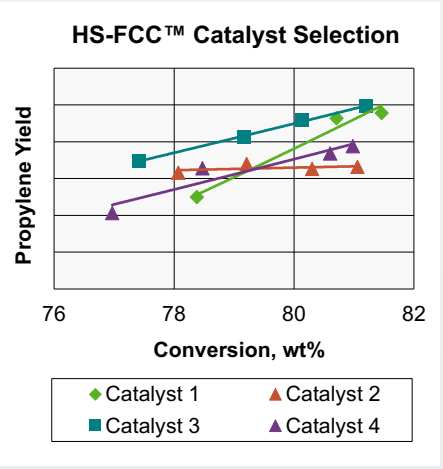


Figure 6: HS-FCC™ Catalyst Selection, Propylene Yield.

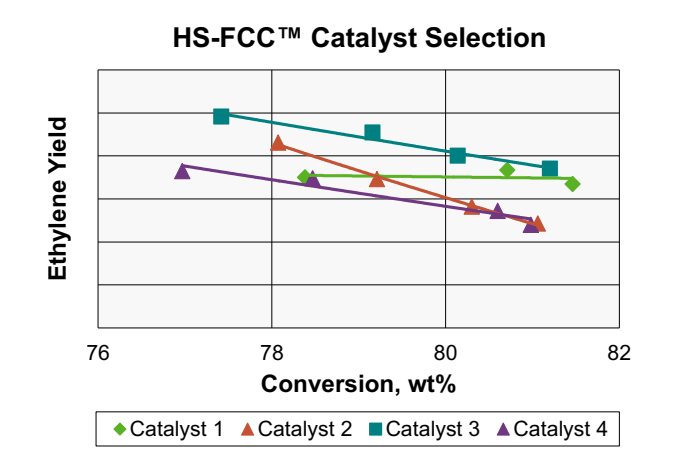


Figure 7: HS-FCC™ Catalyst Selection, Ethylene Yield.

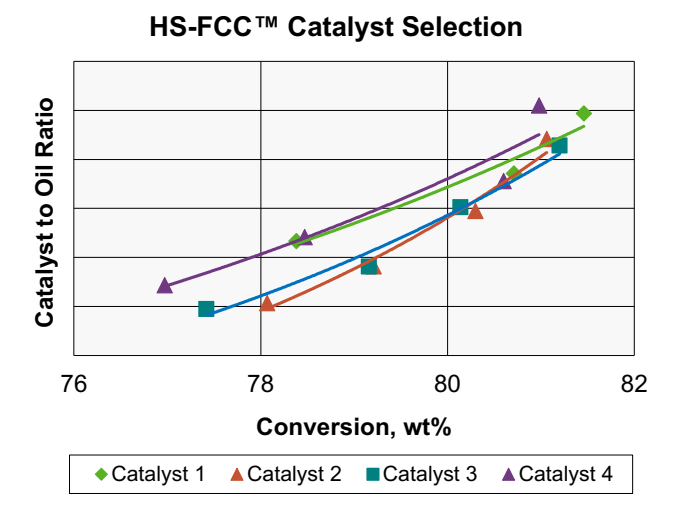


Figure 8: HS-FCC™ Catalyst Selection, Catalyst-to-oil Ratio.

From these results, Grace selected and recommended catalyst system 3 to the refiner. Catalyst system 3 was comprised of:

1. Grace's flagship high-diffusivity, low-Z/M base MIDAS® catalyst technology to provide higher gasoline range olefins through:
    - Optimum zeolite/matrix (Z/M) and rare earth on zeolite (RE/Z) to minimize hydrogen transfer for target activity;
    - Best-in-class Y-zeolite technology for improved coke selectivity and high stability, resulting in lower thermal cracking;
    - High diffusivity to limit non-selective secondary reactions, preserve olefins and provide better bottoms cracking; and
    - Good metals trapping capability for activity retention and coke selectivity.
2. Grace's highest activity propylene selective ZAVANTI™ ZSM-5 technology to crack the gasoline range olefins generated by the MIDAS® catalyst technology into the desired propylene and ethylene products. Grace's ZAVANTI™ ZSM-5 technology offers the following benefits:
    - Maximum activity to crack challenging shorter gasoline range molecules into desired propylene and ethylene yields;
    - High activity retention to prevent activity loss under severe HS-FCC™ conditions; and
    - Improved selectivity to desired light olefins.

The synergistic effect of the high-diffusivity, low-Z/M catalyst with class-leading ZSM-5 technology enabled Grace to demonstrate propylene improvements in pilot testing, unit trial, and, ultimately, during ongoing supply.

Independent, Third-Party Pilot Plant Testing

After Grace provided the catalyst system recommendation and DCR™ test results to the refiner, the refiner requested independent third-party pilot testing to further build confidence in the DCR™ results and gather the internal approvals needed to proceed to unit trial. Grace partnered with the refiner to identify the most suitable third-party testing facility to validate the yield improvements observed in DCR™ testing, and supported the third-party testing to compare the following catalysts:

- Grace's deactivated catalyst (Grace)
- Equilibrium catalyst from the HS-FCC™ unit (Ecat)

Samples of the fresh catalyst system proposed by Grace were metalated and deactivated by the third-party to match the deactivation profile of the unit Ecat, then tested at the third-party testing facility.

The third-party independent testing revealed that Grace's catalyst system exhibited higher propylene and ethylene yields, reduced H_2 and methane (CH_4) yields, and a higher C_3/C_4 ratio (Figures 9-12). The commercial HS-FCC™ unit yield (FCCU) is also plotted on Figures 9-12 for reference. These results provided sufficient evidence for the refiner to proceed with a unit trial.

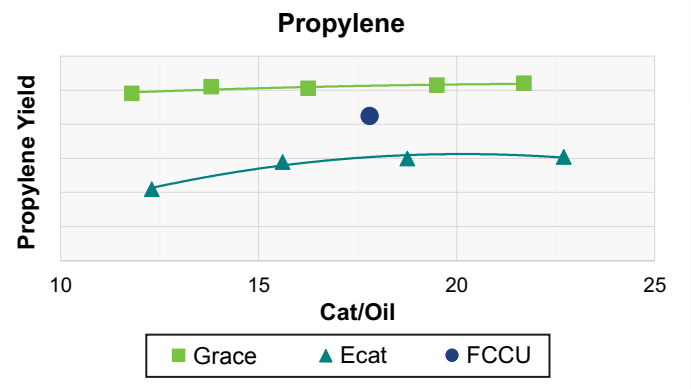


Figure 9: Results of the Third-party Pilot Testing, Propylene.

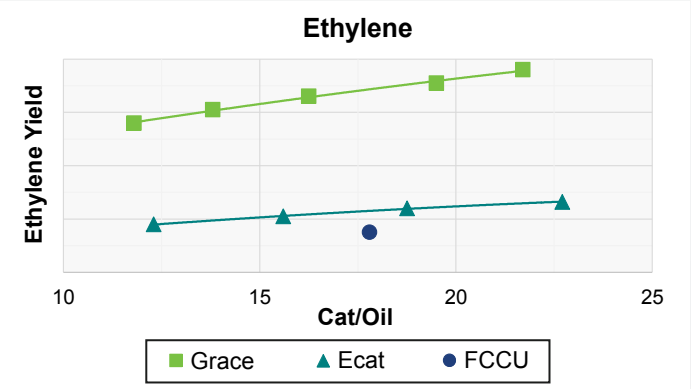


Figure 10: Results of the Third-party Pilot Testing, Ethylene.

