Diesel Creation in the FCC Centered Refinery

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Abstract

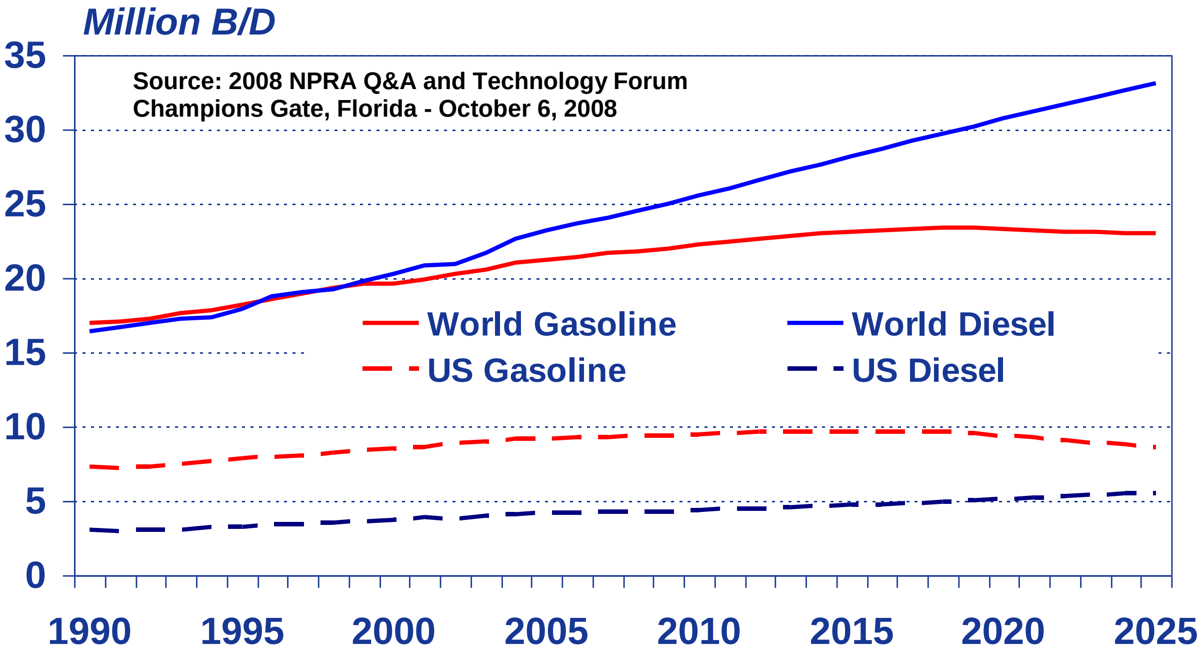
Global product demand trends favor increasing production of diesel fuel over motor gasoline. For refineries that have already invested in an FCC unit as its main conversion vehicle, the question becomes - how can we use our existing refinery assets to economically increase diesel production? The question is challenging because light cycle oil from fluid catalytic cracking operations has limited value as a component in modern diesel transportation fuel due to its aromatic, sulfurous character. To make matters worse, quality virgin distillate included in the FCC feedstock is essentially destroyed during FCC processing. In this paper, methodologies are presented for maximizing the production of high quality diesel in a refinery that relies on FCC as its principal means of heavy oil conversion:

- Preserving straight run distillates for use in diesel blending by preventing its loss to FCC feed
- Increasing yield, quality and recovery of LCO
- Upgrading LCO quality through hydrotreating or hydrocracking
- Preserving FCC naphtha octane and LPG during maximum LCO FCC operations.
- Producing synthetic diesel through oligomerization of lighter olefinic FCC products

Introduction

Globally, the trends in product demand shown in Figure 1 favor increasing production of diesel fuel over motor gasoline[1]. Consequently, many new refineries have utilized hydrocracking (rather than FCC) as the main conversion unit due to the hydrocracker's higher diesel yield and superior diesel quality. For refineries that have already invested in an FCC unit as its main conversion vehicle, the question becomes - how can we use our existing refinery assets to economically increase modern diesel production?

Figure 1
Gasoline and Diesel Demand



Source: 2008 NPRA Q&A and Technology Forum
Champions Gate, Florida - October 6, 2008

FCC units produce a significant quantity of high sulfur, low Cetane Number aromatic distillate commonly referred to as light cycle oil or LCO. Modern diesel quality specifications dictate that LCO must be upgraded in hydrotreating or hydrocracking units to make it an attractive modern diesel blending component. The disconnect between LCO quality and the specifications demanded for modern automotive diesel can be seen in Table 1 comparing the quality of a typical LCO with increasingly stringent diesel specifications[2].

Directionally, the yield and quality of the LCO can be improved by lowering FCC conversion and adjusting the FCC catalyst formulation but the improvement in LCO quality is not sufficient for the LCO to be considered a desirable diesel blending component.

Table 1

LCO Quality vs. Diesel Specifications

Property	**Typical LCO**	**North America Diesel**	**EU (Euro 5) Diesel**
Sulfur, wppm	10,000	≤ 15	≤ 10
Density, kg/m3	900 - 960	-	820 - 845
Cetane Number	20 - 30	≥ 40	≥ 51
PolyNuclearAromatics (PNA), wt%	30 - 60	-	≤ 11
Total Aromatics, vol%	60 - 85	≤ 35	-
D-86 Distillation, °C (°F)	$T_{90} \le 345$ (653)	$T_{90} \le 338$ (640)	$T_{95} \le 360$ (680)

Nicholas Flinn and Salvatore P Torrisi, Jr. (Criterion Catalysts & Technologies), “LCO Upgrading Options: From Simple to Progressive Solutions”, 8th Russia & CIS Refining Technology Conference & Exhibition, Moscow, 25 September 2008

Table 2 contains a sampling of refinery LCO samples from the years 1967 and 1982 showing a shift in the U.S. to higher density and lower Cetane LCO between 1967 and 1982. The decline in LCO quality over the period would in part be the natural result of increasing FCC operating severity and completion of the industry change-over from amorphous catalyst to highly rare earth exchanged zeolite catalyst targeting increased gasoline production.[3] These data are included here to provide perspective on the range of LCO qualities that have been produced from FCC unit operations. The reader can see that while some of the samples have much better diesel qualities than others, they all fall well short of the modern specifications.

Table 2

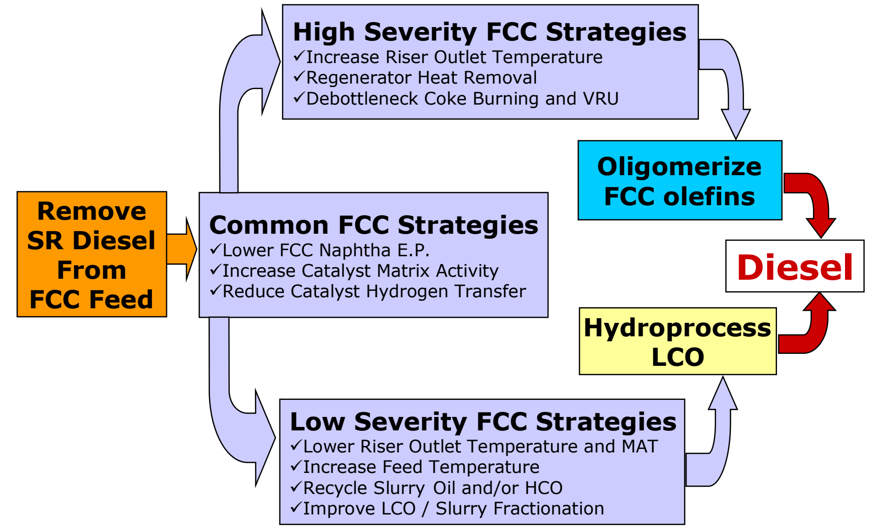
Typical Light Cycle Oil Inspections from U.S. Refineries

