

Better fractionation hikes ULSD yields, hydrotreater run lengths

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Improved fractionation will allow many refiners to increase their ultralow-sulfur diesel (ULSD) yields and hydrotreater run lengths by segregating the easy and difficult-to-treat sulfur species.

When ULSD specifications take effect in the US, refiners will have to control hydrotreater feed stream yields tightly so that the ULSD product sulfur specification is met at an acceptable catalyst life. New high-pressure hydrotreaters are being built based upon assumed feed-stream compositions.

In some instances, high endpoint straight-run (SR) diesel, FCC light cycle oil (LCO), and light coker gas oil (LCGO) stream compositions are assumed to remain unchanged after ULSD production begins. Yet many refiners will have to undercut the ULSD hydrotreater feed streams to lower the endpoint, which will reduce the amount of difficult-to-treat sulfur species feeding the ULSD hydrotreater.

Table 1 shows some data for true boiling point (TBP) distillations of feed streams to the diesel hydrotreater. Although these distillation 90%-end point temperatures are high, today it may be possible to mask the end point with large volumes of kerosene while still meeting sulfur specifications.

Undercutting SR diesel, LCO, and LCGO has several consequences including more diesel-boiling-range material to the FCC feed hydrotreater and FCCU, lower product and pump-around draw temperatures, reduced pump-around

heat removal, lower crude preheat temperature, and other effects.

Some refiners are modifying fractionation systems to allow recovery of nearly the entire range of diesel materials that contain easy-to-treat sulfur species and concentrate difficult-to-remove sulfur compounds by producing vacuum diesel and heavy LCO.

Refinery configuration, crude source

Refinery configuration (Fig. 1) and crude source differences between US and non-US refiners will play a significant role in ULSD hydrotreater catalyst life. FCC capacity outside the US is relatively low and few refiners operate cokers.

Furthermore, many non-US refiners produce light and heavy gas oil (diesel boiling range) products from the crude unit, with most vacuum units producing heavy gas oil. These crude-unit design differences allow non-US refiners better to segregate the 610° F. and lighter portion of the SR diesel from the 610° F. and heavier boiling range material that con-

REFINERY CONFIGURATION

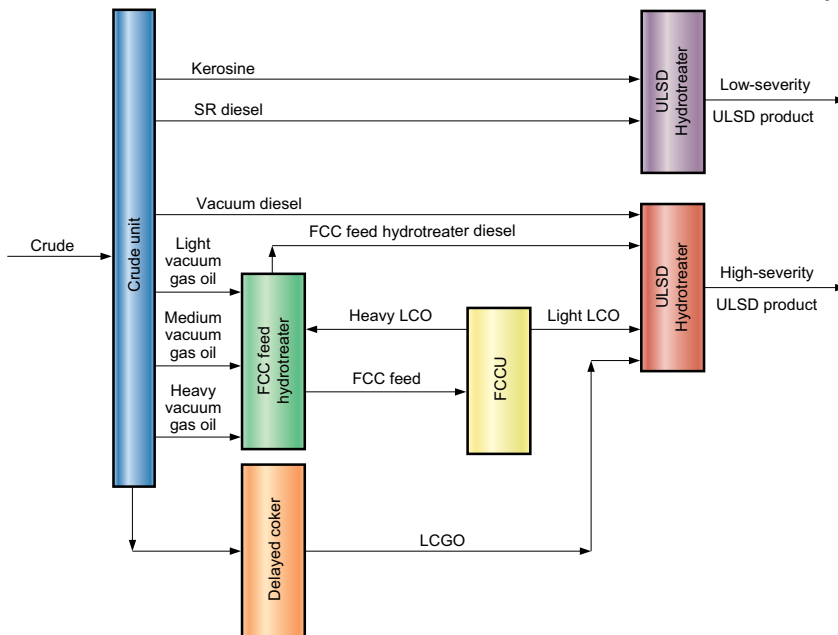
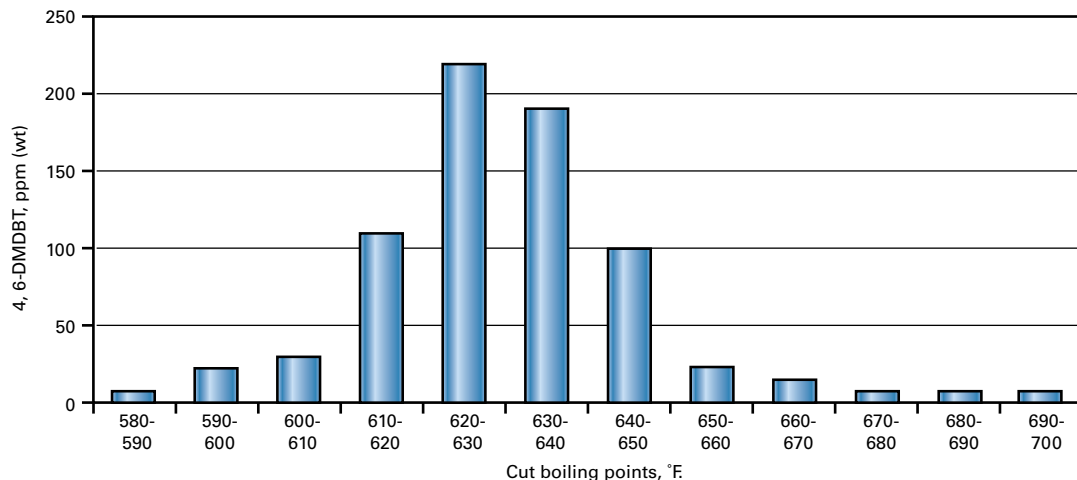


