



LCO UPGRADING

A NOVEL APPROACH FOR GREATER ADDED VALUE AND IMPROVED RETURNS

Vasant P. Thakkar, Suheil F. Abdo, Visnja A. Gembicki, James F. Mc Gehee, and Bart Dziabala
UOP LLC
Des Plaines, Illinois, USA



INTRODUCTION

LCO IN THE CLEAN FUELS REFINERY

As refiners plan to meet regulations for clean fuels, one of the many considerations they face is the disposition of light cycle oil (LCO). It is a poor diesel fuel blending component due to its poor engine ignition performance and its high sulfur. Beyond middle distillate blending, LCO has also historically been used as a blend-stock into heavy fuel oil for viscosity adjustment. This opportunity is also becoming constrained by declining demand for heavy fuel oil. In the overall context of a high conversion, clean-fuels refinery, light cycle oil is an issue, both in terms of product blending and product-value maximization. In addition to the use of conventional hydrotreating, high pressure hydrocracking units have historically been used to crack LCO into naphtha and lighter products. These units are relatively high in capital cost, consume large quantities of hydrogen, and the naphtha product requires reforming before blending to gasoline. This paper will address an alternative LCO processing solution to the growing demand for clean fuels and product slate flexibility with much lower capital investment.

NEW TECHNOLOGY FROM UOP

UOP is pleased to introduce a new and commercially available technology, the LCO Unicracking™ process. The technology solves the problem of LCO disposition by economically converting it to ULSD and high octane gasoline suitable for direct blending without need for further reforming. UOP's new HC™ 190 catalyst, coupled with process innovations, enables an LCO Unicracking unit to operate at much lower pressure relative to conventional hydrocracking unit. The key feature of the technology is selective hydrogen addition, focusing on desulfurization and hydrogen addition to the diesel product, while minimizing naphtha aromatic saturation. The low pressure flow scheme, coupled with efficient hydrogen utilization, provides superior economics compared to a conventional hydrotreating solution.

WORLD WIDE REFINING TRENDS

World oil demand is projected to continue increasing, at a rate of about 1.8% per year, with increased growth of transportation fuels and a decrease in fuel oil. Worldwide the diesel demand now exceeds that of gasoline, with the ratio of diesel to gasoline exceeding 1.0 in some areas, such as Europe. In the US most of the 400,000 barrel annual increase in crude consumption will be used for transportation fuels, with gasoline representing about 45% of the total petroleum consumption.

Coupled with this demand pattern is the changing regulatory picture for transportation fuels. By 2006, the US on-road diesel pool specification will be set at a maximum of 15 ppm sulfur and minimum 40 cetane number (or maximum aromatics level of 35%), with gasoline sulfur specified at a maximum of 30 ppm, a benzene maximum of 1%, and total aromatics at maximum 35%. Beyond 2006, there are pending regulations calling for a gradual merging and harmonization of sulfur specifications for on road and off road diesel. This second wave of regulations is expected to be complete by the end of decade.

How will these trends affect LCO as a distillate pool component? LCO comprises about 15% of the total US distillate pool, and by 2006, it will mainly be suitable as a blend component for lower quality distillate products including off-road diesels, heating oil and marine fuels, or as a cutter stock for heavy fuel oils. It will become increasingly difficult to blend LCO as the specifications for the on-road and off-road diesel pools are harmonized to the same ultra low sulfur levels.

CHARACTERIZATION OF LCO

The total worldwide installed FCC capacity is approximately 14 million BPSD, with an overall production of about 3 million BPSD of LCO. The majority of FCC capacity is in North America, followed by Europe and Asia. Operating severity varies depending upon the market. For example, North American refiners operate their FCC units at high severity to maximize gasoline

production with LCO yield of less than 20%, whereas European refiners operate a lower severity for greater LCO production.

Cracked products such as LCO and coker distillates have a considerably lower cetane value compared to straight run distillates derived from most of the world's crude sources. LCO cetane ranges from 15-25, compared to 40-60 for the straight run distillates produced from the same crude.

