

Technical Moment

ARTICLE

Maximizing medium distillates: the challenge of increasing diesel production in a unit designed to produce gasoline.

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1. Introduction

In a world covered by roads, where terrestrial transportation drives the economy by carrying commodities to the ports and bringing back imported products, one fuel reigns supreme: diesel. But it is not only on roads; it is in electric generators, agricultural machinery, mining, and public transportation. In everyone's daily life, diesel is present.

While the gasoline market faces competition from electric vehicles and ethanol, it is estimated that the global diesel market will grow by more than 4% (1) over the next 10 years and that Latin America will be the region in the world where this market will increase most intensely (2). With this expectation and current prices, the pressure to maximize diesel yield from refineries in the region is increasing, as for many of them this is the most profitable product.

The FCC unit, created to maximize high-octane naphtha from heavy streams, also faces pressure to contribute to increasing the refinery's diesel production by boosting the yield of LCO, a product that can be blended into diesel after treatment. The adjustments to maximize this product at the unit are focused on three fronts:

- Adjustments to the converter's operating conditions;
- Fractionation adjustments;
- Optimization of the catalytic system.

In this article, we will briefly discuss each of these initiatives and their possible impacts on the unit.

2. Adjustments in the converter

For maximizing diesel in a UFCC, the main adjustments in the converter will aim to reduce the severity of catalytic cracking, seeking to minimize the conversion of LCO to naphtha. This reduction in severity involves lowering the reaction temperature and reducing the catalyst/oil ratio, which decreases the availability of catalytic sites and energy for the cracking reactions. For this, the main possible adjustments are:

- Reduction of reaction temperature;
- Increase in feed temperature;
- Reduction of contact time – can be done by increasing the injection of steam into the riser, for example, but some units do reduce the effective length of the riser, either by using feed injections at intermediate positions of the riser or by modifying the dimensions of this riser;
- Increasing the regenerator's dense phase temperature.

Unfortunately, when the severity of catalytic cracking is reduced, the overall conversion decreases, not selectively increasing the LCO, which can affect the profitability of the unit, as in the following example, which shows the results of an industrial test to maximize LCO yield by reducing the reaction temperature. In this case, the increase in volumetric yield of slurry exceeded the increase in LCO, and for that the refinery reversed the changes.

Adjusted yields		
Products (%vol)	TRX 533°C	TRX 516°C DELTA
GLP	Base	-3.9
Naphtha	Base	-1.4
LCO	Base	1.2
Slurry	Base	3.2

Table 1 - Variation of volumetric yields by TRX reduction.
Source: FCCSA database

Each unit will respond differently to the reduction in severity, according to its particularities. Simulation results, combined with financial assessments, can help determine a possible optimal condition.

In addition to the need for economic evaluation, it is important to take into account the limitations of the converter. Reductions in reaction temperature and catalyst circulation can cause coke formation at various points in the unit, as exemplified below:

- **Buildup of coke in the riser's feed zone:** due to the reduced circulation of the catalyst, incomplete vaporization of the feed at the base of the riser may occur. These hydrocarbons that do not vaporize immediately in the riser, besides increasing the formation of non-catalytic coke, can form coke deposits along with the catalyst in the feed nozzle's region.

This problem is more critical in units that incorporate residual fractions into their feedstock.

Increasing the feed temperature and the dispersion steam flow can help reduce the rate of formation of these deposits, but it is important to establish a minimum circulation and minimum reaction temperature to avoid them. For this, process simulations can be very helpful.

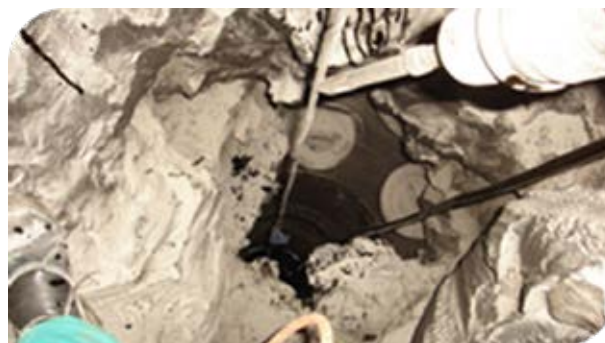


Figure 1 - Coke deposits at the base of the riser.
Source: FCCSA's archives

- **Coke formation inside the reactor's cyclones:** when the internal walls of the reactor's cyclones are at low temperature, it is possible for heavy hydrocarbons to condense inside them. Due to thermal cracking reactions, this liquid film ends up forming a coke layer, which grows over time despite the friction in the area. The heavier the feed and the lower the conversion, the higher the rate of coke formation.