Fig. 1

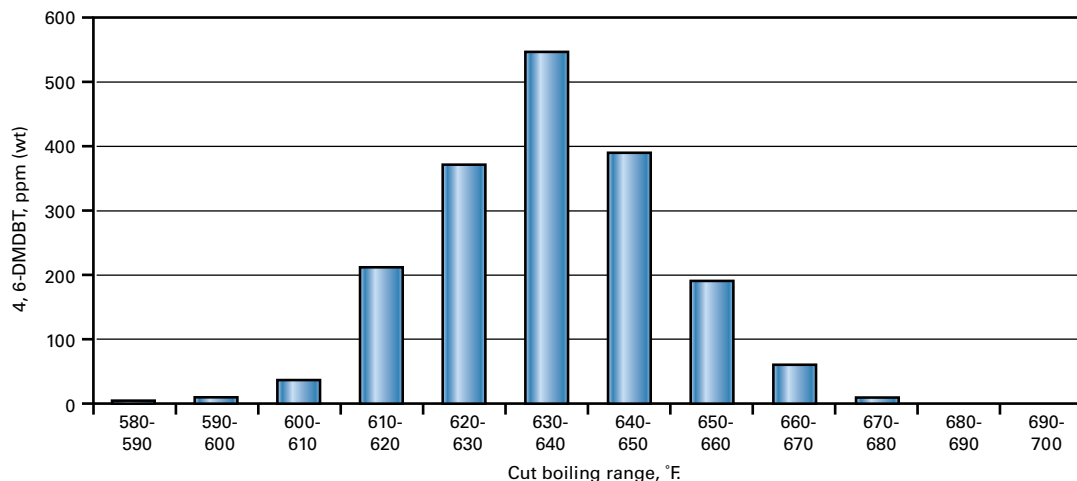
4,6-DMDBT DISTRIBUTION

Fig. 2



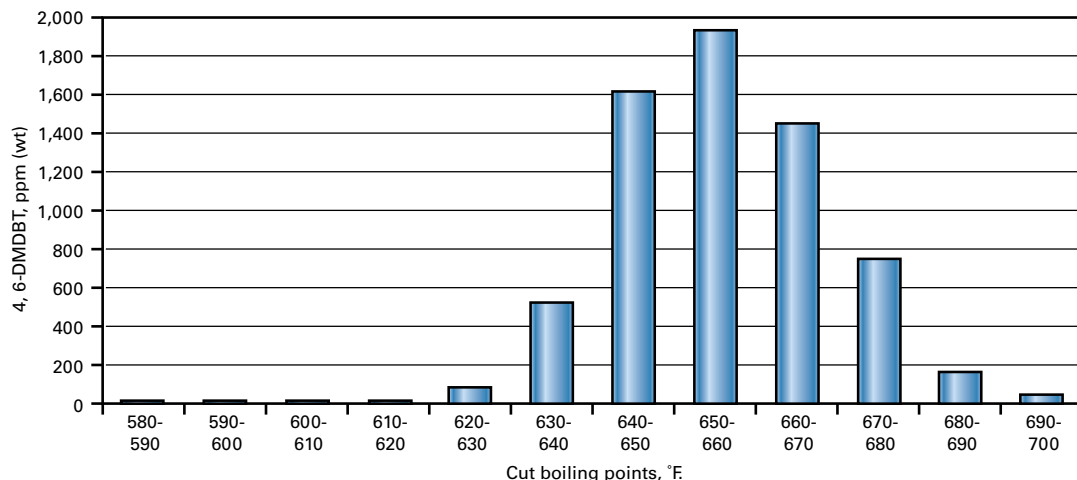
LCGO 4,6-DMDBT DISTRIBUTION

Fig. 3



LCO 4,6-DMDBT DISTRIBUTION

Fig. 4



tains the majority of the hard-to-treat sulfur species.

Segregating difficult-to-treat sulfur compounds allows the refiner to process them in different hydrotreating units, which takes advantage of severity differences. Refiners that have severe FCC feed hydrotreating have an added degree of flexibility.

Crude source also influences the amount of hard-to-treat sulfur feeding the ULSD hydrotreater. Several US refiners process heavy and extra heavy crudes; and future crude supplies will include more oil-sands-based sour crudes from Canada. Some of these contain coker LCGO that is blended with the bitumen to increase API gravity and SR material in the bitumen, which contain much higher percentages of hard-to-treat sulfur species than most crudes.

More coker capacity will be added to US refineries. Ultimately, heavy crudes produce less SR diesel that contains more difficult-to-treat

sulfur species. Heavier crudes produce more FCC feed resulting in a higher LCO product yield; 35% or more of the crude goes to the coker, which increases LCGO product yield. All these make ULSD production more difficult.