	1967						1982					
Sample Number	D39-67	D38-67	D42-67	D64-67	D81-67	D96-67	D22-82	D24-82	D25-82	D26-82	D29-82	D45-82
Gravity, °API	25.7	27.3	29.7	28.9	31.8	20.7	21.4	16.4	18.9	16.8	15.1	19.9
ASTM Distillation, °F @												
IBP	320	394	425	408	472	288	420	438	465	408	398	370
10% Recovered	470	444	487	467	502	466	502	482	490	460	478	441
20%	493	468	497	489	509	490	512	491	508	479	489	456
30%	509	487	506	501	515	506	520	499	520	486	492	466
50%	539	520	518	523	526	529	536	512	540	510	508	485
70%	577	561	532	552	538	560	557	532	568	543	531	513
90%	634	614	560	589	564	617	589	573	618	596	581	573
FBP	685	657	589	618	597	657	618	624	652	630	628	615
Aniline Point, °F	111.0	104.5	126.0	121.0	143.0	73.5	96.5	36.0	82.0	47.0	28.0	21.0
Hydrocarbon Type, vol %												
Aromatics	46.5	53.0	35.5	37.5	30.5	61.5	60.0	80.0	69.0	78.0	83.5	85.0
Olefins	7.5	2.5	8.0	8.0	10.5	6.0	1.0	1.5	2.0	5.0	3.0	1.0
Saturates							39.0	18.5	29.0	17.0	13.5	14.0
Paraffins	21.4	26.5	29.7	29.2	35.4	22.5						
Naphthenes	24.6	18.0	26.8	25.3	23.6	10.0						
Cetane Number Clear	34.5	32.8	41.5	37.2	45.0	25.5	27.0	18.1	24.0	18.8	17.1	19.3
Carbon/Hydrogen Ratio, wt	7.38	7.46	7.19	7.25	6.91	8.09	7.96	8.75	8.20	8.60	8.92	8.56

FCC Based Refinery Strategies for Maximizing Diesel Production

Figure 2 - FCC Diesel Maximization

Orthoflow™ FCC



So what can be done to maximize the FCC based refinery diesel production while taking advantage of an existing FCC asset? The simple answer, depicted in Figure 2, is to avoid the loss of virgin distillate to the FCC feedstock and maximize the production of hydro-processed LCO and diesel synthesized from the oligomerization of lower boiling FCC olefins. The following sections of this paper explore some of the details of how this can be accomplished.

As suggested in Figure 2, after a refiner has taken the steps necessary to minimize the loss of straight run diesel to the FCC feedstock, some FCC operating adjustments are commonly applied in the interest of increasing refinery diesel production. These include the following:

- Lower FCC Naphtha End Point
- Increase FCC catalyst matrix activity and lower rare earth / hydrogen transfer activity
- Maximize LCO End Point
- Hydroprocess the LCO as required

Beyond these commonly applied strategies, two divergent avenues remain for consideration in dealing with the diesel situation: (1) Reduce FCC cracking severity to maximize the production of LCO and take action if needed to mitigate the associated loss of FCC naphtha octane and LPG production., and (2) Increase FCC cracking severity to maximize the production of lower molecular weight olefinic products from the FCC unit and oligomerize these olefins to produce high quality synthetic diesel. Can the FCC based refinery increase diesel production? The answer to this question is certainly “yes”. The more germane question is whether or not the associated investment costs and operating trade-offs are justified by the increased diesel production.

Table 3

FCC Pilot Plant Data

Impact of Changing Operating Severity

	Low Conversion	**Medium Conversion**	**High Conversion**
FCC Feed Properties			
API Gravity, degrees	22.5		
50 vol% boiling point, F	851		
Aniline Point, F	176		
Sulfur, wt%	0.55		
CCR, wt%	0.89		
FCC Pilot Plant Operating Conditions			
Riser Temperature, F	940	979	1020
Feed Temperature, F	416	485	337
Catalyst to Oil Ratio, wt/wt	6.6	6.7	11.4
FCC E-Cat Properties,			
MAT	67		
Rare Earth Oxides, wt%	0.6		
FCC Pilot Plant Yields			
Dry Gas, wt%	1.23	2.08	3.50
C3 LPG, wt%	2.97	4.26	7.27
C4 LPG, wt%	5.98	7.88	11.57
Gasoline (C5-430 °F), wt%	43.21	46.98	46.00
LCO (430 – 680 °F), wt%	27.42	24.47	16.01
Slurry Oil (680 °F+), wt%	13.60	9.06	7.66
Coke, wt%	5.59	5.27	7.99
Conversion, wt %	58.98	66.47	76.33
FCC Pilot Plant Product Qualities			
C3 LPG Olefinicity, wt%	83.8	83.8	85.7
C4 LPG Olefinicity, wt%	66.7	68.5	67.0
Naphtha Gravity, °API	56.6	57.2	55.9
Naphtha Octane, RON / MON	91.7 / 81.1	92.9 / 81.6	95.6 / 84.4
Naphtha PONA, wt%	27.2 / 49.5 / 11.8 / 11.5	25.7 / 49.1 / 10.9 / 14.3	31.3 / 36.8 / 10.5 / 21.4
LCO Gravity, ° API	22.2	17.0	11.3
LCO Hydrogen Content, wt%	10.7	9.9	8.8

	Low Conversion	**Medium Conversion**	**High Conversion**
Slurry Oil Gravity, ºAPI	6.0	-0.8	-7.4
Slurry Oil Hydrogen Content, wt%	9.0	7.8	6.7

Data generated on KBR's FCC pilot plant are presented in Table 3 as an example of how changing the FCC reaction severity can impact FCC yields and product qualities. Three cases are included, all based on the same feedstock and catalyst system. With this as background, now the low severity FCC and high severity routes to increasing refinery diesel production are contrasted.

Reducing FCC cracking severity

Low severity FCC operation can be considered the traditional avenue for maximizing the production of diesel from an FCC centered refinery. As mentioned in the introduction, the quality as well as the yield of LCO improves as cracking severity is lowered. At the same time, reducing cracking severity will generally cause a loss of both LPG production and FCC naphtha octane and also increase the production of low valued slurry oil. There are practical limits to the amount of LCO that can be produced by lowering reaction temperature and catalyst activity because the coke make will become insufficient to heat balance the FCC unit at a sustainable regenerator temperature.

On the positive side of the ledger, reducing FCC severity will not be constrained by regenerator coke burning or vapor recovery unit (VRU) capacity. On the other hand, increasing LCO production increases the burden on the other refining units to create the modern diesel fuel specifications by upgrading the LCO.

Recycling Slurry Oil and Use of a Fired Feed Furnace – These operating strategies are commonly employed to increase LCO yield while directionally helping to maintain regenerator temperature. However, with severely hydroprocessed VGO feedstocks, recycling slurry oil and increasing feed temperature can still be insufficient to maintain adequate regenerator temperature.

There are some non-traditional tactics that can be employed to address the yield, product quality and heat balance issues associated with low severity FCC operations, and two of these are described below:

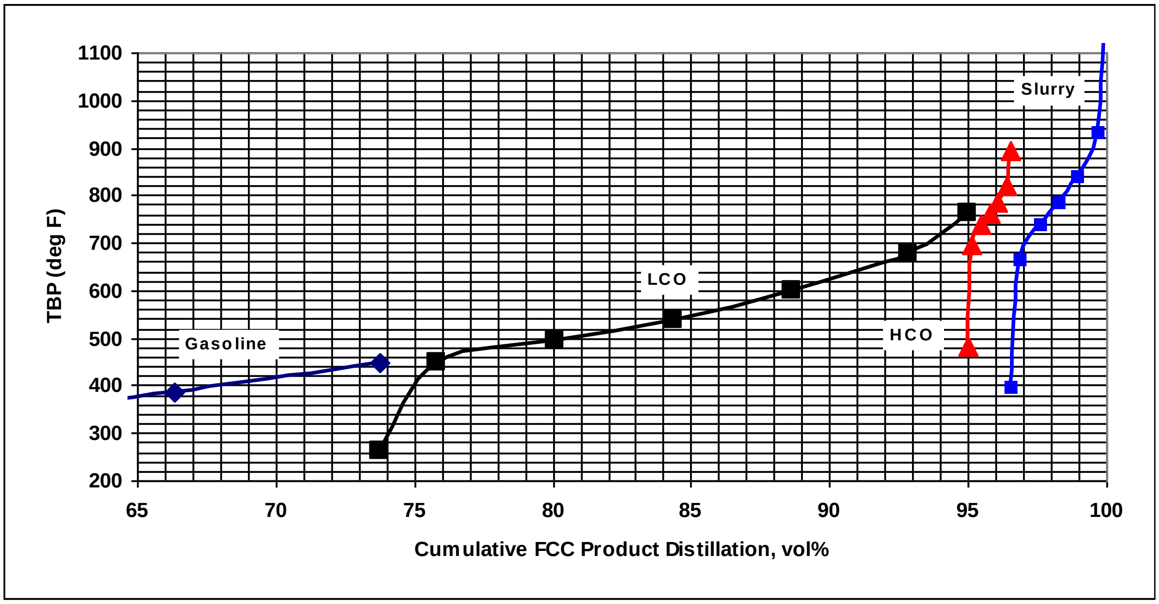
- Use of a dedicated slurry stripping tower to recover incremental LCO from the slurry oil produced by the FCC Main Fractionator and optionally recycle some of the stripped slurry oil to the FCC reactor
- Direct firing of the regenerator with fuel such as fuel gas or slurry oil to maintain regenerator temperature.

