

# **NEW HYDROPROCESSING APPROACHES TO INCREASE PETROCHEMICALS PRODUCTION**

By

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## **Abstract**

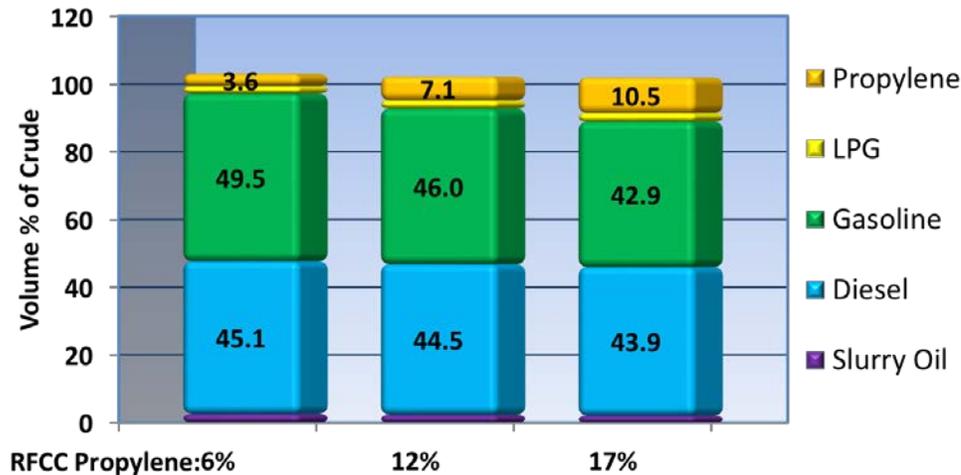
Over the past several years there has been increased interest in combining refinery and petrochemical projects to maximize production of the highest value products while meeting transportation fuel needs. To accomplish these often competing objectives, the hydroprocessing approaches utilized in the refinery are critical. Both the processes and catalysts selected have a significant impact on petrochemical feedstock production. Recently, CLG has been assisting several of our clients with identifying ways to increase their project values based on our extensive portfolio of residue hydrotreating, residue hydrocracking, and VGO/Distillate hydrocracking technologies. This paper shares some of these newer approaches now available and compares their benefits with the traditional paths for producing petrochemical feedstocks.

## **Refinery's Role in Petrochemical Production**

The conventional roles of hydroprocessing in petrochemical production has been to pretreat FCC (or RFCC) feed so as to increase propylene and naphtha yields, especially heavy naphtha as it is an important reformer feedstock, and a source for C8-C10 aromatics. Other refinery streams suitable for petrochemical production include light naphtha and LPG steam cracker feeds.

The manufacture of petrochemical feedstocks frequently competes with the manufacture of transportation fuels. This is because:

- Maximum propylene production requires the (R)FCC to operate at higher severity as compared maximum gasoline production. Figure 1 illustrates this for a RDS/RFCC refinery configuration at different RFCC severities.



**Figure 1: Increasing RFCC severity increases propylene yield at the cost of transportation fuel.**

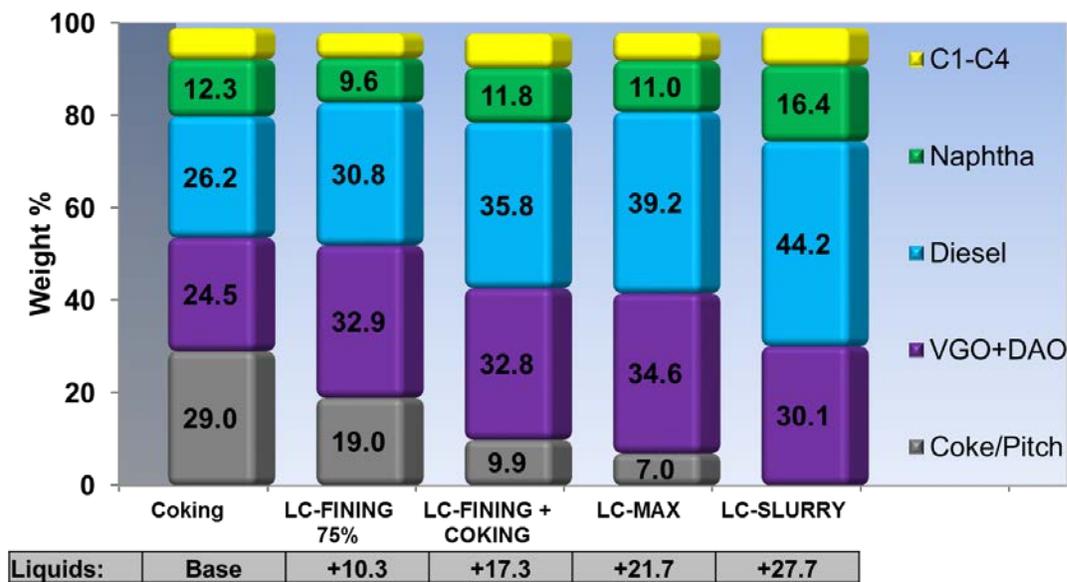
- Maximum aromatics production requires maximum reformatate production, which in turn requires maximum heavy naphtha production. A VGO hydrocracking unit can be tailored toward maximum heavy naphtha production with as high a C8-C10 aromatics content as possible, but maximizing the naphtha-range aromatics yield will be at the cost of the middle distillate yield, in particular the diesel yield. Interestingly, there appears to be a shift in transportation fuel demand from diesel toward gasoline in some of the very same regions that are interested in enhanced production of petrochemical feedstocks.

