MIDW™ Technology as a Drop-in Catalyst Solution

Benefits of Upgrading to a Highly Isomerization-Selective Distillate Dewaxing Catalyst

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MIDW Technology as a Drop-in Catalyst Solution: Benefits of Upgrading to a Highly Isomerization-Selective Distillate Dewaxing Catalyst

ExxonMobil¹, Silver Eagle Refining, Inc.²

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Introduction

Although diesel specifications on cold flow properties vary depending on the region and time of year, the majority of diesel products require improvements to cold flow properties. Using catalysts to improve cold flow properties can be a higher value approach because it maximizes utilization of existing equipment and generates a more profitable product distribution.

During a planned turn-around in September 2015, Silver Eagle Refining, Inc. refinery in Woods Cross, UT implemented ExxonMobil’s MIDW™ isomerization-dewaxing catalyst technology resulting in a net increase in liquid production of up to 15 vol% due to a significant reduction in light ends production and an increase in diesel yield of up to 40 vol%. The catalyst changeout reduced operating cost and improved the quality of the #2 ULSD as evidenced by cetane numbers above 62. This improvement required only minor hardware upgrades and loading more selective isomerization-dewaxing catalyst in place of the former cracking-dewaxing catalyst resulting in a 6 month simple payback for the catalyst changeout costs.

Opportunities for Increased Profitability Through Diesel Technology

Several market forces are creating an opportunity for diesel producers to increase their profitability by optimizing refinery operations and technology around their diesel units. In order to take advantage of these opportunities, the diesel technology that refineries are currently using may need to be optimized, particularly around meeting cold flow property specifications such as cloud point (CP) and cold filter plug point (CFPP). Those opportunities include:

1. Demand growth in both diesel and jet fuel through 2040. As jet fuel demand increases, the use of kerosene as a blend stock into diesel to reduce cold flow properties is less desirable because it can reduce refinery profitability.
2. Diesel specifications continue to become more stringent worldwide. The low sulfur specifications that are already enforced in Europe and North America are soon to be required in the rest of the world. These specifications are only met with additional hydrotreating. The increased hydrotreating in turn reduces aromatics, which have a solubilizing impact on normal paraffins that cause high CP and CFPP. As a result, meeting CP and CFPP targets is more challenging with increased hydrotreating needs.
3. As European refineries close, the demand for diesel exports into Europe will increase. The diesel exported will be required to meet Euro V specifications and may have tighter CP and CFPP specifications than where the diesel is produced today.

4. Use of "Opportunity Crudes", such as tight oils, increase the margin of product coming out of a refinery. However, these crudes present different challenges than traditional crude sources. One challenge is that the diesel range of the crude could have higher paraffin content (and cold flow properties) than the crude it is replacing. This will cause challenges in blending the distillate pool, or lead to additional undercutting of diesel, thus reducing refinery profitability.

In general, refineries built around gasoline production, may be running sub-optimally to boost diesel production and meet tightening diesel specifications. There is a tendency to address only the constraints of existing processes; however, it may be more beneficial to re-evaluate whether the existing processes used to meet diesel specifications are still appropriate given the shifting landscape.

**Cause of Cold Flow Problems in Diesel**

Cold flow properties were highlighted as one of the major challenges in meeting diesel specifications and optimizing profitability when diesel demand grows. To address the problem, the cause must first be understood. What causes high cloud point and CFPP in diesel? The answer is normal paraffins.

Normal paraffins are straight chains of aliphatic hydrocarbons. As the number of carbons in that chain increases, so does the corresponding melting point, as seen in Figure 1. Many of the n-paraffins in the diesel range (C<sub>9</sub>-C<sub>25</sub>) will crystallize above 0°C. Paraffin crystals result in a cloudy appearance of the diesel product and when the crystals agglomerate, they will eventually plug the engine filter.

**Figure 1.** Cetane and Melting Points of N-paraffin by Carbon Number

**Options for Reducing Diesel Cloud Point**
There are many options for reducing diesel cloud point to reach specification limits and the optimal solution will depend on the refinery. General approaches to improve cold flow properties include:

- Restricting Feed Cloud
- Blending Finished Products
- Cold Flow Improvement Additives
- Catalytic Dewaxing

Poor cold flow properties come from crystallization of paraffinic hydrocarbons in the feed. These molecules crystallize at low temperature and agglomerate together, causing cloudy product as measured by cloud point, filter plugging as measured by cold filter plug point (CFPP), and ultimately the inability to flow as measured by pour point. Potential solutions for improving cold flow properties all have advantages and disadvantages that must be weighed on a case-by-case basis.