Deposits can impair the efficiency of cyclones, as they alter their internal geometry, and may fall off during unit shutdowns, since the coke cools, contracts, and eventually cracks. This coke's detachment can lead to blockage of the cyclone's dip legs, high catalyst losses, and the need for prolonged unit shutdown for cleaning. Some units that process residual feeds, where this problem is more common, have anchoring devices for the coke in their cyclones to try to prevent its detachment, but the main tool for preventing these deposits is to establish a minimum reaction temperature that keeps the riser's effluents in the gas phase.

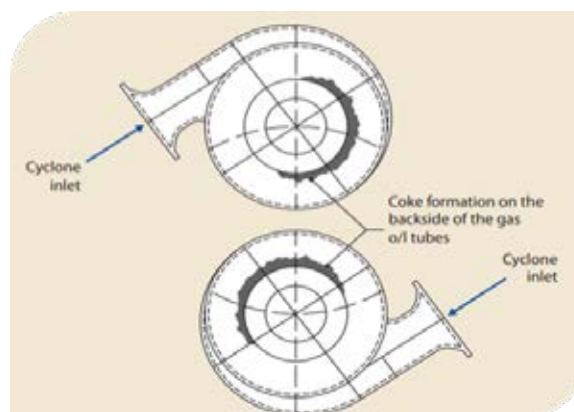


Figure 2 - typical location of coke deposition.
Source: FCCSA's archives



Figure 3 - Coke formed inside cyclones.
Source: FCCSA's archives.

- **Formation of coke on the reactor's cyclones dip legs:** under low circulation conditions, the residence time of the catalyst in the dip legs can be long enough for the hydrocarbons carried by this catalyst to react with each other and form coke inside.

To prevent this occurrence, it is important to maintain catalyst circulation within the cyclone's design range and, if the refinery plans to operate with circulation below the minimum, to replace the dip legs with ones of the appropriate diameter, avoiding excessive residence time.



Figure 4 - Formation of coke inside the cyclone's dip leg.
Source: FCCSA's archives.

- **Formation of coke on the reactor's walls:** it is not uncommon, especially in the overhead region of the reactor and on the external walls of the cyclones, nevertheless operating at low temperatures can lead to the formation of excessive amounts of this coke, which can become a problem for the continuity and safety of the unit. When in excess, during unit shutdowns, this coke can detach due to the temperature variation of the converter and accumulate on the baffles, packings, and debris catchers at the stripping system. During unit startup procedures, at the converter's heating phase, this coke may ignite, requiring the team to carefully control the amount of oxygen present in the reactor to prevent damage to the internals. In addition to the operational risk,

during maintenance this coke can pose a risk to the teams working inside the equipment, and precautions must be taken to prevent workers from being hit by the falling coke.

The formation of coke in the reactor is a particularly important problem in units that have closed cyclone systems but do not have efficient systems for removing hydrocarbons present in the diluted phase, originating from the stripping of the spent catalyst. The continuous and efficient maintenance of dome steam injection, the integrity of the hydrocarbons purge systems, and an adequate temperature in the reactor are the main actions to minimize this coke formation.



Figure 5 - Coke that detached from the reactor walls causing partial obstruction of the catalyst outlet.
Source: FCCSA's archives

- **Formation of coke on the transfer line:** the transfer line is another location where coke formation is common throughout the campaign due to the condensation of heavy hydrocarbons. The operation of the converter at low temperatures and the lack of proper thermal insulation are factors that can accelerate this coke formation, which can lead to process restrictions due to high pressure drop in the line, excessive coke detachment during the startup procedure causing blockage of the bottoms pumps' suctions, and difficulties in installing the blind that isolates the fractionator from the converter.

To minimize coke formation in the transfer line, it is necessary to invest in proper thermal insulation, often with the installation of steam tracing, as well as to ensure that the gas velocity in this line is above the minimum and that the reaction temperature is within the design range.



Figure 6 - coke deposition on the transfer line.
source: FCCSA's archives

All the points raised previously must be taken into consideration when deciding on maximizing LCO by reducing severity in the converter, through lowering the reaction temperature and reducing the catalyst/oil ratio.

3. Fractionation adjustments:

In terms of maximizing diesel, adjustments to the main fractionator can make more difference than adjustments to the converter. These adjustments are aimed at maximizing the incorporation of naphtha and slurry fractions into the LCO, thus increasing the volume produced.

