



Recycle and Catalytic Strategies for Maximum FCC LCO Operations

Ruizhong Hu, Hongbo Ma, Larry Langan, Wu-Cheng Cheng and David Hunt, Grace Davison

New catalysts designed for maximum LCO production can help refiners adjust to higher distillate demand. Distillate demand is expected to exceed gasoline demand in several refining regions. For example, according to a study released in December 2010 by the International Energy Agency (IEA):¹ "Global demand growth (in the oil markets) is heavily biased towards middle distillates, accounting for 62% of total growth by 2015, creating a bottleneck for refiners." Within this context, maximum LCO optimization strategies will benefit many refiners.

LCO Optimization Strategies

LCO as an intermediate FCC product typically reaches 19 wt% production at 40% unit conversion using a typical high zeolite-to-matrix (Z/M) catalyst formulation. A low Z/M formulation with LCO and bottoms selectivity can improve LCO production to more than 23 wt% at 40% unit conversion. A maximum LCO optimization strategy involves the following considerations:

- Reduced gasoline endpoint while maximizing LCO endpoint
- Feedstock: Removal of diesel-range material from FCC feedstock and optimization of FCC feed hydrotreating severity and residual feedstock
- Operating conditions: Lower reactor temperature, higher feed temperature and lower E-cat activity
- Catalyst optimization for additional bottoms results: Increased bottoms conversion,

lower zeolite and higher matrix surface area, lower activity and preserving C₃+ liquid yield and gasoline octane.

To fully maximize LCO, recycle is required to maintain bottoms yield as conversion is reduced. Laboratory simulation of the recycling operation helps refiners select the best recycle stream (e.g., heavy cycle oil or bottoms). Lab simulation also helps determine optimal specific boiling range and to what extent feedstock type plays a role in recycle stream optimization. In one commercial unit, a two-pass Davison Circulating Riser (DCR) + ACE scheme was adopted to simulate the recycling operation in a commercial unit. The DCR generated 650+ °F material over a 75 to 54 wt% conversion range using a resid and VGO feedstock. The 650+ °F stream was distilled into desired bottom cuts, which were blended with the original resid feed. The original

feeds together with the recycle streams were then processed in the ACE fluidized bed pilot plant using the MIDAS® premium bottoms cracking catalyst. The recycle streams at 54% conversion were distilled to:

- 650-750 °F
- 650-800 °F
- 650-850 °F
- 650+ °F
- 750+ °F
- 800+ °F
- 850+ °F.

The recycle streams at 58%, 68% and 75% conversions were distilled to 650-750 °F and the quantity of each recycle stream was measured from first-pass cracking. The properties of each recycle stream were then evaluated. **Table 1** (on page 2) shows the incremental yields of 650-750 °F recycle streams.

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The 650-750 °F fractions from VGO made about the same LCO and bottoms as fresh VGO, while the 650-750 °F fractions from resid made much more LCO. In analyzing the cracking path of the hydrocarbon molecules, the 650-750 °F recycle stream from resid had a significantly higher percentage of di-aromatics (about 17.5%) than the 650-750 °F recycle stream from VGO, leading to higher amounts of LCO (Di-aromatics → LCO + R') as explained further in **Table 2**, while the 650-750 °F recycle stream from VGO had higher levels of Tri-aromatics-producing bottoms (Tri-aromatics → Bottoms + R') and Tetra-aromatics-producing coke (Tetra-aromatics → Coke + R'). Table 2 shows the results when modeling with optimal stream and catalyst system of a full-burn FCCU processing residual feedstock with the following relative product prices:

- Propylene (C₃=) at -13.9 \$/bbl
- Butylene (C₄=) at -2.5 \$/bbl
- Gasoline at 0.0 \$/bbl
- LCO at 8.0 \$/bbl
- Slurry at -18.9 \$/bbl.

