ENHANCING DIESEL COLD FLOW PROPERTIES IN HYDROCRACKING: A CATALYTIC SOLUTION FOR MAXIMIZING MIDDLE DISTILLATES YIELD

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Abstract

Hydrocracking is a complex refining process that converts heavy hydrocarbons into lighter, more valuable products, including diesel fuel. Diesel cold flow properties including cloud point, are essential for ensuring fuel performance and engine reliability in low-temperature environments. Poor cold flow properties can lead to operational issues like fuel gelling and flow blockages, which are particularly problematic in colder climates.

One strategy to maximize middle distillates yield in the hydrocracker is to increase the diesel cut point in the fractionator. However, this approach presents a significant challenge: higher diesel cut points tend to degrade the cold flow properties of the fuel. Even with good fractionation, achieving the desired cold flow properties and product yields can be difficult.

An alternative strategy involves a hydrocracking catalytic solution, which has been developed to improve diesel cold flow properties while simultaneously maximizing middle distillates yields.

In this work, a case study will demonstrate the key benefits of a superior catalytic system including the ability to achieve lower cloud points, even while operating at higher diesel cut points. These benefits are accomplished without compromising the overall yield and quality of middle distillates.

Additionally, this work will highlight the importance of integrating this catalytic solution with optimized operating conditions and good fractionation. By doing so, refineries can achieve a balanced approach that maximizes middle distillate yields while ensuring that the diesel produced meets stringent cold flow performance standards.

Keywords: Hydrocracking, Diesel, Cold Flow Properties, Middle Distillates, Diesel cut point, Catalysts, Cloud Point.

Introduction

Hydrocracking is a key refining process that transforms heavy hydrocarbons into lighter, more valuable products, such as diesel fuel. This process involves breaking down large hydrocarbon molecules into smaller ones, enhancing the overall value of the products. A critical aspect of diesel, particularly in varying climates, is its cold flow properties, including the cloud point. These properties are essential for ensuring diesel's reliable performance in low-temperature conditions.

To increase the yield of middle distillates like diesel, refineries often raise the diesel cut point, which is the temperature range for distilling diesel from crude oil. While this strategy can maximize diesel yield, it poses a significant challenge: higher diesel cut points tend to degrade the fuel's cold flow properties, making it less suitable for cold climates. This degradation can compromise the fuel's performance and reliability.

This work presents a hydrocracking catalytic solution to improve diesel cold flow properties while simultaneously maximizing middle distillates yields without compromising the overall yields and product qualities.

Diesel Cold Flow Properties

The cold flow properties of diesel fuel cuts can be characterized by three properties:

- Cloud Point (CP)
- Cold Filter Plugging Point (CFPP)
- Pour Point (PP)

These properties generally follow the same trend with the concentration of normal paraffins in the diesel cut and are fairly well correlated with each other. In general, the crystallization of a fluid occurs in two stages: first the nucleation step – the appearance of the first crystals and second the crystal growth and agglomeration – where crystals grow and cluster.

The cloud point marks the first stage, when the first crystals appear. The CFPP indicates the point during cooling at which the crystals become too large to pass through a filter. The pour point marks the temperature at which the product can no longer flow because it has become solid. Therefore, the typical temperature order is as follows:

$$CP > CFPP > PP$$

It is important to note that cloud point and CFPP are defined in diesel fuel specifications according to ASTM D975 (1), unlike the pour point.

The maximum allowable cold flow property values for diesel fuels under ASTM D975 vary depending on latitude, climate, and season in each region of the world. Argentina does not publish a unique national standard for cold flow properties but typically aligns with European EN 590 (2) for automotive diesel, especially in colder southern regions (e.g., Patagonia), and ASTM D975 in others.

The European EN 590, that defines the quality and performance requirements for automotive diesel fuel, do not specify fixed Cloud point values, which varies by region and season. However the European standard specifies maximal values for CFPP:

- Temperate climates: CFPP must be ≤ 0°C (summer) and ≤ -15°C (winter).
- Arctic climates: CFPP can go down to -20°C or lower depending on class (Class 0 to Class 4)

There are therefore two cold flow properties to consider when evaluating the quality of a diesel fuel:

- CFPP (Cold Filter Plugging Point):
  The CFPP is the lowest temperature at which a specified volume of a liquid fuel can pass through a standardized filtration device within a set time (60 seconds). This temperature is determined by gradually cooling the sample and passing it through a filter until it can no longer flow properly due to wax crystal formation.