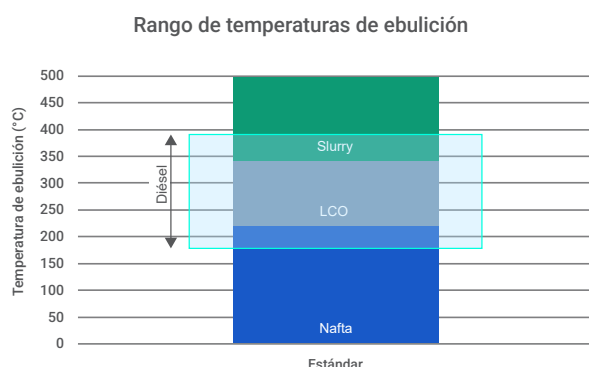


Figure 7 - Comparison between standard cut ranges of FCC products and the distillation range of diesel

LCO was, for a long time, a disregarded product of the FCC unit. Its high content of aromatic and olefinic hydrocarbons, as well as the high levels of nitrogen and sulfur, make its direct incorporation into the refinery's diesel pool difficult or even impossible. Due to the changes in diesel specifications and the increase in the number of hydrotreatment units, which operate with increasing severity and increasingly advanced catalysts, the LCO fraction is now fully incorporated into the diesel pool and becomes important both for volume gain and for property adjustment, such as the cloud point, for example.

As refining schemes have evolved and continue to evolve, FCC units are adapting to the new reality, since the original design of many of the fractionators was not intended for maximizing middle distillates, and sometimes not even for good fractionation. Due to the characteristics of each project, there may be more or less flexibility for adjustments.

4. Adjustments for naphtha incorporation into LCO:

It mainly consists of adjusting the fractionator to minimize the endpoint of the light naphtha by reducing the fractionator's overhead temperature. This adjustment has four main limitations:

- The initial boiling point of the resulting LCO;
- Naphtha's octane number;

- The temperature of salt formation;
- Water's dew point.

In diesel treatment units the fuel must be in liquid phase, though many of them can tolerate very low fractions of vaporized feed. Therefore, the initial boiling point of LCO is an important parameter to be evaluated when it comes to maximizing naphtha incorporation. Each hydrotreatment unit will have its own limitation.

Reducing the end point of cracked naphtha can interfere with its octane rating. This is because some high-octane aromatic compounds have boiling points starting at 100°C, and increasing the final boiling point of the naphtha increases the concentration of these compounds, as exemplified in Figure 8. The refinery must, therefore, internally assess the ideal end point for the cracked naphtha.

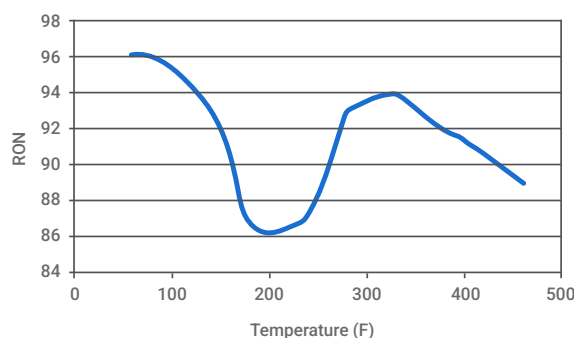


Figure 8 - Variation of the naphtha RON according to the boiling point
Source: PetroSim manual

In addition to the limitations related to product quality, special attention must be given to avoid the formation of chlorine salts at the main fractionator's overhead system. Reducing the overhead temperature to values below the ammonium chloride's deposition point can lead to the accumulation of these salts on the internals, which, besides causing severe corrosion, worsens the fractionation due to inefficient contact between liquid and gas and, consequently, leads to the entrainment of heavier compounds, that should have remained in the heavy naphtha and LCO streams, for the cracked naphtha.

The worsening of the fractionation efficiency raises the end point of the light naphtha and increases its sulfur content, which causes the refinery to reduce the column's overhead temperature even more, thus creating a cumulative effect that is only resolved when an internal cleaning procedure is performed. These deposits can be mitigated through the use of salt dispersants, but it is important to remember that this may lead to the transfer of chlorine salts to the hydrotreatment units, where they can cause corrosion, blockages, and catalyst deactivation. The ideal is to invest in efficient crude desalting and keep the main fractionator's overhead at a temperature of at least 5°C above the salt deposition temperature, as well as to avoid the use of catalyst technologies that contain chlorine.



Figure 9 - Salt formation on trays.
Source: Sulzer (3)

In addition to the deposition of ammonium salts, the formation of an aqueous phase can occur at the main fractionator's overhead system if the temperature is below the water's dewpoint. The presence of this water can cause instabilities in the column and serious fractionation problems if there are no means to remove it, as well as corrosion in internals and damage to heavy naphtha pumps.