The sulfur content in average light cycle oils can range from 0.2 to 2.5 wt%. A detailed sulfur speciation of LCO shows that a significant portion of the sulfur is found in alkyldibenzothiophenes (DBT), which are relatively difficult to desulfurize by hydrotreating. The aromatics content of LCO from FCC units in a normal gasoline-oriented operation can be as high as 80 wt-%. The organic nitrogen is almost entirely composed of non-basic aromatic compounds, such as carbazoles, with a concentration range of 100-750 ppm. The components of LCO boil in the diesel range with a 95% point of 360°C or higher, representing thermally stable cracked hydrocarbons that are not further reacted in the FCC process. Over 70% of the aromatic hydrocarbons present in LCO have two rings, while the remainder is typically evenly split between single ring and 3-plus ring aromatics. Two and 3+ ring aromatics combust poorly in the diesel engine. They have very low cetane values and are the root cause of the low blending quality of LCO.

It is necessary to saturate and open the di-aromatic rings to increase the fuel value of products from LCO upgrading. These reactions are a fundamental pathway in hydrocracking reaction chemistry and thus this process is ideal for converting LCO to a higher quality diesel product. Single ring aromatics boiling in the gasoline range are excellent high octane components in the gasoline pool. Aromatic ring manipulation is the key to producing higher value gasoline and diesel.

OPTIONS FOR UPGRADING LCO

As discussed earlier, pending diesel sulfur specifications effectively eliminate the option to directly blend the LCO into the on-road diesel pool. Further, harmonization of on-road and off-road diesel specifications will mean that blending LCO into off-road diesel will also no longer be possible. Blending raw LCO into the fuel oil and heating oil pool will remain an option but those products will experience market demand shrinkage in the future. Thus, cost-effective upgrading of LCO is becoming increasingly important.

The two main processes for upgrading LCO are hydrotreating and hydrocracking. UOP licenses the Unionfining™ process and the Unicracking process, respectively, for these applications.

UNIONFINING PROCESS

Table 1 shows an inspection of a typical LCO sample containing 0.7 wt-% sulfur. Approximately 300 ppm of the sulfur is contained in molecules that are very difficult to desulfurize by hydrotreating. As a result, hydrotreating LCO to improve its diesel pool blending characteristics is a challenge not only from the standpoint of its high aromatics content but also due to the nature of its sulfur species. Hydrotreating LCO to reduce its sulfur content to an ultra-low level requires high severity operation. However, high pressure hydrotreating results in over saturation of aromatics and inefficient use of hydrogen for only a modest cetane improvement. Some tri- and higher ring aromatics are converted to lower aromatics but the total aromatic content of the LCO still remains high and relatively little cetane improvement is realized. Figures 1 and 2 show that even at low pressure there is significant conversion of polyaromatics to monoaromatics and most of the cetane boost is accomplished at low hydrotreating pressures. As pressure is increased to promote deep desulfurization, little further increase in cetane takes place.

Another important aspect of LCO upgrading is that in the absence of significant conversion of aromatics through cracking reactions, the saturation reactions proceed only to their equilibrium limit. A typical temperature and pressure range of most hydrotreaters places a ceiling on how far the cetane index of the LCO can be improved via simple partial saturation of aromatic rings.

In summary, hydrotreating of LCO for deep sulfur removal requires relatively high pressure and hydrogen consumption, yet achieves only limited improvement in cetane number, total aromatics, and density.

Table 1

Sulfur Speciation of Typical LCO

API	15.4
IBP – EP, °F	410-680
Cetane Index	23.1
Total Sulfur, wt-%	0.7
4,6 dimethyldibenzothiophene, ppm	56
4-methyldibenzothiopene, ppm	231
Other sulfur species, ppm	702
Total Nitrogen, ppm	257