- CP (Cloud Point):
  The cloud point is the temperature at which solid particles first appear in the fuel. To measure it, the sample is first heated until it becomes a clear liquid, then slowly cooled. The temperature at which the liquid becomes cloudy, indicating the formation of the first wax crystals, is detected using an optical sensor (2).

Literature Review

In the literature, there is extensive research on the molecular understanding of cold flow properties in fuels. These studies consistently highlight the critical role of normal paraffins in determining cold flow behavior. Due to their linear and flexible structure, normal paraffins can easily align and form stable crystals upon cooling.

Another important factor is the chain length of the normal paraffins. The longer the paraffin chain (e.g., nP15+), the stronger the axial interactions between normal paraffins through Van der Waals forces within the crystals. Conversely, for shorter linear paraffins, interactions between the chain ends also become significant and can disrupt the crystal organization (1).

As a result, the melting point (MP) of a normal paraffin increases with the length of its carbon chain. In Figure 1 below, it can be observed that normal paraffins with chain lengths beyond 15 carbon atoms have melting points above 10°C.

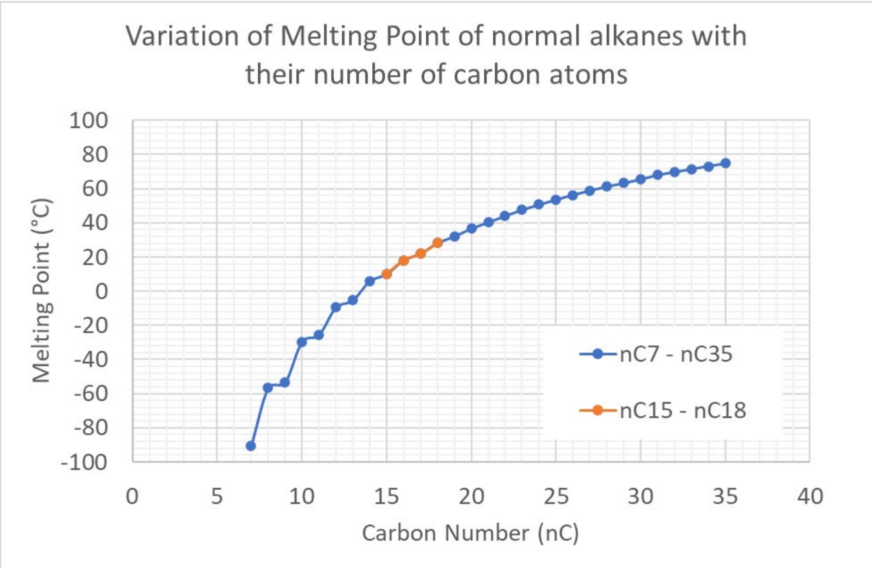

Figure 1. Evolution of the melting point of n paraffins as function of the chain length (2)

Krishna et al. (3) also demonstrated a dependence of the pour point (PP) on both the content of normal paraffins and the average carbon chain length of the normal paraffins. In their study, several narrow cuts (ΔT = 25°C) of diesel and Vacuum Gas Oil (VGO) were obtained by distilling a wide 250–500°C cut from a paraffinic crude oil.

The concentration of normal paraffins in each narrow cut were varied using urea extractive crystallization. Each fraction was characterized to determine its pour point and normal paraffin composition.

The authors observed that short-chain normal paraffins (less than 15 carbon atoms) had less influence on cold flow properties. They also noted that the pour point varied in a non-linear but consistent manner with the mass concentration of normal paraffins (PC) in the cuts, and proposed the following correlation:

$$PP = A_0 \times log(100/PC) + B_1$$

In this correlation:
- A_0 is constant for all diesel and VGO cuts, meaning it is independent of molecular size.
- B_1 depends on the average carbon chain length of the normal paraffins in the cut.
- In fact, B_1 represents the pour point of the average normal paraffin in the cut.