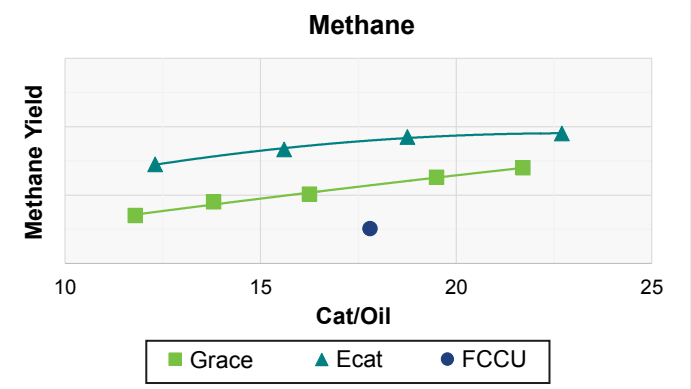


Figure 11: Results of the Third-party Pilot Testing, Methane.

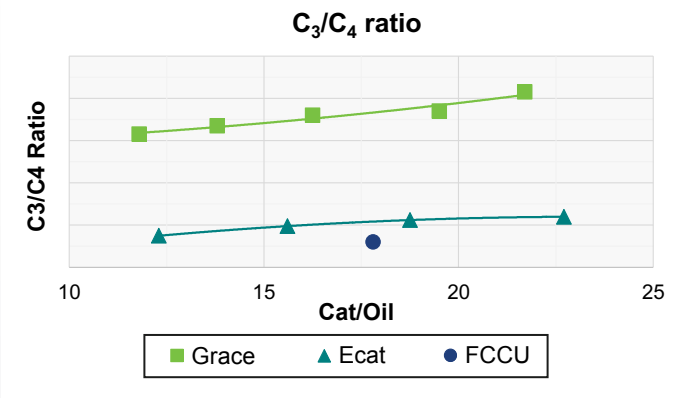


Figure 12: Results of the Third-party Pilot Testing, C_3/C_4 Ratio.

HS-FCC™ Commercial Unit Trial

After observing the positive test results from the third-party pilot testing, the refiner decided to move forward with a six-month trial to test Grace's new catalyst system. During the trial period, the catalyst system demonstrated a 1.5 wt% ff improvement over the incumbent catalyst system.

In addition to the improvements in propylene yield against the incumbent catalyst, Grace's catalyst also demonstrated lower thermal cracking products, including H_2, CH_4, ethane (C_2H_6), and butadienes compared to the competitor catalyst (Table 1).

Table 1: Comparison of Commercial Unit Performance on Grace's Catalyst System vs. the Incumbent Catalyst

Description	HS-FCC™ unit performance vs. incumbent
Throughput	↑
ROT	Base
Catalyst/oil	↑
Feed hydrogen content	Base
Catalyst make-up	Base
Catalyst changeout	75%
Yields	
Propylene	↑
Ethylene	↑
Cracked naphtha	↓
Dry gas (excluding C_2=)	↓

These results confirmed that the improved propylene yield was not only driven by the improved ZSM-5 activity, but also by the increased gasoline olefins generated by the high-diffusivity, low-Z/M MIDAS® catalyst, along with the effective activity optimization of the components in the catalyst system to preferentially favor the desired catalytic cracking reactions and minimize the undesired thermal cracking pathways. The overall performance improvement seen in the unit trial demonstrated the importance of a cohesive and comprehensive approach in designing and optimizing a catalyst system to enhance desired yields for FCC operations.

The refiner expressed complete satisfaction with the performance of Grace's catalyst system and decided to move forward with a long-term supply agreement, which has continued since July 2024.

Conclusion

FCCUs have undergone significant transformation throughout their history and are continually being adapted to meet the evolving needs of the refining industry. During this time, FCCUs have proven to be one of the most flexible and resilient operations in a refinery, positioning them well to play a vital role in the ongoing transition from fuels to petrochemically focused FCC operation.

This article has profiled the approach to catalyst optimization that Grace has taken to help a refiner operating the novel HS-FCC™ unit design to achieve a 1.5 wt% ff higher propylene yield than with the incumbent catalyst. The yield improvement was made possible through a holistic approach to catalyst optimization, utilizing a high-diffusivity, low-Z/M base MIDAS® catalyst to maximize production of gasoline olefins paired with the highest activity ZAVANTI™ ZSM-5 additive available to maximize the cracking from gasoline olefins into the desired propylene and ethylene yields, all while tuning the activity of the catalyst to minimize undesired thermal cracking reaction pathways.

Through pilot testing, unit trials, and ongoing supply, Grace has worked alongside the refiner and licensor to build a deeper understanding of how to optimize catalyst performance in this novel HS-FCC™ design. That experience helps refiners continue adapting as feedstocks, operating conditions, and product priorities shift, with Grace bringing practical insight, technical depth, and a forward-looking approach to catalyst development that can support sustained performance and enhanced profitability over time.

Lessons Learned from FCC Biofeed Co-processing

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The use of existing assets in crude oil refineries can accelerate decarbonization or defossilization efforts, derisking uncertainty with large financing requirements and scale-up risks associated with new processes. As such, co-processing of bio-derived feedstock in crude oil refineries will support the transition to lower carbon intensity fuels, chemical feedstocks, and consumer products. This article offers a survey of learnings from multiple co-processing pilot studies and commercial trials.

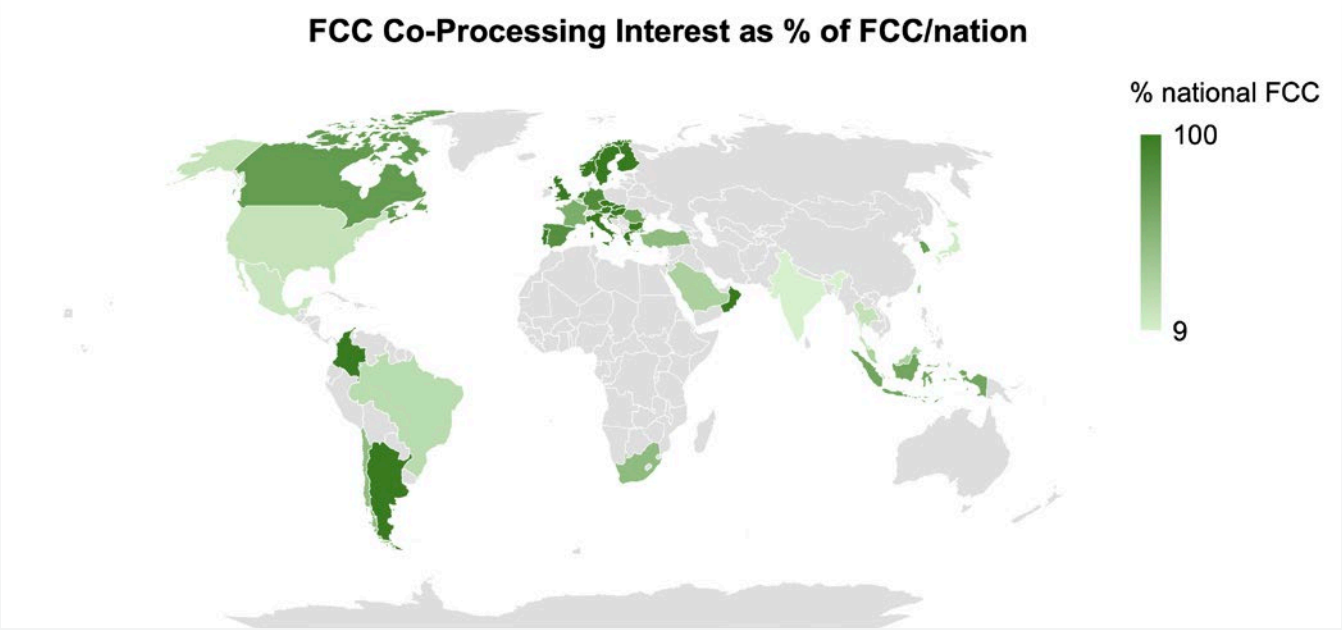


Figure 1: Grace's Visibility of Interest in FCC Co-processing in Percent FCC Units Per Nation

For over 80 years, the fluid catalytic cracking process has proven its adaptability, robustness, and value in modern crude oil refining [1]. The multitude of operating modes and refinery-specific economics around the FCC is a testiment to its flexibility. For example, while some refiners focus FCC operation on upgrading feeds to petrochemical feedstock such as propylene, others might operate their unit to maximize middle distillates, or have strong economics around the FCC bottoms product. In all these scenarios, the complete yield pattern is valorized with refinery specific product economics.