5. Heavy cracked naphtha withdrawal:

The heavy cracked naphtha is the main fractionator's upper pump around. In some units, there is the possibility of sending this product, which has a distillation range close to that of kerosene (200°C-300°C), directly to the hydrotreatment units. This withdrawal can be a good alternative for units where there are flow rate limitations for LCO withdrawal and, since it is easier to treat than LCO due to its lower sulfur content, it can also be sent to units that have limited severity or are having difficulties treating the LCO.

When withdrawing heavy cracked naphtha, attention to the light naphtha's quality is needed. The reduction of liquid flow below the heavy cracked naphtha's withdrawal can interfere with the fractionation between naphtha and LCO, leading to an increase in sulfur in the light cracked naphtha and to the presence of heavy hydrocarbons in this stream, even when distillation curves are normal. To identify this poor fractionation, it is important to observe any anomalies in the cracked naphtha hydrotreatment's deactivation curve and to perform sulfur speciation analysis to identify the presence of high boiling point compounds.

5. Increasing LCO's final boiling point:

While the standard end point of LCO is 343°C, diesel's final boiling point, depending on local specifications, can reach up to 400°C. This opens up the possibility of incorporating a portion of slurry into the LCO. This increase in the final boiling point is achieved by raising the main fractionator's bottom temperature.

For this adjustment, there are two main limitations:

- ➔ The quality of the produced LCO;
- ➔ The coke formation in the main fractionator's bottoms system.

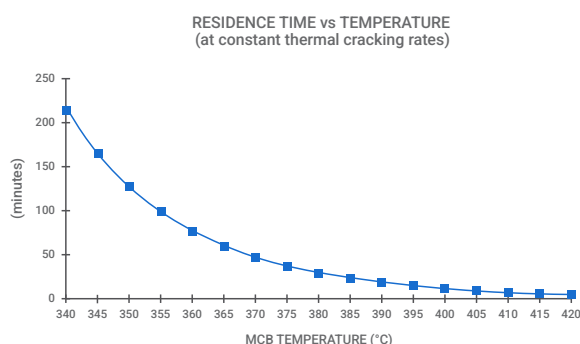
LCO must be treated in diesel hydrotreatment units so that it can be significantly incorporated into the blend. When compared to atmospheric distillation diesel, LCO has a higher concentration of aromatic, olefinic, nitrogen, and sulfur compounds, which makes its treatment more complex, especially when the goal is the production of ultra-low sulfur diesel (ULSD).

In LCO fractions with a boiling point above 310°C, there are sulfur-containing hydrocarbons that are refractory to hydrodesulfurization, such as methyl, dimethyl, and trimethyl-dibenzothiophenes, which require more severe treatment conditions for sulfur removal. This can become a problem in meeting the ultra-low sulfur diesel specifications in units operating under milder reaction conditions. The presence of nitrogen compounds that are also refractory to hydrotreatment, such as alkylated indoles and carbazoles, can affect the quality of the final diesel. Even in medium and high severity units, it is important to know that the higher the presence of these refractory compounds, the shorter the lifespan of the hydrotreatment catalysts. Therefore, properly managing LCO's quality is an investment in extending the inventory's lifespan.

In addition to making LCO's hydrotreatment more difficult, increasing the yield of LCO by increasing its final boiling point endpoint can result in coke formation in the main fractionator's bottoms system, which includes not only the bottom of the column itself but also piping, pumps, and heat exchangers within the slurry circulation's system. This coke formation can have two main causes: high residence time and low velocity inside the heat exchangers.

When increasing the bottoms' temperature, the rate of thermal cracking reactions, that naturally occur in hydrocarbons subjected to high temperatures, increases, which is exacerbated by the fact that the slurry contains a high concentration of polyaromatics, with a greater tendency for condensation and polymerization reactions. At the same time, with the reduction of its yield, the slurry spends more time circulating within the bottoms system, subjected to this high temperature. It is precisely the slurry's residence time that defines the maximum bottom temperature for this column:

$$\text{Residence time} = \frac{\text{Volume of liquid at the bottom of the tower}}{\text{Volume of decanted oil produced}}$$



Residence time	
Temperature (°C)	Time (min)
340	215
345	165
350	127
355	99
360	77
365	60
370	47
375	37
380	29
385	23
390	18
395	15
400	12
405	9
410	8
415	6
420	5

Figure 10 - maximum residence time as a function of temperature.
Source: E. Brevoord, J.R. Wilcox (4)

The formed coke can accumulate in the fractionator itself, pump filters, heat exchanger tubes, and pipes, especially at regions with smaller diameters and lower velocities. Small pieces of

coke can, for example, completely block heat exchangers' tubes. (Figure 11)

There is also a need to monitor the slurry's velocity through the heat exchangers tubes, which creates a minimum limit for this product's pump around. Due to the presence of catalyst, it is important to maintain a minimum velocity inside the tubes (1.5 m/s) to prevent the catalyst from depositing.