<u>Slurry Oil Stripping Tower</u> - The fractionation between LCO and Slurry oil in the bottom of an FCC main fractionator is very coarse because (1) the reactor products feed the fractionator through the bottom of the tower where the slurry oil product is withdrawn and (2) because there are few fractionation trays between the slurry product and the LCO product draws. There is at most a one stage flash available to separate the slurry oil from its equilibrium with the rest of the FCC reactor product stream. For example, Figure 3 presents simulated true boiling point distillations from an FCC main fractionator producing LCO, HCO and slurry oil. In this example, 36 percent of the FCC slurry oil and 50 percent of the HCO boils below the LCO product end point.

It is ironic that in maximum LCO operations, the amount of LCO lost in the slurry oil increases significantly because of the higher volume of slurry oil produced. Another fundamental violation of the maximizing LCO objective is that the recycle of a typical slurry oil also carries LCO boiling range material back into the reactor where the quality will be further degraded, and some of it will be cracked into a non-LCO boiling range material.

Based on the above considerations, it is apparent that to truly maximize the production of LCO from the FCC unit, a sharp fractionation between LCO and heavier liquid products must be achieved. A feature that has been employed to enhance the separation is to use a dedicated LCO/slurry fractionation tower to recover LCO that would otherwise be lost in the slurry oil. In a traditional maximum gasoline FCC operation, downstream recovery of LCO from slurry is not normally economic because of the relatively low slurry oil yield. However, in a maximum LCO operation where the slurry production is higher and LCO is more valuable, the additional fractionating tower may be economically viable.

Figure 3
FCC Product Distillation Example



The LCO/Slurry fractionation tower can be a steam stripper or a tower operated under vacuum to achieve maximum LCO recovery. In addition to prevention of the direct loss of LCO with the slurry product and loss of LCO through its recycle to the reactor, the slurry oil fractionating tower also provides a slurry oil that is a more effective recycle stream for supporting the FCC heat balance due to its higher boiling range and higher CCR content.

HCO Recycle - In low severity FCC operations where maintaining adequate regenerator temperature is not an issue, such as may be the case when processing residue, HCO may preferred over slurry oil as a recycle stream due to its very low carbon residue content and higher hydrogen content[4]. Ideally, the HCO would also have its LCO boiling range material distilled from it before recycling it, but the economic practicality of redistilling the HCO can be questioned if this requires yet another cycle oil fractionator.

Direct Firing of Regenerator with Fuel - The continuous direct firing of the regenerator with fuel can be essential to the operation of a maximum LCO FCC operation when processing non-residue containing FCC feedstocks.

Continuous firing of the regenerator air heater has been utilized for continuous support of the heat balance, but this practice can have an adverse impact on the velocities through the regenerator air distributors as well as the practical issues associated with monitoring the heater firing.

Continuous firing of torch oil, normally only used during start-up, has been practiced. However, this has reportedly been the cause of accelerated catalyst attrition and deactivation. KBR has developed a system for distributing liquid fuel in the regenerator which is commercialized in the KBR Superflex™ process[5, 6]. The system is designed to mitigate the catalyst damage associated with conventional torch oil firing. KBR has now adapted this technology for use in conventional FCC units. A patent pending version is also available for use in conventional FCC operations. In addition to this system for liquid fuels, a system for firing the regenerator with fuel gas, which is often a lower cost fuel, has also been commercialized.

Increasing FCC Cracking Severity

Increasing cracking severity reduces LCO yield and provides the immediate impact of having less LCO to blend into the diesel pool. This can be a net benefit to the diesel blending operation even though the quality of the LCO is diminished. At the same time, the increased LPG olefins can be oligomerized to produce high quality synthetic diesel. Increasing cracking severity can be achieved by increasing reactor temperature and/or increasing catalyst activity. However, unless FCC capacity is reduced, increasing FCC severity may be constrained by regenerator coke burning or VRU capacity. Even with adequate coke and gas handling capacity, increasing regenerator temperature can also pose a limitation to the severity increase. The use of slurry recycle in high conversion FCC operations is usually counter-productive because it only exacerbates the coke burning and regenerator temperature limitation while, referring back to Table 3, the slurry oil from high conversion FCC operations is hydrogen deficient and has little to offer in terms of potential cracking yield. Beyond simply increasing reaction temperature and catalyst activity, these are three hardware related upgrades that warrant mention here to assist in high conversion FCC operations:

- Apply Closed Cyclones to minimize dry gas and coke production at the increased severity
- Apply regenerator catalyst cooling to control the heat balance at the increased severity.

- Recycling FCC C4's and FCC light naphtha to an ultra high severity FCC riser for the purposes of producing incremental C3/C4 olefins and aromatic, high octane naphtha.

Each of these options is further discussed below:

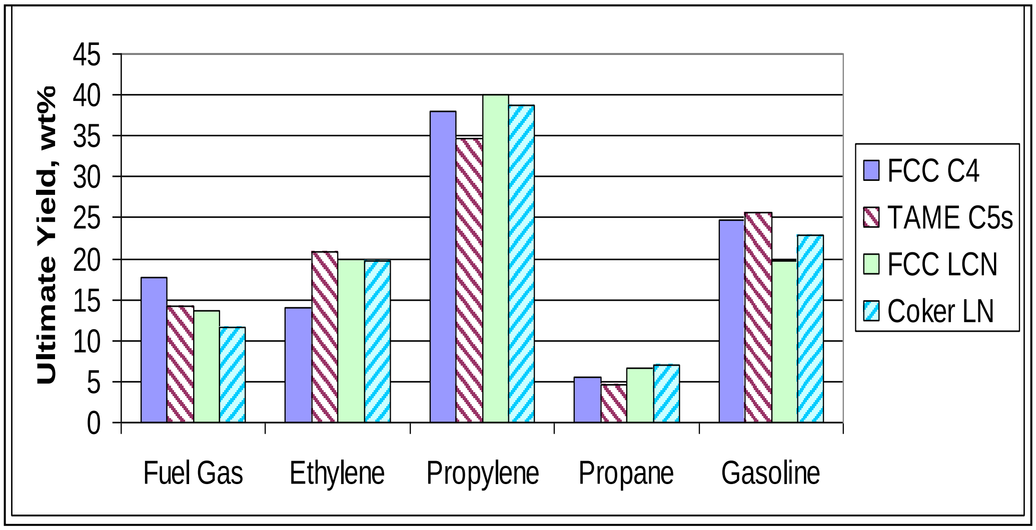
Closed Cyclones – This advanced riser termination system minimizes product vapor residence time between the riser outlet and the main fractionator, reducing the formation of incremental dry gas from post riser thermal cracking. In addition to the reduction in dry gas, the closed cyclone riser termination system also reduces delta coke on units that previously employed low catalyst separation efficiency riser termination devices. Therefore, the closed cyclone system is especially appropriate for use when increasing FCC operating severity because it simultaneously relieves constraints of both vapor recovery unit capacity and regenerator operating temperature. In addition to reducing dry gas production, and of particular relevance to the topic of this paper, Closed Cyclones also increase LCO production by minimizing the thermal condensation reactions that create slurry oil from LCO range material.[7]

Catalyst Cooling - In an unconstrained environment, increasing FCC reactor temperature is easy. However, in most cases FCC units are already operating against several physical and economic constraints. High regenerator temperature can emerge as a major constraint to increasing reactor temperature because of the impact of the higher temperature on the unit heat balance. FCC operators can effect a reduction in equilibrium catalyst activity to mitigate the increasing regenerator temperature but reducing catalyst activity runs counter to the more basic objective of increasing reaction severity. In high severity FCC operations, the catalyst cooler can maintain the regenerator temperature at the optimum value, which increases olefin production. In a recent study, the addition of a catalyst cooler to a regenerator temperature constrained high olefins FCC operation enabled more than a 25% increase in the unit's propylene production.[8]

C4 and Light FCC Naphtha Recycle - The recycle of C4 LPG and light FCC naphtha for the purpose of producing propylene and higher octane FCC gasoline fits in well here because it can achieve the goals of increasing propylene yield and naphtha octane without destroying LCO. This item is further described in literature and patents related to KBR's Superflex and MAXOFIN™ FCC Processes. The potential yields achievable from the recycle of C4's and Light FCC naphtha from KBR's Superflex Process are shown in Figure 4 and may be considered indicative of what can be produced in the high severity second riser of KBR's MAXOFIN FCC process. Ultimately, the application of MAXOFIN FCC catalyst and hardware technology can push the propylene yields into a range of 10 to 20 wt% or more.[6]

Figure 4

Ultimate Yields from KBR's Superflex Catalytic Olefins Process



The recycle of light naphtha and C4's to a high severity second riser can be practiced in both high severity and low severity primary riser operations to improve octane and produce additional LPG olefins without sacrificing LCO yield or quality. There is a synergy between the low severity primary riser operation and a high severity light feed recycle riser because the naphtha and C4's from the low severity primary riser are more olefinic, making these primary riser products better feedstock for the high severity second riser.