The remaining sulfur compounds in current US road diesels are nearly all difficult-to-treat 4,6-dimethyl dibenzothiophene (DMDBT) and other multi-substituted compounds. Hydrotreater operating experience will determine the actual severity and feed stream undercutting needed to maintain acceptable run length when processing high percentages of cracked stock.

US refiners are likely to have some surprises due to difficulties processing cracked stock and because they are not focused on diesel hydrotreater feed quality.

Refinery distillation, sulfur

Each refiner's distillation column design and column heat balance (internal reflux) varies tremendously. Some have many trays and high internal reflux, which leads to excellent product fractionation. Others have few trays, little internal reflux, poor tray design, and operate at high charge rates resulting in poor fractionation.

Reducing product yields and improving fractionation can lower SR diesel, LCGO, and LCO product sulfur levels. Furthermore, refiners charging large volumes of diesel-boiling-range hydrocarbons to the FCC have an additional opportunity to recover the material containing easy-to-treat sulfur compounds.

Table 2 shows a combined atmospheric gas oil, light and heavy vacuum gas oil stream from one refiner's crude distillation unit. This crude unit produces 40,000 b/d of FCC feed.

Recovering the 600° F. and lighter hydrocarbons from the FCC feed and sending it directly to ULSD increases diesel production without materially