A large portion of refining companies are interested in co-processing of unconventional feedstocks in the FCC unit, as shown in Figure 1. Such feed streams can be biomass- or chemical recycling-derived liquids, which can be substantially different from crude oil-derived intermediates.

Biomass-derived feed streams are quite different from crude oil fractions. The class of these liquids spans a heterogeneous chemistry unified by the presence of oxygen as a major or minor component. For FCC operation with conventional feeds, oxygen can be introduced into the riser via entrainment of molecular oxygen carried over from the regenerator along with the circulating catalyst. Oxygen is typically present in trace concentrations in crude oil-derived streams. Oxygen is present in much higher concentrations in the case of unconventional feeds and this can cause new processing and specification challenges in refineries.

On the other hand, liquids from streams like mixed plastic waste, municipal solid waste, sewage sludge, or waste (end-of-life) tires present a heterogeneous feed class with respect to chemistry and the presence of trace contaminants. Challenges and opportunities continue to be monitored in the industry with the increasing availability and processing of these feeds.

With growing interest in co-processing unconventional feedstocks, several FCC units around the globe have trialed and/or implemented continuous co-processing. The Grace technical service team receives many inquiries regarding the opportunities and challenges that come with co-processing and how to avoid problems that others experienced while generating added value. This paper aims to discuss observations, opportunities, and challenges from FCC co-processing of biomass-derived feeds and provide insights from commercial application and pilot plant evaluation.

Feedstock Selection

Bio-derived feedstocks range from fats, oils and greases (FOGs) — or lipid-based materials such as seed oils, animal fats, and waste cooking oils — to lignocellulosic streams like wood-derived pyrolysis oil and tall oil. Selection and supply of such feedstocks in refinery scale quantities can be a hurdle. Early movers in many cases secured supply by direct investment or joint ventures with established market actors.

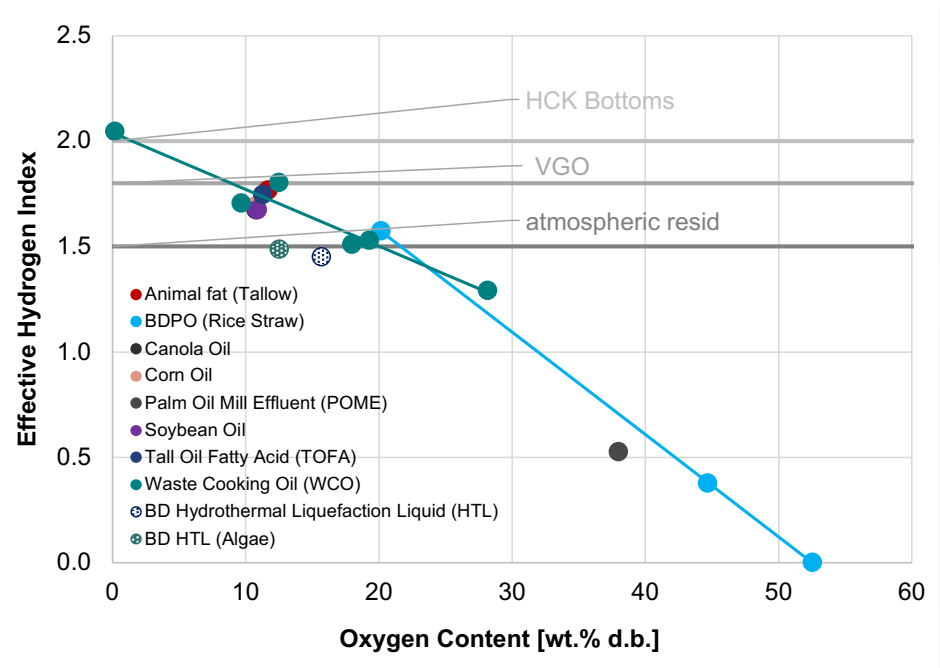


Figure 2: Effective Hydrogen Index [3] Versus Feed Oxygen Content of a Selection of Different Bio-derived Feeds

Edible oils or first-generation biofeeds are an important source of bio-derived feed streams in some regions. Miscibility and thermal stability are typically of lower concern with such streams. Second generation or "advanced" biofeeds, such as tallow/animal fats, waste cooking oils, etc., typically vary from batch to batch to some extent. As a result, increased monitoring is required to mitigate negative effects of contaminants or challenges associated with varying levels of oxygen. Regional regulatory requirements can make advanced biofeeds particularly attractive. For example, high demand for waste cooking oils has driven high prices and rapid supply chain development for those feeds. The FCC co-processing route also competes with the hydroprocessing route (HEFA – hydrotreated esters and fatty acids) to produce renewable diesel or sustainable aviation fuel (SAF), further increasing demand for these feeds.

Much of the supply of lipids stems from specific regions. Asia for example is a large supplier of edible oils and waste cooking oil. Trade flows of these feeds drive local availability. This underscores the need to secure feedstock supply at an early stage. For example, the investments in renewable diesel plants in the USA that came along with favorable investment incentives of the Inflation Reduction Act (IRA) drove significant volume of waste cooking oil supply from Asia towards North America. [2]

While FOGs are limited in quantity and are often directed to the HEFA processing route, lignocellulosic feed streams like bio-derived pyrolysis oil are difficult to process. Overcoming these processing challenges will be important to open the lignocellulosic value chain to more investment and consequently widen availability as the supply of FOGs to refinery value chains is predicted to be limited.

As the FCC process is redistributing hydrogen in feed to products, feed hydrogen content is an important property to assess crackability and product tendencies of FCC feedstocks. When heteroatom content is significant, it needs to be taken into account instead of focusing on pure hydrogen-to-carbon (H/C) ratio. Chen et al. [3] introduced the concept of effective hydrogen index (EHI), with lignocellulosic feeds having a low EHI (Figure 2). This reflects the hydrogen deficiency of such lignocellulosic feeds, indicating lower crackability and lower H/C incremental yield.

Supply chain logistics must be considered in the assessment of co-processing opportunities. The upstream logistics of the unconventional feedstocks are important items to be considered and are typically associated with some investment. Feedstock segregation is often required. The properties of the selected feedstocks in terms of miscibility, interaction with the other components of combined FCC feed, and thermal stability govern considerations about injection points into the feed line to the FCC. While typically unconventional feedstock options can be considered separately, the processing of several unconventional feedstocks should include investigations into the interactions between them. Anecdotal evidence indicates the potential for negative interactions between different biofeeds, which could result in operational difficulties.

All bio-derived liquids have the commonality of introducing a new heteroatom, oxygen, in significant concentration to the FCC. The FCC process is effective in deoxygenating the biogenic compounds without the consumption of precious added hydrogen, especially considering FOGs. The oxygen in such feeds is almost completely converted to water, CO, and CO_2 (see yield section).

In addition to oxygen, bio-derived streams can contain contaminants like alkali and alkaline earth elements as well as phosphorus. While some of these contaminants are well understood due to their presence in traditional feedstocks, others pose new challenges to FCC operation (see the Ecat contaminant section for more information). Catalyst contaminants and deactivation do not appear to be a predominant constraint observed commercially at current low to moderate co-processing rates. As co-processing rates continue increasing and feedstocks with higher contaminant levels are evaluated, catalyst deactivation must be addressed. Development of metals tolerant catalyst technology and feed treatment options will be an active area of research.

Another concern with the properties of bio-derived liquids is often associated with their increased acidity or elevated chloride content. Most of the concern is concentrated around the hardware upstream of the FCC riser with regards to the acidity. Corrosion has to be assessed and monitored in detail during the assessment of co-processing projects [4]. Known effects of increased chloride content of unconventional feeds are discussed below.

