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AM-15-24 Diesel Maximization: Putting a Straw on the FCC Feed

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Diesel Maximization: Putting a Straw on the FCC Feed

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Summary

Alon Big Springs Refinery, with Criterion Catalysts, has worked for over ten years to achieve an impressive track record of successes in their distillate hydrotreater, boosting diesel capacity and production by up to 20%, and greatly improving unit flexibility. With the current strong market for diesel, this gain has allowed them not only to track their product demands, but it has dramatically boosted profitability for their shareholders. The sustained collaboration between Alon and Criterion has been a crucial factor in the success of the whole refinery.

In the early 2000's Criterion worked with Shell Global Solutions to find a cost-effective way to bring Alon's distillate hydrotreater unit to ULSD production. The low operating pressure, difficult feed, and limited hydrogen availability were serious challenges. The refinery chose to install new reactor vessels with reactor internals from Shell Global Solutions. The catalyst was Criterion's first-generation Cobalt-Moly ULSD product.

In the years following their successful transition to ULSD production, Alon continued to work closely with Criterion. The challenge was to extend the catalyst life cycle and increase straight run diesel (SRD) and light cycle oil (LCO) cut-points for improved refinery economics. They needed to push the cycle from about nine months to at least 12 months in order to synchronize with the semi-regen reformer regenerations. Increasing demand for diesel was putting pressure on the refinery to raise cut-points of their straight-run and LCO to maximize diesel yields. In 2010, Alon loaded a first-generation CENTERA™ sandwich system which gave a large boost in activity and enabled significant gains towards increasing the unit's flexibility and profitability.

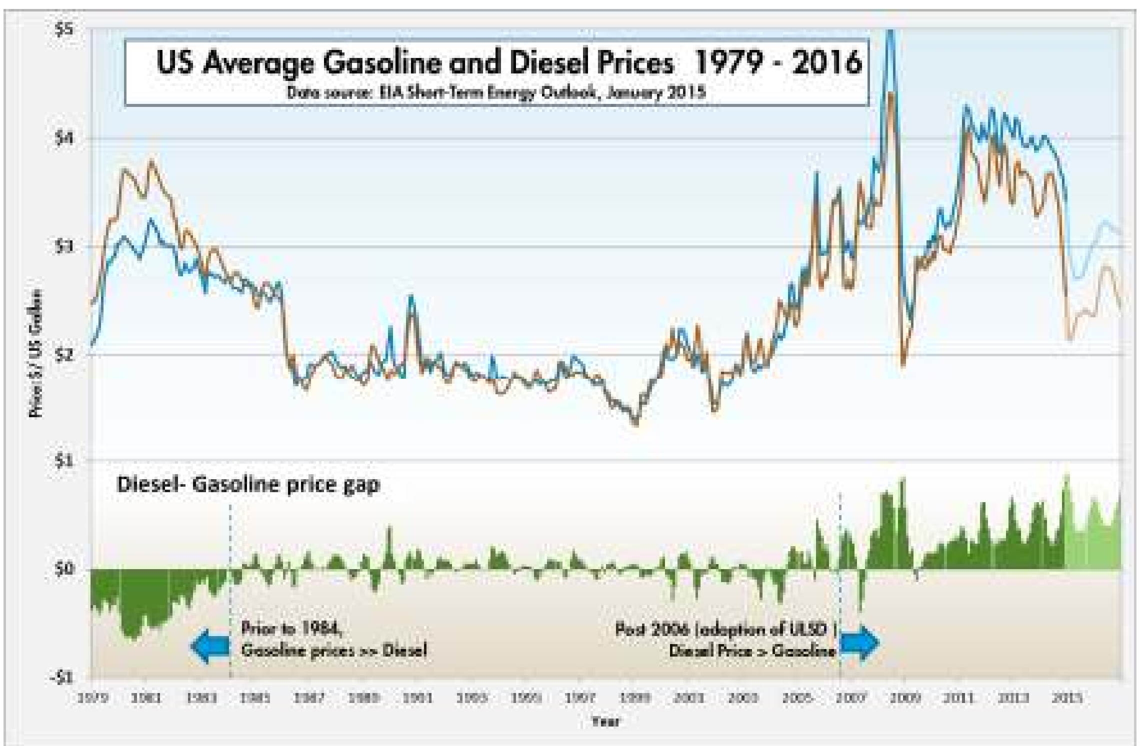
In 2014 Alon implemented a revamp in their crude distillation unit. One of the main objectives of that revamp was to boost straight-run diesel yield which would increase available feed to the ULSD unit for higher diesel production. Again, the success of this project was crucial for the refinery to increase profitability in the face of shifting market demand. Criterion's second-generation CENTERA™ sandwich system with DC-2635 CoMo and DN-3636 NiMo has given the additional activity needed to process the additional difficult feed and, at the same time, maintain catalyst cycle flexibility, once again contributing to Alon's success.

US refiners shift towards increased diesel production

Most of the refineries in North America and other regions in the world were designed and built 40 or more years ago, and in order for them to survive they have had to continually adapt to shifting fuels markets. The major recurring themes in these shifts have been tighter environmental requirements (lower sulfur etc.) and a push towards higher energy efficiency, particularly in transportation fuels. In the Americas, the recent arrival of shale oil with higher yield of naphtha has also had an impact on the fuels market by contributing to gasoline oversupply.

Figure 1 shows the average gasoline and diesel prices in the US since 1979. The diesel-gasoline price gap has been relatively stable over most of the period with some notable exceptions. In the late-seventies/early-eighties, major improvements in automobile fuel efficiency pushed gasoline demand downwards, which had the effect of closing the long-standing gap between the two transportation fuels prior to that time. In 2006, the introduction of ULSD specifications for on-road vehicles marked the beginning of an upward trend in diesel pricing, but the major shift in the price gap which occurred in the 2000-2010 period was driven largely by European and other countries that recognized the higher energy efficiency of diesel over gasoline as a transportation fuel. European governments implemented various forms of vehicle taxation and fuel incentives that favored diesel-powered vehicles. The effect was dramatic. In 1990, diesel-powered cars in Europe represented about 13.8 percent of demand, while by 2009 that proportion had increased to 46 percent. European refiners have been unable to keep up with the demand shift ever since and, as a result, exports of diesel to Europe as well as imports of gasoline from Europe have grown, thus further driving the price gap in the US. In recent years, the arrival of domestic shale oil production has pushed the price gap even further apart due to the higher proportion of condensates and naphtha that are produced from those operations. Today, practically all North American refiners are pushing to maximize their diesel and kerosene production. The resulting increase in yields of diesel-range material in the refinery has increased feed rates and feed difficulty in many ULSD units.