ATMOSPHERIC, VACUUM DIESEL PRODUCTION

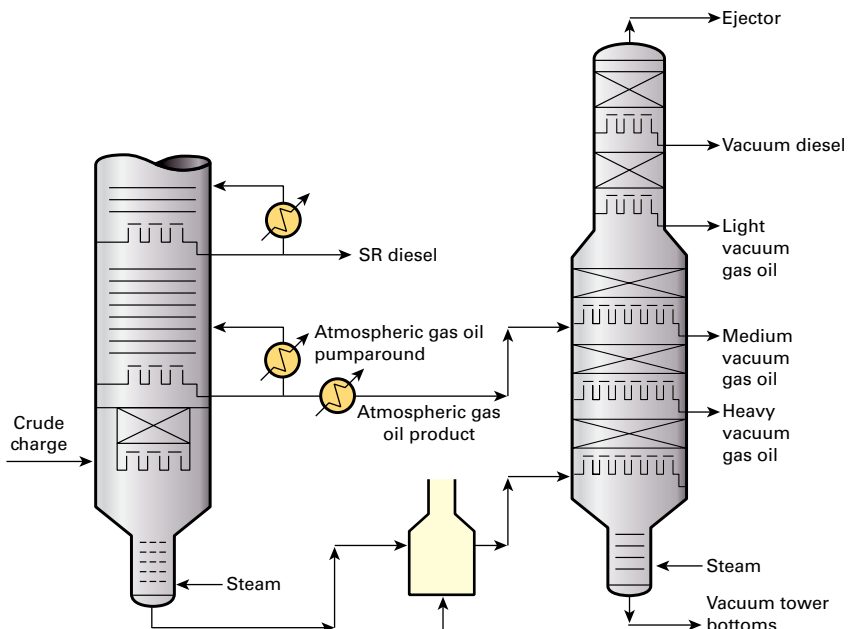


Fig. 5

STREAM DISTILLATION TAILS

Fraction, vol %	Product stream TBP distillations, °F.		
	Straight-run diesel	Light coker gas oil	Light cycle oil
80	620	653	648
90	655	681	683
95	675	719	715
End point	720	777	780

increasing the amount of hard-to-treat sulfur species. But this requires crude-unit modifications.

During a refinery ULSD study, we fractionated hydrotreater feed streams to quantify the amount of hard-to-treat sulfur species in each stream and explore various options for segregating easy and hard-to-treat sulfur species.

SR diesel, LCGO, and LCO were fractionated into 10° F. boiling range cuts in an ASTM 2892 still. We then analyzed each sample for various sulfur species including 4-methyl dibenzothiophene, 4,6-DMDBT, and other multi-substituted dibenzothiophene species.

Determining the quantity of hard-to-treat sulfur species by boiling range helped quantify the influence of fractionation

on the species and screen potential options to segregate easy and hard-to-treat sulfur species feeding the ULSD hydrotreater. Hard-to-treat sulfur distribution was separated by boiling range to allow us to characterize the crude, FCC, and delayed coker feed streams in the process model including the distribution of hard-to-treat sulfur from total sulfur.

Fig. 2 shows the 4,6-DMDBT in the atmospheric column diesel for a medium-sulfur crude. The 4,6-DMDBT begins to distill in the 600-610° F. TBP cut and peaks in the 620-630° F. cut. Very little is present in the 650° F. and heavier cut.

Fig. 3 shows the LCGO product

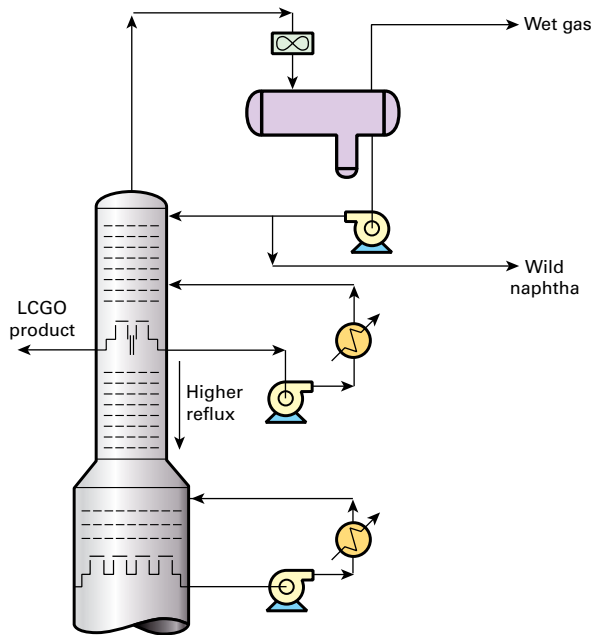
4,6-DMDBT from a coker processing medium-sulfur vacuum residue. The 4,6-DMDBT begins to distill in the 610-620° F. TBP cut and peaks in the 620-630° F. cut. Very little is present in the 660° F. and heavier cut. LCGO contains much more hard-to-treat sulfur than SR diesel.

