

The Importance of Partnership in FCC Bio-Feed Co-Processing: Tackling Contaminant Metal Challenges

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ABSTRACT

The refining industry is crucial for meeting global energy, transportation fuel, and petrochemical needs. As the world strives to reduce the carbon intensity of these essential products, refiners are adapting to new regulations, incentive programs, and carbon taxes aimed at promoting lower-carbon fuels and petrochemicals. One effective strategy is the co-processing of biogenic feedstocks.

Co-processing bio-derived feedstocks in the fluid catalytic cracking unit (FCCU) offers refiners a way to lower the carbon intensity of their products with minimal capital investment. Successful implementation of bio-feed FCC co-processing requires careful planning and change management. By partnering with technology providers, the refiners can leverage pilot plant and commercial experiences, adopt best practices, and accelerate project timelines. Grace collaborates with refiners globally to implement FCC bio-feed co-processing across a range of feedstock types.

Despite its benefits, co-processing introduces challenges. Biogenic feedstocks often contain elevated levels of contaminants that can adversely impact unit performance and profitability. This discussion will examine the impact of these contaminant metals on FCCU performance, demonstrate lab simulation results, and outline mitigation strategies to maintain unit performance and economic viability.

INTRODUCTION

Governments and regulators have identified the urgent need to address and mitigate greenhouse gas (GHG) emissions globally, with many nations setting ambitious reduction targets. For example, the European Union have implemented a range of policies aimed at achieving at least a 55% reduction in GHG emissions relative to 1990 levels by 2030. [7] Similarly, Canada has committed to reducing emission by 40-45% compared to 2005 levels by 2030. [8] The policies supporting this level of reduction include taxation on emissions and requirements for carbon intensity reduction in transportation fuels among other policies. These evolving regulations, incentives, and policies are driving significant action from transportation fuel producers in response to the changing regulatory environment. One key strategy involves the use of biogenic feedstocks, which are increasingly being evaluated as a means to lower the carbon intensity of transportation fuels. These feedstocks help producers comply with regulatory requirements, minimize emissions-related taxes, and generate renewable fuels credits.

Biogenic feedstocks can be processed independently to produce 100% renewable fuel, or co-processed with conventional feedstocks in hydroprocessing or conversion units such as the fluid catalytic cracker (FCC). Grace supports FCC operators worldwide in evaluating and implementing co-processing of biogenic and circular feedstocks. Figure 1 below shows FCC co-processing interest globally as a percentage of FCCs by nation.

FCC Co-Processing Interest as % of FCC/nation

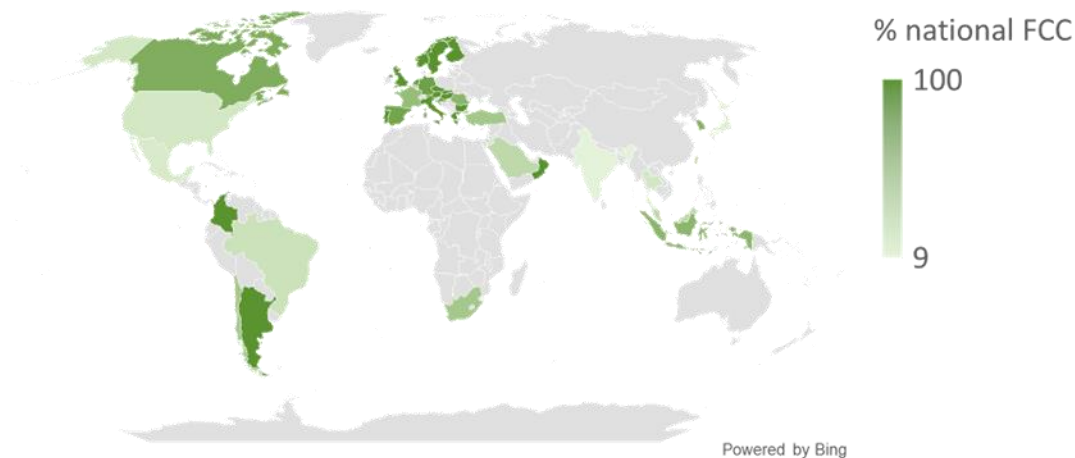


Figure 1: Grace surveyed FCCs interested in co-processing of biogenic and circular feedstock.