The 650-800 °F recycle stream and the 650-850 °F recycle streams produced the highest LCO selectivity (with a slight coke penalty) of about 30 wt% LCO at 64 to 65 wt% conversion. Second pass cracking of the 650-750 °F recycle stream obtained at reduced conversion made more LCO (12 wt% LCO at 55% conversion) than cracking fresh feed with almost no penalty on coke and gasoline. There is a large coke debit at increased conversion (e.g., 20 wt% coke at 75% conversion).

Catalyst Strategies for Maximum LCO

The MIDAS® Technology Platform's optimal matrix surface area, pore size and pore distribution maximizes bottoms cracking to LCO. It is the most effective catalyst formulation for maximum LCO via Type I, II and III cracking as shown in **Figure 1**. Its reduced zeolite surface area minimizes LCO conversion while optimal E-cat MAT provides

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Table 1. Incremental Yields of 650-750 °F Recycle Streams.

Boiling Range	VGO	650-750 °F from VGO	Resid	650-750 °F from Resid
Recycle Ratio, wt%	0	10.5	0	7.3
Cat-to-Oil Ratio	3.29	3.49	3.43	4.8
Dry Gas, wt%	0.7	0.73	1.08	1.13
LPG, wt%	8.39	8.89	7.96	13.34
C5+ Gasoline, wt%	44.01	43.58	40.63	39.79
LCO, wt%	26.04	26.32	24.72	36.97
Bottoms, wt%	18.96	18.68	20.28	8.03
Coke, wt%	1.9	1.81	5.59	5.45

Table 2. Maximum LCO Yields – Fresh Feed Basis – Resid

	Max. Gasoline Base	Base, No Recycle	650-750 °F	650-800 °F	650-850 °F	650+ °F
Conversion, wt%	70	55	61.2	64.2	65.2	64.7
Recycle Ratio	0	0	0.1	0.14	0.16	0.15
Max. Recycle Available			0.1	0.14	0.18	0.24
Hydrogen, wt%	0.11	0.09	0.1	0.11	0.12	0.12
Total C1s & C2s, wt%	1.4	1	1.1	1.3	1.4	1.4
C3=, wt%	3.3	2.1	2.4	2.6	2.7	2.7
Total C3s, wt%	3.9	2.4	2.7	2.9	3.1	3.1
Total C4='s, wt%	5.1	3.9	4.5	4.5	4.7	4.8
Total C4's, wt%	8.5	5.6	6.6	6.6	6.9	7
C5+ Gasoline, wt%	49.4	40.5	44.6	46.8	47	46.4
RON	89.6	89.2	89.4	89.5	89.5	89.7
MON	78.6	77.3	77.7	77.8	77.7	77.9
LCO, wt%	20.5	24.7	28.9	30.2	29.9	29.3
Bottoms, wt%	9.5	20.2	9.9	5.6	5	6
Coke, wt%	6.7	5.6	6.1	6.5	6.7	6.7

Table 3. Maximize Profitability with MIDAS® 300 and OlefinsUltra®

Resid Feedstock Operation	Base	1	2 (optimized)
Catalyst	MIDAS® 100	MIDAS® 100	MIDAS® 300 & OlefinsUltra®
Mode	Max Gasoline	Max LCO	Max LCO
Recycle %FF (650 to 800 F)	0	11	11
Reactor Temp., °F	975	950	950
Air Blower, mscfm	Constraint	Constraint	Constraint
Wet Gas Compressor, scf/bbl	Constraint	75% of Constraint	Constraint
LGP/Gasoline, Vol%	23.9/56.7	19.3/51.9	30.0/44.0
RON/MON	92.6/80.6	90.0/79.5	92.9/80.7
LCO, Vol% FF	22.9	32	33.4
Slurry, Vol% FF	6.8	6	5
C3+, Vol% FF	110.3	109.2	112.4
Incremental \$/bbl	Base	0.1	1.4

the following advantages:

- Lower within slurry yield and liquid yield target
- Optimal rare earth for activity and hydrogen transfer.