Figure 1. Gasoline and Diesel Price Trends in the US

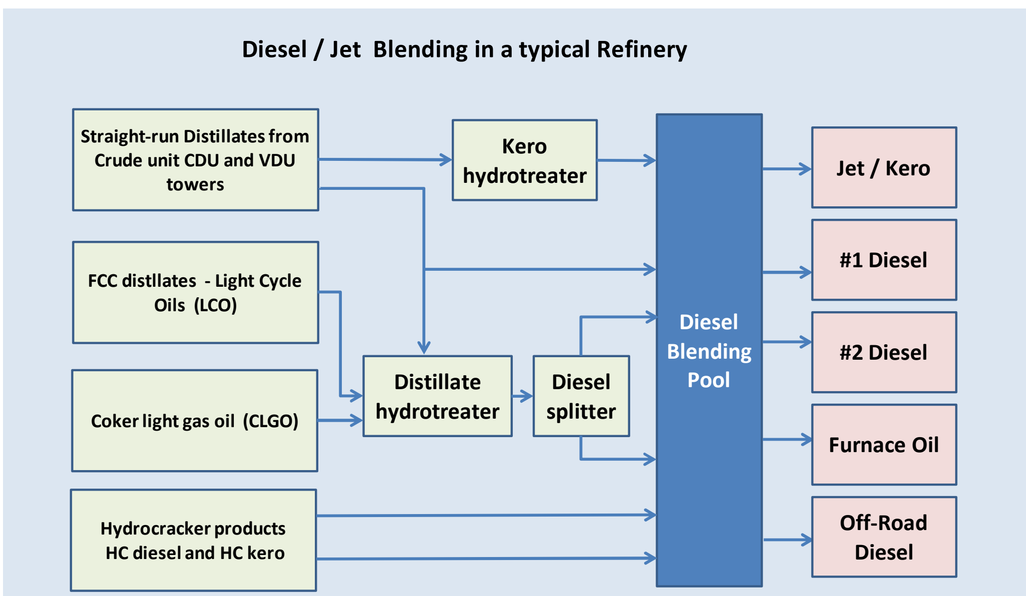


Maximizing distillate production in the refinery

Over the past 20 years or more, refiners have been making large efforts to maximize diesel production by optimizing cut-points, improving fractionation efficiencies and driving their conversion units to maximize diesel range material. In 2010, the US Energy Information Administration (EIA) released an excellent paper[1] on this subject which outlines a range of measures that refineries have implemented to follow this trend.

In a typical refinery, diesel and distillate products are made from blends of a range of refinery streams (Figure 2). The distillate hydrotreater (ULSD unit) is an essential and critical element to diesel production since it has the role of transforming the lower-quality diesel-range material from the crude unit, the FCC and the coker into finished diesel components. As the production of diesel-range material in those upstream units is increased, the DHT unit must have the ability to handle that additional load in terms of higher throughput and higher catalyst activity.

Figure 2. Blending of Diesel, Kerosene and Jet in a typical Refinery



Fractionation improvements in the crude unit for higher diesel yield

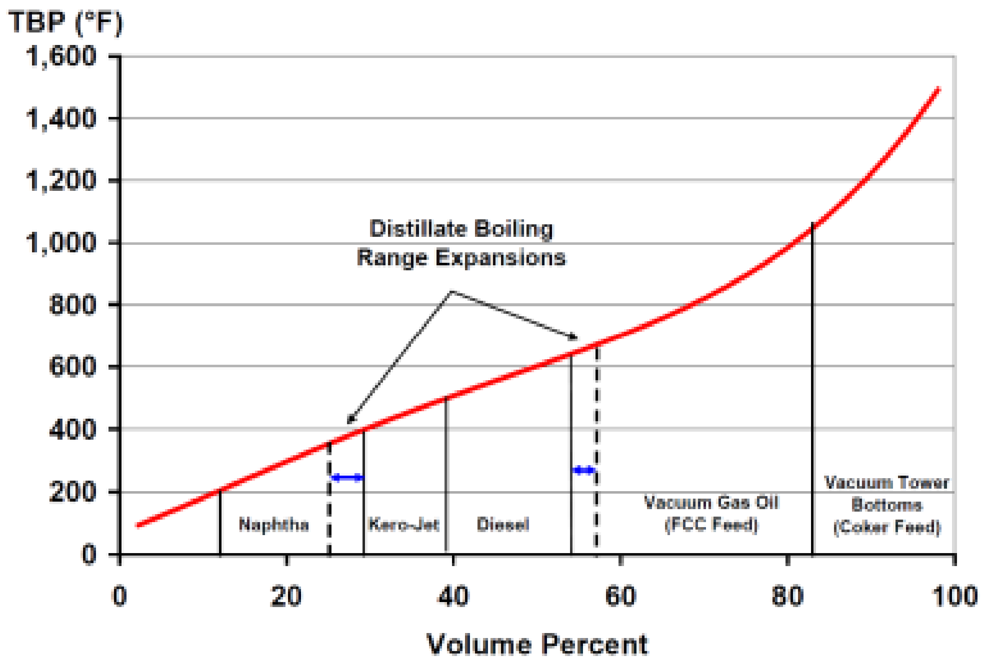
The yield of diesel- and kerosene-range material from a crude distillation column is adjusted by changing the boiling range (cut-points) of the draw stream. Increasing the cut-point range affects properties of the stream such as the specific gravity and the cold flow properties.