### Residue Conversion Approach Implications

Irrespective of a refinery's focus on the manufacture of transportation fuels or of petrochemical feedstocks, the fate of the residual oil is frequently a critical component of the refinery margin. There are three major residue conversion options of interest to most projects:

- **Delayed Coking** has historically been the most popular full conversion technology. However, it has a disadvantage in that this process yields a comparatively large fraction of less desirable products like fuel gas and coke. Coke yields can be as high as 30 to 35 wt%.
- **Residue Hydrotreating (RDS)** is attractive for maximizing gasoline and thereby propylene yields. A disadvantage is that this process exhibits limited feedstock flexibility, and that it struggles in particular to handle the heaviest feedstocks.
- **Residue Hydrocracking (RHC)** is attractive for maximizing the yields of liquid product manufacture with the broadest possible feed slate. Typical residue conversion yields with an ebullated bed process such as LC-FINING are 65-80+ wt%. Combining LC-FINING with coking

can boost conversion levels toward 85-90 wt% and reduce the coke make to 12-14 wt%. This combination results in 15-20 wt% higher liquid yields compared to coking by itself, as shown in Figure 2. Also shown are CLG's latest RHC high conversion offerings of LC-MAX™ and LC-SLURRY™, which have even higher total liquid yields. The higher total liquid yields accessible with the LC-FINING technology platform tend to be in the middle distillates boiling range, so that they require further processing so as to be turned into petrochemical feedstocks.



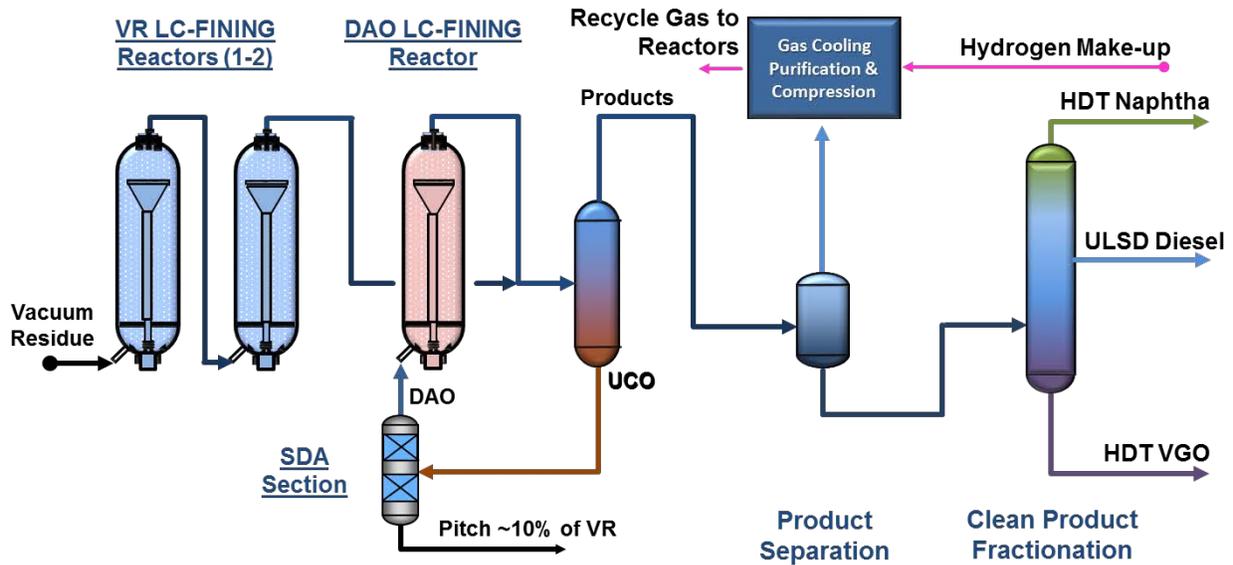
**Figure 2: Yield Comparisons Between Coking and RHC Options**