In addition, the OlefinsMax® and OlefinsUltra® ZSM-5 based additives maintain or increase liquid yield and recover any loss of gasoline octane and LPG olefins as shown in **Table 3 (on page 2)**.

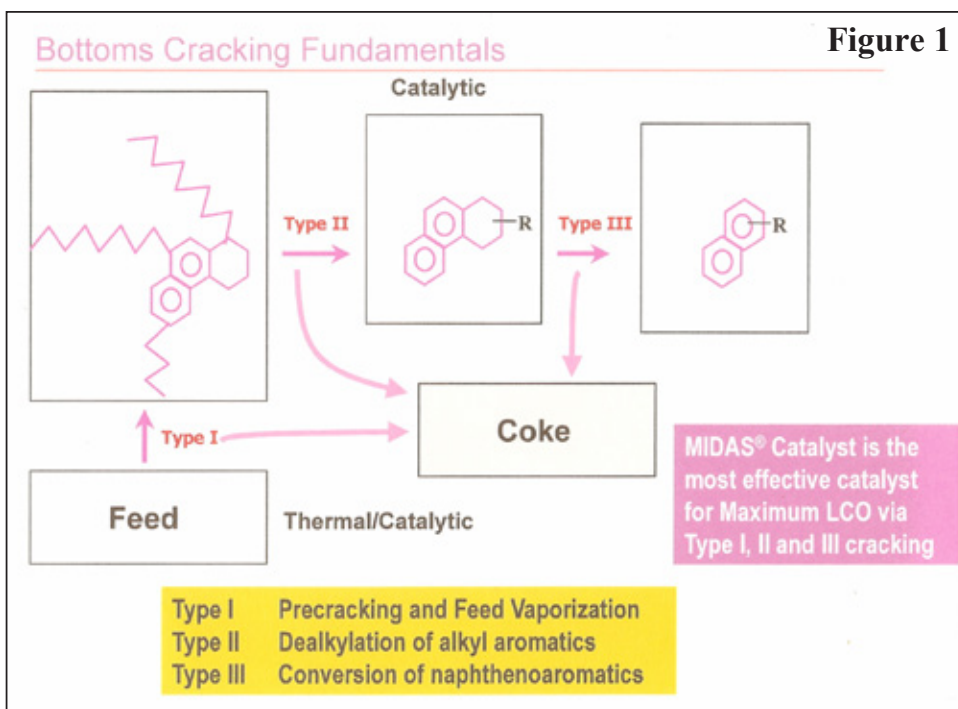
The MIDAS® 300 deep bottoms cracking catalyst (Table 3) was introduced into the market in 2008. The MIDAS® 100 metals tolerant bottoms cracking catalyst was the original invention. In addition, the BX™ 450 LCO maximization additive is based on MIDAS® 300 technology and is used at 10 to 20% of total catalyst additions.

LCO Maximization Challenges

Maximum FCC LCO operation is challenged by bottoms yield and the need to preserve C₃+ liquid yield and octane as conversion is reduced. The MIDAS® 300 catalysts and BX™ 450 additives increase LCO selectivity via improved bottoms cracking, while the OlefinsMax® and OlefinsUltra® ZSM-5 additives maintain liquid yield and gasoline octane during maximum LCO operations.

Recycle is required to fully maximize LCO. In addition, the proper catalyst system and operating conditions ensures a profitable maximum FCC LCO operation from a range of feeds.

Due to the higher di-aromatic and lower tri-aromatic level, a 650-750 °F resid recycle stream results in more LCO and less bottoms compared to



VGO. Recycle produced from first pass conversion of 55% is the optimal among 55%, 58%, 68% and 75%: more LCO is produced with almost no penalty on coke and gasoline selectivity. The 650-800 °F recycle stream produces the highest LCO when processed against a coke constraint. Coke demand will be higher to maximize LCO using a 650+ °F recycle stream. ■

1. Waldron, Michael, "Medium-Term Oil & Gas Markets 2010," International Energy Agency (IEA), December 2010.

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Note: This article is based on a presentation from the Grace Davison Refining Technologies 2010 Houston Seminar.



