



Understanding Cloud Point and Hydrotreating Relationships



Brian Watkins
Manager,
Hydrotreating Pilot
Plant & Technical
Service Engineer

Meredith Lansdown
Technical Service
Engineer

**Advanced
Refining
Technologies**
Chicago, IL, USA

As the distillate markets allow for increased distribution worldwide, refiners need to be more aware of the additional product specifications that can be present at the various locations. One product property that is difficult to modify with general hydrotreating is the ability to improve (lower) the cloud point and cold filter plugging point of the diesel. Cold flow properties are determined by the wax or crystals that are formed as the diesel is cooled. The formation of these crystals can plug filters and lead to poor engine performance.

There are various approaches to meeting cold flow targets, the simplest of which is the blending of lighter material (kerosene or jet) into the fuel. Other options include the use of additives, solvent dewaxing, or adding a separate isomerization reactor. All of these options have disadvantages, including high costs or yield losses. Diluting with blending stocks, such as kerosene, has the added complication that the blending stocks must separately meet all of the same requirements, such as sulfur, of the finished ultra low sulfur diesel (ULSD) and could require that the blending stock undergo additional hydrotreating. This also involves taking a higher value fuel, degrading its value by blending it into diesel, and will have volume limits in order to stay within distillation and flash point specifications for diesel fuel.

The ability to modify the cold flow properties of the diesel in the hydrotreater can have significant economic advantages that the other options do not provide. Use of a specialty catalyst is required in order to do catalytic or hydro-dewaxing (HDW) to improve the cold flow product properties within the ULSD hydrotreater complex, and to avoid making changes to naphthenes or iso-paraffins that already have acceptable cold flow properties. Understanding the cold flow requirements first is necessary to create an individually tailored process and avoid the pitfalls associated with inappropriate quantities of HDS catalyst such as yield losses and not having the flexibility to meet market demands. Figure 1 shows some simple reactions that can effectively improve the cold flow properties of the diesel product. The resultant products contain some olefinic material due to the cracking mechanism and require proper catalyst staging to achieve process goals.

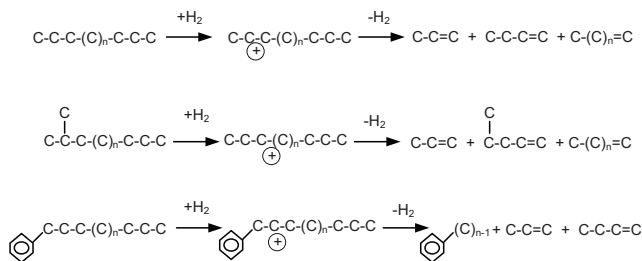


Figure 1: Mechanisms for Dewaxing in a Hydrotreater

		Boiling Point (°F)	Melting Point (°F)
Dodecane	C ₁₂	421	15
Tetradecane	C ₁₄	489	43
Hexadecane (Cetane)	C ₁₆	549	65
Octadecane	C ₁₈	601	83
Eicosane	C ₂₀	649	98
Docosane	C ₂₂	695	112
Tetracosane	C ₂₄	736	129
Hexacosane	C ₂₆	774	134
Octacosane	C ₂₈	809	148

Figure 2: Melting and Boiling Points for n-Paraffins

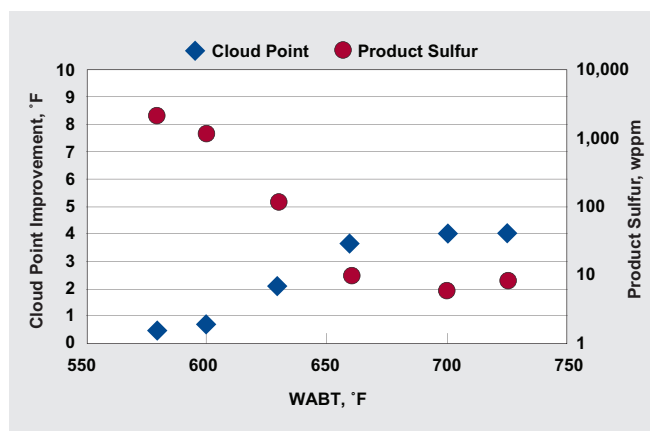


Figure 3: Hydrotreating and Cloud Point Improvement

The typical process of dewaxing utilizes a ZSM-5 type catalyst. The structure of ZSM-5 is such that only straight chained hydrocarbon molecules (normal paraffins or n-paraffins) fit inside the cage structure and are cracked into smaller, lighter molecules. These molecules have significantly lower cloud and pour point characteristics. Figure 2 shows some of the various n-paraffins present in a typical diesel boiling range. The melting point is what influences the cloud point of the diesel if left unconverted, and of course, the higher the carbon content, the higher the boiling point.