Lowering the "front end" of the boiling range brings naphtha-range material into the Kerosene-Jet. This light material lowers the flash point of the kerosene which is limited by the final product specification. Raising the "back end" of the distillation will bring vacuum gas oil range material into the diesel, affecting the cold flow properties and gravity as well as bringing in heavier sulfur and nitrogen species that are more difficult to treat.

In the FCC fractionation column, lowering the front end cut-point of LCO will shift heavy gasoline into the light cycle oil (LCO). This affects not only the flash point, but it also lowers the diesel cetane index. The heavy end of the LCO contains not only difficult sulfur and nitrogen, but also poly-aromatic species which have a large impact on the performance of the ULSD catalyst.

Poor or inefficient fractionation causes overlap of the distillation cuts and will negatively affect important properties such as flash point and cloud point. It limits the ability to expand the cut-point range because the property constraints (flash, cold flow etc.) are reached sooner. Improving product separation is, therefore, an important aspect of maximizing diesel yield.

Figure 3. Increasing Diesel/Kerosene yield by expanding the Distillation Range



Diesel/ VGO separation

Poor separation between the diesel and VGO cut will reduce diesel yield in two ways:

1. Diesel left in the VGO by inefficient separation will result in those molecules going with the VGO to FCC feed. They are subsequently cracked to light naphtha in the FCC reactor.
2. When VGO molecules flash and are recovered in the diesel cut (as “over-flash”) the cold flow properties are affected, and it is often necessary to reduce the cut-point (by reducing diesel draw rate) to correct for this effect.

Improving the separation between diesel and VGO allows more diesel to be recovered by reversing both of these mechanisms. The following describes ways of implementing those improvements in the crude distillation unit.

Atmospheric distillation modifications to improve diesel yield

Figure 4 depicts a typical crude oil distillation unit with an atmospheric and vacuum tower where diesel and kerosene are produced in the atmospheric tower from side draws. The quality of the diesel / VGO separation in the atmospheric tower is affected by the number of theoretical stages between the AGO and diesel draws. Diesel-range material which remains un-flashed in the bottoms of the atmospheric tower is recovered in the LVGO top product of the vacuum tower, which most often is sent to the FCC or hydrocracker. In US refineries (where gasoline yields were historically favored), there may be as few as only 2-5 trays in the AGO and wash sections between the atmospheric tower flash zone and the diesel draw tray. Outside the US, refiners may often have as many as 10-15 trays in this section for better control of diesel endpoint and cold-flow properties.

A recent article in Hydrocarbon Processing[2] describes a project to improve diesel yield by modifications to the atmospheric and vacuum distillation towers. Figure 5a shows a typical atmospheric column flash zone with the AGO and diesel draws. Figure 5b shows the changes to the CDU, which include implementing an AGO wash system and installing structured packing sections above the flash zone. Diesel and AGO “spillbacks” are installed to ensure effective liquid wetting of the separation sections.

Figure 4. Typical Crude oil distillation unit with atmospheric and vacuum fractionation towers