Refiners invariably want the reliability of proven technologies in new projects yet want to maximize profitability by their ability to respond to supply and price volatility for both feedstocks and products. Thanks to recent technical advances, CLG can now offer solutions based on the reliable LC-FINING and RDS technology platforms that expand feedstock optionality and that provide the desired flexibility to diversify product dispositions, e.g. switching emphasis from diesel to naphtha or from transportation fuel to petrochemical feedstock production. These advances include both processes and catalysts.

### Advances in Process Technology

**RDS:** So as to mitigate the feedstock limitations intrinsic to RDS/RFCC and thereby expand the range of RDS applications, CLG offers Upflow Reactor (UFR™) technology for both new and existing units. The UFR reactor is added in front of the fixed bed reactors. Since the UFR reactor has a very low pressure drop it is an excellent solution for revamp applications. UFRs can be isolated from the main fixed bed reactors and the UFR catalyst can be changed out while the main RDS reactors continue in service. An UFR reactor has been successfully employed by several of CLG's licensed RDS units.

**LC-MAX:** One of the more exciting developments for increasing aromatics production has been the development of the LC-MAX process. This is a LC-FINING based process that first hydrocracks residue at low conversion, subsequently utilizes a Solvent Deasphalting step to reject compounds likely to form sediment, and finally achieves nearly complete conversion of the DAO and HVGO products in an additional LC-FINING step.