Hence, when maximizing diesel yields by widening product cut points, it is crucial to convert the long normal paraffinic chains to maintain acceptable cold flow properties. In Hydrocracking technology two catalyst solutions can be foreseen:

- Addition of dewaxing catalysts downstream of traditional mono-zeolite cracking catalysts.
- Implementation of dual-zeolite catalysts as cracking catalysts.

Dewaxing catalysts, commonly based on medium-pore zeolites, promote selective cracking or isomerization of long-chain paraffins taking advantage of their shape selective properties. However, Axens internal studies on these catalysts showed significative increase in light ends while operating in this configuration, specially LPG and light naphtha due to cracking of linear hydrocarbons into very short chained paraffins.

Conversely, dual-zeolite catalysts present both better overall middle distillates selectivity compared with mono-zeolite ones and better diesel cold flow properties, as presented below.

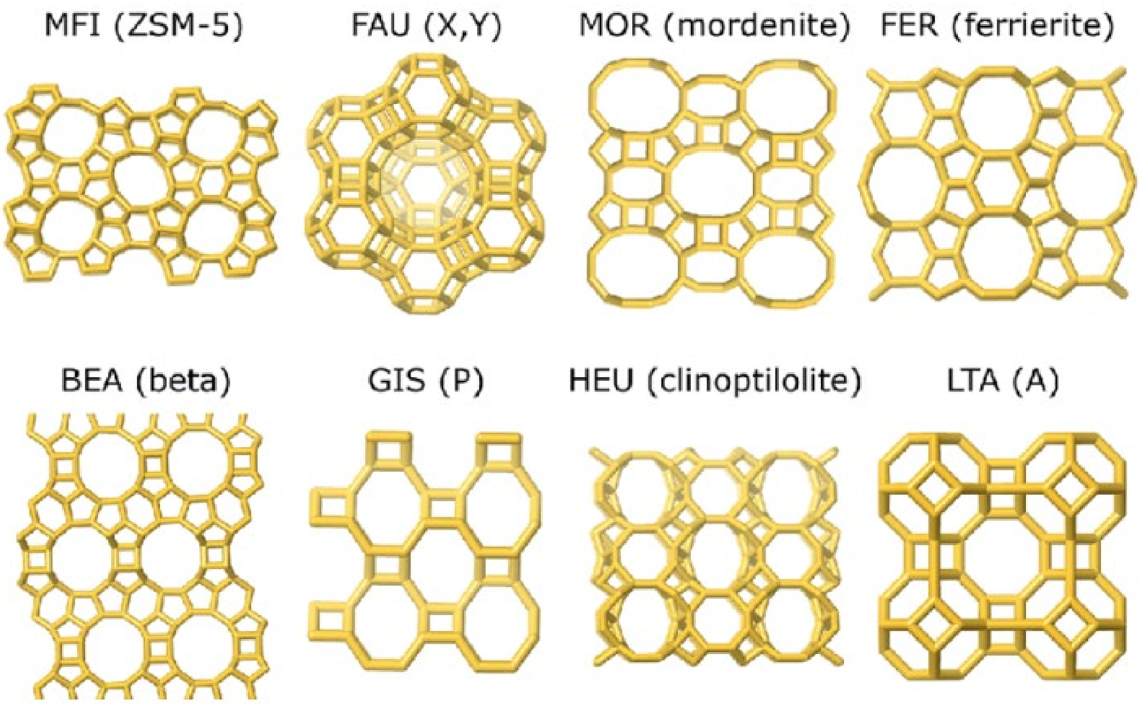

Figure 2. Schemes of the structures of Zeolites (7)

Case Study

This case study involves a Hydrocracking (HCK) unit in North America processing Vacuum Gas Oil (VGO) from a Sweet and Sour Crude mixture and Heavy Cycle Oil (HCO) from an FCC unit.

The unit configuration is Single Stage with Unconverted Oil (UCO) recycle.

The primary objectives of this unit are:

- Maximization of middle distillate production, meeting Euro V standards.
- Improvment of cold flow properties of heavy diesel, specifically targeting a lower cloud point.
- Conversion of 85 to 90 wt%.