Figure 1

Hydrogenation of Aromatics as a Function of Pressure

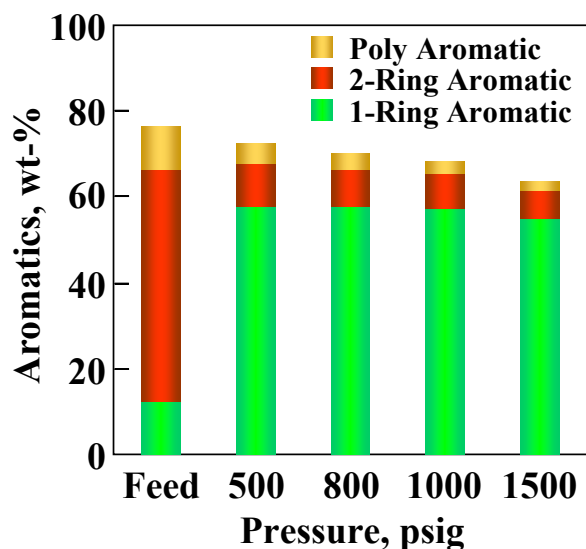
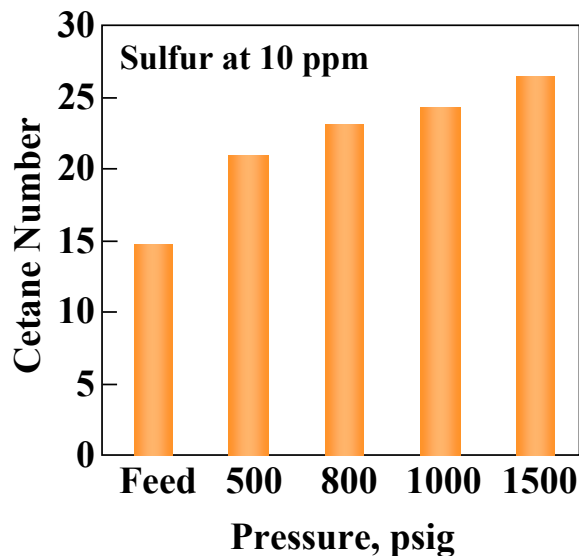


Figure 2

Cetane Number as a Function of Pressure



FULL CONVERSION UNICRACKING PROCESS

As an alternative to conventional hydrotreating, the hydroprocessing severity can be expanded to include hydrocracking reactions. The process goal in this case is to saturate and open the multi ring aromatic compounds to increase the blending value of products. These reactions are a fundamental part of hydrocracking reaction chemistry, and full conversion hydrocracking of LCO to naphtha is a well established commercial process. However, unlike the high octane gasoline made in the LCO Unicracking process, the gasoline boiling-range product from full conversion hydrocracking is a highly naphthenic, low octane naphtha that must be reformed to produce the octane required for product blending, incurring additional operating expense.

NEW UNICRACKING TECHNOLOGY FROM UOP

UOP's newly announced *LCO Unicracking* technology enables substantially reduced capital and operating costs while producing gasoline and diesel streams for direct ULSD and ULSG pool blending. It is highly selective in controlling the hydrocracking reactions in a partial conversion operating mode to achieve good hydrogenation of the diesel fraction, while preserving aromatics in the gasoline range product. Depending on a refiner's product needs and product quality targets, aromatic ring manipulation is the key to producing high-value gasoline and diesel from LCO. In order to accomplish these parallel objectives, UOP has combined process innovations with HC 190 catalyst, a new, high-activity catalyst for effectively upgrading LCO in a partial conversion hydrocracking process configuration.

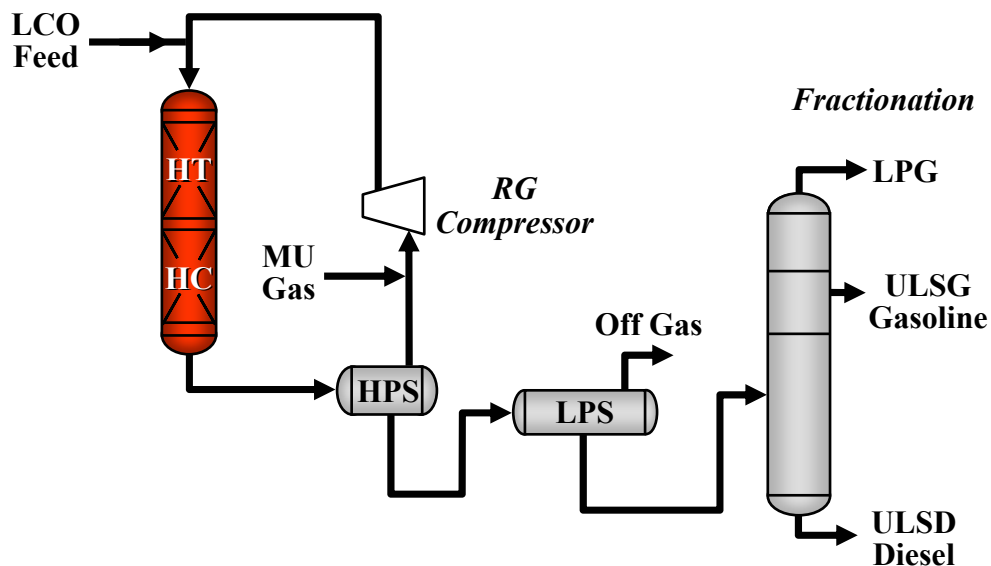
HC 190 CATALYST

HC 190 catalyst was shown to be well suited to accomplish the desired chemistry for partial conversion LCO hydrocracking. It is designed to provide significantly higher activity than the current naphtha hydrocracking catalysts. For example, its performance on a cracked stock blend, containing light cycle oil, shows about 15°F higher activity and higher naphtha yield at equivalent hydrogen consumption compared to current commercial catalysts. It has demonstrated superior performance in pilot plant tests for partial conversion of LCO by maximizing retention of single ring aromatics, thus producing a higher octane naphtha product. It also produces diesel with very low sulfur levels.