One solution is to cut out the “problem” molecules entirely by selecting feeds with low cloud points by limiting the feed to a lighter distillation cut. However, this likely requires more expensive feeds and downgrades a large portion of what could be diesel fuel to lower value products.

Another option is to blend the finished diesel product either a low cloud point product such as kerosene. However, kerosene can be sold as jet fuel, which is a higher value product than diesel in some markets. Therefore, blending kerosene into the diesel pool can reduce the overall profitability of the refinery.

Flow improvement additives called Middle Distillate Flow Improvers (MDFI), may also be used to reduce pour point. Their use can be expensive and has diminishing effectiveness at increasing concentrations. Furthermore, since MDFIs are tailored to the specific blend of products they are added to, reliance on them can make feed flexibility cumbersome. Finally, MDFIs do little to improve cloud point. Therefore, if cloud point is a specification, MDFIs are not a viable option.

Catalytic dewaxing is another alternative. Catalysts are used to facilitate reactions in which the paraffinic hydrocarbons are either cracked to lighter products (cracking-dewaxing) or isomerized into products with lower cloud points (isomerization-dewaxing). The type of catalyst will determine the balance between cracking and isomerizing the paraffins.

There are several advantages to catalytic dewaxing. Kerosene may be pulled out of the diesel blend and instead be sold as jet, obtaining higher margins. Higher cloud feeds are accessible for upgrading, such as heavier cuts or “opportunity” crudes such as tight oils. Catalytic dewaxing lowers cloud point, pour point and CFPP at the same time, and can affect very large changes in these characteristics.

Isomerization-selective catalysts can provide additional advantages over catalysts that primarily crack paraffins. Isomerization-selective catalysts maximize higher value products such as diesel and naphtha, while making less LPG, which can sometimes constrain unit throughput. Additionally, cetane of the resulting diesel is higher than products that result
from cracking. Hydrogen consumption is reduced due to a lower incidence of cracking, which reduces operating costs.

**Figure 2.** The dominant reaction pathway type for each dewaxing technology

![Diagram showing paraffin cracking and isomerization](image)

**Catalytic Dewaxing Overview**

For a better understanding of the differences between paraffin cracking and isomerization, the reactions are depicted in Figure 2. Paraffin cracking improves the cold flow properties by cracking long, paraffinic hydrocarbons to form shorter chains that have lower cloud point temperatures and boiling points. Paraffin isomerization removes a portion of a long hydrocarbon chain and inserts that small chain into the long hydrocarbon backbone. This retains the carbon number and boiling point while lowering the cloud point temperature. Therefore, at equivalent cloud point reduction, the isomerization dewaxing technology will yield more distillate product than the cracking dewaxing technology.

The directional impact that paraffin cracking and isomerization have on cold flow properties is illustrated in Figure 3, where the melting point of normal paraffins is plotted against carbon number. Cracking-selective dewaxing catalysts shift the melting point by reducing carbon number, pushing some of those molecules out of the diesel range and into naphtha and LPG. Alternatively, the isomerization-selective dewaxing technology reduces melting point by adding branches to the paraffins, retaining carbon number, but dropping the melting temperature.

**Figure 3.** The melting point as a function of carbon number and how each dewaxing technology improves the cold flow properties.
ExxonMobil first invented a cracking-dewaxing catalyst for distillate dewaxing in the 1970's and has deployed this technology in 25 refineries around the world. As part of the continuous improvement process, in 1990 ExxonMobil developed the first isomerization-dewaxing catalyst for distillate-range feeds called MIDW™ process. This technology has also evolved over time, leading to the development of a suite of catalysts, shown in Figure 4, which address a wide range of refinery needs, including catalysts with:

- High isomerization-selectivity for high delta cloud point requirements
- Higher activity catalyst with high selectivity where space velocity may be an issue
- Robust sulfur and nitrogen tolerance for sour environments