The typical feed properties are shown in the following table:

Property	UOM	Value
Density @ 15°C	g/cm^3	0.90 – 0.92
Sulfur, wt%	wt%	0.5 – 0.7
Nitrogen, wtppm	wt ppm	800 – 1000
Ni+ V	wt ppm	1.0
CCR, wt%	wt%	< 0.3
Simulated Distillation		
10%	°C	306
50%	°C	368
90%	°C	488
EBP	°C	580

Table 1. Feed Properties

The main products of the fractionator are Light Naphtha (LN), Heavy Naphtha (HN), Light Distillate (LD), Heavy Distillate (HD) and Unconverted Oil (UCO).

A general process scheme of the unit is illustrated in the following figure.

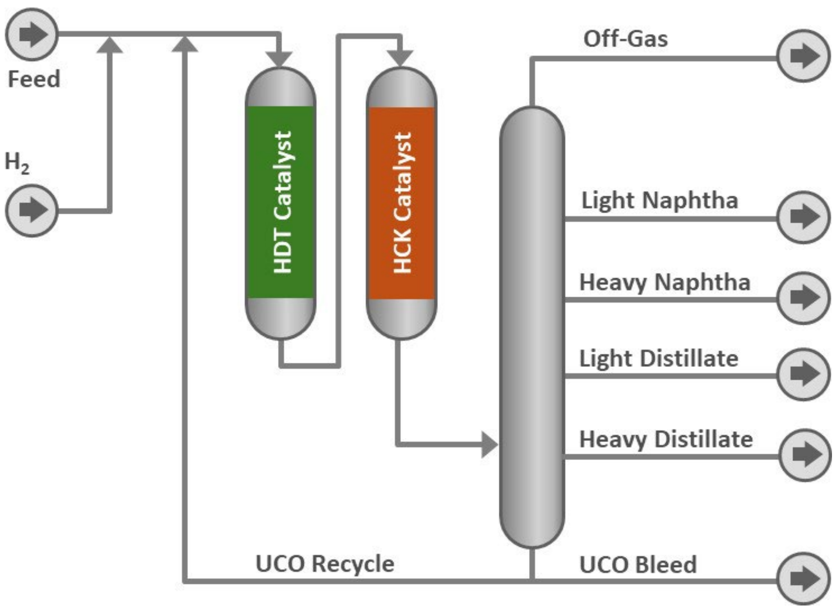

Figure 3. General Process Scheme of the unit.

The catalyst configurations for two consecutive operating cycles are shown in Figure 4.

The Hydrotreating (HDT) section is loaded with inert grading for pressure drop mitigation, followed by a dedicated Hydrodemetalization (HDM) catalyst for metal removal from the feed, protecting the main HDT catalyst downstream of this section. This HDT configuration is the same for both cycles.

The Hydrocracking (HCK) section is loaded as follows:

- **Cycle 1:** 50% mono zeolite zeolite + 50% optimized dual-zeolite catalyst.
- **Cycle 2:** 100% optimized dual-zeolite catalyst.

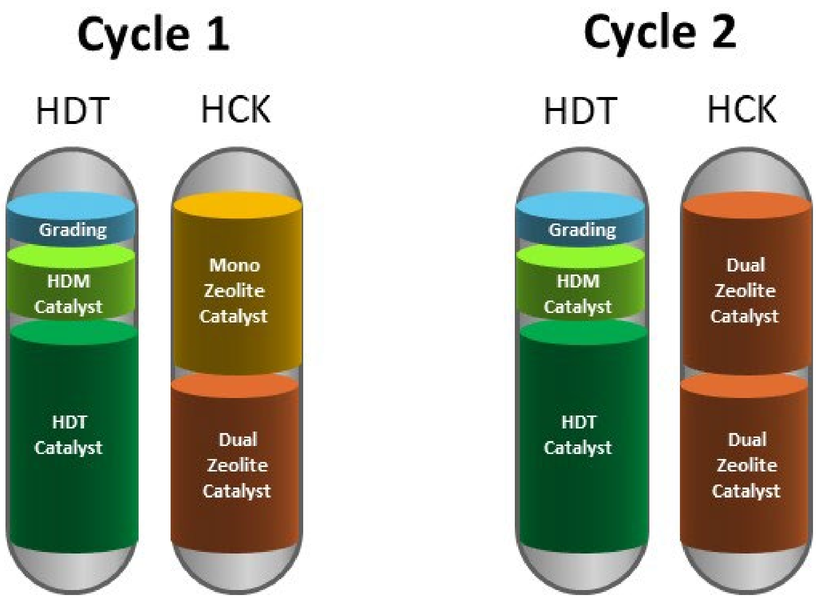

Figure 4. Catalyst configuration for Cycle 1 & Cycle 2.