Figure 11 - Heat exchanger blockage by coke.
Source: FCCSA's archives

6. Optimization of the catalytic system

The UFCC's catalytic system optimization for maximizing diesel is a valuable resource, as it allows for an additional increase in LCO yield while the unit operates within its safe limits. These special formulations maintain the conversion of bottoms to LCO while limiting the cracking of LCO to naphtha, allowing an increase in LCO yield under the same operating conditions.

In these formulations, zeolite is no longer the main protagonist, and the focus is on using matrices with high activity and high accessibility to maximize bottoms conversion. The zeolite/matrix ratio in these catalysts is balanced to maintain the production of high-quality naphtha and the possibility of maximizing olefins if that is the unit's objective.

Some refineries that use catalysts with a high zeolite-to-matrix ratio end up reducing the catalyst's specific makeup in an attempt to increase the LCO yield, reasoning that increasing the concentration of contaminants in the inventory will naturally reduce zeolite activity, which in turn decreases the conversion of LCO to naphtha. This strategy is risky and can cause a series of inconveniences to the refiner:

- ➔ Increase in slurry yield due to low availability of active matrix;
- ➔ Reduction of the cracked naphtha's octane number;
- ➔ Severe loss of inventory quality;
- ➔ Reduction in the production of light olefins;
- ➔ Increase in coke and dry gas yields due to the increased concentration of metals in the equilibrium catalyst;
- ➔ Risk of critical iron contamination.

The desired characteristics for a catalyst dedicated to maximizing diesel are:

- Balanced zeolite/matrix ratio;
- High activity and high accessibility matrix;
- Resistance to metals;
- Use of high-resistance zeolites, with balanced activity for maintaining the quality of cracked naphtha;
- Flexibility for olefin maximization.

FCCSA offers a family of catalysts that combines all these characteristics: UPGRADER™ MD. These are catalysts that promote not only an increase in LCO yield but also an increase in the LCO/slurry ratio.

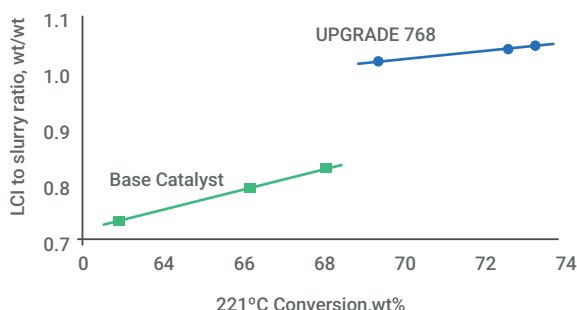


Figure 12 - Effect of UPGRADER™ MD on the LCO/bottoms ratio, (m/m %). (5)

The experience of replacing high zeolite/matrix ratio catalysts with UPGRADER™ MD family catalysts demonstrates that, at the same reaction temperature, it is possible to increase the LCO yield without increasing slurry production, which enhances the unit's profitability without the need for excessive severity reduction, helping to preserve the unit's integrity.

TRX 532°C Yield Comparison		
Yield (%m)	BASE CATALYST	DELTA UPGRADER™ MD
GC	Base	0.1
GLP	Base	-1.9
Naphtha	Base	0.0
LCO	Base	2.3
Slurry	Base	-0.4
Coke (fuel)	Base	0.0

Table 2 - Variation of mass yields with the change of base catalyst for the UPGRADER™ MD.
Source: Ketjen database

FCCSA's technical services team can help you optimize your unit. We are specialists with a broad perspective, with experience in refining and advanced knowledge in process optimization. We are at your service.

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MEET OUR SPECIALIST



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Chemical Engineer specializing in oil processing, with over 14 years of experience in the refining industry, including 11 years as an FCC Monitoring Engineer. She currently serves as a Technical Consultant at FCCSA, providing specialized technical support.

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FCCSA is a leading-edge technology company, with headquarters in Rio de Janeiro, comprising the Petrobras S.A. and Ketjen companies. Being the sole manufacturer of catalytic cracking catalysts and additives for petroleum refining in the South-American market.



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