LCO UNICRACKING PROCESS

The LCO Unicracking process uses partial conversion hydrocracking to produce high quality gasoline and diesel stocks in a simple once-through flow scheme. The basic scheme is shown in Figure 3.

Figure 3
LCO Unicracking Process



The feedstock is processed over a pretreatment catalyst and then hydrocracked in the same stage. The products are subsequently separated without the need for liquid recycle. The advantage of the LCO Unicracking process is that it can be designed for lower pressure operation. The pressure requirement will be somewhat higher than high severity hydrotreating but significantly lower than a conventional partial conversion and full conversion hydrocracking unit design. The upgraded middle distillate product makes a suitable ultra-low sulfur diesel (ULSD) blending

component. The naphtha product from low-pressure hydrocracking of LCO has ultra-low sulfur and high octane and can be directly blended into the ultra-low sulfur gasoline (ULSG) pool. Thus, the LCO Unicracking process offers excellent flexibility to increase the value of LCO by upgrading its products to ULSG and ULSD blending targets.

ANALYTICAL TECHNIQUES

Recent advances in hydrocarbon analysis have made it possible to speciate distillate fuels at the molecular level. UOP has developed a technique, which uses comprehensive gas chromatography, also called GCxGC, that enables resolution of hydrocarbon species in a three-dimensional map. One axis distinguishes by boiling point, the second axis distinguishes by polarity, and the vertical axis measures the relative concentration (Figures 4 and 5). This type of graphical representation significantly enhances the understanding of complex hydrocarbon mixtures like LCO. Advanced procedures to analyze and interpret this data are being developed at UOP and have been crucial in understanding the fundamental chemistry and pathways associated with different catalysts and reaction conditions. It will allow more precise feedstock characterization and facilitate better understanding and control of the desired molecular transformations