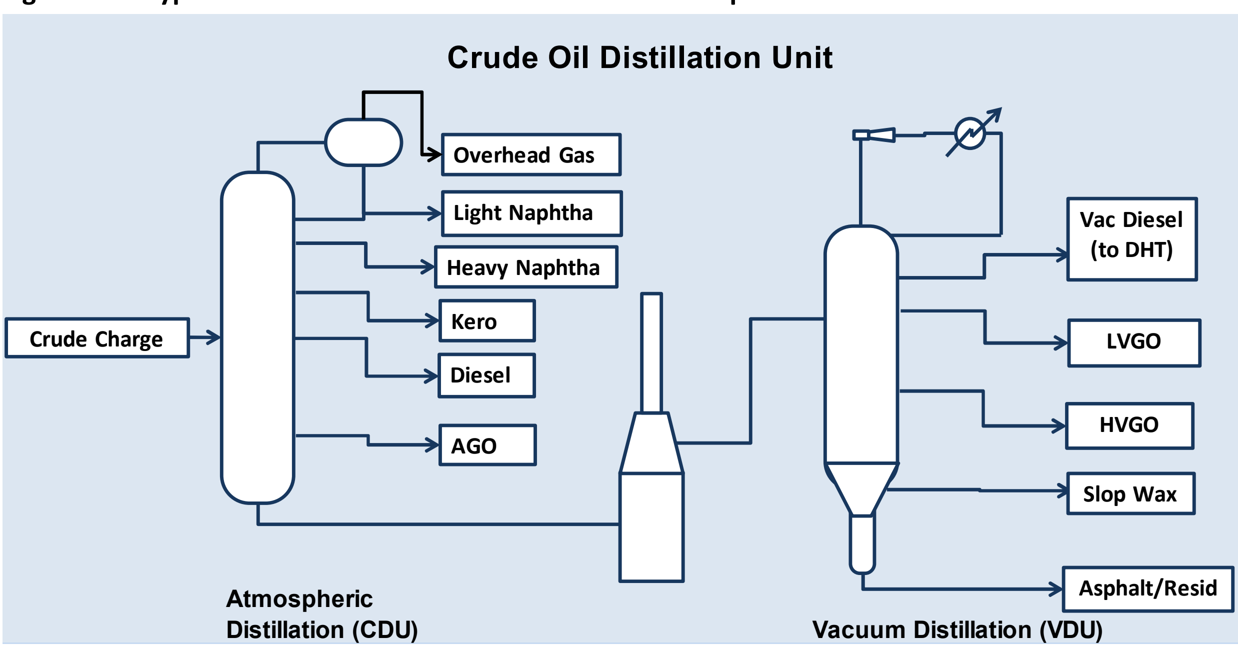


Figure 5a – Typical Flash-Zone arrangement of the Atmospheric Distillation Tower

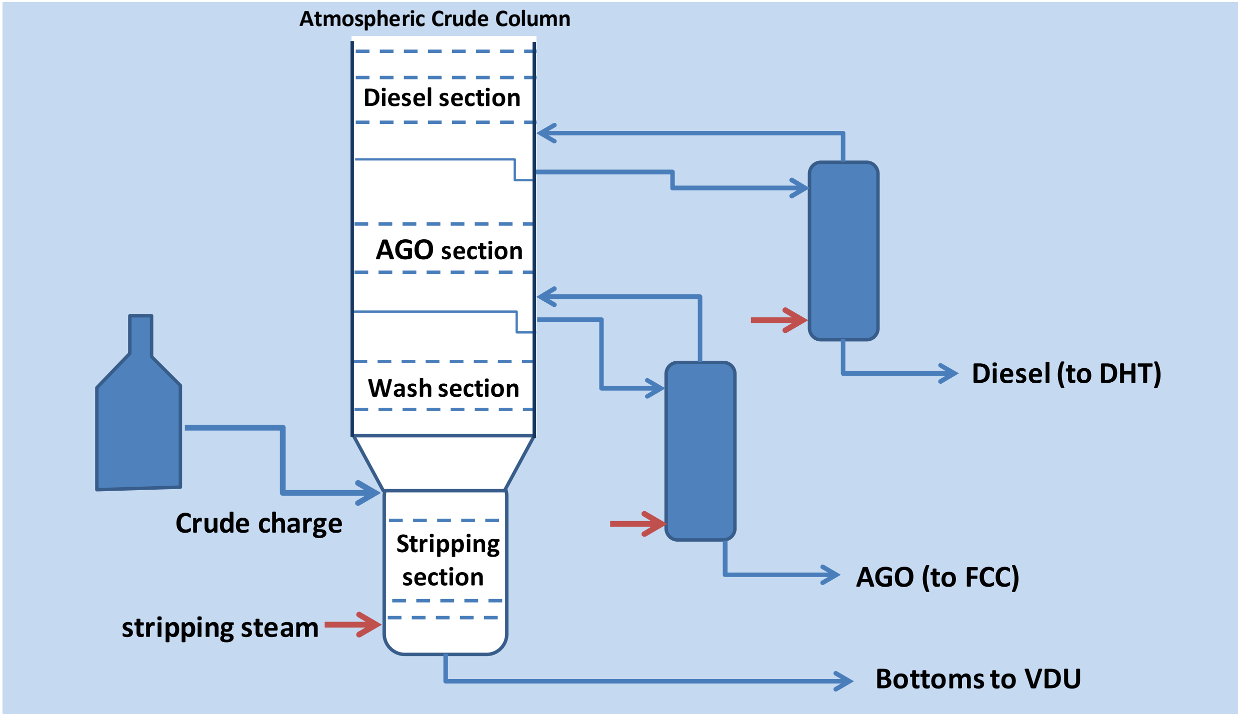
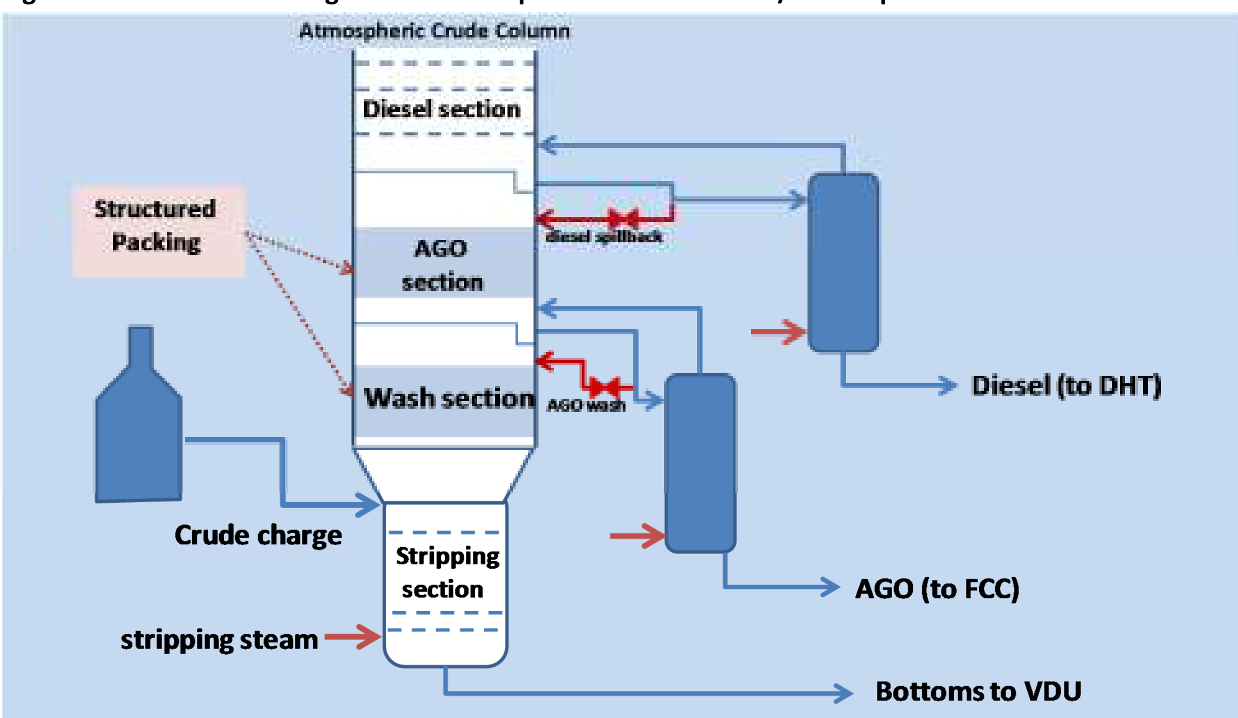


Figure 5b Flash-Zone arrangement with improvements to Diesel/VGO separation



Vacuum Tower Modifications for recovering diesel

The Alon refinery implemented a complete revamp of their VDU which added a new top-product draw to allow the diesel range material from the CDU bottoms stream to be recovered.

Typical vacuum towers have three distillate draws above the flash zone. Resid is the bottom product. The draw trays are separated by spray sections which offer heat recovery with low pressure drop but have poor separation efficiency. This arrangement gives the lowest possible resid yield for asphalt or bunker fuel operation, but because of the low efficiency of the spray sections the separation between the products (wash oil, LVGO and HVGO) is poor.