Figure 5 shows a comparison of Cloud Point of Heavy Distillate (HD) cut for both cycles as a function of T95 (D86), and it is possible to see that for a given T95 (D86) in the Heavy Diesel (HD) the Cloud Point is improved by around 8°C in Cycle 2, allowing this cut to be incorporated into the diesel pool while meeting strict product specifications for the winter season, which was not possible in the Cycle 1.

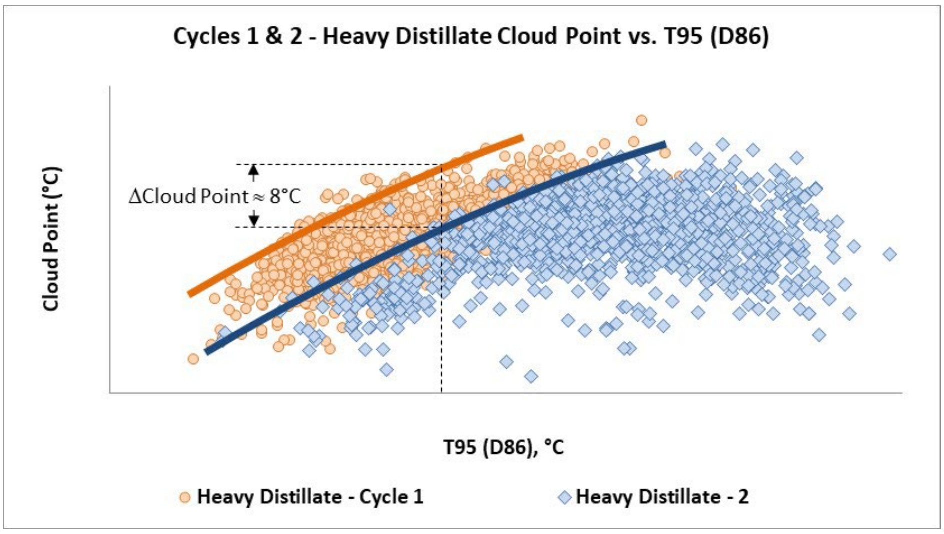

Figure 5. Cloud point of Heavy Distillate as a function of T95 (D86).

The total Middle Distillate yield (Light Distillate + Heavy Distillate) are very stable for both cycles, as shown in Figure 6. This figure also indicates a higher HD/LD ratio for Cycle 2 using 100% dual-zeolite catalyst, indicating better selectivity towards Heavy Distillate compared to using some mono-zeolite catalyst, which provides a great benefit when the goal is to maximize the diesel pool.

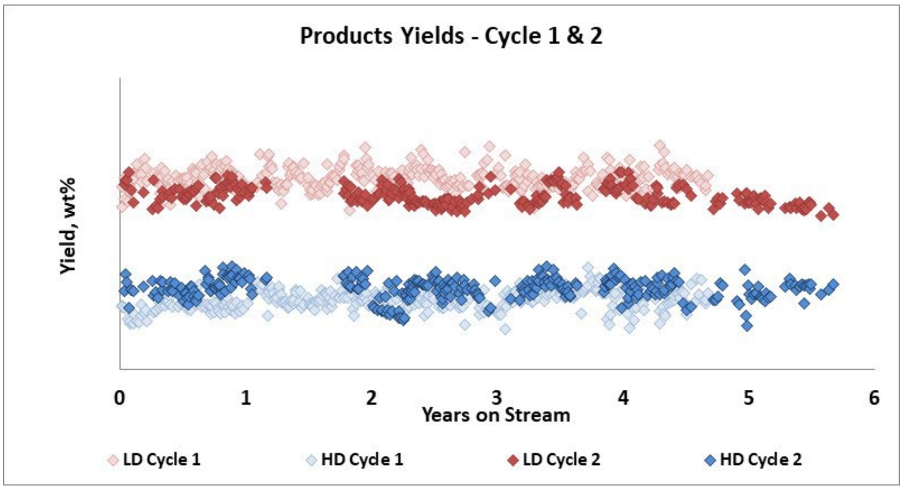

Figure 6. Product Yields for Cycle 1 & Cycle 2.