Some of the bio-derived feedstocks, especially bio-derived pyrolysis oils, might not be thermally stable and therefore require bypassing of the FCC preheat train, including separate feed injection. FCC licensors offer technical solutions for such feedstocks.

The water content of the bio-derived feedstocks could be high. Free water should be removed upstream from the feed injectors to prevent uncontrolled water vaporization leading to riser vibration or feed nozzle damage. A feed drum with a water boot will reduce the risk of free water entrainment, for example.

Feed Introduction

Renewable Feedstock Atomization Injectors and Handling

Once feedstock supply is secured and stored on site, refiners must address the issues associated with injecting the feed to the FCC. Feedstock stability at elevated temperatures, miscibility issues, increased corrosion rates, and higher amounts of light ends relative to traditional feedstock can result in problematic operation of the feed preheat train and injection nozzles [5]. One or more of these issues may require the refiner to use a dedicated feed injection nozzle.

Plugging of traditional nozzles from polymerization has been observed, limiting the processing of some challenging bio-based pyrolysis oil. Additional use and monitoring of filter/strainer systems in the biofeed supply line might be required depending on bio feedstock type and source, its thermal stability, and general quality.

Feed injection nozzles specifically designed for bio-based feed, particularly the pyrolysis oils, are offered by several licensors. These feed injection systems employ enhanced metallurgies such as 317L stainless steel or even Hastelloy and minimize the temperature of the biobased feedstock inside the nozzle prior to injection into the FCC riser. Minimizing temperature of the renewable feedstock is a task accomplished by using a design with strategic insulation and atomizing the feedstock with alternate fluids instead of steam [6].

Several refiners are successfully processing renewable feeds through their primary feed or recycle nozzles. For these cases, extra precaution is required to avoid excessive corrosion and nozzle plugging. Many refineries that employ a dedicated feed injection nozzle especially designed for bio-based feedstocks are processing more difficult pyrolysis oils, which can degrade and plug the nozzle at traditional FCC feedstock temperatures.

Renewable feedstocks are almost always stored in dedicated containers or tanks. In some cases, the renewable feedstock is mixed with the primary FCC feedstock upstream of preheat exchangers. However, the more common approach is for the renewable feedstock to be mixed with the primary feedstock immediately upstream of the feed injection nozzles to minimize the mixing time with the primary feedstock.

Riser/Reactor Section

Heat Balance Effects from Lower Heat of Reaction

The exothermic formation of carbon monoxide, carbon dioxide, and water will reduce the overall endothermic heat of reaction when co-processing renewable FCC feedstocks.

Bryden et al. described a ~15% lower endothermic heat of reaction from 100% soybean oil processing relative to cracking vacuum gasoil (VGO) in a Davison Circulating Riser (DCR™) pilot plant [7]. The FCC heat balance responds to the lower heat of reaction by requiring a lower cat/oil to maintain the same riser outlet temperature (ROT), thereby reducing coke yield. Many units limited by catalyst circulation and/or air blower capacity may alleviate that constraint by replacing some traditional feedstock with a renewable bio-based feedstock. Reduced catalyst-to-oil ratio and coke demand results in lower conversion of the base feedstock. This can be offset by increasing ROT or equilibrium catalyst activity.

For example, the heat balance effects associated with co-processing of 20% soybean oil allow ROT to be raised at a constant air blower and catalyst circulation capacity resulting in a gain in conversion of the base feedstock as demonstrated in a pilot study. (Table 1)

Table 1: Reaction Conditions of DCR™ Testing of VGO and VGO and Soybean Oil Blend

	100% VGO	80%/20% VGO/soybean oil	
ROT, °F	Base	Base	+6
Preheat, °F	Base	Base	Base
Cat/Oil	Base	-0.1	Base
Coke, wt% ff	Base	-0.1	Base
Heat of Reaction, Btu/lb	Base	-5	-5
Base Feedstock Conversion, wt% ff	Base	-1.5	+0.7

Lower Flue Gas Opacity

Some refiners processing pyrolysis oil in FCC units observed a decrease in flue gas opacity alongside an increase in slurry ash content. During the cracking of pyrolysis oil in the FCC, biochar – a solid, carbon-rich byproduct of thermochemical biomass conversion – can form. Froehle et al. [8] explain that biochar within the FCC reactor has alkali metal properties that enable it to attract catalyst fines. Due to its low density compared to FCC catalysts, biochar and the attached catalyst fines are more likely to be lost from the reactor, leading to a higher concentration of catalyst fines in the slurry product. The lower flue gas opacity observed is attributed to the reduced presence of catalyst fines in the regenerator. Increased slurry solids content may require additional monitoring and mitigation from equipment reliability and finished product property perspectives.

Catalyst Inventory

Bio-derived feedstocks will introduce known or new catalyst poisons and inhibitors into the FCC unit. These contaminants include alkaline and alkaline earth elements and phosphorus (see Table 2).

Alkali and alkaline earth elements are known FCC catalyst poisons. Zeolite deactivation is the consequence for increasing concentration of alkali elements, while alkaline earth elements like calcium (Ca), are known to exhibit pore mouth blocking effects [10]. Phosphorus, while currently hardly present in fossil FCC feedstocks, is expected to be introduced by biofeed co-processing, and research indicates that this also contributes to pore mouth plugging.

These contaminants provide new issues for catalyst technology companies to address through development of enhanced contaminant tolerant technology and traps. Effective management of these contaminants can be achieved with the use of advanced adsorbents like TRISYL® silica, which is employed extensively for the purification of lipid feedstocks in the edible oil industry [11].

Biofeeds such as waste cooking oils can also contain mg/kg levels of chlorine as a contaminant. This can contribute to a corresponding increase in the chloride content in the sour water stream and cause an adverse impact.

Yield Structure and Downstream Considerations

The FCC catalyst and the process provide high activity for oxygen removal. Commercial observations and extensive pilot plant evaluation studies provide significant insight on the deoxygenation reaction pathways in the FCC process while co-processing biofeeds. Most of the feed oxygen is converted to water, CO, and CO_2 with the remaining oxygen resulting in trace (mg/kg) levels of organic oxygenates present in gas, liquid product, and sour water streams. While small amounts of oxygen containing products can be formed during the processing of conventional petroleum feedstocks, the concentration of oxygen-containing products greatly increases while processing biofeed.

Table 2: Contaminants in Bioderived Feeds [9]

	Soybean Oil	Rapeseed Oil	Palm Oil (refined)	Waste Cooking Oil	Tallow	Pine Based Pyrolysis Oil	Crude Tall Oil	Typical Ranges FCC Feedstock
Na [mg/kg]	0 – 2	5	0	0 – 30	55	5	Alkali and alkaline earth metals reported as 56 mg/kg	0 – 10
K [mg/kg]	0 - 88	0	0	0 – 20	No data	160		0 – 5
Ca [mg/kg]	3 – 60	14	0	1 – 20	40	400		0 – 20
P [mg/kg]	6 – 150	4	0	10 – 50	60	No data	36	0 – 5

Yield structure impact of co-processing bio-derived feed streams cannot be generalized apart from the increased yields of water, CO, and CO_2. As such, the amount of the biofeed co-processed contributes to the sellable product pool based on the rate minus oxygen in feed, coke, and dry gas yield. Some biogenic carbon is lost from the product pool via the conversion of oxygen to CO and CO_2. With lipidic feedstocks, nearly all oxygen is converted to water and CO_x (CO and CO_2) and the product distribution is about 80:10:10 for water, CO, and CO_2 respectively with trace levels of oxygenate byproducts present in LPG, cracked naphtha, and heavier liquid streams. Other biogenic feedstock types might show a different pattern. In FCC process monitoring, it is important to consider the mass balance impact of increased water yield and the higher CO and CO_2 levels in sponge gas to reflect the FCC yield pattern accurately. Accurate quantification of water yield is complicated by the multiple steam use and entry points in unit and downstream operation. Additionally, a low co-processing rate relative to fossil feed complicates an accurate quantification of additional sour water production and CO_x in sponge gas.