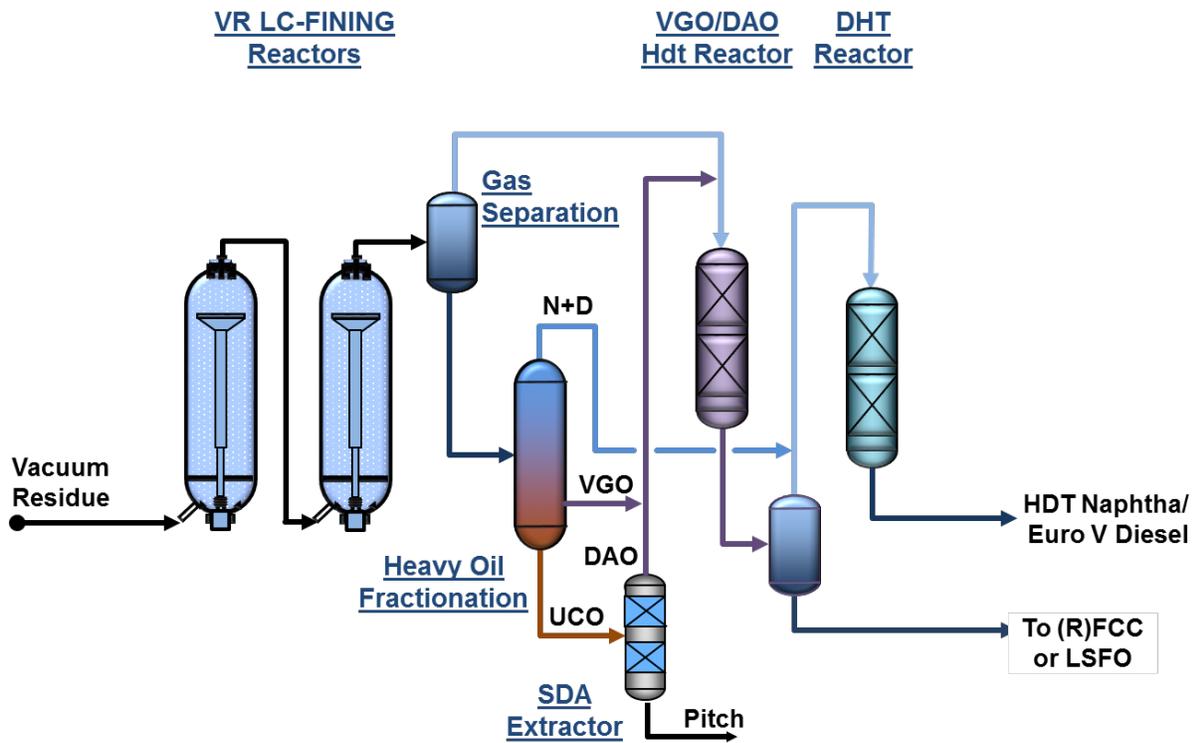


**Figure 3: LC-MAX for maximum liquids production using standard technology platforms**

Figure 3 illustrates this LC-MAX process. LC-MAX makes about 10 wt% more VGO and 13 wt% more distillates as compared to coking. Figure 2 highlights the LC-MAX yield advantage over conventional technologies. LC-MAX has been selected for 2 large residue conversion projects, both in the engineering phases.

An added advantage of LC-MAX is that its VGO is a better hydrocracker feedstock than that of conventional higher conversion RHC. This is because the combination of solvent deasphalting and high conversion residue hydrocracking effectively eliminates the feed components that make highly refractory VGOs.

**LC-MAX-G:** For applications where increased FCC feedstocks are desired a modified LC-MAX-G, a modification of the original LC-MAX process is available. In this version of LC-MAX the hydrocracked residue is fractionated and only the unconverted oil is deasphalted. The VGO and DAO are subsequently combined and hydrotreated (Figure 4). The desired VGO/DAO hydrotreating severity depends on the desired FCC performance. High quality distillates and naphtha can be manufactured more or less independent of the VGO/DAO quality objectives.