Figure 4
Comprehensive GC Speciation of LCO

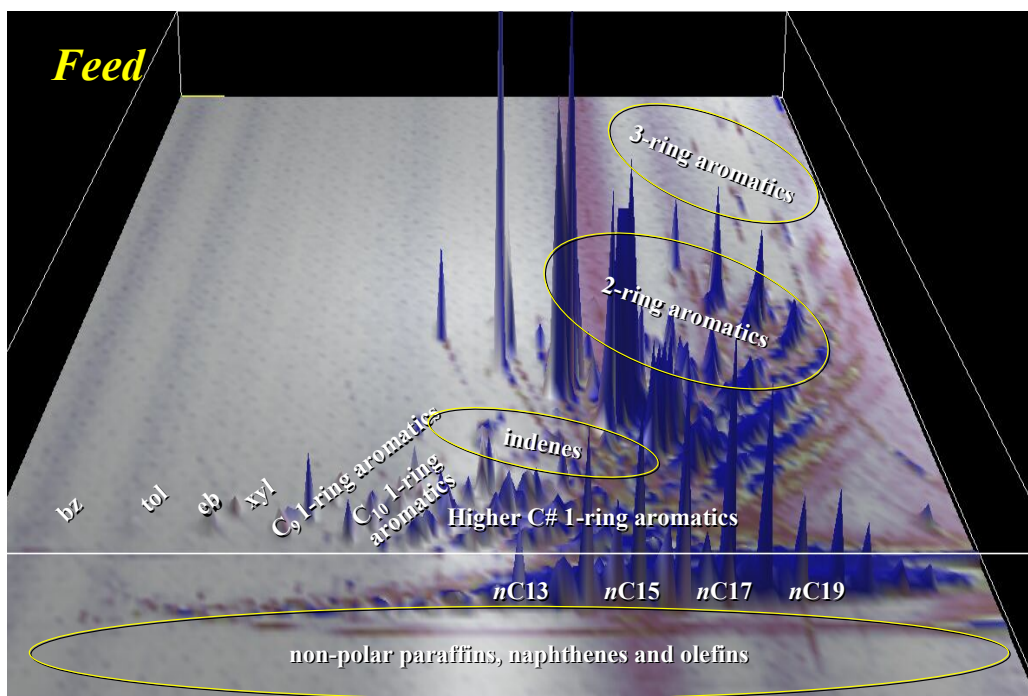
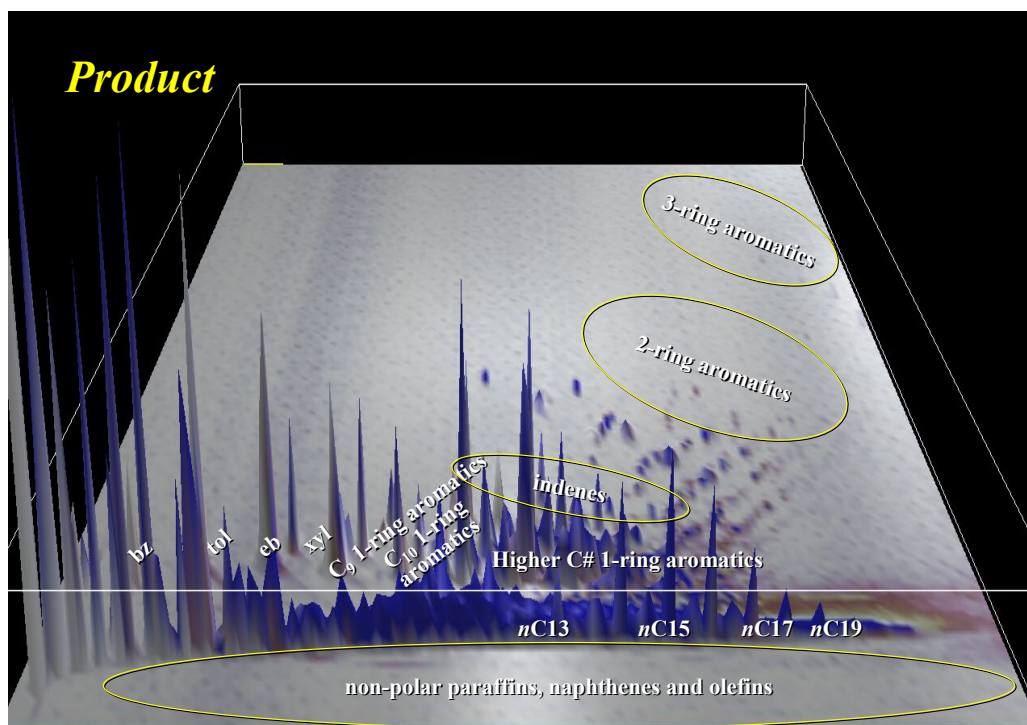


Figure 5
Comprehensive GC Speciation of Hydrocracked LCO



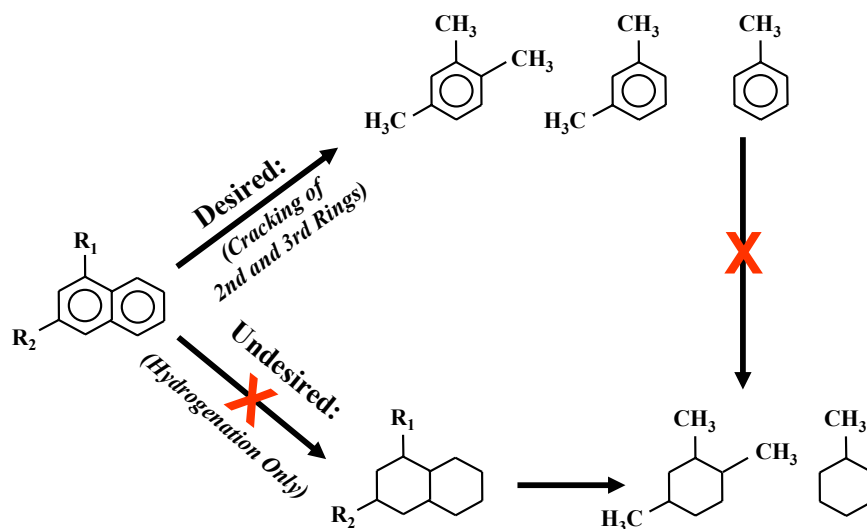
PILOT PLANT EVALUATION

In partial conversion hydrocracking of LCO, the severity must be optimized so that the naphtha product has high octane for direct blending to gasoline without the need for reforming. At the same time, the diesel product must be hydrogenated to produce a higher cetane, ultra-low sulfur blendstock. Finally, ring saturation and ring opening need to be highly selective to make efficient use of hydrogen. These objectives require unique catalyst chemistry and operating conditions to maximize the yields and qualities of the desired products.