**Figure 4. ExxonMobil’s Current Dewaxing Catalyst Offering**

<table>
<thead>
<tr>
<th>Offering</th>
<th>Technology Summary</th>
<th>Activity</th>
<th>Diesel Selectivity</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cracking Dewaxing</td>
<td>Lowest cost catalytic solution if naphtha and LPG production are not concerns and not cetane limited.</td>
<td>+++</td>
<td>Low</td>
<td>Sweet or Sour</td>
</tr>
<tr>
<td>4th Gen MIDW™</td>
<td>Optimal for high ΔCP in low and moderate S/N environments</td>
<td>+++</td>
<td>High</td>
<td>Sweet or Sour</td>
</tr>
<tr>
<td>5th Gen MIDW™</td>
<td>Optimal for deep dewaxing applications</td>
<td>+++</td>
<td>High</td>
<td>Sweet or Sour</td>
</tr>
<tr>
<td>6th Gen MIDW™</td>
<td>Optimal for low and moderate ΔCP in high S/N environments</td>
<td>++</td>
<td>Moderate</td>
<td>Sour</td>
</tr>
</tbody>
</table>

**MIDW™ Catalytic Dewaxing Process**

The MIDW™ process can be applied to a single reactor train (Sour) or to a dual reactor train with interstage separation of H₂S/NH₃ (Sweet). ExxonMobil can also provide drop-in catalyst solutions with little-to-no capital investment. As shown in Figure 5, dewaxing catalyst may be added to the bottom bed of an existing hydrotreater or placed in a separate
post-treat reactor. A key part of the dewaxing technology allows the refiner to switch the dewaxing function off. At times of the year when cloud point reduction is not required, the unit can be returned to ULSD mode by either cooling the dewaxing catalyst bed with quench or bypassing the dewaxing post treat reactor entirely to maximize catalyst life.

In addition to process configuration flexibility, MIDW™ technology has worked effectively in a broad operating envelope. This technology has been deployed in 14 units worldwide. These units have ranged from sweet to sour, single reactor to multiple reactors, low and high pressure, and trim to deep dewaxing.

Drop-in catalyst solutions provide an opportunity to add value to the refinery with minimal or zero capital expenditure. The high isomerization selectivity from the MIDW™ catalyst suite can deliver value by allowing the refinery to better optimize molecules in the refinery to higher value streams:

- Uplift from adding heavier, high-cloud feeds
- Reduce product conversion to LPG and Naphtha
- Eliminate or reduce blending of high-value, low cloud products to meet cloud specification
- Eliminate or reduce MDFI additive addition
- Selection of light feeds containing paraffins (tight oils)

Silver Eagle Refining, Inc.’s Refinery in Woods Cross, UT is an example of where a drop-in catalyst solution with only minor hardware modification has provided significant value to the customer.

**Figure 5. MIDW™ Technology Reactor Configurations.**

**Silver Eagle Case Study**

In early 2015, Silver Eagle Refining, Inc. (Silver Eagle) needed to replace the dewaxing catalyst at their refinery in Woods Cross, UT. In addition to other catalyst companies, ExxonMobil was contacted for a bid. ExxonMobil provided yield estimates that
demonstrated higher diesel retention and corresponding lower naphtha and LPG production than the incumbent catalyst. In addition, ExxonMobil understood the unique challenges of running the paraffinic feed used at Silver Eagle.

ExxonMobil worked with Silver Eagle to identify key enablers for reaching longer cycle lengths and having more reliable, productive operation. A new distributor tray was needed to improve distribution of feed over the catalyst, reducing the likelihood of hot spots and catalyst bypassing. Reactor thermometry was improved by adding new thermocouples to monitor catalyst activity and detect hot spot formation. In addition, Silver Eagle replaced their bottom catalyst support grid with an elephant stool and addressed issues with reactor internals.

**Leveraging ExxonMobil’s Operating Experience**

Although there was a narrow timeframe in which to execute the hardware and catalyst changes, there was a consistent focus on safe and reliable operations. In addition to optimizing hardware design, ExxonMobil provided Silver Eagle with recommendations for updated safety measures and provided procedures to ensure safe operation of the unit. For example, the thermometry was redesigned to add 18 additional thermocouples to the design. ExxonMobil’s technical experts provided training to the full Silver Eagle staff and were present for the distributor tray leak test, installation, catalyst loading and unit start-up.