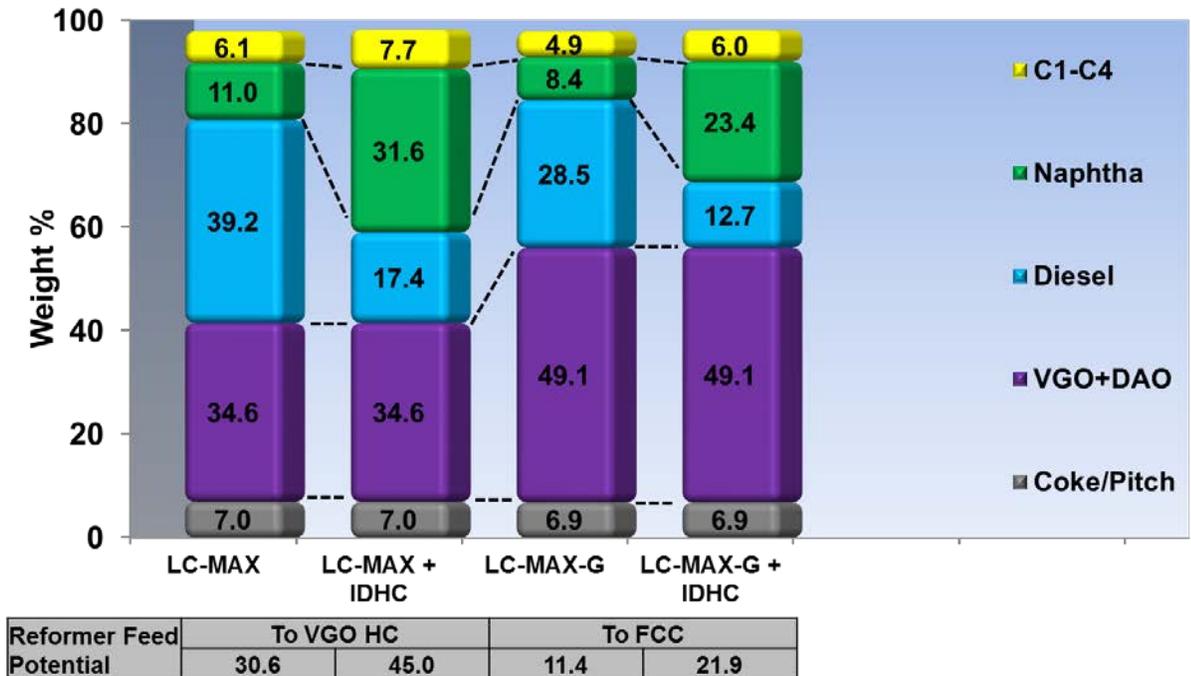


**Figure 4: LC-MAX-G for maximum petrochemical feedstock production at low process complexity**

**Hydrocracking RHC Distillate Product:** CLG has pioneered the integration of RHC and both RHC product hydrotreating and RHC product hydrocracking into a shared RHC high pressure loop. This results in a highly cost-effective operation as compared to a RHC product hydroprocessing facility that is disconnected from the RHC operation. With LC-MAX-G addition of an integrated product hydroprocessing option is fairly straightforward, requiring only a few additional catalyst beds or a small additional cracking reactor.

With integrated distillate hydrocracking there is a significant shift from distillates to naphtha, implying an increased production of reformate and FCC feedstocks that can be used for petrochemical production. Figure 5 shows how LC-MAX can shift yields depending on the product objectives.

LC-MAX VGO can be processed in a high conversion, naphtha selective hydrocracker. In this scenario the yield of reformer feed can be as high as 45 wt% of the vacuum residue. For the LC-MAX-G cases where the objective is maximum propylene yield the potential reformer feed can approach 22 wt%, after the FCC heart cut naphtha is sent to the reformer. In this case, the vacuum residue yields some 8 wt% overall propylene after conversion of the hydrotreated VGO/DAO in the FCC unit.