PROCESS OPERATIONS

Tüpra Selects UOP Hydroprocessing to Boost ULSD Yields

Tüpraş will use UOP process technologies and catalysts to improve yields and boost performance at its Izmit Refinery in Turkey. Working closely with Tüpraş personnel, UOP engineers

developed an approach integrating three new units projected to deliver about \$30 million in capital expenditure savings and greater than \$20 million per year in yield improvement benefits.

Located in the heart of the largest Turkish consumption region for petroleum products, the Izmit refinery is one of four refineries owned and operated by Tüpraş, an integrated **Cont. page 4**



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petroleum company and Turkey's largest industrial enterprise. Tüpraş has the system-wide capacity to process 28.1 million tons (about 211 million barrels) of crude oil per year. The Izmit refinery has an 11 million ton (82.5 million barrels) annual capacity. The Izmit refinery processed 10.3 million tons of crude oil in 2008, achieving 94 percent of capacity and breaking production records for the facility and for several products, including diesel and jet fuel.

UOP recommended that the refinery use an enhanced two-stage hydrocracking process to upgrade vacuum gas oil (VGO) and heavy coker gas oil (HCGO) to high value kerosene and diesel products that fully meet today's rigorous specifications. The company's engineers were able to provide a flexible hydrocracking solution tailored for the specific needs of the Izmit

refinery, based on the proven UOP Unicracking technology.

The UOP proposal recognized that creating capacity to produce more kerosene and low-sulfur diesel was the primary value driver for Tüpraş. By tailoring the Unicracking process and catalysts to meet the refinery's specific objectives, UOP engineers were able to improve yields and increase flexibility by enabling the unit to produce the highest yield of kerosene and diesel from the available feedstock available in the market.

Editor's Note: A detailed process and operations discussion on enhanced two-stage hydrocracking for upgrading VGO and HCGO is beyond the scope of this report and will be discussed in more detail in the **Innovations in Hydrocracking & Hydrotreating** special report scheduled for Spring 2011. ■

Heater Safety Practice in Hydro-processing Operations

Installation of emergency isolation equipment at the outlet of hydroprocessing reactor charge heaters is recommended on a case-by-case basis in the event of a tube rupture. The decision to install check valves or actuators at reactor charge heater outlets depends on a range of factors, including the unit's design configuration. Other important factors were discussed at the most recent NPRA Q&A and Technology Forum. It was noted during the discussion that installation of a check valve would require the valve to be placed on a periodic inspection and test program due to its designation as a "safety critical device." As many refiners are aware, the decision to install a check valve at the heater outlet would also depend on

the layers of protection required for safe operations, based on the volume of process throughput, pressure requirements (i.e., hydroprocessing operating pressures are generally increasing), type of feedstock, etc. A layer of protection analysis (LOPA) may indeed show the need for a check valve. Additional details on LOPA analysis, process hazard analysis (PHA), independent protection layers (IPLs), and other related procedures that play a role in enhancing heater safety practice can be found at the following websites:

www.primatech.com
www.process-improvement-institute.com
www.dyadem.com
www.processengr.com ■

Remedies for Meeting 2012 Benzene Limits

Mobile source air toxics (MSAT), such as benzene are a subcategory of volatile organic compounds (VOCs) discussed in detail in the EPA's "Final Regulatory

Impact Analysis" (EPA 420-R-07-002, Feb. 2007). Refinery produced benzene, 1,3 butadiene, formaldehyde and other related compounds

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fall under the MSAT category. The EPA began limiting benzene in gasoline to 0.62 vol% on January 1, 2011. In addition, a 1.3 vol% maximum average benzene standard will go into effect by July 1, 2012. However, EPA-registered small refiners will have a four-year grace period to comply with the benzene standard by 2015. According to EPA estimates, the industry-wide refin-

ery capital investment will be over \$1.1 billion or \$22,400/ton benzene.