Commonalities in Basic Process Strategy

Even as the chosen strategy drives the refinery down a selected avenue of either a high or low conversion FCC operation, there will be some commonalities among the two strategies:

FCC Main Fractionator Cut Point Adjustment - Adjusting the FCC naphtha end point would be considered standard practice in most refineries for making seasonal adjustments for swings in gasoline vs. distillate demand. Reducing the end point of the FCC naphtha product shifts heavy naphtha into the LCO product. The limitation to the adjustment can be gasoline octane, the flash point specification of the LCO product, pool Cetane considerations or a limitation related to the minimum FCC main fractionator overhead temperature that can be practiced without condensing water and fouling or corroding the top of the main fractionator or its overhead system.[9] Typically, the FCC naphtha ASTM D-86 end point would not be reduced to less than about 300 ºF in order to stay above a minimum acceptable main fractionator overhead temperature.

Figure 5 provides a typical example of how changes in gasoline end point impact the naphtha yield and LCO yield by implication. In addition to changes in the FCC naphtha and LCO yields due to the cut point adjustments, there will be changes in the product distillations, gravities, octanes, sulfur contents and cetane values.

Because of the wide variation in heavy FCC naphtha molecular composition from one FCC operation to the next, a rule of thumb is not provided for the impact of the cut point adjustments on octane, sulfur content or Cetane. These effects are best taken from empirical observations on the operating unit.

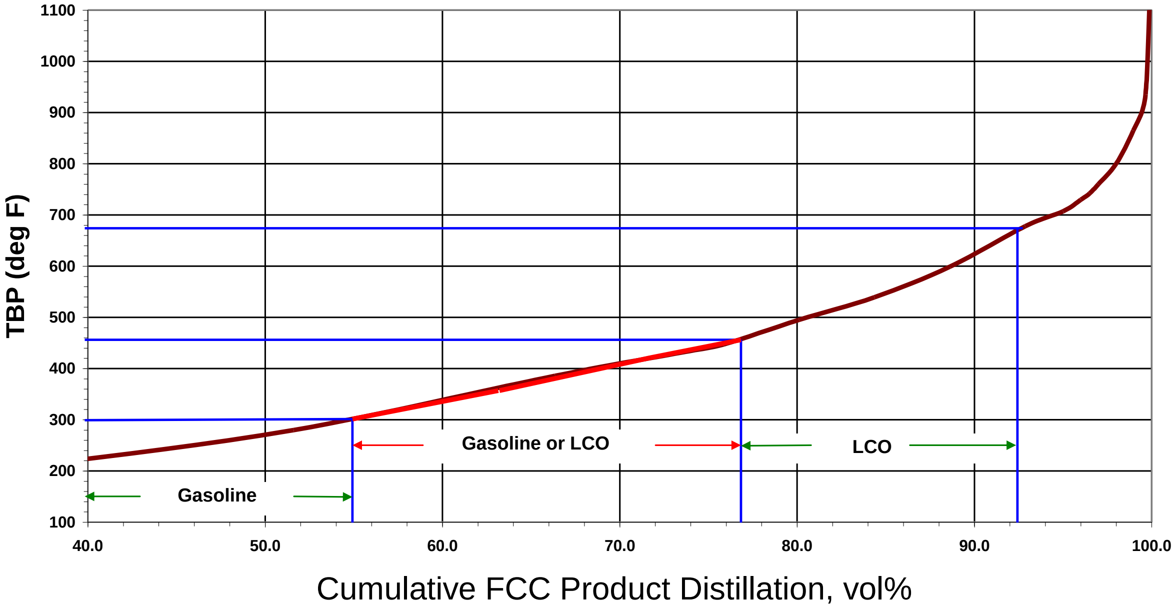
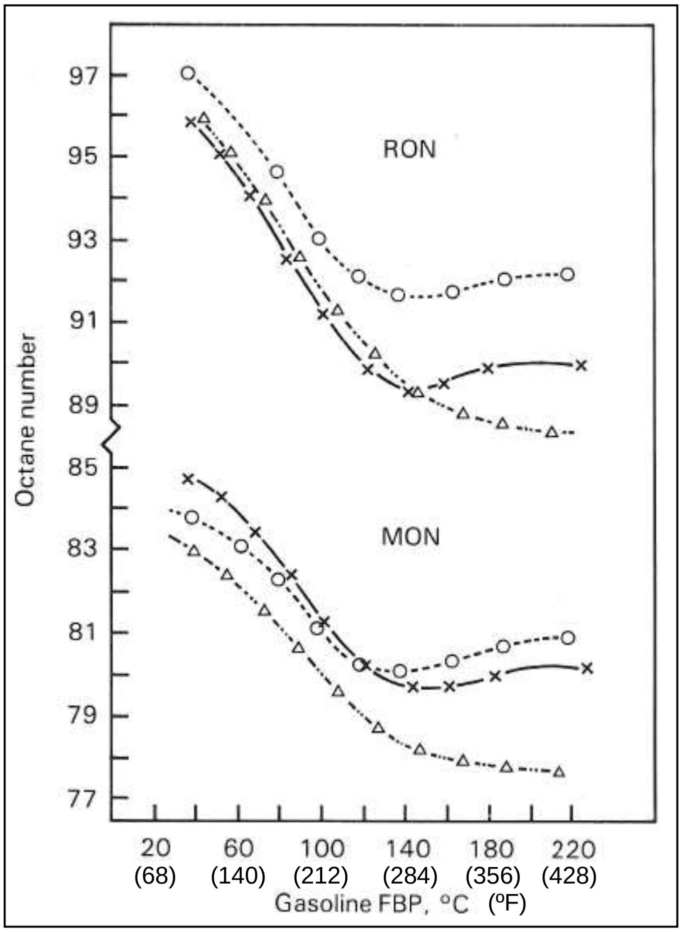


Figure 5 – Example FCC Liquid Product Distribution

As an example of the variability of product property trends with cut point, Figure 6 shows the impact of FCC gasoline end point on octane calculated from narrow boiling range octane data for three different FCC situations operating with a variety of feedstocks, catalysts and operating conditions.[10]

Figure 6 - FCC Gasoline Octane Examples



In many cases, the seasonal demand swings are accommodated with changes in the FCC gasoline cut point with no change to the true (430 deg. F) FCC conversion level as this strategy works to preserve the LPG production, octane and total liquid volume associated with the higher conversion operations.

Crude Distillation – Another common practice is maximizing diesel production from the crude distillation processes so that losses of potential diesel to the FCC feed are minimized. There are intermediate swing cuts from some crude distillation operations that can be routed to the FCC unit when gasoline is demanded and routed to diesel production when the objective is maximizing diesel. As a side benefit, keeping the diesel out of the FCC feed also improves FCC gasoline octane.[11]

Pilot plant data have shown that in moderate or high severity FCC operations, most of the straight run diesel will be converted to gasoline and lighter products with only 20 to 30 percent leaving the FCC in the LCO product. The data have also shown the LCO made from the distillate will have Cetane values 10 to 15 numbers below that of the distillate feed but still higher than that of typical FCC LCO.

Beyond standard operating adjustments, there may be investment opportunities in crude distillation hardware that can achieve a sharper separation between the diesel product and FCC feed streams, reducing the loss of potential diesel to the FCC feed.

A survey of over 100 refineries has indicated that FCC feed typically contains between 10 and 15 volume percent of material, mostly diesel, boiling below 650 deg. F.[12] In environments where gasoline production is maximized, the loss of diesel to the FCC unit has little negative impact, but if the objective is diesel maximization, better crude fractionation efficiency between diesel and FCC feed can be economically justified.

There are a number of ways to reduce the loss of virgin diesel to the FCC feed.[13] Some of these options are listed below:

- ✓ Revamp the atmospheric distillation column to increase the degree of fractionation between the diesel and atmospheric gas oil products
- ✓ Revamp the vacuum column to produce a diesel product
- ✓ Add a gas oil tower or a vacuum preflash tower in between the atmospheric and vacuum distillation columns and recover diesel from the vacuum tower feedstock.
- ✓ Add a splitter column to process the light vacuum gas oil and produce a diesel stream.

Table 4 shows examples of calculated incremental diesel production that were reported for some of these options.[13] The best option(s) for a given refinery are a function of the site specifics of the application, but the data in Table 4 can indicate the magnitude of diesel production increases that are possible.

