Maximizing Diesel from Existing Assets

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1. Abstract

The growth in diesel consumption globally continues to outpace the growth in gasoline consumption. To capitalize on this trend refineries need to shift their product slate towards increased diesel output while preferably avoiding major capital projects. Depending on the configuration of the refinery, either the product density or the product distillation specifications may limit the increase in diesel production.

In this paper, Albemarle will highlight the strategies that refineries can use to overcome these limitations and increase the diesel production from their existing assets. By employing a molecular approach to the product quality specifications limiting the increase in the refinery diesel yield, maximization of the diesel production can be achieved while minimizing the byproduct formation. Commercial case studies will be used to illustrate the various concepts.

2. Introduction

The global trend of the growth in diesel demand outpacing the growth of other mineral fuels, observed over the last few years, shows no sign of abating. To address this growth, refineries need to look for opportunities to increase the diesel yield of the refinery. Given the high cost and long duration of the construction of new facilities, optimizing the use of existing assets with innovative catalyst solutions can be an economically attractive opportunity.

Refineries can be divided into two general categories; those with hydrocrackers and those without hydrocrackers. These two types of refineries face different challenges when trying to increase their diesel pool.

For refineries without hydrocrackers, the specifications on the density, cetane number and cetane index of the diesel product can be a limiting factor in increasing diesel production. As a result, many operate below the ASTM D86 T95 specification to meet these density and cetane targets. Increasing the density reduction achieved in the diesel hydrotreaters will allow these refineries to extend the endpoint of the feeds to the ASTM D86 T95 specification of 360°C, thereby increasing the diesel yield of the refinery.

In refineries with high-pressure hydrocrackers, hydrocracked diesel provides a source of low density, high cetane blending material that can be used to correct these deficiencies from the diesel hydrotreaters. However, the application of these blending materials may be limited, particularly in refineries that frequently produce a diesel pool that is too low in density. This may force the refinery to sell low-density products separately, even when the margins on those products are lower than the diesel margin. Increasing the distillation endpoints of the feed is a relatively easy option to increase the density of the diesel pool. However, since aromatics saturation can only give limited T95 reduction, the specification on the ASTM D86 T95 will determine the maximum end-point of the feed. Incorporating some form of T95 reduction in the diesel hydrotreaters would allow these refineries to extend the boiling range of the diesel hydrotreater feed and increase the diesel yield of the refinery.

3. Ultra Deep Aromatics Saturation

As with any mineral oil, diesel fuel is a blend of paraffins, naphthenes and aromatics. Considering the effect of hydrotreating on these three component groups provides insight into the reaction pathways that can be employed to increase the diesel production from existing hydrotreaters.

New analysis techniques, such as coupled gas chromatography (GCxGC-FID), give an unparalleled view of the detailed carbon distribution of diesel fuels. In a GCxGC-FID measurement the sample is first separated by boiling point. Effluent samples from the first GC are then injected into a second GC at five second intervals, which separates the components by polarity. Since aromatics have a higher polarity than paraffins, their retention time in the GC will be longer for separation. Finally, a flame ionization detector measures the concentration of each species in the sample.

The result of the analyses is a three dimensional (boiling point, polarity and concentration) map of an oil sample. Figure 1 provides an example of a two dimensional (2D) projection of a GCxGC-FID diagram for a typical untreated diesel fuel, where the third dimension (concentration) is indicated by the color of the species (black = low concentration, white = high concentration).