The Alon refinery re-designed their column in a revamp to include structured packing for improved separation in the upper sections and an additional draw for recovering the cleaned-up diesel-range material at the top of the column. Figure 6a shows a typical vacuum column arrangement with spray-sections. Figure 6b shows an example of a revamped vacuum column with low pressure-drop structured packing and an additional product draw for vacuum diesel.

Figure 6.a Typical Vacuum tower arrangement

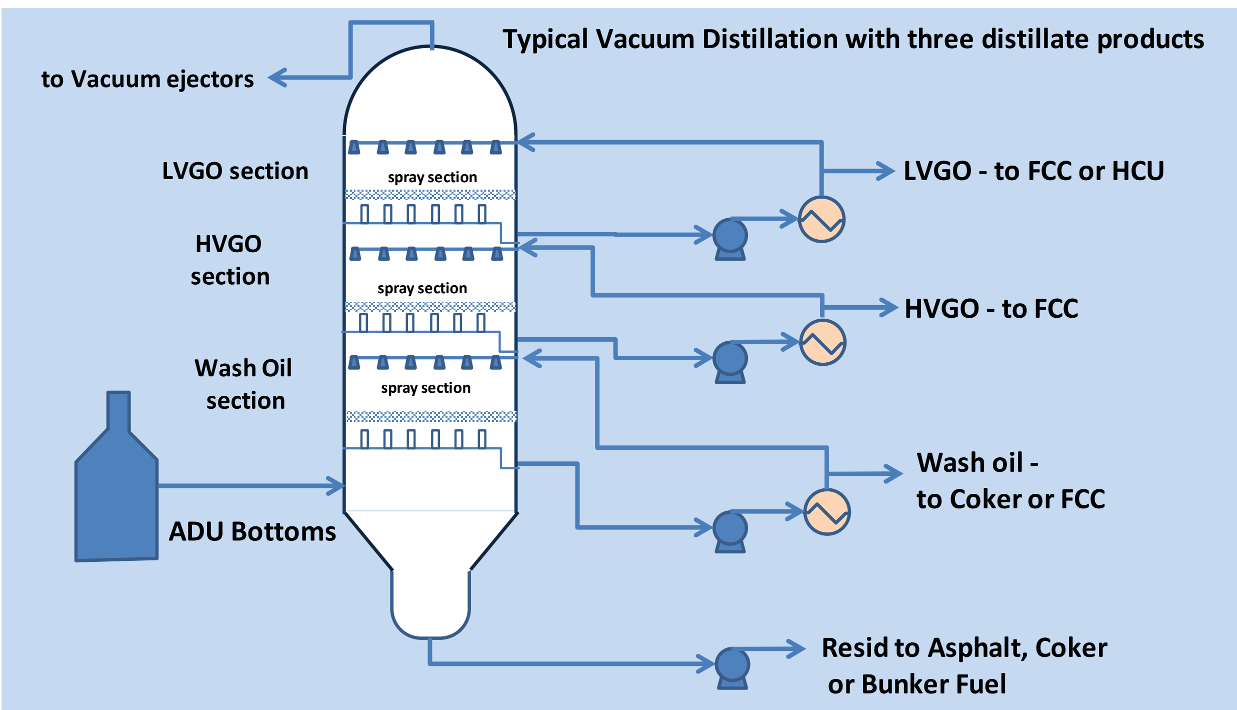
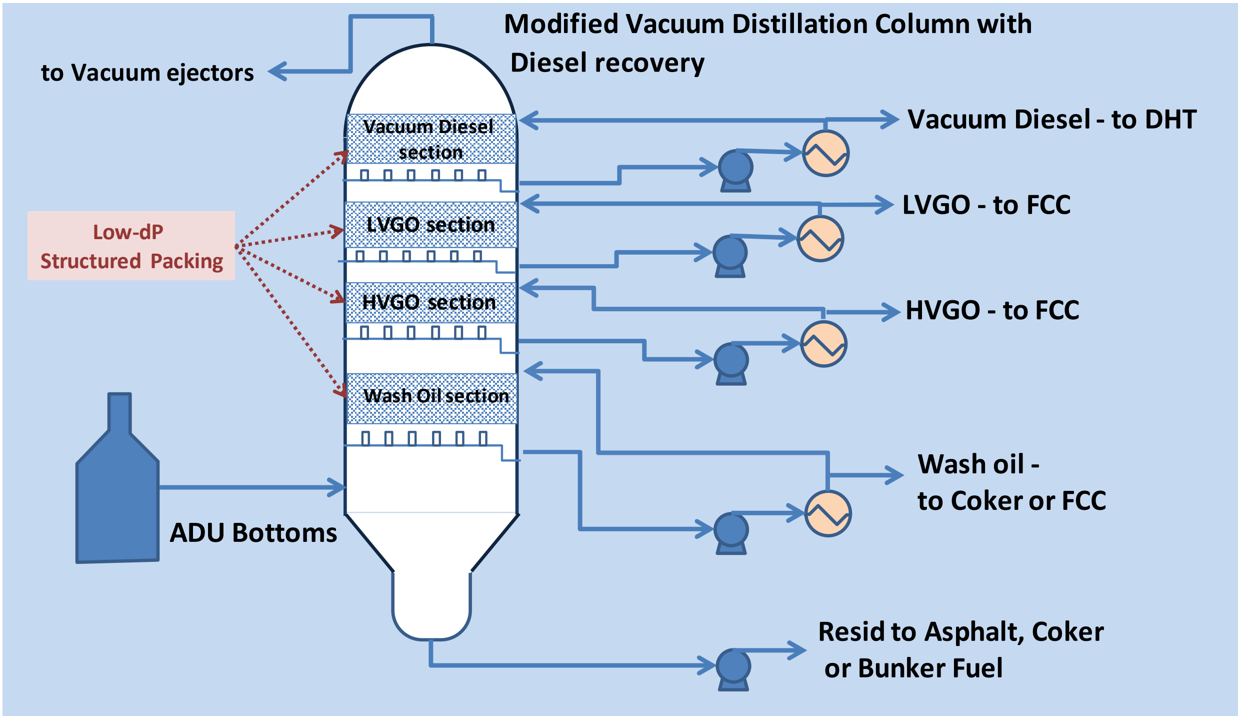


Figure 6.b Vacuum tower with improved internals for additional vacuum diesel draw



Maximization of LCO at the FCC

Maximizing LCO yield at the FCC is an important lever to increase overall diesel production in the refinery, and a range of effective tactics have been reported to that end in recent literature[3] .