Due to the nature and structure of the zeolite, the catalysis choice is important as these structures can easily be poisoned by nitrogen and olefins present in the feed. Even in high-pressure applications hydrotreating has only a small impact on product cloud point. Figure 3 shows the effect of hydrotreating on cloud point at 1400 Psi hydrogen partial pressure and with a feed containing 50% cracked material. This figure examines the cloud point improvement across a wide range of product sulfur and operating temperatures. Even at high temperatures, well beyond that required to produce ULSD, there is little change in product cloud point.

Typically, the target market for these products requires more than several degrees decrease in cloud point below the value of the feed. This suggests the use of hydro dewaxing in conjunction with the ULSD unit is desirable.

As mentioned previously, for HDW catalyst to perform most efficiently requires some hydrotreating first since it is susceptible to poisoning from the organic sulfur and nitrogen present in the feed. Figure 4 shows pilot plant results from operating a system using untreated feed over dewax catalyst at 5.75 LHSV to simulate the feed rate over a dewax bed in a hydrotreater. This work was completed over the entire range of temperatures for a ULSD hydrotreater from start of run to end of run. As the figure shows, there is very little change in product values. The cloud point of the product is improved only slightly and this corresponds with a small increase in bromine number, which is expected based on the reactions listed in Figure 1. It is important to note that it also shows that there is very little sulfur and nitrogen removal, and interestingly enough there is actually a slight increase in the volume percent for mono and poly aromatic species in the product, as indicated by a negative percent change.

Decreasing the LHSV over the dewax catalyst bed produces similar trends for the total and poly aromatics conversion as well as the HDN and HDS conversions. There are only a few degrees change in cloud point and almost no change in the bromine number from the higher LHSV. This clearly indicates that it is important to provide some level of hydrotreating in advance of the HDW catalyst in order to be able to utilize the zeolitic acid function. It is also important to note that there needs to be enough hydrotreating catalyst available in the system in order to meet the other product specifications such as sulfur and aromatics, since the HDW catalyst provides no sulfur or nitrogen removal.

One of the keys to successfully combining a dewaxing catalyst with an HDS system is an understanding of the tradeoffs between dewaxing and HDS activity as the amount of dewax catalyst is changed. ART completed a number of pilot plant tests with two different amounts of dewax catalyst and ART's NDXi, a premium nickel molybdenum catalyst for ULSD applications. The pilot plant work consisted of testing loadings of 10% and 20% dewax.

The first set of data examines the ability of the system to meet 10 wppm sulfur in the diesel at both low pressure (500 Psi hydrogen partial pressure) and at a higher pressure (975 Psi hydrogen pressure). Figure 6 compares the two systems and the base case is the 10% dewax system at low pressure. This base condition is for producing 10 wppm product sulfur and is the zero point on the temperature axis. As expected, the higher pressure system outperforms the low pressure application by almost 30°F (~17°C). At lower pressure, the difference between the systems shows a 10°F (~6°C) higher temp required with the increased dewax catalyst volume. The additional temperature required to meet ULSD also needs to be considered as this could mean a debit of 4-8 months in cycle life if too much HDW catalyst is loaded into the hydrotreater.

The ability to determine product cloud point and how it is expected to change over time is also important. Similar to a hydrocracking reactor, as the temperatures are increased over the bed of HDW catalyst, the ability to break the n-paraffins increases. There is a clear difference in the ability to make a cloud point change based on not only LHSV over the dewax bed, but also the operating pressure of the unit, much like that for producing ULSD. In Figure 7, the base case is again the 10% dewax bed, and the zero point on the chart is the point at which 10 ppm sulfur is produced. Moving from left to right is changing the WABT relative to the expected SOR temperature for 10 wppm sulfur.

Once the temperature is high enough to begin dewaxing, the kinetic response for converting the n-paraffins is linear for both catalyst systems. In these cases, with the combination of hydrotreating catalyst and dewax catalyst (HDT-HDW), there is still a requirement for the removal of sulfur and nitrogen in order for the system to perform well. At 20°F (~11°C) below the expected SOR temperatures, the system is still capable of decreasing the cloud point 5-7 numbers with the remaining sulfur to the HDW catalyst between 60-100 wppm. Increasing the residence time over the HDW catalyst has a significant impact on the product cloud point. At the temperature required to produce 10 ppm product sulfur the 20% HDW case results in 8-10 degrees more cloud point reduction compared to the 10% HDW case.