Table 4 – Impact of Crude Unit Modifications

	Base Case	**Additional Diesel Recovery Options**				
	Atmospheric Tower Revamp	Add Standard Diesel Draw to VDU	Add High Recovery Diesel Draw to VDU	Install Gas Oil Tower in Front of VDU	Install Vacuum Preflash Tower in Front of VDU	Install LVGO Splitter Tower
Incremental Diesel, vol% of Crude	1.3	3.0*	3.2*	2.2*	2.3*	3.4*
Number of Fractionation Stages Between Diesel and Gas Oil	5	2	6	4	4	12

* Incremental yield of selected option relative to Base Case

<u>FCC Catalyst Selection</u> – Some catalyst recommendations apply to both high severity and low severity FCC operations. Low hydrogen transfer FCC catalyst* is recommended for maximizing refinery diesel production as this type of catalyst will generally produce a higher yield and higher quality LCO (that can be hydroprocessed) while increasing the

yield of FCC olefins (that can be oligomerized). Similarly, active matrix functionality also benefits LCO yield and quality.

- Hydrogen transfer reactions strip hydrogen from saturated LCO molecules (such as naphthenes) and transfer it into gasoline boiling range olefins. The net impact of these hydrogen transfer reactions is that the LCO becomes more aromatic (lower Cetane Number and more dense); the gasoline becomes more saturated (lower olefin content and lower octane); naphtha yield increases; and LPG olefins yield declines.
- In FCC operations intended to maximize gasoline production, the hydrogen transfer reactions provide a net benefit due to the increased gasoline volume that results from the saturation of the gasoline olefins before they catalytically crack further into LPG olefins. The negative impact of hydrogen transfer activity on LPG olefin yield and naphtha octane have been widely documented while the negative Impact on LCO quality has been less widely publicized.

In high LCO yield FCC operations where LCO quality, gasoline octane and LPG yield considerations are more important than sheer gasoline volume, hydrogen transfer reactions are counter-productive.

Refer to Table 5 below for an example of how FCC catalyst Rare Earth content can impact FCC yields and product qualities.[14]

Table 5

FCC Pilot Plant Data

Comparison of Yields and Product Qualities
with Super D and Octacat® Catalysts
at Constant Pilot Plant Feedstock and Operating Conditions
(23.9 °API VGO, 40 WHSV, 4 c/o and 950 °F)

Catalyst	Super D (Higher Rare Earth, REY Catalyst)	Octacat® (Lower Rare Earth USY Octane Catalyst)
Conversion, vol%	72.5	72.5
Yields		
H2, wt%	0.02	0.02
C1+ C2, wt%	1.28	1.13
C3, vol%	1.9	1.4
C3=, vol%	6.0	7.6
C4's, vol%	13.6	15.1
Gasoline, vol%	59.0	58.0
LCO, vol%	18.1	19.5
640 °F Residue, vol%	9.4	8.0
Coke, wt%	4.6	4.0
Gasoline Octane, RON + 0	86.0	90.4
Gasoline Octane, MON + 0	78.0	80.0
LCO Gravity, °API	18.4	20.1
LCO Aniline Point, °F	62	75

- The base catalyst can also be used in combination with ZSM-5 containing catalyst additive to further preserve the gasoline octane and C3/C4 olefins at low conversion levels. The ZSM-5 is also applicable to maximizing olefins production from high severity FCC operations. The data in Table 6 provide an example of how ZSM-5 additive can change the yields and product qualities in a moderate severity FCC operation. [15]

Table 6

FCC Pilot Plant Data

Effect of ZSM-5 Additive (O-HS) on Yields and Product Qualities
at Constant Pilot Plant Feedstock (27.0 ºAPI VGO) and Operating Conditions (960 ºF)

Catalyst	Astra-378 (Davison octane-barrel FCC Catalyst)	Astra-378 With 4% ZSM-5 Additive	Delta
Conversion, vol%	68	68	
Yields			
H2, C1+ C2, wt%	2.38	2.49	0.11
C3, vol%	2.0	1.9	-0.1
C3=, vol%	6.8	7.4	0.6
C4=, vol%	6.1	6.9	0.8
iC4, vol%	4.2	4.0	-0.2
nC4, vol%	1.1	0.9	-0.2
Total LPG	20.2	21.1	0.9
Gasoline (450 ºF TBP) , vol%	57.6	56.8	-0.8
LCO, vol%	18.0	17.9	-0.1
Bottoms, wt%	14.0	14.1	0.1
Coke, wt%	3.9	3.8	-0.1
Gasoline Octane, RON + 0	90.2	91.6	1.4
Gasoline Octane, MON + 0	79.2	79.6	0.4

In low severity, high LCO yield FCC unit operations, ZSM-5 additives have also been shown to convert higher boiling FCC products into both gasoline and LPG. Two examples of the impact of ZSM-5 additions in low severity FCC operations are shown in Table 7. In these data it is apparent that the cracking of heavier molecules in the low severity FCC products by the ZSM-5 results in a loss of total cycle oil (302 to 698 ºF) production and increases in both 302 ºF TBP gasoline and LPG production.[16]

Table 7

Commercial Low Conversion FCC Plant Data

Effect of ZSM-5 Additive on Yields and Product Qualities
Feedstock: Bombay High VGO – Typically 27.3 ºAPI

Low Conversion FCC Operation	Plant A	Plant B
Catalyst System	REY Zeolite With ZSM-5 Additive	REY Zeolite With ZSM-5 Additive
Incremental Yields from ZSM-5 Addition		
Dry Gas, wt%	+ 0.3	0.0
LPG, vol%	+ 2.4	+ 2.9
Gasoline (IBP - 302 ºF) , vol%	+ 4.8	+ 3.3
Total Cycle Oil (302 - 698 ºF)	- 3.2	- 6.7
Bottoms (698 ºF +)	- 4.5	+ 0.2
Coke, wt%	0.0	+ 0.2

The paper which originally published the data shown in Table 7 also reported that based on a large sampling of pilot plant product from runs having an average conversion level of 40 percent and a 0.5 wt% ZSM-5 crystal addition, the average Research Octane Number changes were as follows:

+ 2.4 numbers for the IBP to 302 ºF gasoline
+ 3.3 numbers for the IBP to 410 ºF gasoline

- Low equilibrium catalyst MAT activity is often employed when maximizing LCO production.

- Active matrix FCC catalysts are also recommended for LCO maximization as they enable the cracking of LCO boiling range aliphatic side chains from high molecular weight feed components. In addition to increasing LCO yield, the aliphatic side chains that report to the LCO boiling range improve LCO Cetane. The active matrix also contributes to Cetane improvements because matrix cracking does not possess the higher hydrogen transfer characteristic of a zeolite. Refer to Table 8 for representative data concerning the impact of changing the catalyst matrix activity.[17]

Table 8

FCC Pilot Plant Study

Mid Continent Feed

Catalyst Matrix Surface Area	**Low**	**High**
Conversion	69.5	69.7
Gasoline (C5-421 F)		
Yield	53.0	53.1
RON	87.7	90.0
MON	77.8	78.5
P / O / N / A	36/23/15/27	26/36/14/24
LCO (421-602 F)		
Yield	16.3	19.2
Cetane Index	24.5	28.5
API	21.8	23.8
Carbon NMR		
Aromatic Carbon, %	49.5	45.9
Aliphatic Carbon, %	50.5	54.1
Bottoms (+602 F)		
Yield	14.2	11.1
API	13.0	7.6
Carbon NMR		
Aromatic Carbon, %	39.0	57.4
Aliphatic Carbon, %	61.0	42.6
Viscosity @ 210 F, cSt	7.87	5.8
Viscosity @ 100 F, cSt	116.4	68.14

Maximize LCO End Point

The maximization of LCO end point is a common operating strategy for maximizing LCO production at the expense of low valued FCC slurry oil. In many FCC operations, concern for coking in the FCC main fractionator bottoms circuit limits the LCO end point. There are a number of FCC operating parameters that influence the propensity of the bottoms circuit to suffer coking problems.

- Bottoms circuit temperature
- Bottoms circuit liquid residence time
- Concentration of unconverted paraffins in the slurry oil

In high conversion FCC operations the slurry oil is more aromatic and can be held at higher temperatures and longer residence times without coking. Some of the slurry oil quality data that FCC operators monitor as indicators of coking tendency are the gravity and viscosity. The more aromatic slurry oil produced by high conversion FCC operations will allow the unit to operate with lower API gravities while respecting bottoms viscosity targets selected to avoid the fractionator coking.

FCC Product Considerations

Changing FCC cracking severity directly impacts the FCC product yield distribution and product qualities. In the FCC pilot plant example presented earlier in Table 3, the VGO is of average quality as an FCC feedstock, and the catalyst is a low rare earth catalyst with some matrix activity. The pilot plant runs covered reactor temperatures and conversion levels ranging from low to high relative to industry norms.