It is noteworthy that a significant percentage of FCC units focused on co-processing are in Europe and Canada - regions known for their ambitious emission reduction targets and supportive legislation framework. Figure 2 further illustrates the growing interest among refiners with FCCs, highlighting a sharp increase over the past 5 years. This trend is based on Grace's engagement with refiners exploring co-processing opportunities

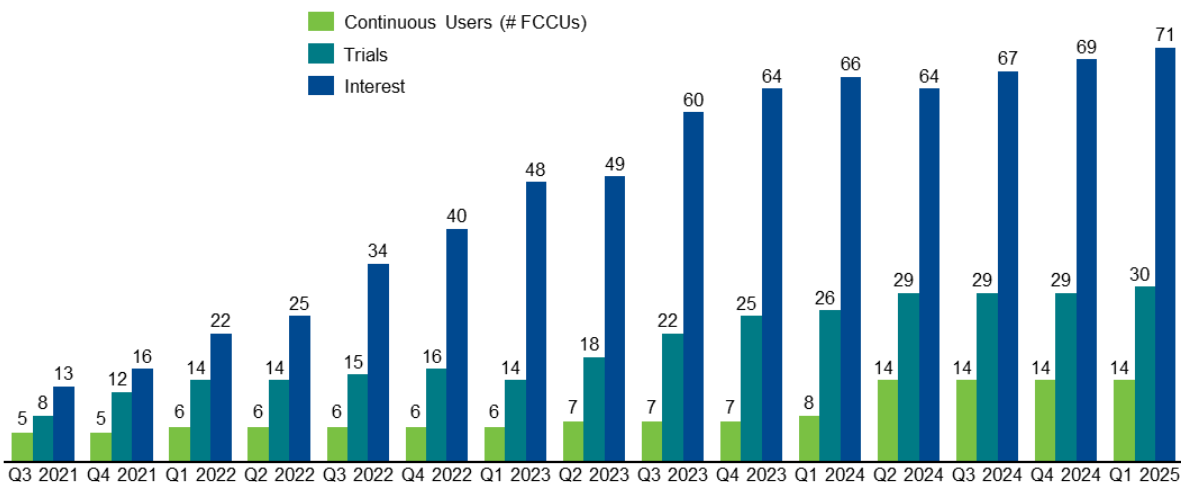


Figure 2: FCC operators expressing interest in, conducting trials, or continuously co-processing biogenic or circular feedstocks.

Figures 1 and 2 show significant growth in FCC co-processing interest globally, regardless of established regulatory incentives. Part of this momentum is driven by the premium values placed on low carbon intensity petrochemical feedstocks.

Grace continues to support refiners in evaluating suitable feedstock for co-processing and understanding their impact to operation and catalyst. This support ranges from initial evaluation and pilot plant testing to trial monitoring and driving higher continuous co-processing rates. Two primary challenges in co-

processing biogenic feedstocks are managing contaminant metals and addressing high oxygen content. This discussion focuses on the importance of partnership and collaboration in identifying and mitigating the unique contaminants commonly present at elevated levels in biogenic feedstocks.

BODY OF WORK

Once the value drivers and magnitude of uplift from co-processing are well understood, refiners must identify a target feedstock and evaluate its availability and quality. At the same time, they need to assess their infrastructure and operational capability to source, handle and process the new feedstock. Figure 3 below illustrates the types of feedstocks that are commercially co-processed across the industry.

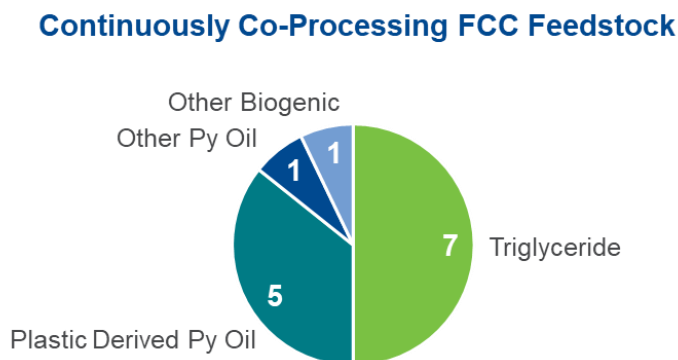


Figure 3. Commercially co-processed biogenic and circular feedstocks.