Although water is generated by reaction of oxygenates, the overall sour water increase can be worsened by the direct introduction of water from the co-processed feed. Some alternative feeds may contain significant amounts of water, either from production or contamination during logistic operations. For example, some biomass-based pyrolysis oils have been observed to contain water up to 25 wt%.

The FCC is often referred to as a carbon rejection process but could also be defined as a hydrogen redistribution process. The hydrogen content of the FCC feed is redistributed amongst the products of the cracking process with the unconverted product (by definition LCO and bottoms) and coke having lower hydrogen content while the gaseous products and cracked naphtha are higher in hydrogen content. As such, the formation of water from the oxygen in the biofeed adds to the consumption of hydrogen. Pilot plant testing shows a respective lower hydrogen yield for co-processing of biofeeds [12].

Other yield pattern impacts are dependent on a multitude of factors like biogenic feedstock type and quality, base fossil feed quality, unit operation, catalyst, and additives. Exemplary data have been shared in publications [12, 13].

Table 3 summarizes yield data from a DCR™ pilot plant study for the co-processing of canola oil with VGO as reference fossil feed and a typical equilibrium catalyst (Ecat). This study shows the blending of canola oil with VGO to cause slightly higher propylene yield, slightly lower C4= and gasoline yield, higher LCO yield, and significantly lower bottoms yield. As expected, CO_x and water yield increased with canola oil content.

Table 3: Reactor Yields at Constant Severity Data From DCR™ Testing of VGO and VGO and Canola Oil Blend and Incremental Canola Oil Yield [14]

Yield, wt% ff	VGO	VGO/Canola Oil (8:2)	Incremental Canola Oil Yield
Conversion	74.9	75.2	76.5
H_2 Yield	0.02	0.03	0.03
C_1 + C_2's	1.7	1.7	1.6
C_3	0.70	0.65	0.43
C_3=	5.4	5.6	6.3
iC_4	2.6	2.4	1.6
nC_4	0.55	0.48	0.23
Total C_4=	6.8	6.2	4.0
Gasoline	52.7	51.5	46.7
LCO	18.2	18.7	20.8
Bottoms	6.9	6.0	2.7
Coke	4.2	4.2	4.2
CO	0.00	0.23	1.2
CO_2	0.02	0.13	0.55
H_2O	0.0	2.2	11.2

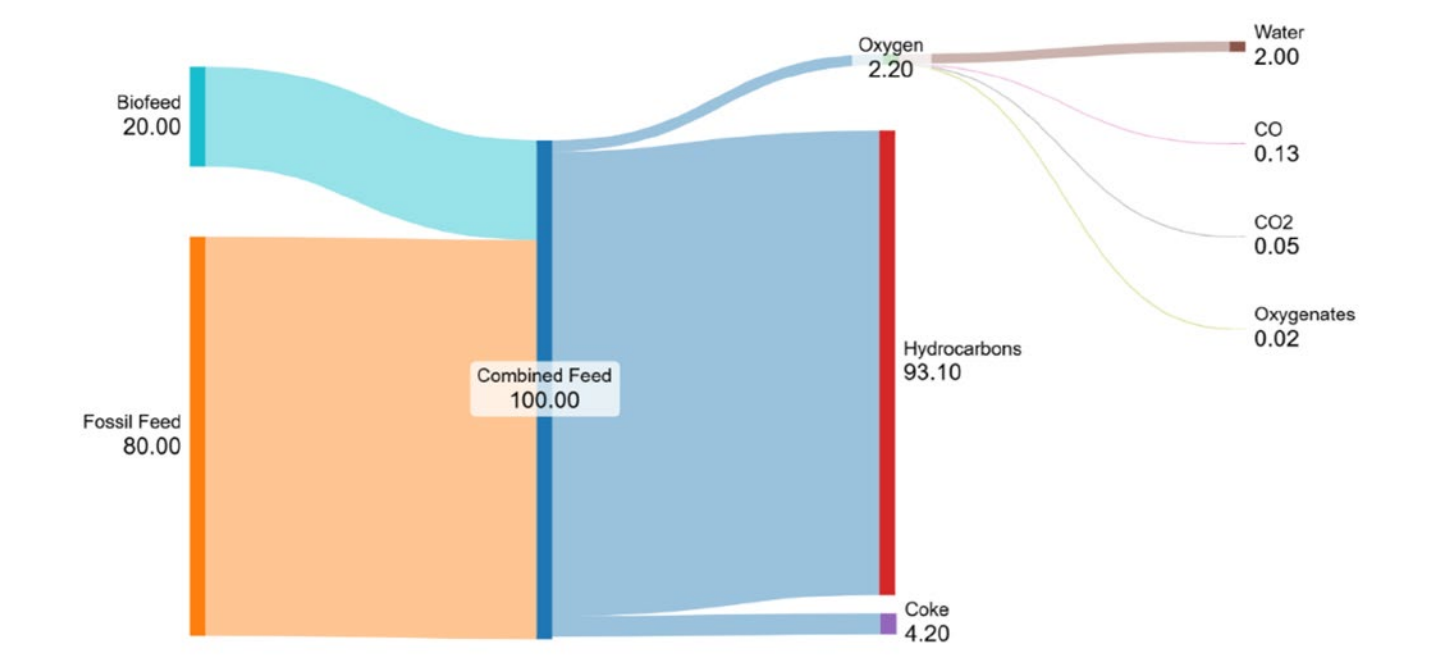


Figure 3: Oxygen Balance from DCR™ Testing of a VGO: Canola Oil Blend (8:2)

In addition to the yield structure impact, the distribution of the biogenic carbon content to the final products might have a governing impact on the FCC co-processing economics. Determination of the biogenic carbon content by ASTM D6866 enables the assessment of biogenic carbon distribution in FCC products, including sponge and flue gas. Depending on the regulatory framework, such testing might be required to generate value from FCC co-processing.

In the case of low co-processing rates, the quantification of yield effects and biogenic carbon distribution may be within the variability of normal FCC operation.

Pilot plant studies routinely incorporate the evaluation of product properties such as naphtha sulfur and octane. The starting quality of the FCC base feed is also important when evaluating the impact on both yield structure and product quality. For FCC processing a deeply hydrotreated feedstock, there could be an increase in the portion of sulfur ending up in the gasoline range. Also at significant biofeed amounts in the feed (>15%), sulfur in the gasoline fraction may increase, whereas at very high levels, the effect of dilution with zero to low sulfur biofeeds will be the dominating factor. Pilot studies and field observations also have shown that at appreciable biofeed co-processing levels, carbonyl sulfide (COS) can be formed due to the reaction of CO_x with H_2S. This will lead to COS enrichment in the propylene stream. These observations indicate an effect of biofeed co-processing on total sulfur distribution amongst FCC products.

Increased reactor side CO and CO_2 are most likely to impact the FCC operation through increased load on the wet gas compressor and higher vapor traffic in the absorber tower and to the dry gas amine scrubber. Figure 3 generated from Grace DCR™ pilot plant data co-processing 20% canola oil with a gas oil base feedstock demonstrates the expected magnitude of increased CO and CO_2 from the oxygen in the feed.

For units operating at wet gas compressor limitations or co-processing significant percentages of oxygen containing feedstock, the increase in non-condensable gases can cause wet gas compressor bottlenecks and reduced profitability due to a need to reduce conversion to accommodate the incremental compressor load. Examining operation downstream of the wet gas compressor yields similar conclusions with increased vapor traffic in the absorber tower and amine treating of the FCC dry gas.

Additionally, CO and CO_2 pose challenges to units downstream of the FCC including amine capacity to adsorb H_2S and fuel gas system limitations. The primary purpose of treating the FCC dry gas (ethane and lighter) is the removal of H_2S prior to routing the stream to refinery fuel gas. The solvents used for this dry gas sweetening are not only selective toward adsorbing H_2S but also CO and CO_2 [15]. This presents additional challenges for sweetening the dry gas, which may require increased amine circulation rates and larger ancillary equipment, as well as poorer operation of the sulfur recovery unit [16]. There are different types of amines with or without CO/CO_2 adsorption.