The pilot plant data show the trade-offs between LCO production and quality and the production and quality of FCC naphtha. As shown in Table 3, even without adjusting the LCO cut points, the LCO yield changes by a factor of almost two by adjusting the FCC reaction severity. At the same time, among the runs presented in Table 3, the gravity of the LCO increases by about 11 degrees API as the operating severity is lowered.

Figure 7 summarizes a positive relationship between increasing LCO production rate and LCO quality taken from a larger sampling of the same pilot plant study data.

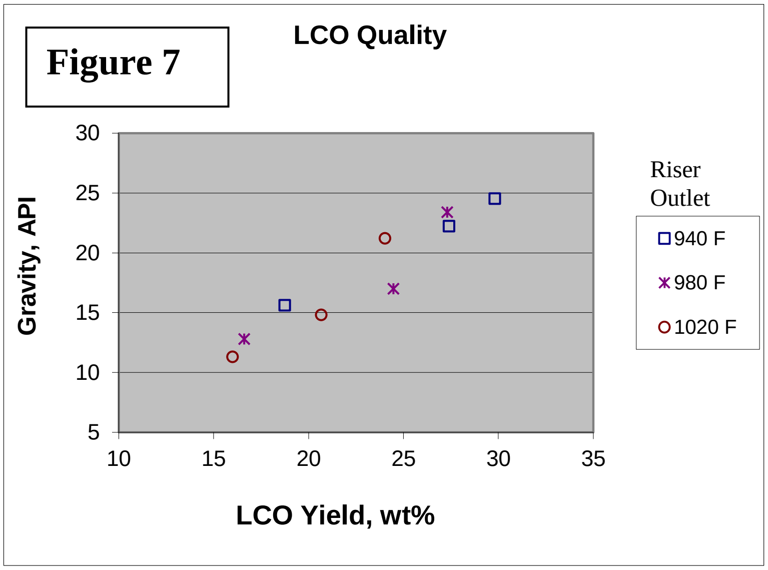
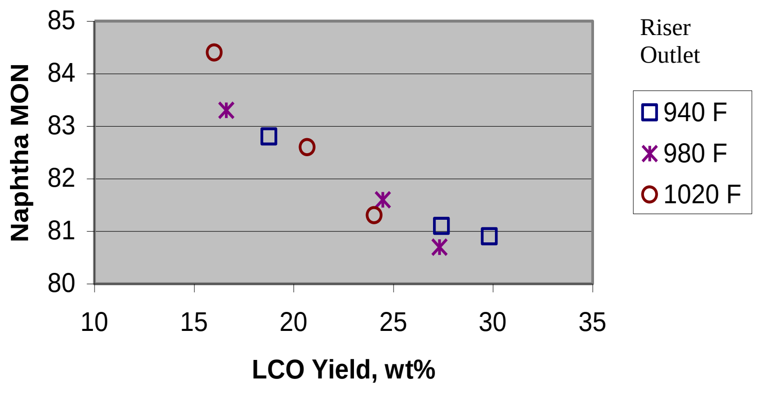


Figure 7

Figure 8

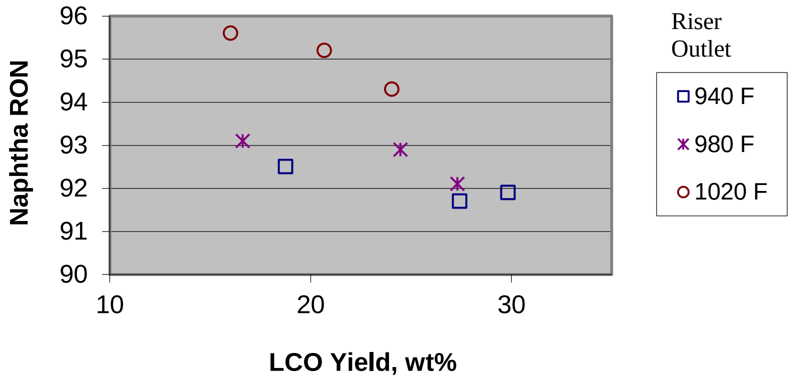
FCC Naphtha Quality



Conversely, Figures 8 and 9 show a very direct and negative correlation between LCO yield and FCC naphtha octane. Figure 8 demonstrates that irrespective of the indicated FCC reaction temperature, FCC naphtha motor octane will suffer as LCO yield increases. Figure 9 shows that the negative impact of increasing LCO yield on the olefin dependent Research Octane can be mitigated to some extent, if high FCC reaction temperature is maintained.

Figure 9

FCC Naphtha Quality



The data in Table 3 also provides examples of how changing FCC reaction severity can impact LPG yield and naphtha octane.

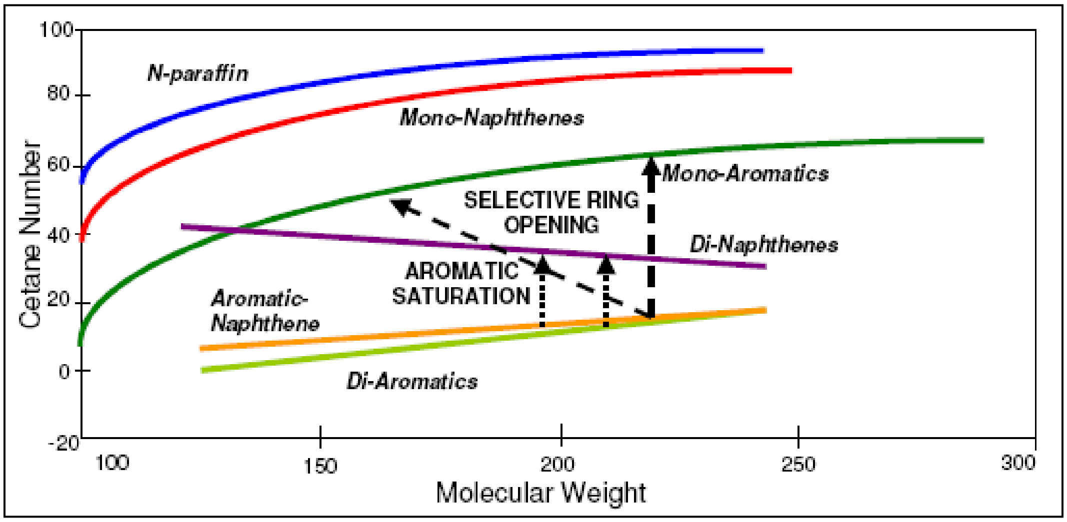
Comparing the low conversion and high conversion cases, the data show that the low conversion case produces less than one-half the LPG and 3 to 4 numbers lower octane than the high conversion case.

Table 3 also provides an apt example of the degradation of LCO as a potential feedstock for upgrading into diesel as the FCC conversion is increased; the LCO hydrogen content decreases from 10.7 wt% to 8.8 wt% as the FCC conversion level is increased from 59 wt% to over 76 wt%.

Hydroprocessing Options

There is a wide array of hydrotreating and hydrocracking processes being applied for upgrading of LCO. These range from mild hydrodesulfurization to full conversion hydrocracking. Figure 10 depicts some of the chemistry responsible for improving the cetane, density and aromatics content of the LCO. For purposes of this paper, three upgrading processes (hydrotreating, aromatics saturation, and mild hydrocracking) are described as representative examples of some of the processes being used today.[18]

Figure 10 – Hydrocarbon Comoponents and Cetane Number



LCO Hydrotreating – Mild hydrotreating of LCO will reduce its sulfur content significantly, but this will only modestly improve the product qualities related to aromatic content. In examples presented in Table 9, LCO in a 10 percent concentration, in a mixture including straight run gas oil, is hydrotreated. Two options are presented, with the later representing a higher degree of desulfurization and more aromatics reduction. These examples demonstrate that based on the product cetane and sulfur levels, it is possible to include about 10 percent LCO in the diesel pool by hydrotreating the LCO/SRGO mixture.