Triglycerides are by far the most common and highest volume material co-processed in the FCC. Triglycerides include fats, oils and greases (FOGs), such as seed oils, used or waste cooking oil (UCO), and animal fats. Plastics based pyrolysis oils are also a widely co-processed material, but is typically only available in limited quantities and co-processed at levels of 1% or less of total FCC feedstock. These feeds vary significantly in terms of the type of contaminants present and their effects on FCC operation and profitability. Figure 4 below summarizes some key contaminants of interest, their concentration, and effects on FCC catalyst.

	Effects	Soybean Oil	Rapeseed Oil	Palm Oil (refined)	Waste Cooking Oil	Tallow	Pine Based Pyrolysis Oil	Crude Tall Oil	Median Value FCC Feedstock	Typical Ranges FCC Feedstock
Oxygen [wt%]	CO, CO ₂ , H ₂ O Oxygenates Amine system impacts	10.5	10.6	11.3	0 – 30	12.6	51	9.9	0	0 – 0.5
Na [mg/kg]	Zeolite deactivation	0 – 2	5	0	0 – 30	55	5	Alkali and alkaline earth metals reported as 56	0.3	0 – 10
K [mg/kg]	Zeolite deactivation	0 - 88	0	0	0 – 20	No data	160		0	0 – 5
Ca [mg/kg]	Zeolite deactivation Pore mouth plugging	3 – 60	14	0	1 – 20	40	400		0.4	0 – 20
P [mg/kg]	Pore mouth plugging	6 – 150	4	0	10 – 50	60	No data	36	0	0 – 5
Reference		[1], [5]	[1]	[1]	[5], [6]	[2]	[3]	[4]	[5]	[5]

Figure 4: Summary of oxygen content and contaminant metals for various feedstocks.

Figure 4 illustrates the wide range of contaminants present in these alternative feedstocks, which typically are not present in appreciable amounts in FCC feeds. Not only is there variability between different types of feed, there can also be significant variation from batch to batch depending on its source and level of

refinement. This presents additional challenges to refiners who seek to meet regulatory requirements and capture incremental value through bio-feed co-processing.

Grace supports customers in these evaluations starting with basic feedstock characterization and miscibility testing to help inform strategies around feedstock handling. This characterization is then used to construct metals balances and understand what levels of contaminants will accumulate on the FCC unit's circulating catalyst. More advanced evaluations such as cracking in single receiver short contact time MAT (SR-SCT MAT) units are also leveraged to understand the impact on FCC unit yields and profitability. As refiners continue advancing toward trials and ongoing co-processing efforts, Grace conducts larger scale evaluation of these feeds in advanced cracking evaluation (ACE[®]) and Davison circulating riser (DCR[™]) units. This allows for a better representation of effects in a commercial unit and can help identify operability concerns. Additionally, sufficient FCC product can be generated to perform biogenic carbon ¹⁴C testing to determine the distribution of biogenic carbon and product oxygenates (CO, CO₂, water, and organic oxygenates).

In addition to this testing, Grace has developed the capability to deactivate catalysts using the unique contaminants found in co-processing feedstocks to simulate their effect on FCC catalyst performance. Grace's **Co-Protocol[™]** deactivation method is utilized to study the effects of contaminants such as Na, Ca, K, and P on catalyst activity, zeolite stability, and diffusivity. This approach allows Grace and its refining partners to anticipate and respond to the challenges posed by elevated levels of these contaminant metals, while also driving innovation in catalyst technologies to enhance profitability in co-processing operations.

Grace works closely with customers to implement a range of strategies to mitigate the impact of contaminant metals. Although the contaminant species are different than the "usual suspects" in typical FCC feeds, their management is not very different from an FCC processing residual feeds. These strategies fall into two main categories: limit the accumulation of contaminants on circulating Ecat and deploy catalyst technologies that are resistant to the detrimental effects of the contaminants.

In the first category, it is important to continually monitor the quality of the purchased feedstocks and construct detailed metals balances to guide catalyst addition rates. Establishing contaminant specification limits for co-processed feedstocks can help mitigate the risk of operational disruptions. Grace also partners with refiners to identify high quality purchased catalyst (Ecat) and leverage it for contaminant flushing. Additionally, optimizing fresh catalyst activity may be necessary to meet yield objectives while enabling higher addition rates that help control contaminant metal accumulation.