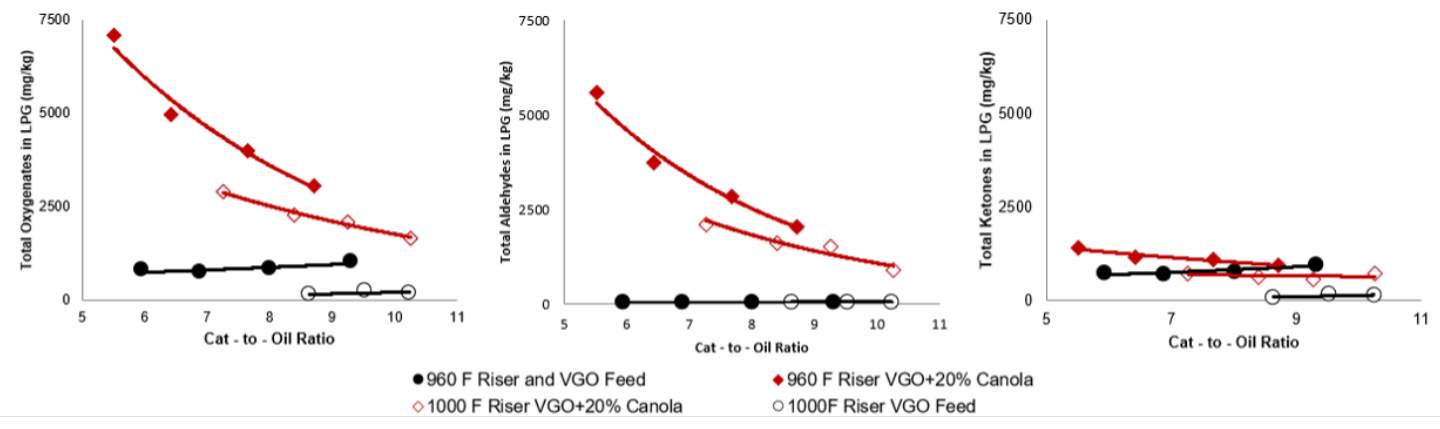


Figure 4: LPG Oxygenates Yields Comparing VGO and VGO: Canola Oil Feedstocks in DCR™

It is possible to selectively remove COS/CO/CO_2 from the dry gas but it requires a change to the amine type and potential redesign of the amine regeneration unit.

CO and CO_2 that are not captured in the amine scrubber enter the refinery fuel gas system, resulting in a lower heat of combustion. This lower heat of combustion may have significant impacts to refining operation if there are furnaces operating at burner tip pressure limits. This may result in a wide range of consequences including lower unit throughput or recovery, incremental natural gas purchases, or the need to vaporize and fuel propane to deliver incremental heat of combustion to the refinery fuel mix.

In LPG products (C_3s and C_4s), Grace and refiners have observed increased oxygenates, with the primary species comprising of aldehydes and ketones, especially when co-processing lipidic feedstocks. Figure 4 shows that co-processing 20% canola oil in the DCR™ results in a substantial increase in total LPG oxygenates.

This pilot plant study demonstrates that aldehydes increase more than ketones. In addition, aldehydes have a stronger correlation to FCC severity, with cat/oil ratio influencing aldehydes to a greater degree than reactor temperature. Additionally, it is important to note that aldehydes are not typically observed in FCC products in appreciable amounts without co-processing of oxygen-containing feedstock. Not only does oxygenate content increase, there is the introduction of a compound that is not widely encountered in normal FCC operation.

In the LPG product treatment section, oxygenates are thought to play a major role in foaming, emulsion formation, and fouling in caustic treater and amine systems. In other industries (including ethylene plants) aldehydes are well documented as the cause of “red oil” formation. Red oil forms as the result of an aldol condensation reaction catalyzed by a base, where oxygenate species react and form a heavy reddish oil [17]. This red oil can result in fouling or emulsions in the treater systems and has been observed in co-processing FCCs.

FCC product oxygenates in LPG and naphtha can also cause issues downstream of the amine, caustic product treatment sections. Any oxygenates that are not removed in these washing steps will end up in the feed to various C_3= and C_4= processing units including cumene, polygasoline, MTBE/ETBE, and alkylation units. In alkylation units oxygenates, such as acetone, result in water formation and increased formation of acid soluble oils, ultimately resulting in higher acid consumption [18]. In some cases, reaction of side products in downstream conversion processes may result in higher boiling range sulfur molecules and impact the gasoline pool blending. Unlike alkylation where increased acid consumption may be relatively straight forward to handle, conversion processes using fixed bed catalysts present acute pain points during co-processing activities.

A common area of contact with a basic medium is in mercaptan extraction and/or sweetening units, which are used for reducing sulfur in both LPG and naphtha streams. As organic oxygenates can absorb into an aqueous phase and react under basic conditions, there is potential for accumulation of atypical species in the caustic streams, and the routing of spent caustic is an important issue to consider. The disposal of this caustic can become difficult and expensive, especially for refiners without any neutralization facilities. Caution is necessary when this spent caustic is routed elsewhere within the refinery as combinations of conditions can result in fouling from red oils [17]. Furthermore, the presence of phenols or higher tendency to form stable emulsions can cause increased carryover of aqueous phases resulting in hazy naphtha and increased tank draining requirements.

As mentioned earlier, elevated concentrations of COS can impact the propylene stream quality and poison the catalyst downstream of the FCC.

There is significant potential for increased sour water rates due to generation from oxygenates or direct introduction. With knowledge of the total water and oxygen content in the feed, it is possible to model the effect on sour water production. The pH of sour water should be monitored and maintained in the typical range (< 9) to avoid corrosion, as the stream will contain higher amounts of phenols and organic acids.

Co-processed feeds can also include chloride, sometimes in high concentrations. Chloride directly entering the riser reactor has the potential to cause salt deposits in the main fractionator and its overheads system [19], increasing the importance of effective washing (and therefore further increasing sour water loads).

When co-processing oxygen-containing feeds in the FCC, it is critical to assess the routing of sour water in the refinery. Some refiners route the FCC stripped sour water to crude desalters, which under typical conditions will drive phenols into the oil phase and reduce the load on the Waste Water Treatment Plant (WWTP). This option can present environmental concerns if there is a crude unit outage. Other refiners route stripped sour water directly to the WWTP, which typically incorporates a biological treatment plant. For some refiners, this is acceptable as the WWTP can tolerate and remove moderate levels of organic oxygenates such as phenols to meet environmental obligations. However, this can be a difficult constraint, especially during winter months when colder temperatures affect the microbial activity of the biological treatment plant.

The presence of low levels of oxygenates and reactive species in product streams and sour water impacts have the potential to cause significant hurdles. Beyond the immediate FCC impacts, preparation of lab facilities and affected downstream processes are critical to successful commercial co-processing trials and applications. Lead times for specialized analytical equipment and calibration standards can be long and the importance of establishing pre-trial baselines should not be underestimated when planning project timelines. In the case of analytical data collection, the location of sample points within the process are important to assess. Product treatment steps may impact the concentration of components of interest. For example, collection of oxygenate samples after a water washing step could show a much lower concentration than actual.

Conclusion

There is substantial interest in the refining industry in co-processing bio-derived feed streams in the FCC unit to produce lower carbon intensity products. With the flexibility and robustness of the FCC, co-processing low amounts of biogenic feedstocks is possible with limited impact and capital investment. A significant number of FCC units globally have performed commercial trials, some of which have converted to continuous operation. This paper provides a high-level overview of the lessons learned from biofeed co-processing to enable enhanced understanding of required preparation and monitoring activities in FCC biofeed co-processing.

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How to Optimize Feedstock Pretreatment for Renewable Diesel and SAF

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The rapid growth of the biofuels industry over the last decade has contributed to new and unforeseen challenges as refineries today look to lipid-based feedstocks to produce renewable diesel (RD) and sustainable aviation fuel (SAF). While economic growth of the edible oil market has increased the demand for oil and fat products globally, the emerging biofuel industry is challenged with identifying non-food-competing feedstocks and converting them into transportation fuels.