**Silver Eagle Project Execution**

From the initial discussions between Silver Eagle and ExxonMobil to the catalyst deployment and unit start up was less than 6 months. In order to meet this challenging deadline, Silver Eagle and ExxonMobil worked closely to align and progress. ExxonMobil provided the preliminary distributor tray design 1 week after contracts were signed and final drawings were issued 3 weeks later. In parallel to this, the Operating Guide and training packages were developed with Silver Eagle to mitigate any safety concerns of the existing unit.

Silver Eagle worked with an approved ASME code certified fabrication shop to quickly fabricate the new hardware. Early in the turn-around, inspection of the reactor vessel indicated the internals were compromised and needed to be replaced. Once all of those replacements were made, Silver Eagle and ExxonMobil worked side-by-side to ensure the fabrication and installation of the hardware was done correctly. Silver Eagle personnel installed the internals and loaded the catalyst.

With hardware modifications complete, ExxonMobil’s catalyst experts were present to oversee the addition of catalyst to the unit and to troubleshoot any issues experienced during start-up. The unit started up in October 2015 without issue.

**Figure 6.** Timeline for MIDW™ Technology Deployment at Silver Eagle
MIDW Unit Results

Silver Eagle opted for an in-kind replacement of the previous cracking-selective dewaxing catalyst with MIDW™ technology. Their existing unit configuration was used, in which the dewaxing catalyst was in a sour environment in the bottom bed of the diesel hydrotreater. Based on feed and process considerations, diesel yield estimates were provided for summer and winter dewaxing conditions. Unit performance in the first year have exceeded or met both estimates, as shown in Figure 7.

**Figure 7.** Actual distillate yield at Silver Eagle compared to estimates vs. cloud point reduction.

For comparison to cracking-selective dewaxing catalysts, estimates of diesel yield at summer and winter cloud point reduction targets were generated. These estimates are based on models that ExxonMobil has developed of their own cracking-selective dewaxing catalysts, which include 40+ years of commercial experience. The estimates indicate that approximately 45 wt% of additional distillate would be converted to naphtha and LPG if cracking dewaxing were to be used again.

The minimization of LPG production was the primary driver for Silver Eagle’s selection of ExxonMobil’s MIDW™ technology. The plot in Figure 8 shows the total liquid yield (naphtha + distillate) over the wide range of cloud point reduction experienced at Silver Eagle. This
plot shows that even at very high cloud reduction where cracking dewaxing technology typically converts naptha and distillate to LPG, there is high liquid yield retention when MIDW™ technology is utilized. Silver Eagle stated that they went from being natural gas balanced to having to increase natural gas purchase by ~2X due to the reduction in LPG production on the dewaxing unit. The cost of additional natural gas purchase was more than offset by the lower $H_2$ consumption of the HDT, leading to an overall operating expense savings.

**Figure 8.** Total liquid yield as a function of cloud point reduction of Silver Eagle’s diesel HDT unit.

Due to the increase in total liquid yield at the expense of lower value LPG and the overall operating expense savings, Silver Eagle was able to reach the payout for this catalyst changeout in 6 months. An additional benefit was the increase of cetane they saw with the catalyst switch. Silver Eagle uses high-quality virgin straight-run diesel feed for their hydroprocessing and dewaxing units. With ExxonMobil’s MIDW™ catalyst technology, they are able to retain the high cetane of their feed, as seen in Figure 9, resulting in some of the highest cetane diesel in their market.

**Figure 9.** Increase in Diesel Product Cetane at Silver Eagle from 2014 to 2016
Conclusion

ExxonMobil provides several solutions for catalytic dewaxing of distillate fuel. We work with customers to develop solutions for their needs that ultimately improve their profitability. In many cases, the solution may be as simple as a catalyst change-out.

The solution for Silver Eagle Refining, Inc. involved installing a new distributor tray and replacing their cracking dewaxing catalyst with MIDW™ catalyst technology. ExxonMobil and Silver Eagle worked closely together to meet a very aggressive timeline for a minor unit revamp and catalyst changeout. Through the technology deployment, there was a strong focus and commitment to safety and reliability both of which translate to improved profitability.

The result was an increase in refinery profitability and a reduction in operating expense. Silver Eagle was able to achieve this by reducing their LPG yields while improving diesel yields and lowering hydrogen consumption. In addition, the quality of their distillate product improved markedly. The payout for the catalyst changeout was achieved in 6 months.