Grace's support for managing co-processing contaminant metals extends beyond limiting their increase. Using the **Co-Protocol[™]** deactivation method, Grace has developed catalyst technologies specifically designed to mitigate the effects of co-processing contaminants and maintain a profitable FCC yield profile, even in the presence of elevated metals. Many of the common contaminants in co-processing, such as sodium, potassium, calcium, and phosphorus, are zeolite deactivators from the alkali and alkaline earth families, as shown in Figure 4 above.

To address this, Grace has focused on zeolite stabilization in the development of Co-Pro[™] FCC catalyst. This technology incorporates Grace's proprietary stabilization ingredient, yttrium (also referred to as GSI), as a replacement for lanthanum to enhance Y zeolite stability.

The GSI stabilization in Co-Pro[™] catalyst technology imparts increased Brønsted and Lewis acidity, as illustrated in Figure 5 below.

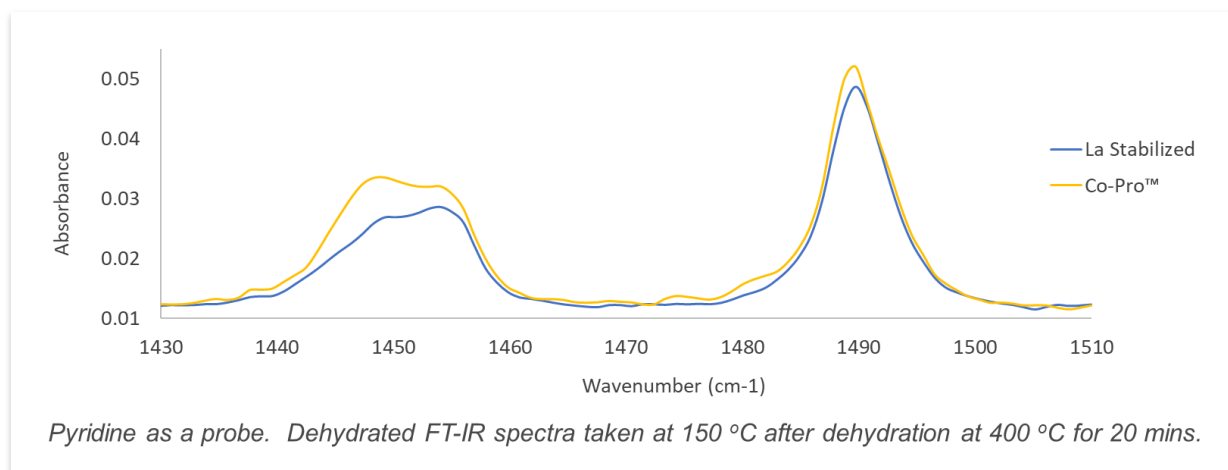


Figure 5: FT IR spectra of lanthanum stabilized FCC catalyst and a corresponding Co-Pro™ catalyst with GSI stabilization.

The increased acidity drives higher cracking activity and improved tolerance against basic contaminant metal deactivation, resulting in improved zeolite surface area (ZSA) and activity retention in the presence of co-processing contaminant metals. Figure 6 below illustrates the improvement in zeolite stability and tolerance indicated by zeolite surface area (ZSA) retention for Co-Pro™ catalyst relative to its lanthanum stabilized counterpart when deactivated with elevated levels of various co-processing contaminant metals.