Renewable diesel (RD) is a hydrocarbon fuel, chemically identical to traditional petroleum-based diesel. Primarily produced by hydroprocessing renewable fats, oils, and greases (FOG), RD is sometimes referred to as hydrotreated vegetable oil (HVO) or green diesel. Unlike first generation biodiesel (also known as fatty acid methyl esters), RD is a highly stable hydrocarbon that does not contain oxygen, making it a drop-in replacement for petroleum-based diesel up to 100%. SAF is produced similarly to RD, however the fuel needs to be further "cracked" to create smaller hydrocarbons for jet engine utilization. In petroleum-based jet fuel there is also a fraction of aromatics, therefore SAF can only be a drop-in replacement for up to 50% of aviation fuel. With a high cetane index, low carbon intensity, high blending limits, and clean emissions, RD and SAF are highly attractive to both consumers and businesses globally to help reach sustainability targets.

Renewable fuel production is aimed at converting natural triglyceride FOG to diesel via specialized hydrotreating catalysts. Feedstock contaminants, such as metals in the form of salts and soaps, and phosphorus-based species in the form of phospholipids, can severely affect a refinery's production efficiency and profitability. These impurities are known to deactivate hydroprocessing catalysts, precipitate, self-polymerize, foul the catalyst bed, and cause large pressure build-ups at elevated reaction temperatures. Removing these contaminants prior to contact with catalysts downstream is critical to help ensure seamless fuel production and to utilize the equipment and catalyst's full potential. With an optimized and robust pretreatment process, renewable fuel producers can utilize a wide range of feedstocks and blend them accordingly based on which feedstock is readily available.

Not All Adsorbents are Created Equal

It is no secret that feedstock cost is often the largest expense for producing RD and SAF. To maximize profit, comply with legislation, and stay competitive, refiners are looking at all avenues to reduce their overall cost of production, especially in their pretreatment units (PTU). The pretreatment process typically consists of the sequence of operations as seen in Figures 1 and 2.

First, the feedstock is blended and homogenized with other available feedstocks, followed by a series of strainers to remove large particulates. During "dry degumming," acid conditioning follows the strainers and consists of mixing the feedstock blend with a mild acid (i.e. citric acid) to chelate metal contaminants prior to an adsorption step. However, if "wet degumming" is preferred, a water washing step follows acid conditioning to physically remove the majority of contaminants prior to the adsorption process. During impurity adsorption, the feedstock is sent to a slurry tank, then an adsorbent is added to remove the remaining contaminants down to trace levels as specified by catalyst technology licensors. The majority of licensors set a phosphorus limit of 3 mg/kg and a metals limits of 7 mg/kg in the feedstock before it can be sent to the renewable diesel unit (RDU) consisting of various hydroprocessing catalysts.

Traditionally, PTU engineering designs are similar to those from the edible oil industry and thus start up utilizing activated bleaching earth (ABE). However, for RD and SAF production, color is not a specification for the catalyst technology licensors, so there is no need for "bleaching" in the PTU. For the last 30 years, Grace's TRISYL® silica has been recognized as a more efficient adsorbent compared to ABE for removing both phosphorus- and metal-based contaminants during the refining of various oils and fats across both the edible oil and biofuels industry.

Cleaning bio-based feedstocks for the biofuel industry introduces more challenging targets as the specification for phospholipids and metals are much lower in RD and SAF production than what is typically needed to serve the edible oil industry. Additionally, non-food competing feedstocks usually come at the expense of high free fatty acids (FFA) or metal



Figure 1: Typical Sequence of Operations in a PTU with Dry Degumming



Figure 2: Typical Sequence of Operations in a PTU with Wet Degumming

contaminants. If the adsorbent used contains metals, the adsorption equilibrium will be hindered, reducing the capacity of that adsorbent, resulting in less contaminants removed from the feedstock. In extreme cases, metals from the adsorbent can leach back into the feedstock, causing metals to actually increase rather than decrease. Unlike ABE, Grace's silicas, including TRISYL® and TRISYL® 300, have highly pure SiO_2 compositions with no detectable levels of metal oxides present, as seen in Table 1. In addition to its pure composition, TRISYL® silica has a significantly larger surface area and higher moisture content compared to ABE, resulting in a much higher capacity to adsorb polar and ionic impurities, illustrated in Figure 3.

	TRISYL®	TRISYL®300	ABE
Total Volatile @ 954˚C (wt.%)	65	65	20
pH	4.5	2.5	3.6-4.5
Average Particle Size (µm)	20	20	13
Bulk Density Packed (g/cm^3)	0.48	0.48	0.56
Surface Area (m^2/g)	700	700	300
Chemical Analysis [c]			
SiO_2 (wt%)	99.6	98.8	70.0
Na_2O (wt%)	<0.1	<0.1	0.3
SO_4 (mg/kg)	<0.1	<0.1	7.9
Fe_2O_3 (mg/kg)	<0.1	<0.1	2.4
Al_2O_3 (mg/kg)	<0.1	<0.1	10.1
MgO (mg/kg)	<0.1	<0.1	1.6
CaO (mg/kg)	<0.1	<0.1	4.2

Table 1: Typical Properties of TRISYL® Silica, TRISYL® 300 Silica and ABE

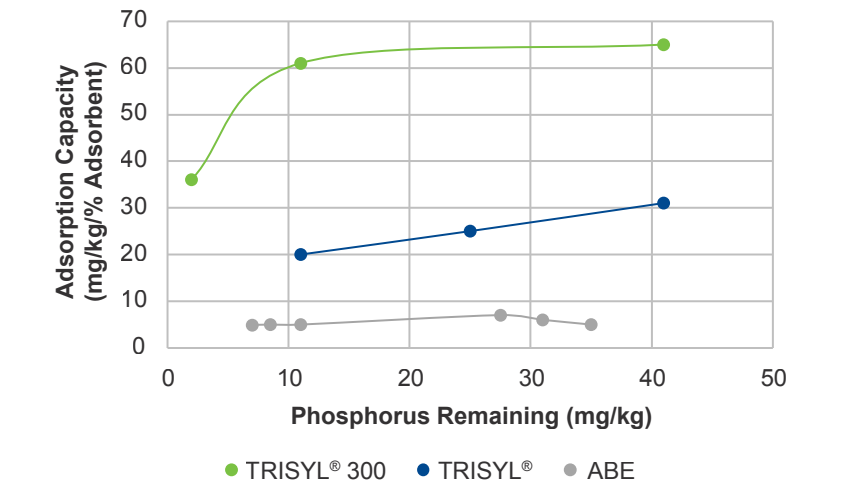


Figure 3: Adsorption Capacity Comparison of TRISYL® Silica, TRISYL® 300 Silica, and ABE in Soybean Oil Where:

$$Adsorption\ Capacity\ \left[\frac{mg/kg}{g}\right] = \frac{Phosphorus\ Removed\ [mg/kg]}{Adsorbent\ Mass\ [g]}$$

Although soft vegetable oils (i.e. soybean, canola, sunflower, etc.) are technically adequate for the production of RD and SAF, producers are challenged with sourcing inedible, waste feedstocks that do not compete with the food industry and create fuels with a much lower carbon intensity (CI) score.

Even in severely contaminated feedstocks and blends, TRISYL® 300 silica maintains a higher adsorption capacity for contaminants (i.e. phosphorus and metals) than ABE, as illustrated in Figure 4.