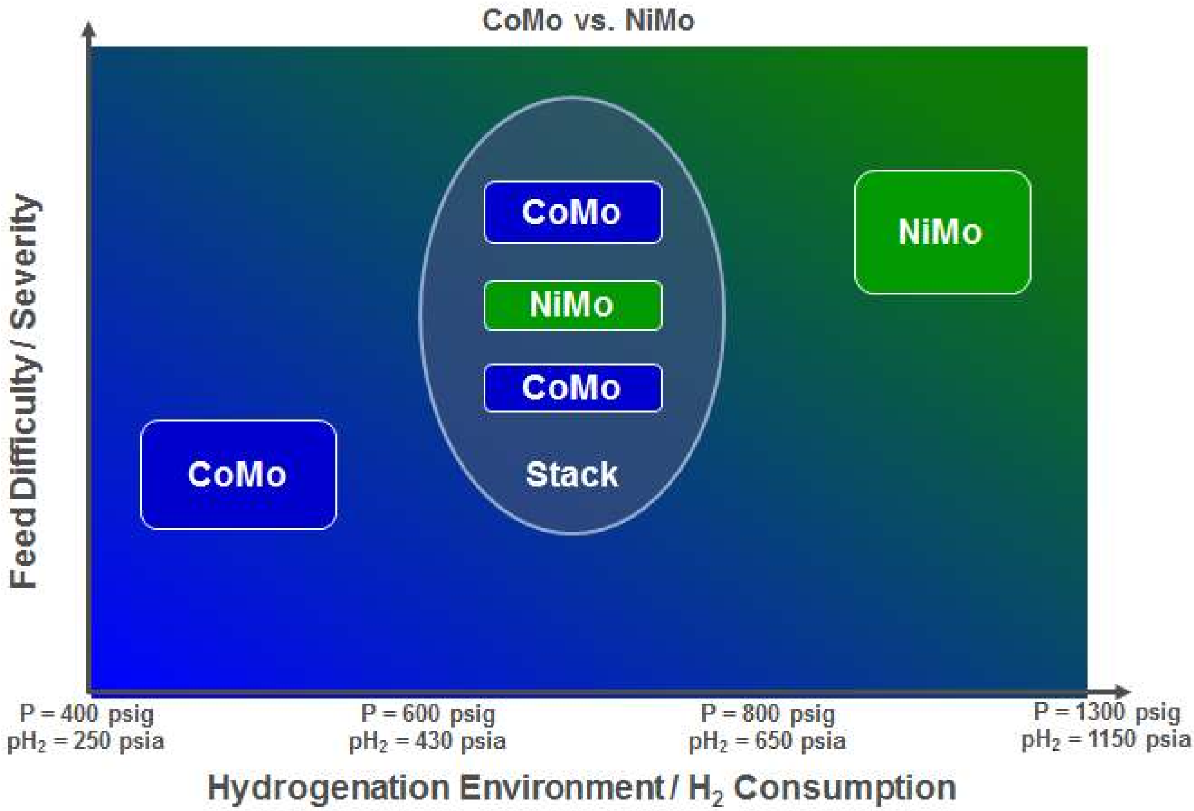
Shifting the cut-point in the fractionator is the most direct way to adjust the LCO yield; however the high aromatic content of the FCC product makes it increasingly difficult to process at the distillate hydrotreater as endpoint is increased. Lowering the FCC reactor temperature can have the effect of increasing LCO, but the associated reduction in conversion increases slurry oil yield, and reduces gasoline and lighter products. For most refiners this is not an economically attractive option. Recycling heavy cycle oil from the fractionator back to the FCC reactor feed can improve LCO yield. Often this practice is combined with the use of more zeolytic FCC catalysts which are designed to promote conversion of the heavier cycle oils.

Minimizing diesel-range (650°F-material) in the FCC feed by recovering it in the crude fractionation towers is perhaps the most direct and effective strategy for maximizing overall diesel yield in a refinery. The Alon refinery reported FCC feed containing up to 20% diesel range material prior to their unit revamp. That percentage dropped to the 4-6% range following the revamp.

Catalyst Choice

In a hydrogen-constrained environment such as the Alon Big Spring ULSD unit, the processing capacity is maximized by choosing a catalyst system which provides maximum activity while it minimizes chemical hydrogen consumption. Figure 8 presents the chart that Criterion uses for making catalyst selections for a ULSD unit.

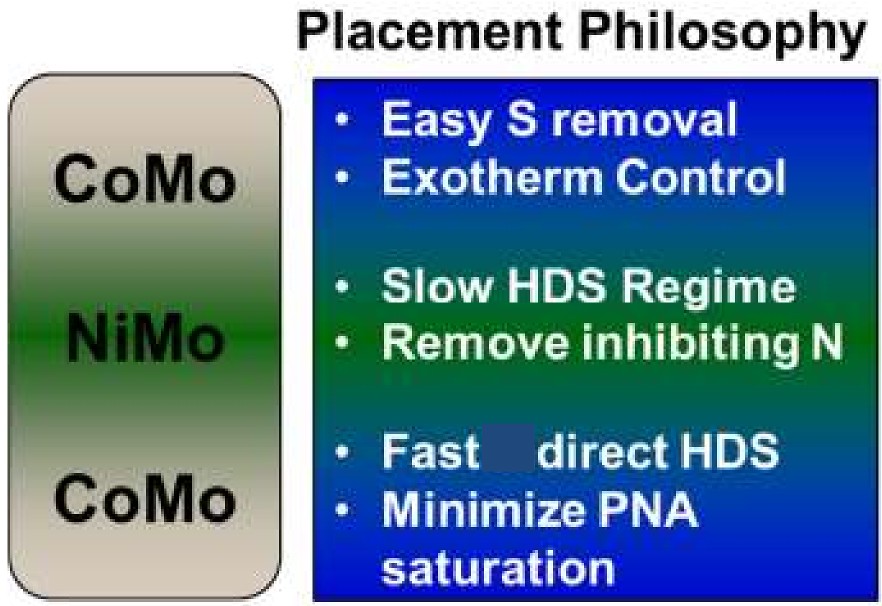
Figure 8. Criterion Catalyst selection map for ULSD