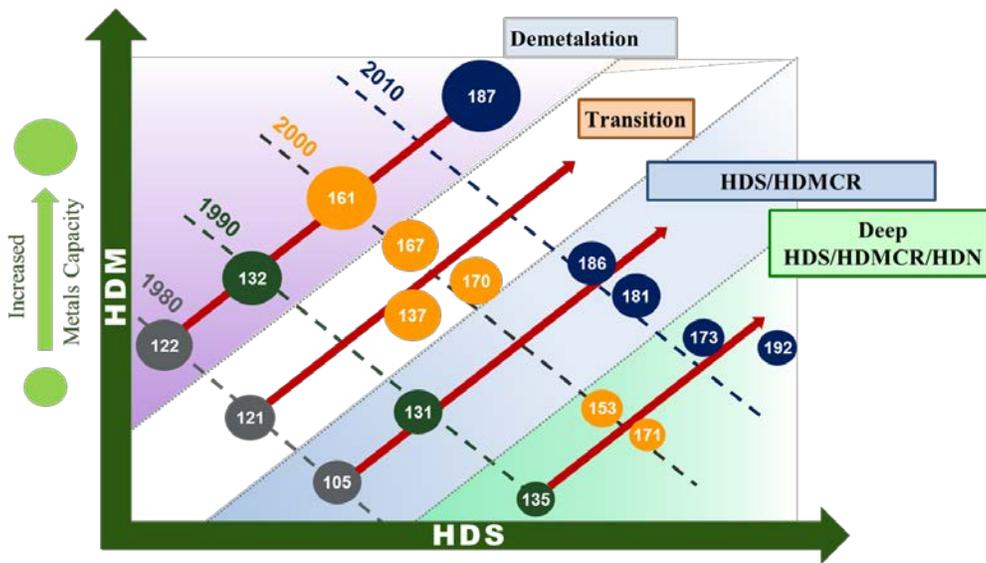


**Figure 5: LC-MAX Process Options can tailor the Yield Structure for maximum Petrochemicals Production**

### Advances in Catalyst Technology

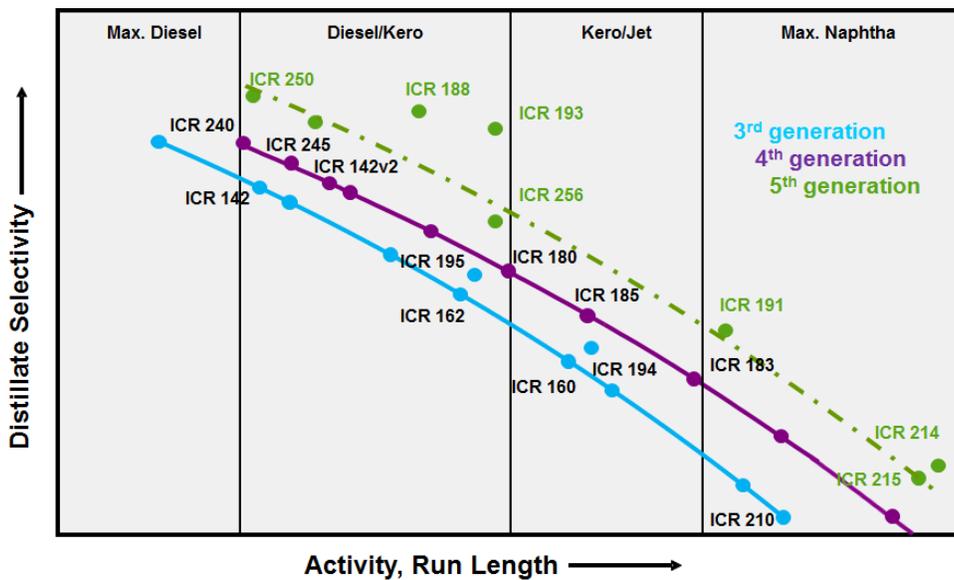
CLG and its catalyst partner, Advanced Refining Technologies (ART™), offer world class residue hydroconversion catalysts with continuously evolving performance as shown in Figure 6. The proper choice of catalysts leads to a higher tolerance of feedstock contaminants, and to an RDS atmospheric residue product with a higher hydrogen content. The overall impact is a better selectivity toward propylene and naphtha in the (R)FCC unit.

The relentless focus of both CLG and of its catalyst partner ART at residuum upgrading has made CLG the only licensor that offers a complete portfolio of processes and catalysts to maximize the value derived from residue. An integral and often underestimated part of this monetization of residue is the upgrading of the RHC products. These products contain an unusually high concentration of refractory components (particularly polynuclear aromatic hydrocarbons) that seriously threaten run length if left untreated. Specially designed co-gel catalysts, such as ICR™ 1000, exemplify a class of catalysts that combine the required high aromatics saturation capability with a high selectivity to specifically hydroconvert these most refractory components. Early elimination of these residue-derived poisons is essential to the conversion of particularly the VGO into transportation fuel or into petrochemical feedstocks.



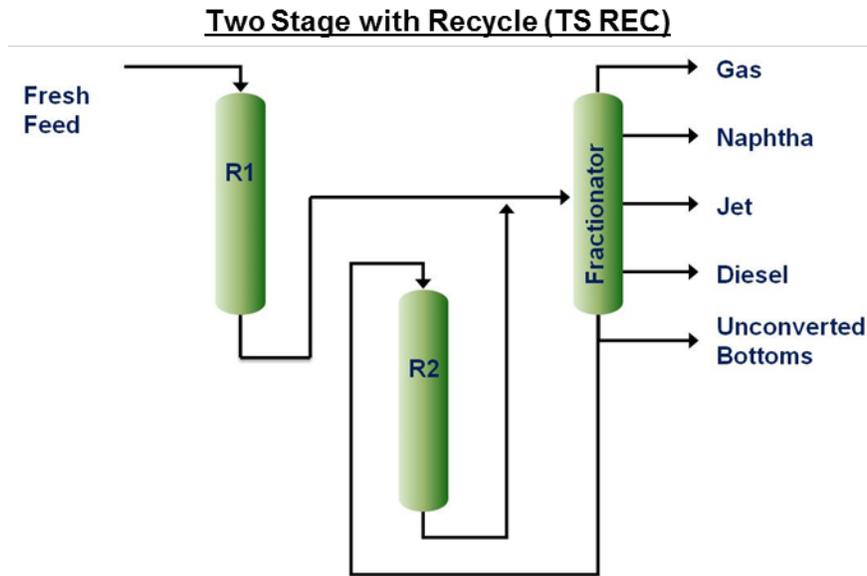
**Figure 6: CLG/ART’s continuously evolving RDS Catalyst Offerings**

After sufficiently deep hydrogenation, the boiling point of RHC products can be further reduced in a hydrocracking step. Figure 7 shows the continued evolution of hydrocracking catalysts, each generation exhibiting an improved tradeoff between yield structure (“selectivity”) and sustainable run length (“activity”). Provided the ancillary equipment has the capacity to handle the changes in product streams, a straightforward change in catalyst from a catalyst geared toward jet or diesel such as ICR 180 to a catalyst geared toward naphtha and jet, such as ICR 215 can impart a dramatic change in hydrocracking yield structure from diesel to naphtha-range aromatics, suitable for both reforming and petrochemicals production.