Similar trends are observed when the two catalyst systems are operated at higher pressure, as shown in Figure 8 for both 10% and 20% HDW catalyst systems. The zero point on the x-axis is where the 10% HDW system is able to produce 10 ppm product sulfur. The important item to note is that the total cloud point improvement is much greater in this application than at lower pressures. In this case, the

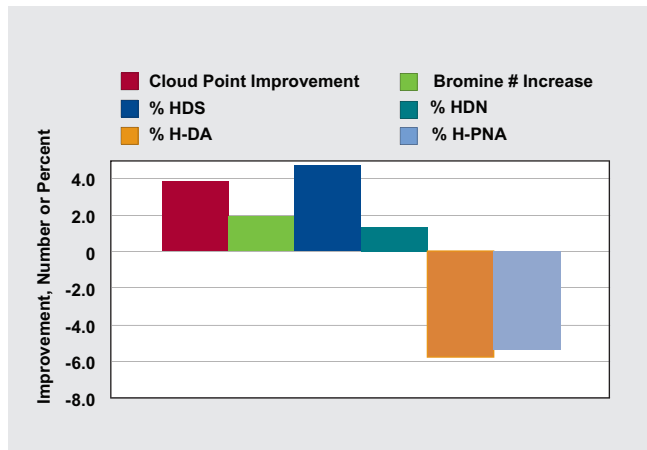


Figure 4: Dewax Catalyst with Untreated Feedstock at High LHSV

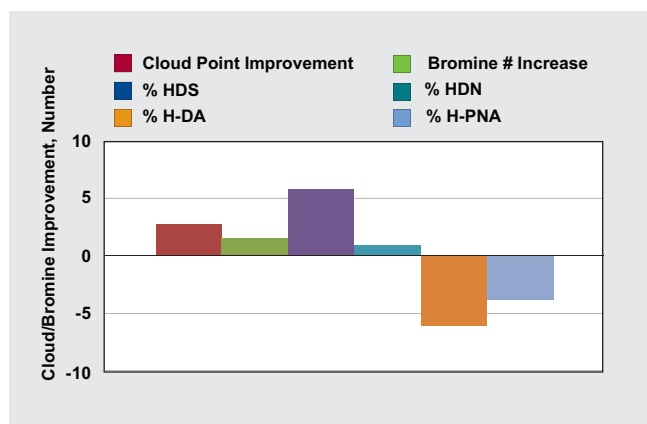


Figure 5: Dewax Catalyst with Untreated Feedstock at Low LHSV

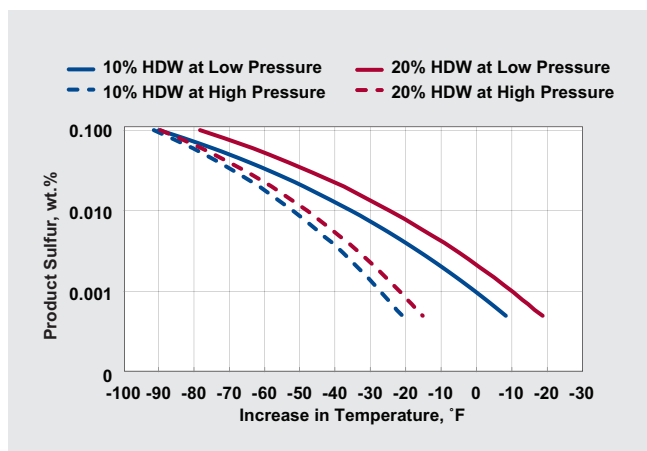


Figure 6: Changes in LHSV and Pressure over the HDW Catalyst System

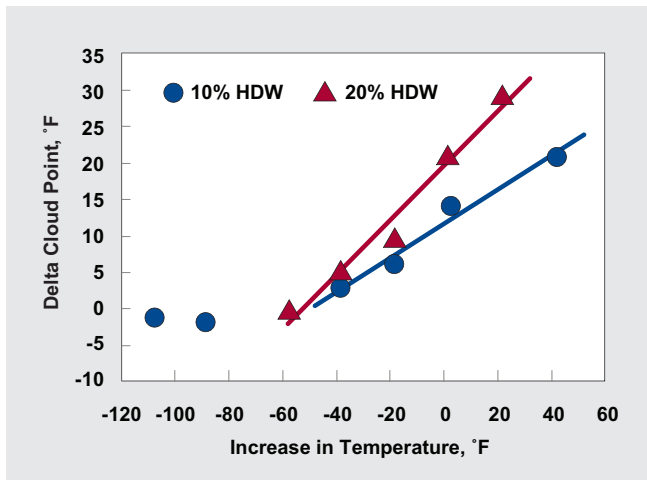


Figure 7: Low Pressure Effects on HDW Performance

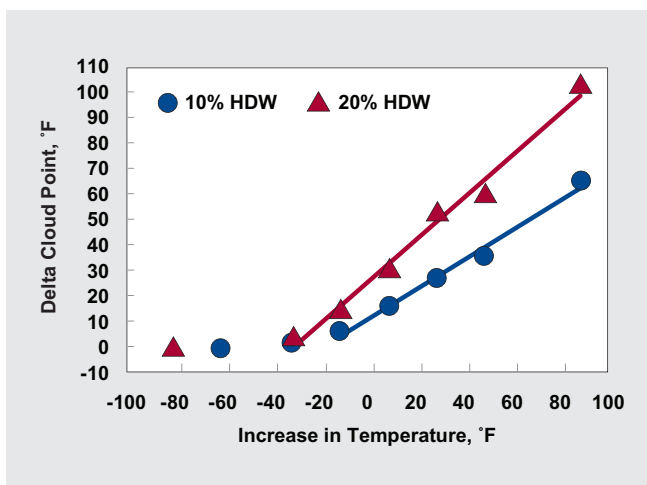


Figure 8: High Pressure effects on HDW Performance

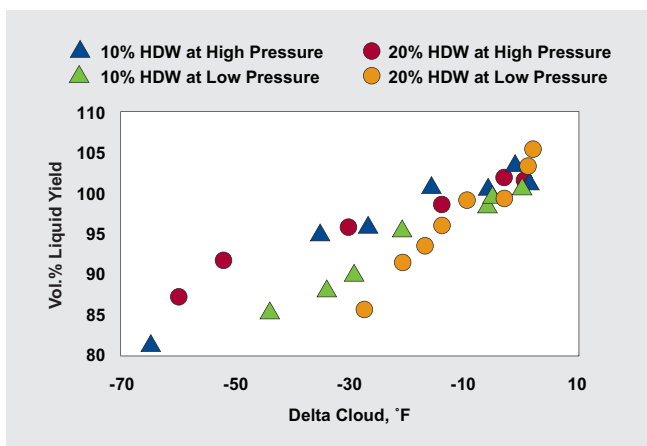


Figure 9: Yield Losses and HDW

20% HDW case 20-25°F (~11-14°C) of cloud point improvement is achieved at the temperature required for 10 ppm sulfur. Similar cloud point reduction was achieved for the 20% HDW case at 10 ppm sulfur at low pressure, but as shown in Figure 6, there is 20-30°F (~11-17°C) difference in WABT for 10 ppm sulfur between low and high pressure. The impact of residence time in the dewax bed is a little larger at high pressure as well. The 20% dewax system gives about 10-12°F (5.5-6.6°C) more cloud point reduction compared to the 10% case at 10 ppm product sulfur.

As discussed earlier, the HDW function is to break the n-paraffins into smaller molecules in order create less waxy molecules in the finished diesel product. This chain breaking reaction, although somewhat selective, does have the potential disadvantage that it can convert diesel boiling range material into naphtha or possibly lighter materials. These