The HD/LD ratio is shown in the Figure 7, which confirms the higher selectivity toward Heavy Distillate of the dual-zeolite catalyst (Cycle 2).

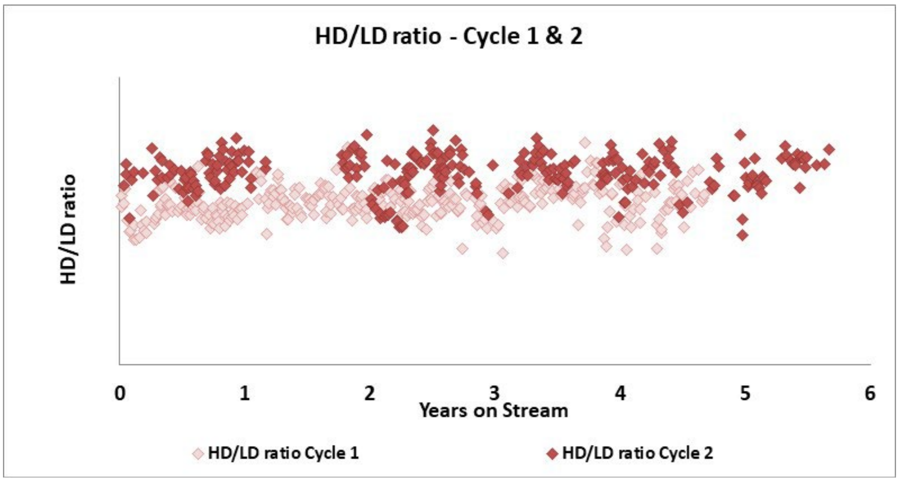

Figure 7. HD/LD ratio for Cycle 1 & Cycle 2.

Another important aspect are product properties, e.g., the Middle Distillate Cetane Index (ASTM D4737), which is improved by adding the Heavy Distillate into the pool, in addition to exhibiting outstanding stability during the two cycles as shown in Figure 8.

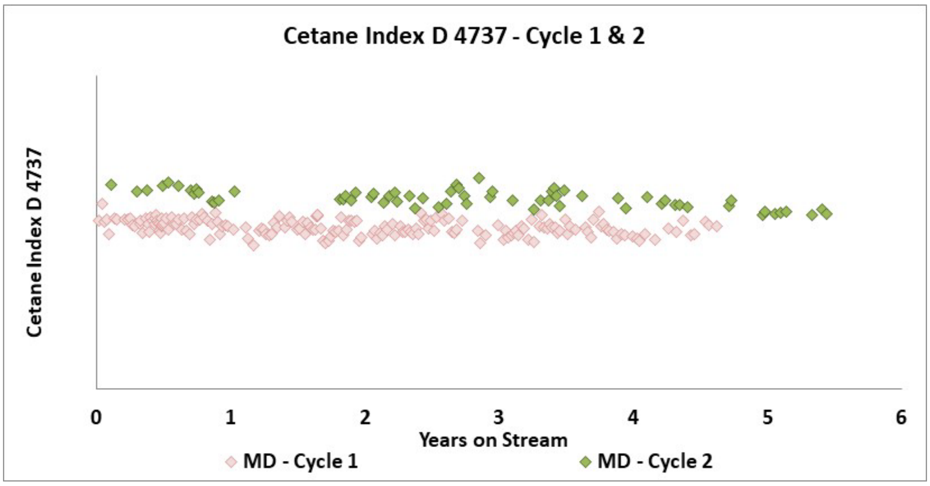

Figure 8. Middle Distillate Cetane Index ASTM D 4737 – Cycle 1 &Cycle 2.