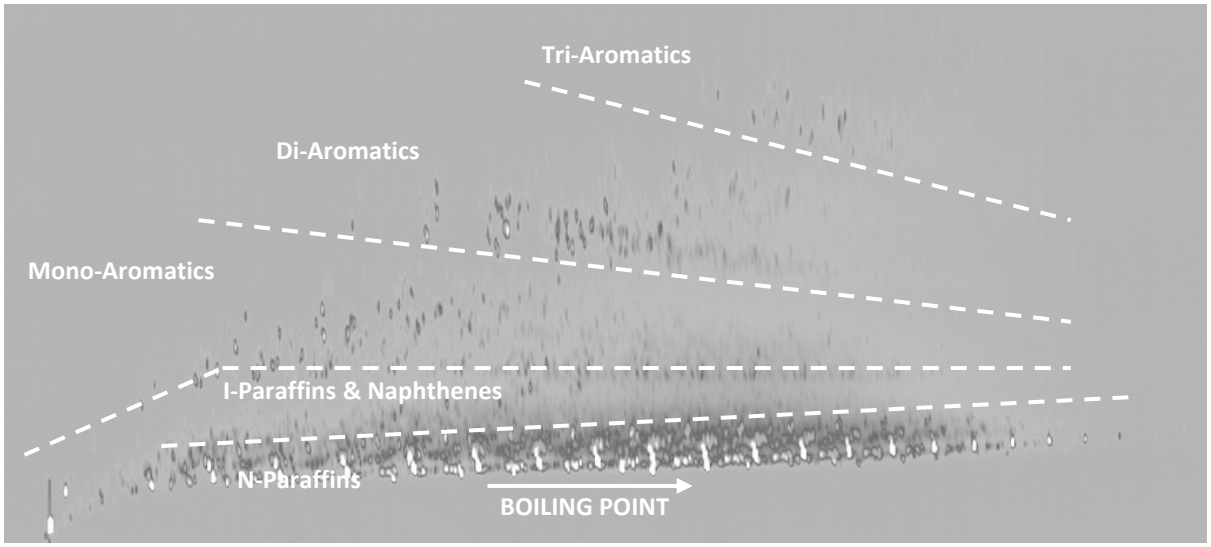

Figure 1: Carbon Distribution of a Typical Diesel Fuel

The typical untreated diesel feed shown in Figure 1 contains significant quantities of aromatics and particularly di- and tri-aromatics with high boiling points. For example, subsequent saturation of the three rings of phenanthrene, a simple tri-aromatic, with a boiling point of 332°C, reduces the density of the hydrogenated molecule from 1.18 g/ml to 0.914 g/ml. The presence of polyaromatics in diesel and their saturation provide an effective means for reducing the density of diesel fuels.

Since naphthenes have better combustion characteristics than aromatics, the cetane value, the ASTM D4737A cetane index and the ASTM D613 cetane number, will improve with aromatics saturation.

The level of aromatics saturation achieved in a particular hydrotreating unit depends on the operating conditions, the detailed chemical composition of the feed and the catalyst used.

The reactivity of aromatics decreases with a decreasing number of rings. For example, Cobalt-Molybdenum catalyst will readily saturate di- and tri-aromatics to mono-aromatics, while further conversion of the mono-aromatics to naphthenes will hardly occur. However, significant conversion of mono-aromatics to naphthenes can occur with Nickel-Molybdenum catalysts and units designed for density reduction and cetane uplift. This typically occurs in the DHDT units in most Indian refineries operating at very high pressures using a Nickel-Molybdenum catalyst. Still, even under these severe conditions, the level of mono-aromatics saturation achieved is limited to approximately 50%.

Figure 2 shows the carbon distribution obtained after the feed from Figure 1 is hydrotreated at moderate pressure with a Nickel-Molybdenum catalyst. Nearly all the di- and tri-aromatics have been saturated to their monoaromatic equivalent and although some conversion of the mono-aromatic to the fully saturated naphthenes has occurred, significant quantities of mono-aromatics remain in the product.