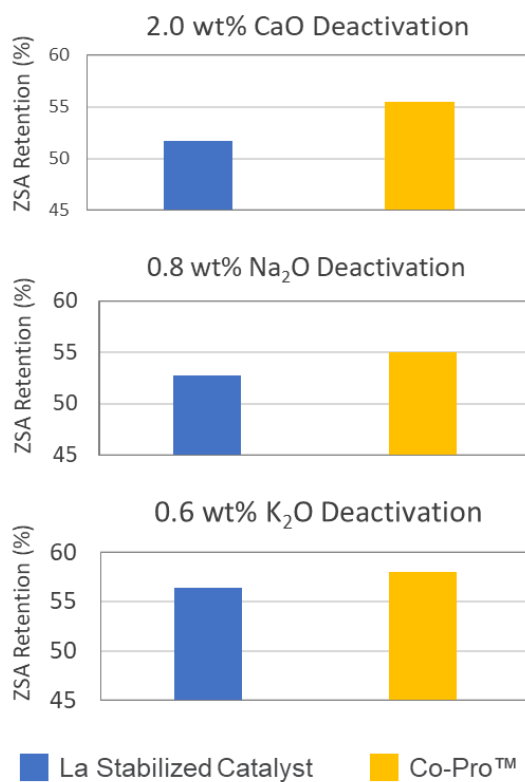


Figure 6. ZSA retention of lanthanum stabilized and Co-Pro™ catalysts with co-processing contaminant metals deactivation applied.

This improvement in zeolite stability leads to improved catalyst cracking activity, as demonstrated in Figure 7. The data shows a consistent increase in conversion at constant cat to oil ratio, based on results from ACE® testing.

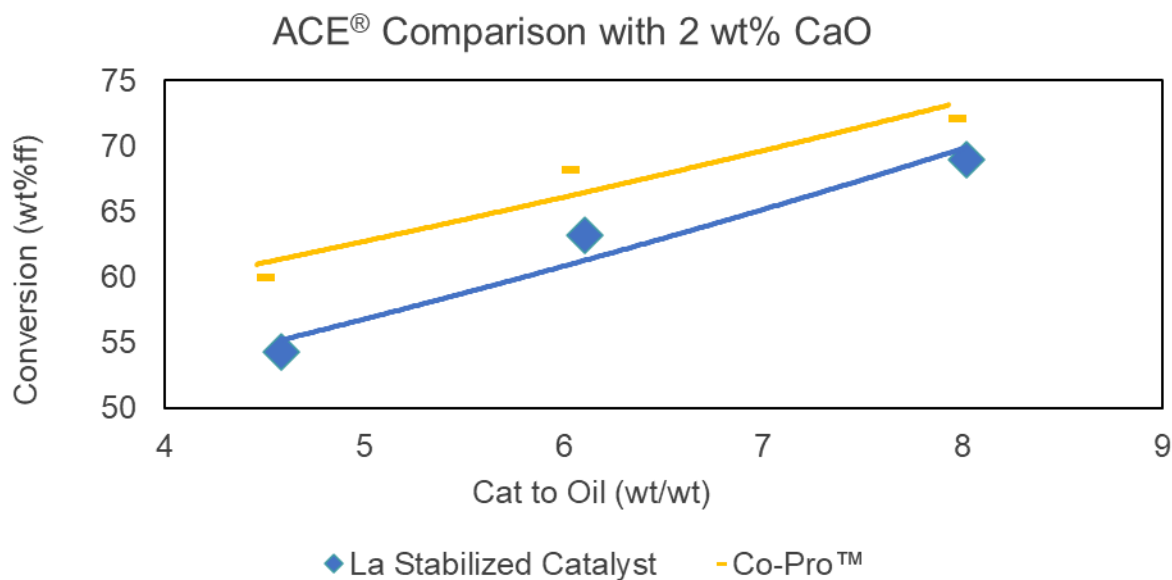


Figure 7. ACE® results showing improved activity profile for Co-Pro™ catalyst relative to lanthanum stabilized catalyst

This enhanced activity profile offers refiners flexibility to adapt based on their specific objectives, operational constraints, and feedstock availability. If additional co-processed feedstock is accessible, refiners can increase co-processing rates and tolerate higher contaminant metal levels while maintaining existing catalyst addition rates and activity. Alternatively, if the FCC unit is already operating at its maximum co-processed feedstock capacity, transitioning to the Co-Pro™ catalyst can help sustain unit profitability by enabling lower catalyst addition rates without compromising performance.

CONCLUSION

The evolving regulatory environment and growing product premiums are prompting refiners to explore co-processing of biogenic and circular feedstocks in the FCC. While this shift presents new opportunities, it also introduces new challenges—including securing a reliable feedstock supply, developing appropriate handling strategies, and managing elevated levels of oxygen and other contaminants that can impact FCC performance and profitability. Close collaboration with catalyst partners is essential to proactively address these challenges. By leveraging a combination of mitigation strategies, refiners can better manage the effects of co-processing contaminant metals and optimize the overall operational and economic performance of their FCC unit.

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CV

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