**Figure 7: ISOCRACKING Catalyst Advances**

CLG combines access to state-of-the-art catalysts with 60 years of experience on how best to deploy these hydroprocessing catalysts. For maximum VGO hydroconversion into transportation fuel or chemicals, CLG has traditionally offered a two-stage hydrocracking process. Figure 8 illustrates this process lay-out.



**Figure 8: CLG Two-Stage ISOCRACKING™ Process for maximum sustainable VGO Conversion**

The increasing demands for propylene and gasoline increase the attractiveness of RDS + RFCC. There have been tremendous advances in RDS and FCC designs and catalysts that further enhance propylene production.

### **Case Studies – Residue Conversion Option and Hydrocracker Catalyst Type Impacts on Petrochemical Feedstock Production**

To illustrate the opportunities associated with the addition of various Residue Hydrocracking technologies and VGO Conversion approaches, CLG evaluated several options utilizing our comprehensive process planning and optimization models.

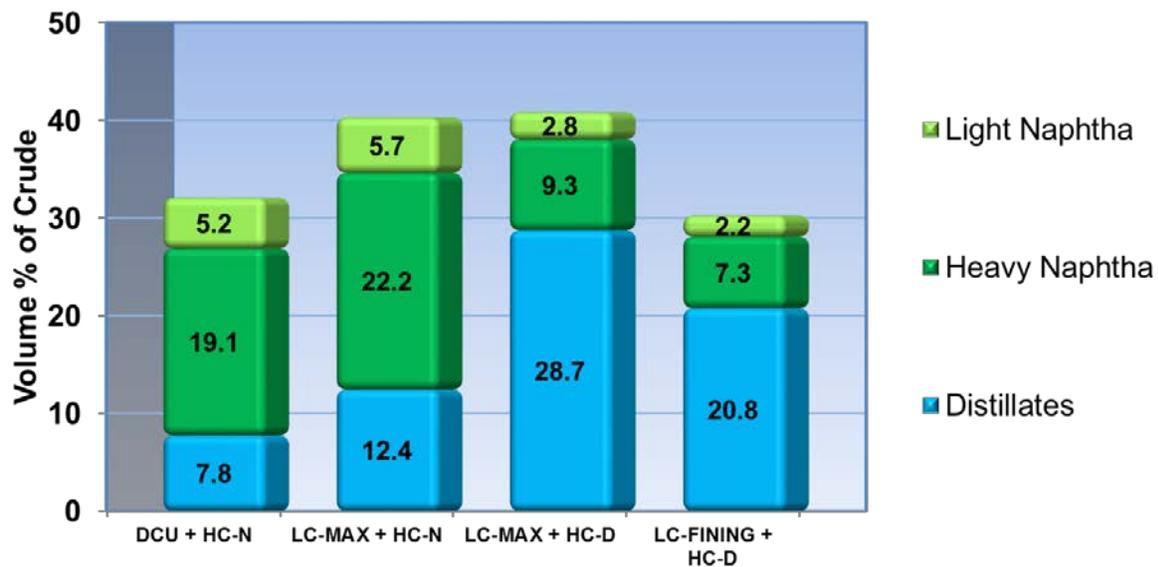
#### **Case Study 1 – Heavy Naphtha Production**

Production of Heavy Naphtha can vary significantly, based on the following:

- Residue Conversion Yields
- VGO Hydrocracking Selectivity
- Synergies between the Residue Conversion and VGO Conversion processes

When comparing processes such as Delayed Coking to LC-MAX the combined light and heavy naphtha yields are within about 1 wt% of each other. This by itself would suggest that these processes would result in similar C8-C10 aromatics yields after reforming. But because the VGO yield difference is 13 wt% the impact of the downstream VGO conversion unit also needs to be taken into account.

Figure 9 shows the combined yields of the Naphtha and Distillate products from the Residue Conversion Unit and a high conversion VGO Hydrocracker operating in various modes. Because the LC-MAX case converts significantly more residue into liquids as compared to coking, the resulting naphtha + distillate yields of this option are the highest.