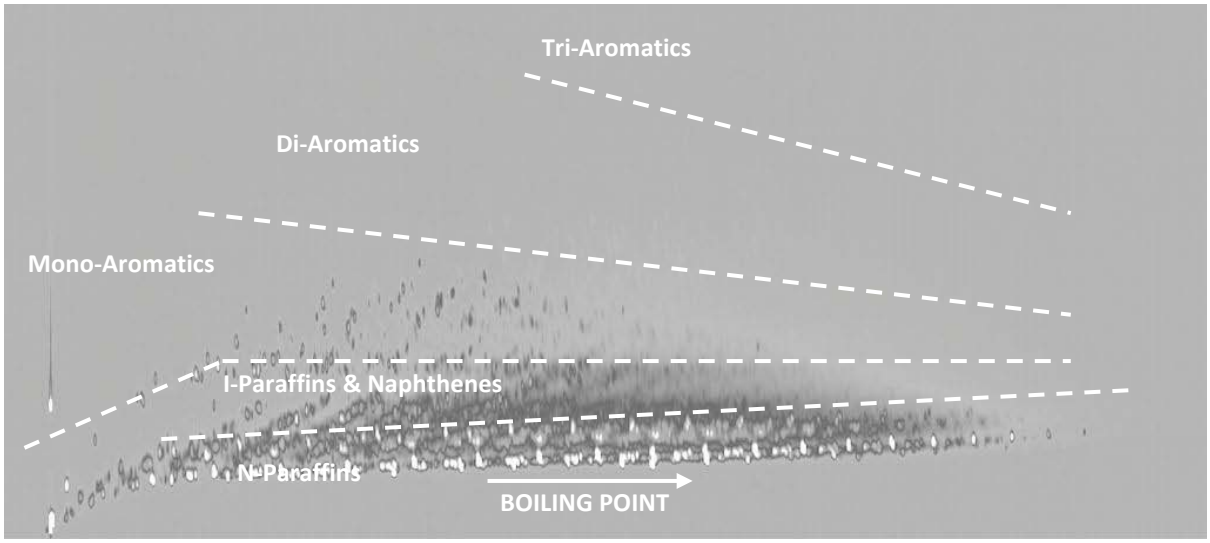

Figure 2: Carbon Distribution of the Diesel Fuel of Figure 1 after Hydrotreating at 75 barg Hydrogen Partial Pressure with the Nickel-Molybdenum KF 848 STARS® catalyst

If further reduction of the product density is required to achieve the diesel specifications or the refinery has excess hydrogen available that can be used to increase the volume of the diesel pool, historically the only option available was to use a noble metal

Platinum/Palladium catalyst. As these catalysts cannot tolerate the presence of sulfur and nitrogen, a two-stage unit with inter-reactor removal of H_2S and NH_3 was necessary.

The introduction of the Nebula family of catalysts provided a solution for refineries limited by the product density. Nebula is a base metal catalyst technology that can operate in an H_2S and NH_3 rich atmosphere while giving an aromatics saturation activity rivaling that of Noble metal based catalysts. This makes Nebula a drop-in solution for refineries looking to achieve unparalleled, ultra deep aromatics saturation for maximum density reduction and cetane improvement. Furthermore, in combination with Albemarle's STAX™ methodology for optimizing hydrotreating catalysts loads, the quantity of Nebula required to achieve a defined objective can be reduced to typically 20 to 25% of the total catalyst volume, thus minimizing costs.

Table 1 shows the results of two commercially operating diesel hydrotreaters. Apart from the catalyst system, the units process very similar feeds at comparable operating conditions. Despite the limited hydrogen partial pressure of 65 barg in the two units, a regular NiMo STARS catalyst can achieve significant density reduction. However, for the second refinery, the diesel product density was limiting the diesel blending flexibility and spare hydrogen was available.

By employing a Nebula STAX system designed for additional mono-aromatics saturation, the density reduction improved by 12 kg/m^3 and the ASTM D4737A cetane index improved by 3 points when compared to the unit loaded with conventional catalysts.

Table 1: Effect of Ultra Deep Aromatics Saturation at 65 barg Hydrogen Partial Pressure

		NiMo STARS	Nebula STAX™
Product Density	kg/m^3	base	base – 12
Product Cetane Index	ASTM D4737A	base	base + 3
Product ASTM D86 T95	°C	base	base – 2

Thus ultra deep aromatics saturation can be an attractive option for refineries where the diesel yield of the refinery is limited by the density or cetane index of the diesel pool. Applying ultra deep aromatics saturation can relieve constraints on the end-point of the feed. As a result, the product quality giveaway on the ASTM D86 T95 can be reduced or eliminated.

Ultra deep aromatics saturation is the most attractive option available to refineries when compared to other technologies for decreasing the product density, as it has the lowest naphtha make while also maximizing diesel yield.

4. Selective T95 Reduction

As shown by the commercial operating data in Table 1, ultra deep aromatics saturation can substantially improve the density reduction and cetane uplift. However, the ASTM D86 T95 reduction does not increase significantly due to the increased aromatics saturation. The reason for the limited increase in T95 reduction on increased aromatics saturation is related to the composition of the heavy fraction of the diesel fuel after hydrotreating.

Examination of the pure component data for phenanthrene reveals that the saturation of each of the aromatic rings the molecule reduces the boiling point by 14°C, 23°C and 22°C respectively. Since the starting boiling point of phenanthrene is 332°C, saturation of two of the three rings will already reduce the boiling point by 37°C, thus bringing the hydrogenated product into the kerosene boiling range.

Looking back at Figure 2 shows that hydrotreating will saturate the high boiling aromatics present in the diesel feed to components with a lower boiling point. Since the fraction of material in the high boiling range is reduced, so too will the T95.