Cobalt-molybdenum (CoMo) catalysts tend to use less hydrogen than nickel-molybdenum catalysts because they have a lower hydrogenation power, and CoMo catalysts will favor the direct-HDS reaction mechanisms (which use less hydrogen) over indirect. Their weakness is that they are more prone to nitrogen inhibition and thus less robust for processing more difficult feeds. To overcome the CoMo catalyst limitations while at the same time minimizing hydrogen consumption, Criterion pioneered the development of combined CoMo/NiMo/CoMo stacked catalyst systems in the early-mid 2000's.

The three-zone CoMo / NiMo / CoMo stacked system functions by removing easy sulfurs in the upper part of the reactor using Cobalt Molybdenum catalyst, then nitrogen species are reduced in a layer of NiMo catalyst placed in the upper-mid-section of the reactor. The NiMo layer is sized to provide maximum nitrogen removal while minimizing aromatic saturation and hence hydrogen consumption as well. High-activity Cobalt-Molybdenum catalyst is loaded in the lower sections of the reactor to complete the desulfurization reactions by direct desulfurization, again minimizing hydrogen consumption. The CoMo / NiMo/ CoMo sandwich catalyst system enables the refiner to process much more difficult feeds than pure CoMo catalysts, and has been proven in many applications in the refining world (ref. 5, 6, 7).

Figure 9. Catalyst placement in the CoMo/NiMo/ CoMo sandwich design



Alon Big Springs Refinery – Collaboration yields success with the ULSD unit

The Alon Big Springs refinery in West Texas has operated for over 75 years and currently processes about 73,000 B/d of crude from Texas and other areas. It is configured with an FCC and a propane deasphalting unit to extract heavy PDA gas oil, and it has four hydrotreaters – an NHT, a jet hydrotreater, a DHT and a gasoil hydrotreater. The hydrogen for all of the hydrotreaters is supplied by a semi-regen naphtha reformer.

Prior to early 2005, the Alon refinery had only a single diesel hydrotreater which operated at 700 psi. The unit had been revamped in 1992 for 500 ppm diesel production. With ULSD requirements on the horizon, they realised that their unit was not capable of desulfurizing their tough feeds containing 25 % LCO to the 8 – 10 ppm ULSD product at the required rates. Capital was very tight, and they could not afford to build a new high-pressure ULSD unit like many other refiners were doing. Hydrogen supply was also very limited so a key requirement for their ULSD unit was low hydrogen consumption.

The refinery canvassed five catalyst vendors for a solution – they found that processing their feed was too challenging with the existing unit, considering the low pressure, the single reactor volume and the difficulty of the feedstock. At the time, Criterion and Shell Global Solutions proposed a low-cost unit revamp which would have two reactors in series, lowering the LHSV to 0.83 hr^{-1}. The reactors would be loaded with Criterion's highest-activity cobalt-molybdenum catalyst. The high-activity cobalt-molybdenum catalyst would achieve maximum desulfurization while minimizing hydrogen consumption from aromatic saturation. With these modifications, Alon successfully migrated to ULSD production, however over the first years of operation the unit struggled to process their difficult feeds. The initial catalyst cycles with all CoMo catalyst did not have enough activity to process the available LCO and to synchronize with the reformer regeneration cycles. The refinery was forced to reduce endpoint by as much as 35-40°F on the LCO and straight-run diesel cuts to restore enough flexibility in the operation.

Since that time, the Alon refinery has worked closely with Criterion to improve the unit performance and to respond to large incentives to upgrade more LCO for diesel production. Over years the unit saw a steady increase in both feed rate and the cut-points of the feed components, which resulted from collaborative efforts by Alon and Criterion to optimize the unit operation. In 2009, Criterion tested the CENTERA™ sandwich catalyst system. The robustness and improved activity of the CENTERA™ sandwich over the CoMo catalyst allowed an increase in the D-86 T90 of the LCO of about 25°F – from 630-635°F to the 655-665°F range. Straight run diesel D-86 T90 increased from 627°F to 650-655°F range with cold flow constraints applied in the winter months. The sandwich system enabled these improvements with only a very nominal 5% increase in hydrogen consumption.

In 2012, the most recent sandwich design with second generation CENTERA™ catalysts was tested against the original CENTERA™ system and a 100% CENTERA™ CoMo catalyst for this unit. Figures 10 and 11 show the results from those tests. The new generation CENTERA™ sandwich system demonstrated even higher levels of activity and, again, with only very small increases in hydrogen consumption. Coupled with Alon's improvements to the crude unit towers implemented in the 2014 revamp, loading this new catalyst system has allowed a dramatic increase in unit throughput and further increases in the LCO and straight-run cut-points .