Benzene removal strategies typically revolve around catalytic reformer operations as reformate from the catalytic reformer is generally around 4-9 vol% benzene (in comparison: crudes are less than 0.1 vol% benzene; CDU naphtha and FCC naphtha between 0.5 to 1.5 vol% benzene). One of

the most effective benzene removal strategies involves removing benzene precursors from reformer feed. Other strategies typically involve proprietary processes, of which there are various configurations, depending on overall refinery configuration, and will be discussed in the upcoming issues of *Refinery Operations*. ■

Compressor and Turbine Training Modules for Operators

A company known as RDC (Resource Development Corporation) that was the exclusive content developer for the American Petroleum Institute dating back to 50 years has posted its critical fundamental courses that are designed to progress someone with little or no knowledge of the mechanics and operation of turbines or compressors, such as the following curricula:

1052a Positive Displacement Compressors: Introduction:

In the hydrocarbon processing and production industry, gas is compressed for transportation to consuming markets and for use in processing operations. This program is an introduction to positive displacement compressors. This program teaches the operating principles of reciprocating compressors, different types of rotary compressors, and techniques for controlling compressor output.

1052b Positive Displacement Compressors: Construction & Operation:

In the hydrocarbon processing and production industry, gas is compressed for transportation to consuming markets and for use in processing operations. This program is about the construction and operation of compressors. In this program refiners will learn the construction, principal parts, and operation of reciprocating compressors.

1082a Steam Turbines: Introduction:

Steam turbines may differ from one another in size, appearance, and construction, but all steam turbines are similar in operation and work on similar principles. This program teaches how impulse and reaction turbines convert thermal energy to mechanical energy, how condensing and non-condensing turbines work, how turbine speed is controlled, and how the over-speed trip protects the turbine against failure of other speed controls.

1082b Steam Turbines: Equipment and Operation:

This program teaches about the construction of the turbine, including rotor and casing, diaphragms, seals, and packing boxes, and labyrinth and carbon ring packing. Also discussed is the construction of the bearings and bearing combinations used in turbines, of single- and multi-valve governors, and of the oil circulation system. And finally, turbine operation and operating problems are discussed; the effects of pressure, heat, and steam condensation; uneven heating and cooling; leakage of steam; vibration; lubrication and lubrication problems; speed adjustment, instrumentation, and the visual inspections that must be conducted before startup. With this understanding of turbine principles, construction and control, refinery personnel will be able to ensure the efficiency and safety of turbine operations.

1083a Combustion Gas Turbines: Introduction:

In Combustion Gas Turbines the operating principles of the compressor, the combustion chamber, and turbine section are discussed, including compressor construction, combustion chamber, and turbine section; the blading arrangement; and the use of the turbine as a driver and hot-gas generator. Also covered is turbine auxiliary equipment such as starting devices, governors, and overspeed mechanisms, and their functions.

1083b Combustion Gas Turbines: Equipment and Operation:

This course discusses the functions of casing seals, bearings and lubrication in a combustion gas turbine. The program also covers the control and operation of combustion gas turbines, including start-up, operating, and shutdown procedures, and the control of vibration, critical speed, and turbine imbalance. Also discussed are temperature control, the use of turning gears, and turbine control using the automated control panel. Through this understanding of turbine principles, construction, and control.

More information on these training modules are available from Brian Cormier, Director of Oil & Gas Solutions, www.rdc.us.com, bcormier@resourcedev.com. ■

EDITORIALLY SPEAKING

Feedstock Chemistry Continues to Challenge Refiners



Rene Gonzalez, Editor
Refinery Operations

Try running certain types of Canadian crudes without any plans on how to deal with corrosion to crude unit overheads and you'll be surprised how fast \$200 million worth of metallurgy can be destroyed in less than two years. One U.S. Gulf Coast refiner did just that, but still plans to continue running Canadian crudes after making significant process changes to the crude unit.