Economical benefit

Thanks to the Cloud Point improvement in the Heavy Distillate cut, this stream is incorporated into the diesel pool, which means a **great economic impact** by incorporating more than 15wt% of the yield into the diesel pool, as it is shonw in Figure 9.

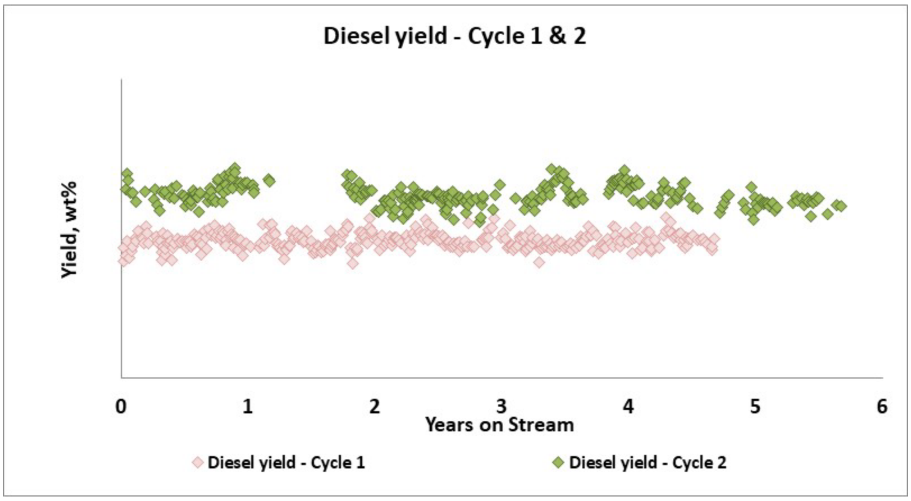

Figure 9. Diesel yield – Cycle 1 & Cycle 2.

Finally, effective fractionation combined with the best catalytic solution are critical in hydrocracking units to achieve a balanced approach that maximizes middle distillate yields while ensuring diesel meets stringent cold flow performance standards. A good fractionation is equally important, as it ensures the precise separation of hydrocracked products into distinct boiling range fractions, thereby maintaining the quality and specifications of each product stream. This separation is crucial for meeting market demands and regulatory requirements, particularly for diesel cloud point and T95 in the ASTM D86 distillation curve.

Conclusions

The use of dual zeolite catalyst in HCK units has been industrially proven to deliver:

- Better selectivity toward Heavy Distillate compared to mono-zeolite catalysts.
- Enhanced product properties, notably the cold flow properties of diesel.
- Increase Cetane Index by adding the Heavy Distillate into the diesel pool.
- Gain of more than 15wt% of diesel yield, thanks to the incorporation of Heavy Distillate into the pool without degradation of the Cold Flow Properties.
- Outstanding and stable performance throughout the cycle.

Dual-zeolite catalysts play a pivotal role in refining operations aimed at producing high-quality diesel with improved cold flow properties, meeting stringent environmental and performance standards.

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Roger Torres has over 20 years of experience in the oil refining industry. Since 2013, he has been with Axens Solutions, currently as Senior Technology Engineer in North America, leading the Hydrocracking technology. From 2003 to 2013, at PDVSA Intevep – Venezuela, he held roles such as Lead Technical Services Engineer, coordinating technical assistance for refineries in hydroprocessing units. Roger has strong technical expertise and leadership in hydroprocessing technologies.

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Tiago Sozinho has over 19 years of experience in the oil refining industry, specializing in hydroprocessing and hydroconversion technologies. Since 2020, he has been with Axens Solutions, where he currently serves as a Principal Technology Engineer for North America. In this role, he provides technical leadership and expertise in Distillates and bottom-of-the-barrel upgrading, supporting clients worldwide. Prior to joining Axens, Tiago spent a decade at IFP Energies nouvelles (IFPEN), where he worked as a Research & Innovation (R&I) researcher from 2010 to 2020. His work focused on pilot plant testing and multiphase reactor modeling, contributing to the development and optimization of advanced hydroprocessing technologies. Tiago holds a Ph.D. in Heterogeneous Catalysis from the Université de Poitiers in France. His doctoral research provided a strong foundation in catalyst design and reaction engineering, which continues to inform his work in industrial process development and innovation.

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