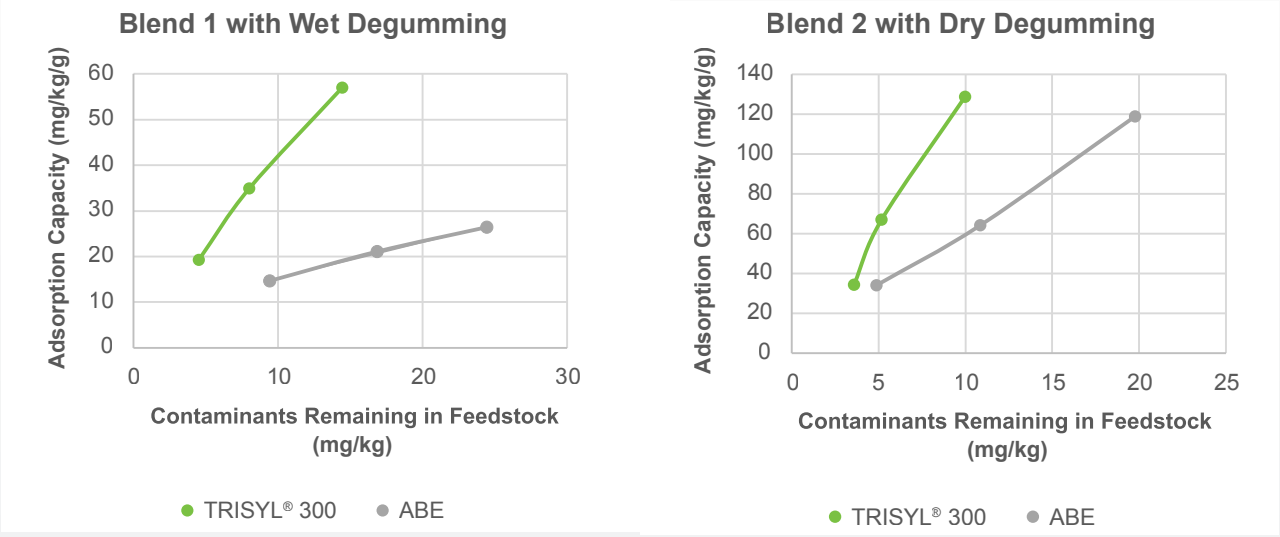


Figure 4: Adsorption Capacity Comparison of TRISYL® 300 and ABE in Various Feedstock Blends.
Blend 1 = 30% Soybean Oil and 70% Tallow. Blend 2 = 30% Soybean Oil, 30% Used Cooking Oil, and 40% Tallow.

$$Adsorption\ Capacity\ \left[\frac{mg/kg}{g}\right] = \frac{Phosphorus\ Removed\ [mg/kg] + Metals\ Removed\ [mg/kg]}{Adsorbent\ Mass\ [g]}$$

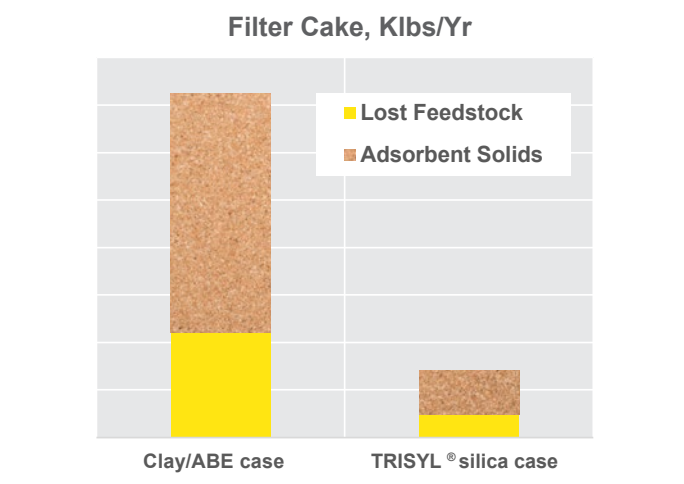


Figure 5: An Example of Filter Cake Composition when Clay/ABE is Used vs. TRISYL® Silica

Because of TRISYL® silica's larger adsorption capacity in both wet and dry degumming — compared to ABE — adsorbent dosages are reduced significantly. Using less adsorbent with a lower solids content will not only lower solid waste generated and emissions related to disposal transportation, but also reduce the amount of feedstock lost during pretreatment process. Figure 5 shows the relative filter cake reduction and composition when using TRISYL® silicas compared to ABE. Without the need for additional feedstock, overall productivity of the refinery is increased, while at the same time the environmental footprint of the refinery can be significantly reduced.

TRISYL® Silica: Optimized Process-of-Use

When using Grace's TRISYL® silica as an adsorbent for renewable feedstock pretreatment, it is recommended to add TRISYL® silica to the slurry tank under atmospheric pressure once the oil contains less than 0.5 wt% moisture. If the feedstock contains moisture over this threshold, the adsorption equilibrium could be hindered and a vacuum dryer should be installed prior to the slurry tank. Once TRISYL® is added, the slurry should mix for approximately 15-30 minutes between 60 and 70 °C to allow it to reach equilibrium and maximize TRISYL® silica's full capacity to remove contaminants, as demonstrated in Figure 6. The moisture in the pores enhances adsorption by attracting polar and ionic contaminants to the surface of the hydrophilic particles. The mixture is then sent through a vacuum dryer to remove the water from TRISYL®, shrinking the particles' pores, while trapping the phospholipids and metals within its internal structure. The dried mixture is then passed through a filter (horizontal or vertical leaf, candle, or press) to remove the particles and trapped impurities from the feedstock.

Conclusion

As the transportation sector continues to demand more sustainable fuels to help governments around the world meet emission reduction targets, renewable fuel producers will continue to look for options to optimize their processes and generate lower carbon intensity fuels. When refiners switch from ABE to Grace's TRISYL® silica adsorbents for the pretreatment of renewable feedstocks they can expect not only a reduction of solid waste up to 85%, but also a reduction of feedstock losses, ultimately leading to higher yields of renewable fuels.

For more information on how TRISYL® silica adsorbents can improve your pretreatment process, please visit grace.com/biofuels or contact your local Grace sales representative.

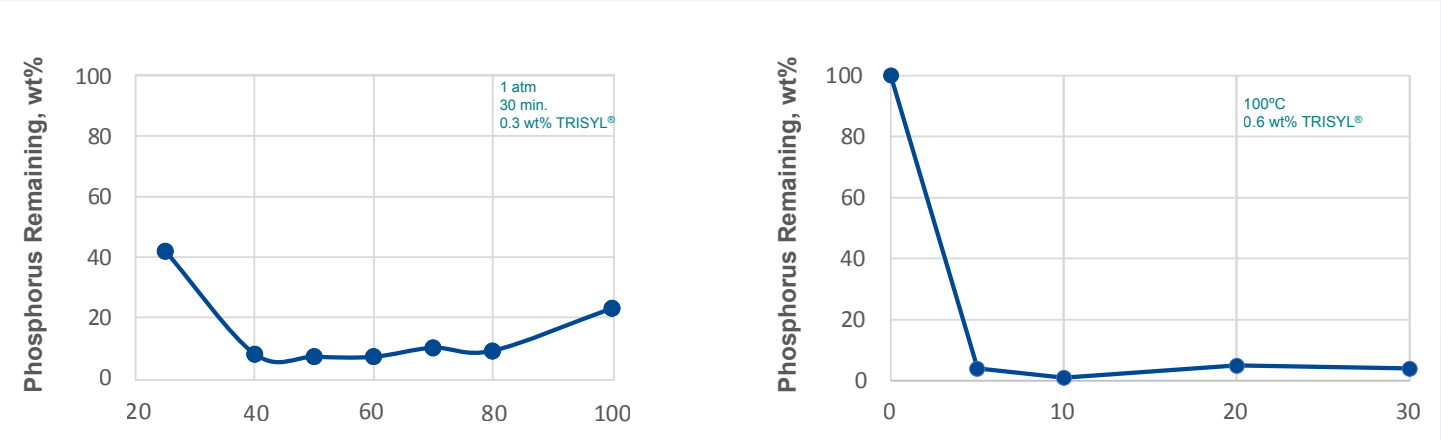


Figure 6: Phospholipid Removal as a Function of Temperature and Time with TRISYL® Silica

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