Figure 10. Comparison of Hydrogen Consumption - 2012 Catalyst testing Program

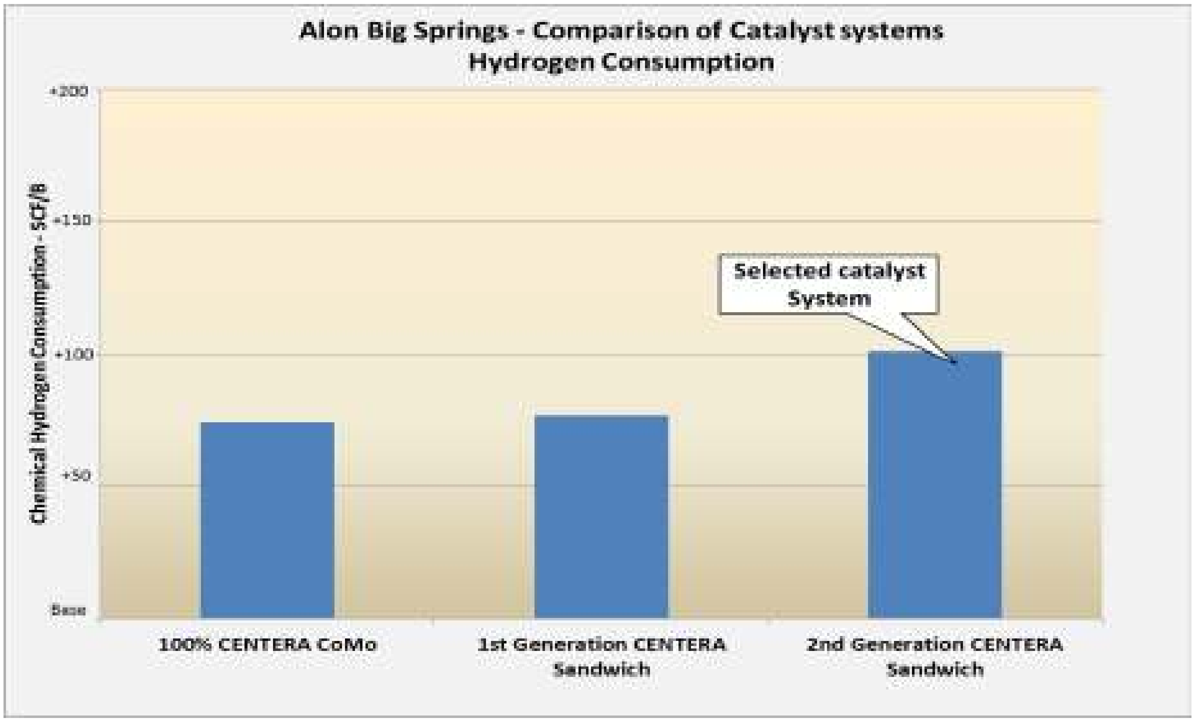
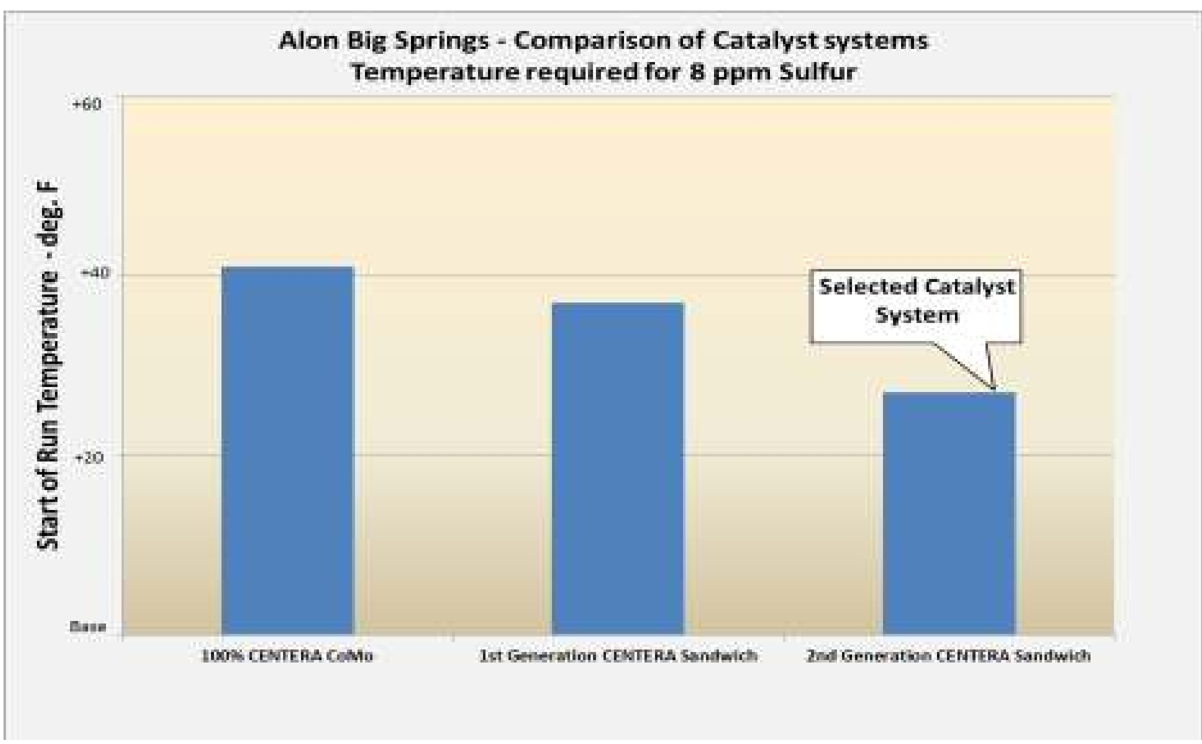


Figure 11. Comparison of Temperature Requirement for 8 ppm Product Sulfur - 2012 Catalyst testing Program



Conclusion

Refiners in North America and around the world are adapting to shifting fuels markets. In recent years, demand and prices for diesel have outpaced gasoline quite substantially. Refiners have increased their efforts to maximize production of diesel-range material in all the units of the refinery. The distillate hydrotreater in many refineries has seen increases in feed rate and feed difficulty, thus increasing demands on the catalysts.

Maintaining consistent, long term collaboration with Criterion, the Alon refinery in West Texas has implemented a series of improvements to their low-pressure, tightly-constrained ULSD unit to allow it to process more difficult feeds and to increase operational flexibility.

The implementation of Criterion's first-generation CENTERA™ sandwich system in 2010 and the second-generation CENTERA™ sandwich system in 2014 yielded substantial gains in this progress. These major steps on their journey contributed in a large way to the overall refinery profitability. The success Alon has had with the distillate hydrotreater unit over the past almost ten years is an outstanding demonstration of beneficial results from a continued collaboration with Criterion Catalysts & Technologies and unit improvements to take advantages of the opportunities provided.

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