Table 9

Processing 10% LCO Blend with ULSD Catalyst Systems

		Feed 90% SRGO 10% LCO	**Product**	
			CoMo	NiMo
Operating Pressure			Medium	High
Density	kg/m^3	880	863	853
Sulfur	wppm	15,300	50	10
D-86 T10	°F	543	534	523
D-86 T50	°F	586	579	570
D-86 T90	°F	660	657	649
IP391 Mono Aromatics	wt%	16.7	22.6	21.4
IP391 PNA	wt%	15.0	9.2	2.8
IP391 Total Aromatics	wt%	31.8	31.8	24.2
Cetane Number	CN	47.0	51.0	52.5
H2 Consumption	Nm^3/m^3		37	72

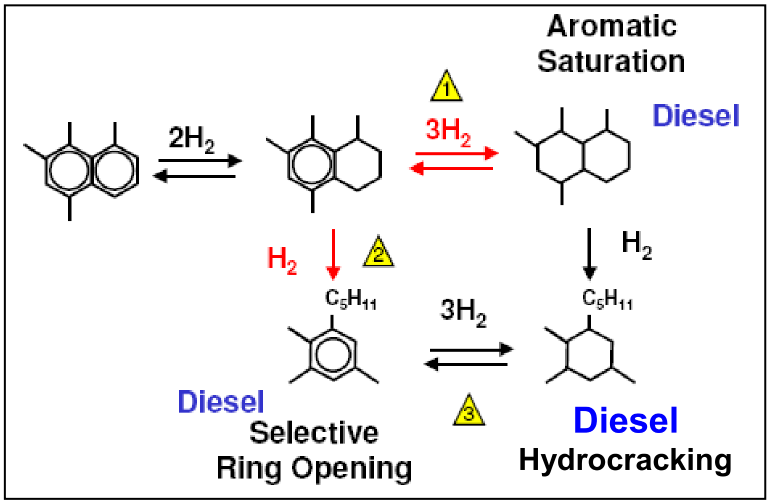
Table 10 shows what is possible utilizing a 2-stage Aromatic Saturation unit to process 100% LCO.[18] The drawback of ring saturation is high hydrogen consumption.

Table 10

Two-Stage LCO Aromatic Saturation

		100% LCO	**Product**
Operating Mode			2-Stage
Operating Pressure			Medium
Density	kg/m^3	960	859
Sulfur	wppm	7300	<10
Total Aromatics (FIA)	vol%	79.1	2.5
Cetane Index	D-976	24.1	40.2
Cetane Number	CN	<20	44.9
Delta Cetane Number			25+
Liquid Yield	vol%		115.7
H2 Consumption	Nm^3/m^3		473

Figure 11
Three Reactions to Upgrade LCO Quality



Mild Hydrocracking - An alternative is to rely on ring opening with mild hydrocracking (MHC) as shown in Figure 11 which also moves some of the aromatics out of the LCO boiling range into gasoline.[18] This approach can provide substantive LCO quality improvement with lower hydrogen consumption. Table 11 provides an example of co-processing LCO along with SR distillate and other cracked products.[18]

Table 11
ULSD and MHC on Feed Blend Containing 10% LCO and 35% Coker Diesel

Property	**Units**	**Feed**	**ULSD Product**	**MHC Product**	**MHC Product**
Density	Kg/m3	866	842	829	822
Delta Density			24	37	44
Sulfur	wppm	8000	<10	<10	<10
SFC Aromatics, Total	wt%	**42.4**	**23.0**	**13.2**	**14.0**
Mono	wt%	30.0	20.0	12.8	13.5
PNA	wt%	12.4	3	0.4	0.5
Total Product Cetane Index	**D-4737**	**36.8**	**43.8**	**46.2**	**46.8**
Delta Cetane Index			7.0	9.4	10.0
Chemical H2 Consumption	Nm³/m³		116	150	155
Incremental 379 °F minus	Vol%		1.1	10	20

Diesel Product is 2-3 Cetane higher than Total Product for MHC cases

Non-Traditional Processing Operations for Creating Diesel from FCC Byproducts

Two processing options deserve to be in a separate category because their application to date has been limited. These options are (1) the creation of synthetic diesel from FCC olefins and (2) the extraction of aromatics from FCC naphtha. These options can be integrated into the over-all processing scheme along with the other options described earlier.

Reprocessing of C3 – C9 Olefins into Distillate – Olefins can be used to produce good quality diesel with oligomerization processes. For example, based on a zeolite catalyst co-developed by Süd-Chemie with the Central Energy Fund of South Africa, as shown in Table 12, an oligomerization unit distillate yield from a C3 through C9 olefin feed was reported to be 78% distillate with a byproduct gasoline yield of 19%. After hydrotreating to saturate the olefins, the distillate was reported to have a Cetane Number of 52 to 54, zero sulfur and less than 2 % aromatics[19].

Therefore, for FCC based refineries working to maximize diesel production, oligomerization of olefin containing FCC light gasoline and LPG may provide viable investment opportunities.

FCC Naphtha Extraction – Extractive techniques are available for separating a mid boiling fraction of FCC gasoline into a higher octane, aromatic rich fraction and an olefin and paraffin rich fraction.[20] A patent recently granted to KBR describes a combined FCC/extraction process wherein an aromatic rich, higher octane fraction of FCC gasoline can be produced as a gasoline product while a paraffinic/olefinic naphtha fraction can be produced for recycle to an FCC riser for the purpose of producing propylene and other olefins.[21]

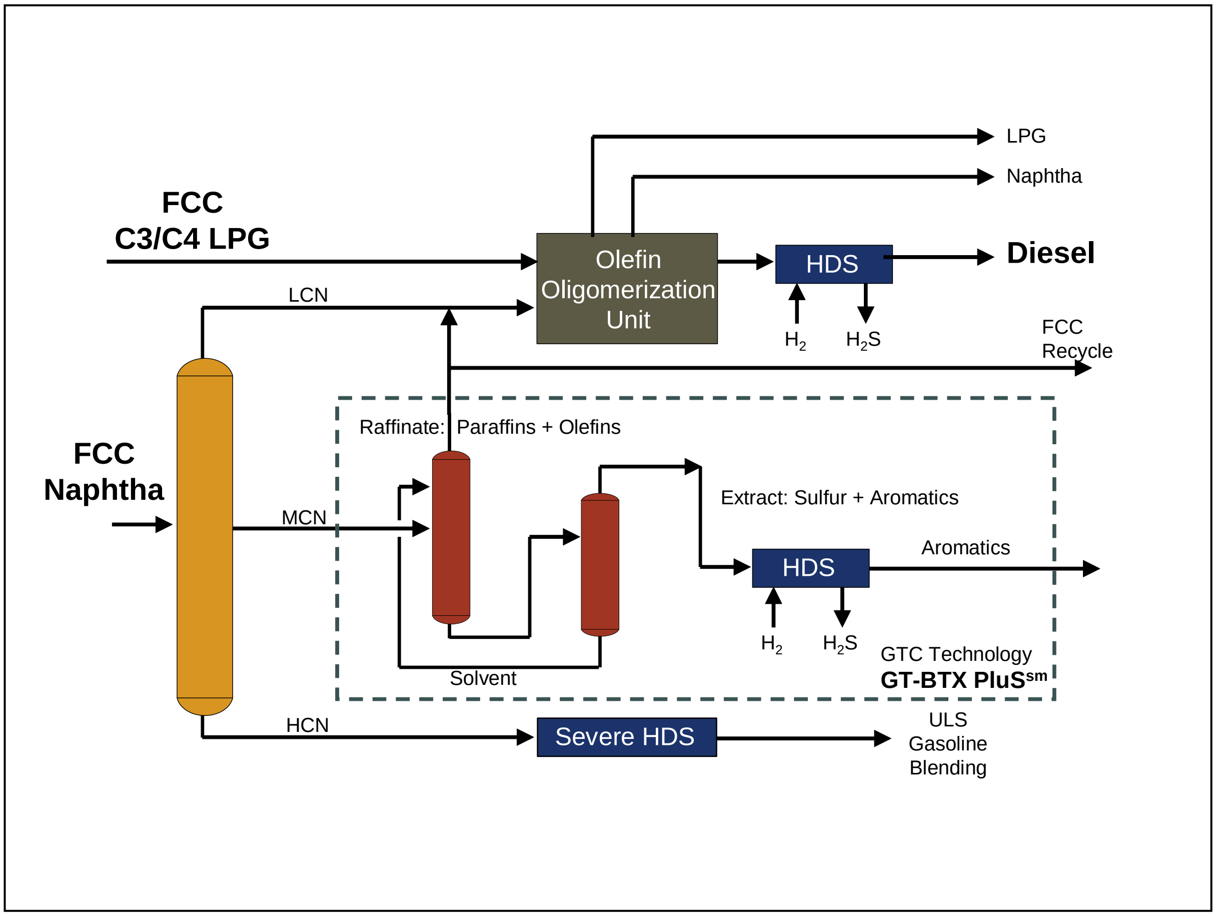
This FCC naphtha extraction concept and oligomerization technology can be used together as shown in Figure 12 to maximize the production of synthetic diesel from FCC olefins[22]. The combination can be especially useful in the context of a high LCO yield, low severity FCC operation because the low severity FCC naphtha will have a higher olefins content than the more aromatic, more paraffinic naphtha from a high severity FCC operation. Thus, the non-aromatic naphtha raffinate from a low severity FCC operation will make a better quality oligomerization feedstock or better quality FCC recycle stream for the purpose of increasing lighter FCC olefins production because olefins are easier to crack than paraffins.