An example of a preferred reaction is shown for a typical two-ring aromatic hydrocarbon, 1,3-dialkylnaphthalene, in Figure 6. The desired reactions shown in the figure are those to saturate and open one ring to yield a mixture of alkylaromatics in the naphtha boiling range.

Pilot plant tests were conducted on representative commercial LCO feedstocks. The key properties of these feeds covered wide ranges of aromatic content and distribution, sulfur and nitrogen content and distillation characteristics. Their properties are listed in Table 2. The tests were all conducted in partial conversion hydrocracking mode at relatively mild conditions.

Figure 6
Preferred Reaction Pathway



Typical cracked product characteristics using HC 190 catalyst are listed in Table 2. It can be seen that the high activity and unique cracking characteristic of HC 190 catalyst enable good

Table 2

LCO Unicracking Process Pilot Plant Evaluation

Feedstocks:	
Origin	Commercially derived LCOs
API Gravity	15.1 – 19.0
Sulfur, ppm	2290 – 7350
Nitrogen, ppm	255 – 605
Aromatics, IP391, wt-%	
1 – ring	12 – 21
2 – ring	40 – 55
3+ rings	8 – 14
Distillation, ASTM D-2887, °F	
95%	660 – 710
EP	725 – 790
Cetane Index, ASTM D-4737	22 – 25
Operating Mode:	Partial Conversion
Products:	
Light Naphtha Yield, wt-%	10.5 – 13.5
Heavy Naphtha	
Yield, wt-%	35 – 37
RONC	90 – 95
Sulfur, ppm	< 10
Diesel	
Yield, wt-%	46 – 51
Cetane Index Improvement	+6 to +8
Sulfur, ppm	<10

aromatic retention in the gasoline range product as demonstrated by the high research octane number. The diesel range product contains less than 10 ppm sulfur and low aromatic content, well within ULSD fuel specification limits. Its cetane index ranges from 6 to 8 numbers higher than the LCO feed.

Extended stability tests of more than six months of continuous operation at low pressure have confirmed excellent catalyst stability while maintaining the cracking conversion and product qualities. Stable yields of products were obtained over the entire period, with slight improvement observed in the gasoline octane with time on stream.

REFINERY APPLICATIONS

The potential impact of LCO Unicracking employed in a typical US refinery was examined by comparing it against the alternative of deep LCO desulfurization by high pressure hydrotreating.

BLENDING OF TRANSPORTATION FUEL POOLS

In order to assess the potential impact of upgrading these two options, a “typical” US coker/FCC-based refinery was considered. The refinery capacity was set at 300,000 BPSD of crude oil. The refinery and gasoline pools had the following products available for blending:

Gasoline Pool

Treated FCC gasoline
Hydrotreated light straight run naphtha
Reformate
Alkylate (to premium)
Purchased MTBE (to meet oxygen specification for RFG)
Butanes for RVP adjustment
LCO Unicracking unit gasoline

Diesel Pool

Jet Fuel blending components
 Kerosene
 Hydrotreated kerosene

Ultra-low sulfur diesel components
 Hydrotreated kerosene
 Hydrotreated straight run diesel
 LCO Unicracking unit diesel or hydrotreated LCO (case study)

All process units were sized to be consistent with the design crude oil capacity, and assumed to operate at “typical” conditions for a US refinery. The new LCO Unicracking unit or the hydrotreating unit cases were sized at a 20,000 bpsd capacity. The gasoline and diesel pools were blended to meet the 2006 US quality regulations. In order to reflect the next wave of diesel regulations, the diesel pool blend was based on harmonized on-road and off-road diesel specifications, i.e. the entire pool must attain an ultra low sulfur level of 15 ppm or less.