**Figure 9: Combined Residue and VGO Hydrocracking  
Key Product Yields Illustrate the Advantages of LC-MAX**

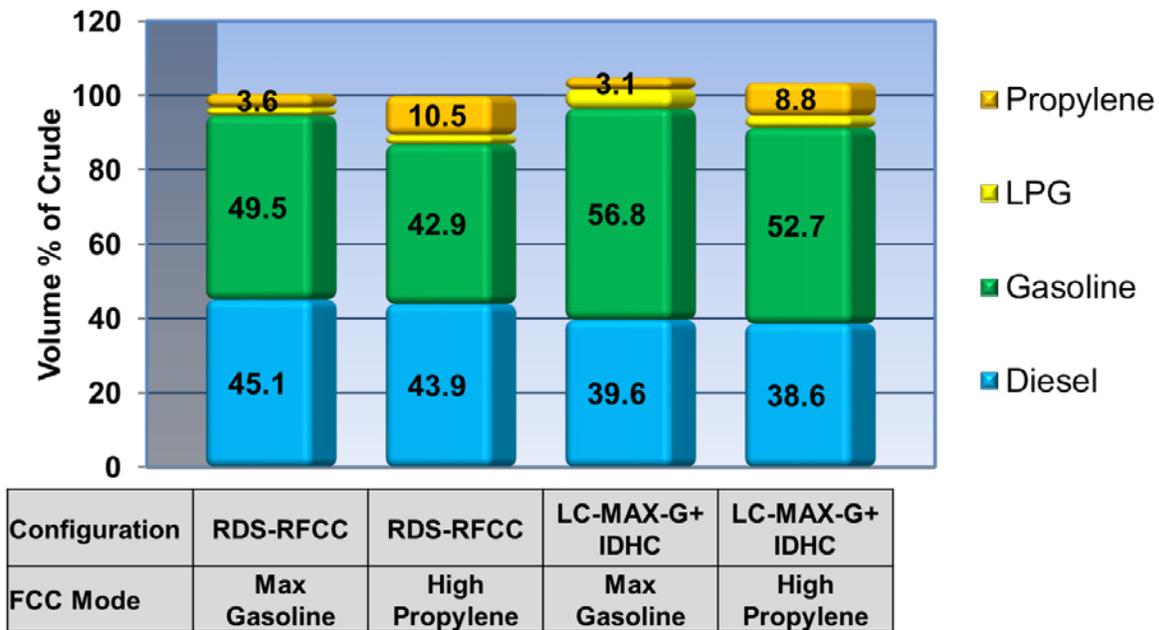
For the LC-MAX case the second and third columns show the shifts in yields dependent on the VGO hydrocracker selectivity. As can be seen both heavy and light Naphtha can be increased considerably with a naphtha selective operation, resulting in more steam cracker and C8-C10 aromatics feed stocks.

Although LC-FINING by itself does not show an enticingly high naphtha and distillate yield, its Unconverted Oil could be processed in a delayed coker, which in turn would significantly augment these yields.

## Case Study 2 – Maximizing Gasoline and Propylene

Figure 10 shows the overall refinery yields for both RDS + RFCC and LC-MAX-G + FCC flow schemes. The respective yields from each option also depend on the operating mode of the (R)FCC unit.

For the RDS + RFCC flow scheme the gasoline yield could be significantly reduced when the RFCC is geared toward maximizing the propylene yield. In this operation propylene yield can be further enhanced if also the C4 production that is usually of use for alkylate production can be minimized.



**Figure 10: Residue and VGO Hydrocracking Key Product Yields**

LC-MAX-G with the integrated distillate product hydrocracking option can result in higher gasoline yields compared to a RDS + RFCC flow scheme. Although LC-MAX-G has less (R)FCC feed stock, the FCC feed quality is higher. In addition, LC-MAX-G produces a significant amount of naphtha by itself. The effective result is high overall gasoline and C8-C10 aromatics yields. RDS + RFCC will be preferred in case high propylene yield is preferred.

### Summary:

Residue and VGO conversion are important aspects for maximizing the production of petrochemical feedstocks. CLG can help with tailoring combinations of LC-FINING or LC-MAX with VGO hydrocracking toward maximum production of feedstocks for ethylene cracker and aromatics plants while minimizing residue byproducts. Proper integration of RDS + RFCC can maximize propylene production. Advances in RDS catalysts and a combination of UFR and traditional RDS reactors expands the feedstock range for this application. LC-MAX-G + FCC facilitates both high propylene and gasoline yields.

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