CRUDE UNIT FCC FEED TBP DISTILLATION

Fraction, vol %	FCC stream TBP distillations, °F.
Initial boiling point	430
5	560
10	600
15	615
20	641

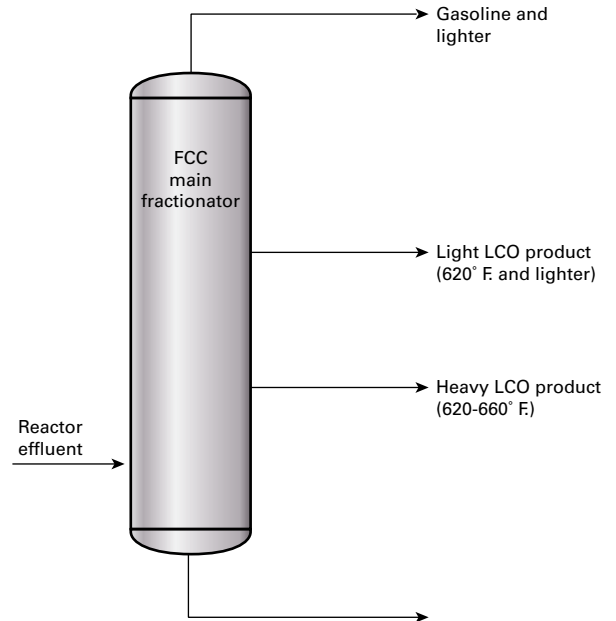
DELAYED COKER MAIN FRACTIONATOR MODIFICATIONS

Fig. 6



HEAVY LCO DRAW

Fig. 7



FCC LCO contains the highest quantity of hard-to-treat sulfur compounds.

Fig. 4 shows the 4,6-DMDBT in the FCC LCO from a hydrotreated FCC feed processed from a medium-sulfur crude. The 4,6-DMDBT begins to distill in the 630-640° F. TBP cut and peaks in the 650-660° F. cut. Very little is present in the 680° F. and heavier cut.

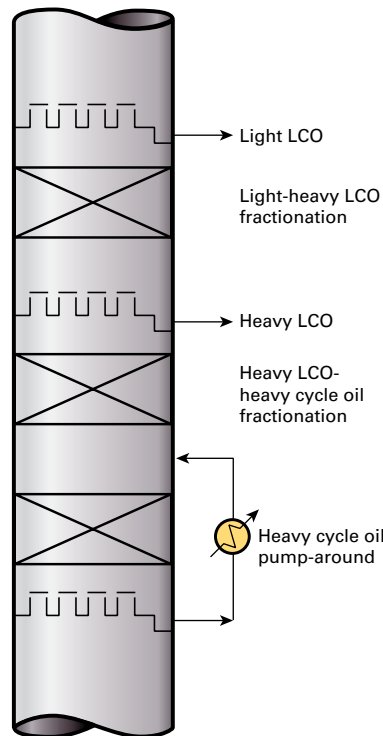
Product undercutting

Most difficult-to-treat sulfur compounds feeding the ULSD hydrotreater are in the LCO product with lesser amounts in crude diesel and coker LCGO streams. Undercutting both crude unit diesel and LCGO product increases the FCC charge rate unless the FCC feed hydrotreater has a fractionator. Undercutting LCO product increases slurry production and sometimes raises slurry product API gravity above carbon black market specifications.

Undercutting decreases product and pump-around draw temperatures, which makes product fractionation increasingly difficult because exchanging pump-around heat generates column internal refluxes. For example, decreasing LCO product draw temperature reduces the amount of heat that can

FCC MAIN FRACTIONATOR

Fig. 8



removed from the LCO pump-around.

Often a refiner increases slurry pump-around duty to avoid higher

overhead condenser duty, thereby reducing reflux below the LCO product draw. This results in more undercutting required as fractionation deteriorates.

If a refiner's FCC charge rate is already limited, undercutting crude unit diesel and LCGO product has a high cost. Undercutting may appear to be an inexpensive option to reduce hard-to-treat sulfur in the ULSD hydrotreater feed, but it may be costly.

Crude units

Most US refiners produce diesel from the atmospheric distillation column. Yet maximizing recovery of 610° F. and lighter hydrocarbons and segregating the 610-660° F. boiling range requires diesel production from both the atmospheric and vacuum columns.

Most European refiners already do this because their motor fuels market is predominantly diesel; maximum recovery has always been important. Because US refiners focus on gasoline production, many have poor recovery of diesel and high quantities of diesel-boiling-range hydrocarbons in the FCC feed.

Fig. 5 shows an optimized crude-unit design with diesel produced in the atmospheric and vacuum columns.

Most US refineries' crude units are currently running at maximum capacity. Typically this reduces diesel recovery because the crude heater outlet temperature must be reduced to process more crude.

A lower temperature increases the amount of diesel-boiling-range material feeding the vacuum column and reduces atmospheric column internal reflux below the diesel draw. A low liquid-vapor ratio below the diesel draw increases the amount of 610° F. and lighter hydrocarbons containing the easy-to-treat sulfur species into the atmospheric gas oil product.