The estimated quantities and qualities of the blended gasoline and diesel products are detailed in Table 3. The results show that both solutions, i.e. the LCO Unicracking process or high pressure hydrotreating will enable production of acceptable ultra-low sulfur diesel which can be entirely blended into the diesel pool. Due to selective chemistry of the LCO Unicracking process however, this route produces 3-5 points higher cetane index than the hydrotreating route. Both routes produced a cetane index in excess of the 2006 specification. By employing the LCO Unicracking solution, the refiner will be better prepared for expected future upward changes in the cetane specifications. Additionally, LCO Unicracking process yields a high octane and ultra low sulfur gasoline, which can be blended directly into the gasoline pool without jeopardizing the pool specifications for octane, sulfur, or aromatics. The small amount of naphtha produced in the hydrotreating case is sent to a reformer prior to blending into the pool. Due to the high octane of the gasoline produced via the LCO Unicracking process, the overall refinery pool octane is not changed by direct blending of this product into the pool.

The installation of an LCO Unicracking unit increased gasoline production by about 10% while decreasing the diesel production by 13% compared to the hydrotreating unit option. The addition of an LCO Unicracking unit has the benefit of varying diesel/gasoline slate to meet the refiner’s seasonal demand.

Table 3
Refinery Gasoline and Diesel Pool Yields and Qualities
As a Function of the LCO Upgrading Option

<i>Type of LCO Upgrading</i>	<i>Hydrotreating</i>	<i>LCO Unicracking Process</i>
Gasoline pool:		
Volume, BPSD	134,616	148,242
RONC / MONC	92.2/83.7	92.1/83.8
Sulfur, ppm	<30	<30
ULSD Pool:		
Volume, BPSD	104,763	92,871
Cetane Index	45	48
Sulfur, ppm	<10	< 10

ECONOMICS OF LCO UPGRADING OPTIONS

The economics of LCO upgrading are a function of many factors, such as product pricing, and also the value assigned to LCO feedstock, which is in turn a function of its end-product disposition. The refiner has generally three options:

- Invest in a hydrotreating unit, which requires lower capital investment and operating cost, but results in inflexible product slate, i.e. mainly diesel product.
- Invest in an LCO Unicracking unit, which requires higher capital and operating cost than the hydrotreating unit. This solution enables a flexible yield of both ULSD and high octane gasoline, ready for the pool blending.
- In a special case where the refiner needs to add new unit capacity for straight run or coker distillate hydrotreating, in addition to investing in an LCO Unicracking unit, an integrated plant solution is a very attractive option. The synergy resulting from parallel reaction system for hydrocracking LCO and hydrotreating the other refinery distillate streams within the shared recycle gas system and common downstream separation, can provide as much as 30-40% capital savings compared to building two stand alone units. Furthermore, with this strategy a refiner's ULSD project and capital investment can be consolidated into a single project versus multiple unit revamps.

ECONOMIC PROJECTION CASE STUDY

The following study compares the relative economics for upgrading light cycle oil using an LCO Unicracking process versus an LCO hydrotreating process. The scenario is that of a nominal 300,000 bbl/d FCC-coker based US refinery. The refiner wishes to upgrade LCO to produce both ULSD and ULSG products. Prices for this study are based on market averages from early 2004 period.^(2,3) The value of LCO was derived from its alternate use as a fuel oil blending component. Additional hydrogen need was met with purchased hydrogen, while the estimated ISBL erected costs are based on US Gulf Coast construction for the 4th quarter of 2004.

The purpose of the case study was to:

- Determine the investment payback on an LCO Unicracking unit designed to produce a flexible product slate of both ultra-low sulfur diesel and high octane gasoline blendstocks, and compare the economics to hydrotreating only.
- Determine the sensitivity of payback and net present value to the price differentials between the primary products, gasoline and ULSD, and to the differential between LCO and ULSD value.

PERFORMANCE AND ECONOMICS

Table 4 summarizes economic projections for the addition of either a hydrotreating unit or an LCO Unicracking unit solution for LCO upgrading in the refinery study.

Table 4
Process Economics

<u><i>Type of LCO Upgrading</i></u>	<u><i>Hydrotreating</i></u>	<u><i>LCOUnicracking</i></u>
Unit Capacity, BPSD	20,000	20,000
Yield, Lt and Hvy Naphtha, wt-%	1.6	57
Yield, ULSD, wt%	98.9	41.6
Estimated ISBL Investment Cost, \$M	36.4	61.4
10 yr NPV, \$M	(1)	203
Simple Payout, yrs	6.5	2.1

The LCO Unicracking project produces a very attractive positive 10 yr NPV of \$203M and results in a simple payout of two years. LCO hydrotreating option has a negative NPV and a payout time of six years, i.e. it is a ‘stay-in-business’ solution imposed by the regulatory requirements.