One consultant who specializes in crude unit design noted that "you can't buy enough chemical treatment programs to deal with this type of corrosive situation," you must instead address errors with the original design of the crude unit and the entire refinery in general." Further downstream from the crude unit, severe catalyst poisons such as arsenic (As) are becoming a serious issue for refiners processing feedstocks such as Canadian Synthetic, and certain other crudes from Russia, Venezuela and elsewhere.

Only small amounts of arsenic can permanently deactivate catalysts. In these cases, pretreatment utilizing a guard bed layer of specially designed catalysts capable of "trapping" arsenic and other catalyst deactivators (e.g., silicon) are being commercialized.



"As many Chinese refining facilities, such as the one pictured here, process a wider variety of feedstocks, the chances of encountering problems with processing high-acid, high-sulfur crudes makes planning for targeted run-lengths more challenging."

One U.S. Gulf Coast refiner and two Asia-Pacific refiners are adding a guard bed of a new generation of trapping catalyst to their hydrotreaters.

One region with a lot of new refining capacity is seeing a "diversity" of process challenges as a result of so many variations in feedstock chemistry. As China diversifies its crude oil processing sources and expands its own domestic oil production, they will have to adjust to the continuously changing crude slate obtained from regions throughout the world. Traditionally, many of China's refineries were built to handle relatively light and sweet crude oils, such as Daqing.

In recent years, new or upgraded Chinese facilities have been designed to process significantly higher volumes of heavy and sour Middle Eastern crudes. China's refiners have also had to plan for processing high-acid

feedstocks. Much of the country's planned new oil production from their offshore oil fields is considered high-acid, and China is the largest importer of Sudan's Dar Blend, a high-acid crude. High-acid crude oil tends to be light and sweet, but refiners must install stainless steel metallurgy (e.g., 316 S.S.) or utilize other advanced processes to process high-acid and high-sulfur feeds, as the previously mentioned U.S. Gulf Coast refiner discovered after two years of running a Canadian crude.

In today's highly competitive refining market, poor economics can shut down or significantly reduce unit throughput even if it's not encountering any significant process and operational problems. In summary, prepare for dealing with the worse types of feedstock chemistry, even at small quantities. ■

Rene Gonzalez

CALENDAR OF EVENTS

FEBRUARY

13-16, *Hydrogen Conference & Expo*, National Hydrogen Association, Washington D.C., info@hydrogenconference.org, www.hydrogenconference.org

23-25, *ERS FCC & Hydrocracking*, Eurotek Refining Services Ltd, Windsor, London, enquiries@eurotek-refining.co.uk, www.eurotek-refining.co.uk

MARCH

8-11, *European Fuels Conference, 12th Annual Meeting*, World Refining Association, Paris, +44 (0) 20 7067 1800, www.wraconferences.com.

13-17, *2011 AIChE Spring Meeting & 7th Global Conference on Process Safety*, American Institute of Chemical Engineers, Chicago, Illinois, +1 203 702 7660, www.aiche.org.

20-22, *NPRA Annual Meeting*, National Petrochemical and Refiners Association, San Antonio, Texas, +1 202 457 0480, www.npra.org

27-31, *ACS Spring 2011 National Meeting & Exposition*, American Chemical Society, Anaheim, California, +1 508 743 0192, www.acs.org.

30-31, *14th Annual ARTC Meeting*, Singapore, Incisive Media & Global Technology Forum, +852 3411 4829 www.gtforum.com

APRIL

3-6, *The Middle East Downstream Week, 12th Annual Meeting*, World Refining Association, Paris, +44 (0) 20 7067 1800, www.wraconferences.com.

MAY

2-6, *Coking Safety Seminar*, Coking.com, Galveston, Texas, +1 360 966 7251, www.coking.com.

24-27, *NPRA Reliability & Maintenance Conference & Exhibition*, NPRA, Denver, Colorado, +1 202 457 0480 www.npra.org.

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