There is an upper limit to the T95 reduction that can be achieved with aromatics saturation. Once all the high boiling polyaromatics have been saturated, the naphthenes and paraffins remaining in the high boiling range of the feed are essentially inert and will remain unchanged in the product. Although the front end of the boiling curve will still shift when applying ultra deep aromatics saturation, this will only have a limited effect on the back end of the distillation curve. In practice this means that the T95 reduction achievable with aromatics saturation is limited to 5 to 7°C for straight run feeds and 8 to 10°C for feeds containing an aromatic stream such as light cycle oil.

If the diesel pool of the refinery is limited by the end-point of the feed, some form of T95 reduction through a cracking mechanism is required to increase the diesel yield of the refinery. The instinctive response of most refineries is to dismiss it straight away, as the perception is that the refinery diesel yield will decrease.

However, the objective described in this article is to increase the endpoint of the feed while keeping the remainder of the feed constant. Thus, the feed rate to the unit will increase as the end-point is increased. Although the naphtha make will increase, both in tons and as a percentage of fresh feed, the increase in the diesel yield compensates for the increased naphtha make.

Figure 3 shows a numerical example of the effects of a simultaneous increase in the feed end-point and the application of T95 reduction. In this example, the base case naphtha yield of the diesel hydrotreater is 2 metric tons per hour, or 2 wt%.

When T95 reduction through a cracking mechanism is applied, the naphtha yield in this example increases to 6 metric tons per hour, or 5.4 wt%. Most refineries will conclude that this option is not economically attractive.

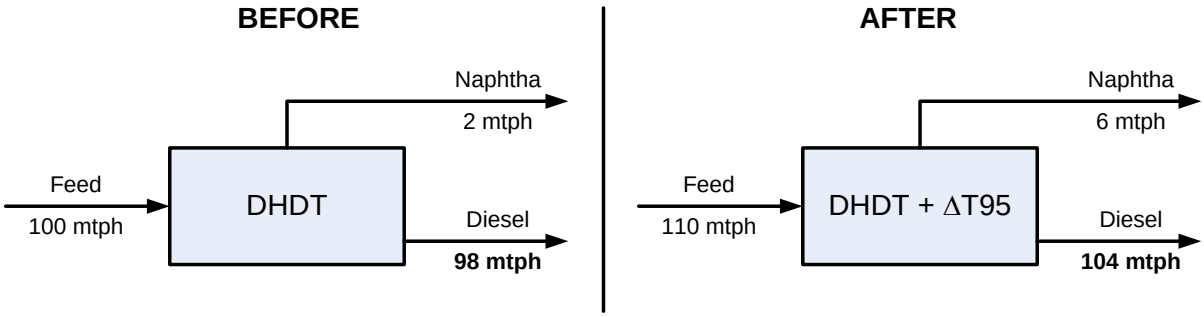

Figure 3: Comparative Unit Mass Balance Before and After the Implementation of T95 reduction

However, since the feed rate also increases from 100 to 110 mtph due to the extension of the end-points of the feed, the diesel output of the unit increases from 98 mtph to 104 mtph for a net gain in diesel output of 6 mtph. Evaluating the application of T95 reduction only in terms of percentages can be very misleading and may lead refineries to dismiss profitable opportunities.

If the capacity of the DHDT is already fully utilized, but spare capacity is available in a lower pressure DHDS unit, the same increase in the overall diesel pool can be achieved by shifting some of the lighter feed components from the DHDT to the DHDS unit and applying T95 reduction on the heavier feed to the DHDT.

4.1 Implementation of T95 Reduction

When implementing T95 reduction in a commercial unit, catalyst selection can be crucial in achieving the right selectivity to maximize the diesel product yield. Figure 4 compares the naphtha yield between a “standard” mild hydrocracking catalyst and a catalyst specifically designed for T95 reduction of heavy diesel fractions at 100 barg total reactor pressure.

The standard mild hydrocracking catalyst, designed to crack heavier VGO feeds, will overcrack the lighter portion of the diesel feed to naphtha and results in higher naphtha make per degree of T95 reduction. Moving up the selectivity–activity curve towards a higher selectivity and lower activity catalyst will increase the required start-of-run temperature and therefore reduce the cycle length to unacceptably low levels.

In contrast, a dedicated selective T95 reduction catalyst that operates on a different principle can achieve the right combination of activity and selectivity to reduce the naphtha make to acceptable levels.