The sensitivity analysis of the two solutions was done using two comparative parameters; price differential between ULSD and LCO, and a price differential between gasoline and ULSD. The results are depicted in Figures 7 and 8. It is shown that the LCO Unicracking solution retains the same advantage over the hydrotreating solution for a range of price differentials. As expected, the Unicracking solution advantage increases as the price differential between gasoline and diesel increases. It should be noted that this analysis is specific to market where gasoline is a higher priced product, as for example, in the US. A somewhat different case study was described recently in another publication which was focused on the European refinery setting and market pricing ⁽¹⁾.

Figure 7

NPV Sensitivity to ULSD-LCO Differential

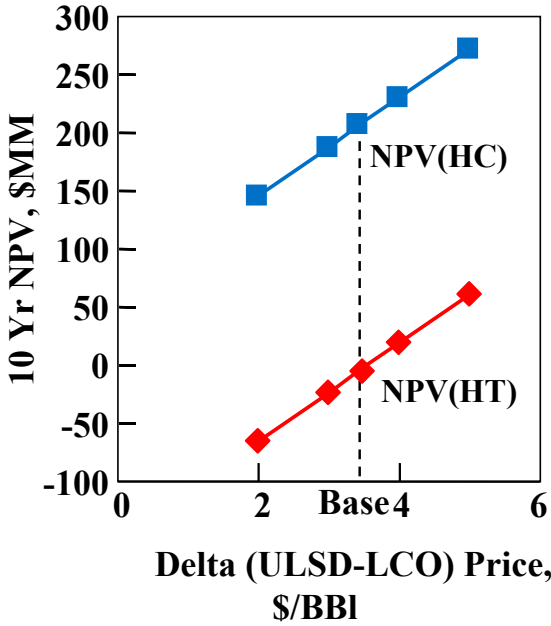
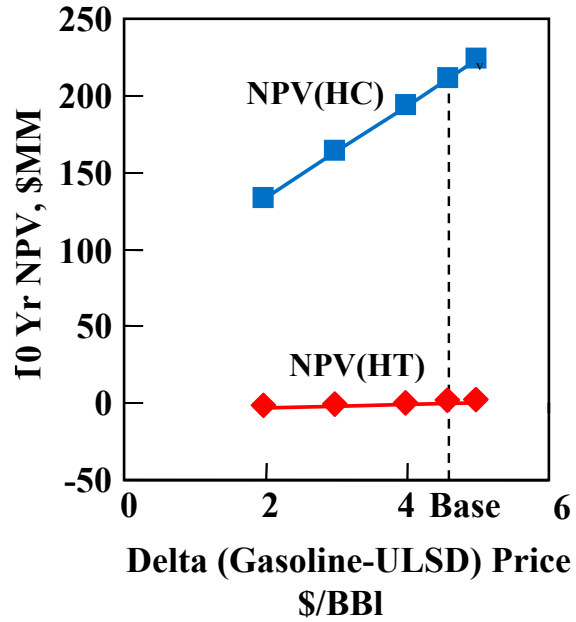


Figure 8

NPV Sensitivity to Gasoline-ULSD Differential



CONCLUSIONS

LCO is a distressed refinery stream with limited future disposition options without further significant upgrading. Refiners will have to consider investments in technology to upgrade the LCO to higher value transportation fuels as they prepare for clean fuels production and increased market demand in the future.

In this paper we have announced our new, commercially available technology, the LCO Unicracking process, ideally suited for production of ULSD and ULSG blendstocks from LCO at relatively mild conditions. The unique selectivity characteristics of our new HC-190 catalyst are also an important enabler in the new process. The LCO Unicracking process makes efficient use of hydrogen by employing advanced catalytic know-how to selectively increase the hydrogen content of the diesel range product while minimizing saturation of aromatics in the naphtha range.

The process economics for a US based refinery have shown that the investment in an LCO Unicracking unit yields superior NPV and provides a good payout compared to a conventional hydrotreating solution.

REFERENCES

1. V. P. Thakkar, V.A. Gembicki, D. Kocher-Cowan, S. Simpson, “LCO Unicracking Technology – A Novel Approach for Greater Added Value and Improved Returns,” ERTC, 2004
2. Crude Oil Prices, EIA petroleum marketing Monthly, www.eia.gov
3. Product prices obtained from historical North American data of Platts, and CMAI, www.platts.com, and www.cmaiglobal.com

UOP LLC
25 East Algonquin Road
Des Plaines, IL 60017-5017
© 2005 UOP LLC. All rights reserved.

UOP 4399B