Table 12

Product Yields and Properties from Oligomerization of Olefins

Feed Composition	82 Percent C3 through C9 Olefins
Product Yields (based on feed olefins), vol%	
Gasoline	19
Distillate	78
Distillate Qualities after Mild Hydrotreating	
Boiling Range, Deg. F (IP 123/84)	388 – 676
Density, kg/m3 @ 20 ºC	787
Cetane Number	52 to 54
Aromatics Content, wt%	< 2
Sulfur Content, wt%	0
Viscosity, cSt @ 104 ºF	2.55

Figure 12
Production of Diesel from FCC LPG and FCC Naphtha



Refinery Diesel Balance

With all the processing options presented in this paper, an obvious question would be, how much can the refinery diesel production be increased if many of these options were applied in a retrofit of an existing refinery? The answer depends on the specifics of the application. Table 13 shows estimated results from isolated examples provided in this paper, and this can provide insight into the question.

Table 13
Refinery Diesel Increase Examples

Volume Percent of Refinery Crude Input Assuming 27 percent crude oil to FCC unit and LCO hydroprocessing to maximize diesel in all cases	**Lower Severity FCC**	**Moderate Severity FCC**	**Higher Severity FCC**
Changing FCC Severity Assuming constant MAT and no Recycle	0.9	0.0	-2.5
Minimize Diesel in FCC Feedstock	3.2	3.4	3.6
Lower FCC Naphtha End Point	5.1	5.3	4.6
Change FCC Catalyst Formulation Increase FCC Catalyst Matrix Activity and Reduce Hydrogen Transfer Activity	1.3	1.3	1.3
Refractionate Slurry Oil Recover 30 vol% LCO from slurry	1.1	0.7	0.6
Oligomerize C3 - C5 Olefins	3.1	3.7	5.1
Oligomerize C6+ Naphtha Olefins	3.8	4.3	2.6
Total Increase in Diesel Production, vol%	**18.4**	**18.6**	**15.3**

Conclusions

Assuming the demand for diesel continues to increase faster than the growth in gasoline, a number of reactions can be broadly expected across the refining industry.

- The loss of virgin diesel to the FCC unit will diminish through crude distillation unit improvements.
- FCC gasoline end point will be minimized.
- Hydrocracking and hydrotreating units designed to upgrade LCO quality will proliferate.
- Low hydrogen transfer, higher matrix surface area FCC catalyst will be used to improve LCO yield and quality while increasing LPG olefin production and naphtha octane.
- In some cases, ZSM-5 catalyst additives will be used to further increase LPG olefin production and octane, but in low severity FCC operations this may come at the expense of some LCO yield.

For refiners that also place high values on propylene production, high octane gasoline, and minimization of refinery bottoms production, the high severity FCC route to making more diesel will gain favor though the oligomerization of C4 and higher FCC olefins while continuing to hydroprocess the LCO production. If a refiner has a more singular focus on the production of diesel, the low severity, traditional FCC route to increasing diesel can be optimized and economically favored with some of the following enhancements.

- The loss of LCO in slurry oil product or recycle will diminish through the use of dedicated slurry distillation hardware.
- Synergistically, some of the stripped slurry oil may be recycled to the FCC reactor to produce more LCO and help maintain FCC heat balance, while HCO recycle may also be advantageous.
- Low severity FCC operations will rely on increasing feed temperature and in some cases direct firing of the regenerator with a liquid or gaseous fuel using technology designed to minimize damage to the catalyst.
- FCC produced LPG and naphtha olefins will be converted into good quality diesel blending stock using oligomerization processes.

An ultimate vision for maximizing diesel production in a specific FCC centric refinery may also include a selective combination of the following elements:

- Extraction processes will separate aromatics rich fractions of FCC gasoline from fractions enriched in olefins and paraffins. The aromatic fraction can be used for BTX production or high octane motor fuel; the non-aromatic fraction can be recycled to the FCC reactor for the production of more olefins (diesel precursors) or the olefins in the non-aromatic fraction may be directly oligomerized into diesel .
- FCC C4's and FCC light naphtha can be recycled to an ultra-high severity FCC riser to increase propylene and aromatic naphtha yields without diminishing LCO production.

A case by case analysis based on refinery specific data is needed to accurately contrast the costs and benefits associated with the application of various options for increasing diesel production from the FCC centered refinery. The performance of the study requires both refinery-wide and FCC specific experience and related modeling capabilities. In the final analysis, it is just a question of economics. Technologies are available to maximize diesel production from the FCC centered refinery.

References

1. Blake Eskew, “The Diesel Challenge – and Other Issues Facing U.S. Refiners”, NPRA Q&A and Technology Forum, Champions Gate, Florida - October 6, 2008
2. Nicholas Flinn and Salvatore P Torrisi, Jr. (Criterion Catalysts & Technologies), “LCO Upgrading Options: From Simple to Progressive Solutions”, 8th Russia & CIS Refining Technology Conference & Exhibition, Moscow, 25 September 2008
3. Re G.H. Unzelman, “Potential Impact of Cracking on Diesel Fuel Quality”, Katalistiks Fourth Annual Fluid Cat Cracking Symposium, Amsterdam, May 18-19, 1983.
4. David Hunt, Ruizhong Hu, Hongbo Ma, Larry Langan and Wu-Cheng Cheng, “Recycle Strategies and MIDAS-300® for Maximizing FCC Light Cycle Oil”, Catalagram Number 105, W.R. Grace &Co., Spring, 2009
5. Robert B. Peterson, Chris Santner and Michael Tallman, U.S. Patent 7,153,479
6. Maureen F. Gilbert, Michael J.Tallman, William C. Petterson and Phillip K. Niccum, “Light Olefin Production From SUPERFLEX^{sm} And MAXOFIN™ FCC Technologies”, ARTC Petrochemical Conference in Malaysia, 12 February 2001
7. Rik Miller, Tiffin Johnson, Chris Santner, Amos Avidan and David Johnson, “FCC Reactor Product-Catalyst Separation – Ten Years of Commercial Experience with Closed Cyclones”, NPRA Annual Meeting, March 19-21, 1995, San Francisco, CA
8. Rahul Pillai and Phillip K. Niccum, “FCC Catalyst Coolers Open Window to Increased Propylene”, Grace Davison FCC Conference, Munich – September 2011
9. Michel Melin, Colin Baillie and Gordon McElhiney, “Salt Deposition in FCC Gas Concentration Units”, Catalagram Number 107, W.R. Grace &Co., 2010
10. M. Akbar, B. Claverin, M. Borley and H. Otto, “Some experiences with FCC octane enhancement”, Ketjen Catalysts Symposium, May 25-28, 1986, Kurhaus, Scheveningen, The Netherlands
11. Ray Fletcher, Meeting Transcript, 1997 NPRA Q&A Session – Refining and Petrochemical Technology, October 1997, New Orleans, LA, Question 18, page 66
12. Andrew Sloley, Refinery Process Services - FCC Network News, Volume 35, January 2010
13. A.W. Sloley, “Increase diesel recovery”, Hydrocarbon Processing, June 2008
14. “Ronald Ritter, David Wallace, James Maselli, “Fluid Cracking Catalyst to Enhance Gasoline Octane, Catalagram Number 72, W.R. Grace &Co., 1985
15. Philip Thiel, “Additive O-HS Davison’s Octane/Olefin Enhancing Additive”, Catalagram Number 81, W.R. Grace &Co, 1990
16. A.K. Das, YV. Kumar, V.R. Lenin and S Ghosh, “Performance of ZSM-5 Additive in Distillate FCC Units”, Akzo Catalyst Symposium 1991 Fluid Catalytic Cracking, June 1991, Scheveningen, The Netherlands, 1991
17. L.D. Silverman, S. Winkler, J.A. Tiethof and A. Witoshkin, “Matrix Effects in Catalytic Cracking”, 1986 NPRA Annual Meeting, March 23-25, Los Angeles, California
18. Nicholas Flinn and Salvatore P. Torrisi, Jr. (Criterion Catalysts & Technologies), “LCO Upgrading Options: From Simple to Progressive Solutions”, 8th Russia & CIS Refining Technology Conference & Exhibition, Moscow, 25 September 2008
19. Ernst Kohler, Mike De Pontes, Friedrich Schmidt and Hans J. Wernicke, “Converting olefins to diesel – the COD process”, Hydrocarbon Technology International, Summer 1995
20. J. Gentry and W. Jin, “FCC gasoline and C4 streams for BTX production, PTQ Q4 2009
21. Anand Subramanian and Alan Claude, U.S. Patent 7,883,618

22. Phillip K. Niccum, “Maximizing Diesel Production in the FCC Centered Refinery”, AFPM (NPRA) Annual Meeting, March 11-13, 2012, San Diego, California