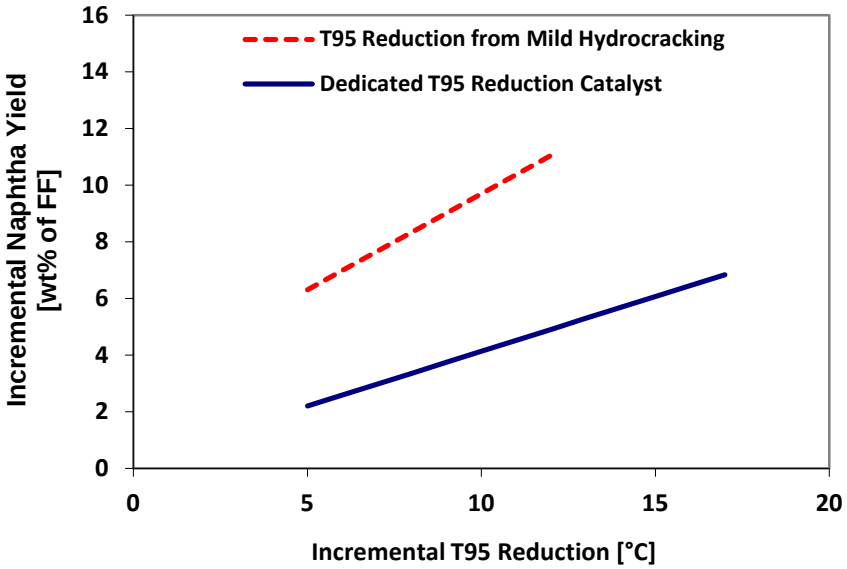

Figure 4: Incremental Naphtha Yield versus Incremental T95 Reduction

Table 2 shows an example of a commercial application of T95 reduction using Albemarle's dedicated selective T95 reduction catalyst. In this unit, the catalyst system has been designed in such a way that the refinery can switch off the T95 reduction activity whenever necessary. The data shown compares a period where the unit was operated as a hydrotreater to a period where the T95 reduction capability of the catalyst system was used.

Table 2: Commercial Example of T95 Reduction at 65 barg hydrogen partial pressure

		HT Only	HT + ΔT95
Product ASTM D86 T95	°C	base	base – 8
Feed Rate	wt% of FF	base	base + 10
Diesel Yield	wt% of FF	base	base + 6

In this particular unit, the T95 reduction operation provided an additional 8°C of T95 reduction with an incremental naphtha yield of 4.2 wt%. By extending the end-point of the feed by 8°C this refinery was able to increase the feed rate by 10 wt%. Consequently, the overall diesel output of the unit increased by 5.8 wt%.

T95 reduction can be an effective means of increasing the diesel output of existing units in a refinery. Optimizing the feed diet and reallocating the feed to other hydrotreating units can be exploited to maximize this benefit. An important question to consider when evaluating T95 reduction is whether the naphtha yield of the entire complex actually changes. If, for example, the heavy diesel stream is taken from the FCC or hydrocracker feed, the overall naphtha make of the refinery may not change, as both of those units produce copious amounts of naphtha.

5. Conclusion

Refineries exploring options to increase their diesel pool can be faced with several challenges on product quality. By maximizing the capabilities of their existing units, the refineries can achieve a significant increase in their diesel output.

For refineries where the diesel pool is limited by the product density or cetane number, ultra deep aromatics saturation is an attractive option to minimize T95 give-away. Using Albemarle's Nebula catalyst in combination with the STAX technology for optimizing catalyst systems, the density reduction and the cetane index number can be increased by up to 50%.

If the distillation specifications are hindering a further increase in the diesel pool, a reduction in T95 using an optimized T95 reduction catalyst, will allow an increase in the end-point of the feeds and thus increase diesel production while minimizing the naphtha make.

An important aspect to keep in mind is whether the incremental naphtha yield from the diesel hydrotreater using T95 reduction will actually increase the naphtha production of the refinery, since processing the heavy diesel in one of the conversion units (FCC or Hydrocracker) will also convert some if not all of the heavy diesel into naphtha.

Author Biography:

Pieter Lusse holds a MSc degree in Chemical Engineering from the Delft University of Technology in The Netherlands. He joined Albemarle Catalysts in 2003, working in the Technology Licensing division and later for the UOP-Albemarle Hydroprocessing Alliance. From 2008 until 2013 he provides technical services for Hydroprocessing and FCC catalysts in the Middle East and India. Since 2014 he is the Technical Manager Hydroprocessing catalysts in the Americas.