Many US refiners commonly have 10% or more 610° F. and lighter hydrocarbons in the FCC feed.

Maximizing crude unit diesel recovery requires the production of a diesel-boiling-range product from the vacuum unit. This allows a lower atmospheric-column diesel product end point while recovering the 610-660° F. boiling range hydrocarbons as vacuum diesel.

Processing atmospheric gas oil through the vacuum column further increases recovery. Producing two crude-unit diesel streams allows the refiner to process the lower-sulfur atmospheric column diesel in the lower-severity ULSD hydrotreater and process the vacuum diesel in a higher-severity unit.

Delayed coker main fractionator

LCGO yield will depend on the ULSD hydrotreater severity and targeted unit run length. Most cokers can increase the recovery of 620° F. and lighter hydrocarbons from the HCGO product.

A low internal reflux between the LCGO and HCGO and an inferior tray design cause poor fractionation. In some instances, the refiner can reduce the amount of hard-to-remove sulfur

FCC FEED HYDROTREATING

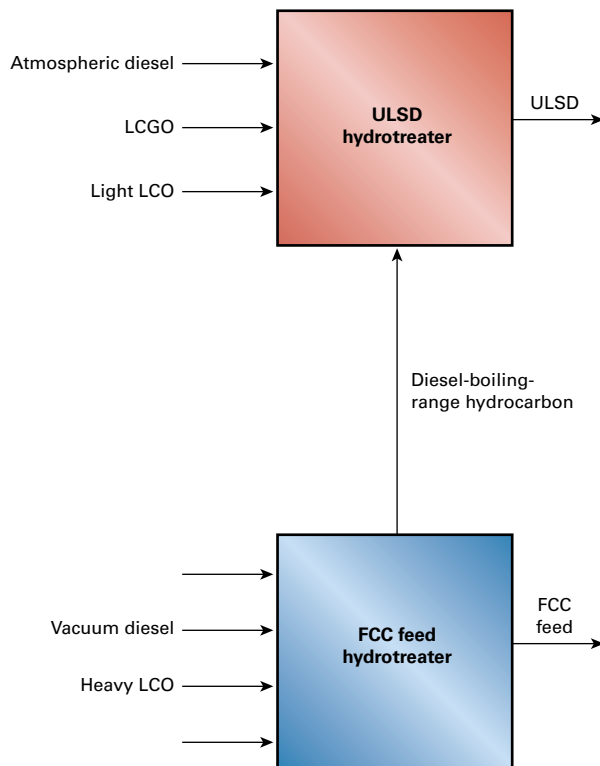


Fig. 9

compounds in the LCGO product by more than 50% while minimizing product yield loss at relatively low cost (Fig. 6).

Undercutting LCGO without improving fractionation significantly increases FCC charge rate. Those refiners that have an FCC feed hydrotreater can recover some of the diesel-boiling-range material and feed this stream to the ULSD hydrotreater. The FCC feed hydrotreater severity will determine whether this makes sense.

FCC main fractionator

LCO contains the highest percentages of the most refractory sulfur compounds of any of the hydrotreater feed streams; therefore, many refiners will have to undercut LCO to reduce its end point to manage catalyst life and run length. Furthermore, those refiners selling slurry product as decant oil will have to be ensure that the slurry API gravity still meets carbon black market specifications.

Some refiners are already producing HCO that is blended to fuel oil. But the fuel oil market cannot take all the future LCO undercutting. Some refiners have already installed a heavy LCO product draw that allow them to produce 620° F. and lighter LCO and a 620° F. and heavier LCO draw (Fig. 7).

Fig. 8 schematic shows a recent main fractionator design with a new light-heavy LCO fractionation. Heavy LCO product is drawn between the light LCO and heavy-cycle-oil product draws. The heavy LCO material boils at 620-660° F.

The advantage of over-producing a heavy-cycle oil is that the heavy LCO can feed a high-severity ULSD hydrotreater whereas heavy-cycle oil will have an 850-900° F. end point. In a few cases the heavy LCO material can feed a high-severity FCC feed hydrotreater (Fig. 9).

In some instances this heavy LCO must be sold as a low-value stream to maintain acceptable ULSD hydrotreater run length. ♦

The author

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