materials, if the refinery is able to tolerate and utilize them, can be considered quite valuable as well. One concern is that if a significant volume of diesel is converted to lighter products, the downstream equipment might not be capable of handling excess light materials.

Figure 9 compares the two loadings and the two pressures in terms of liquid volume yields of 250°F (121°C) plus boiling material. There is a clear importance to understanding the limits of placing too much HDW catalyst into a hydrotreater. Tailoring a system to be able to control the activity of the HDW catalyst is important so that as EOR temperatures are reached, the system is capable of being controlled so that the yield losses are within expectations. Note that the high pressure system, regardless of the percent of HDW catalyst, is able to maintain better liquid yields benefiting from an environment in the hydrotreater that allows it to be highly selective in what molecules it will work on. This is also due to the ability of the NiMo catalyst to saturate and modify the hydrocarbon molecules before it has a chance to be converted by the HDW catalyst. In the lower pressure system, ring saturation does not occur as easily, and the HDW catalyst is unable to be as selective in which molecules it is converting and results in a greater liquid yield loss.

ART's extensive pilot testing has shown that there is a complex interaction between dewaxing and hydrotreating in ULSD applications. There is a balance between dewaxing activity and HDS activity, which needs to be understood when designing a catalyst system. Furthermore, the liquid yield needs to be considered at both SOR and EOR as this is highly dependent on the amount of dewax catalyst in the system. ART's technical services staff can work with refiners in order to provide the right catalyst system tailored for maximum refinery profit.