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Upgrading Residuum to Finished Products In Integrated Hydroprocessing Platforms: Solutions and Challenges

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Upgrading Residuum to Finished Products in Integrated Hydroprocessing Platforms – Solutions and Challenges

Several European, Canadian, Asian and Middle Eastern refiners are planning residual oil upgrading projects. The incentive for refiners to process heavier, high-sulfur crudes is greater than ever before due to the large differentials between sweet and sour crudes. Processing less expensive, heavier crudes that contain more sulfur makes it even more urgent to invest in bottom-of-the-barrel upgrading to meet the new specifications and to maximize refinery margins. This paper presents the most relevant residue hydroprocessing technologies and scenarios where an integrated platform provides the biggest economic incentives.

Chevron Lummus Global's Residuum Hydroprocessing Technologies

Residuum conversion to distillates by hydrogen addition technology is well suited for reducing the sulfur level in fuel oil and for producing at the same time, valuable mid-distillate products that meet the current and future specifications. Chevron Lummus Global (CLG) has extensive experience in heavy oil upgrading and is the market leader in both fixed bed and ebullating bed residuum hydroprocessing technologies.

The fixed bed residuum hydroprocessing technologies licensed by CLG are RDS and VRDS. CLG also licenses the ebullating bed LC-FINING technology. For each of these technologies, CLG is proud to announce recent projects that are the largest of their kind in the world:

- At Shell Canada, CLG has completed the design of an LC-FINING unit that will be added to the existing unit, making it the largest single train LC-FINING unit in the world (47,300 BPSD).
- In 2005, KNPC awarded CLG the largest RDS complex, to be built in Kuwait. This complex will be hydrotreating 330,000 BPSD atmospheric residue to produce low sulfur fuel oil.

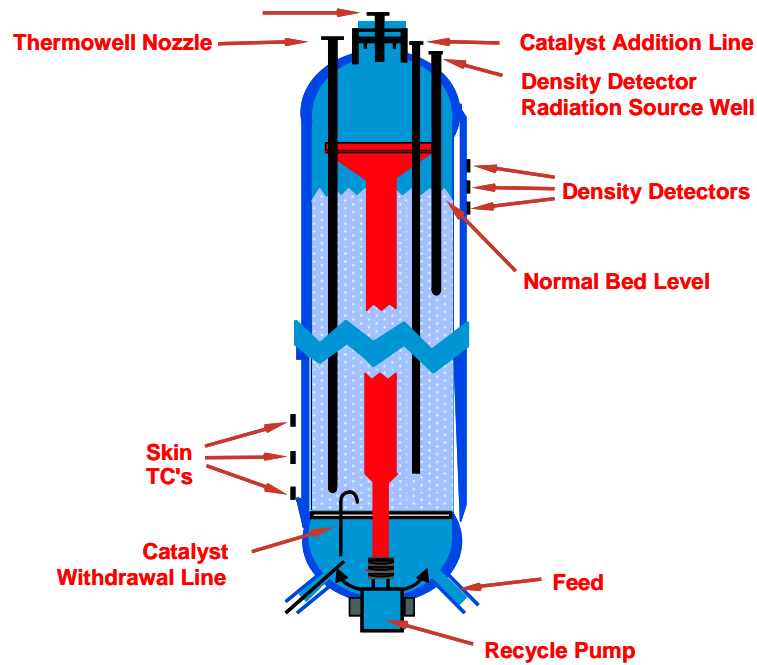
In this paper, we will give an overview of these two technologies and new developments, highlight the key drivers for these projects and reveal why these refiners decided to invest in bottom-of-the-barrel upgrading with CLG technologies.

LC-FINING Technology

LC-FINING technology is an ebullating bed residuum hydrocracking process. Petroleum residuum and other heavy hydrocarbon streams in the refinery such as heavy cycle oil are readily converted into white products. The remaining stable residuum is low in sulfur and is a good blending stock for low sulfur fuel oil that will meet the new EU limit of 1.5 wt % sulfur, even at moderate conversion levels. At higher conversion, the LC-FINING bottoms stream can be sent to a downstream unit in the refinery for further processing, such as a partial oxidation unit or an integrated gasification combined cycle unit. Alternatively, the residuum can be fed to a delayed coking unit. Depending on the refinery scheme and its position in the market, different outlets for the residuum are possible. During the project development phase, CLG works together with the refinery to optimize the LC-FINING unit configuration in the overall refinery scheme.

The key process feature of the LC-FINING unit is the expanded (ebullated) bed reactor. Feed enters the reactor at the bottom and moves upward towards the reactor exit. In the reactor, the feed is converted by the presence of hydrogen and catalyst into distillate products (vacuum gas oil, diesel, kerosene and naphtha).

Figure 1: Schematic of Reactor Using LC-FINING Technology



The catalyst is continuously added and removed from the reactor, thereby keeping a constant catalyst activity throughout the run. This also has the advantage of no pressure drop buildup over the reactor as would be the case with fixed bed residuum hydrocracking units. Therefore it is possible to continuously process heavy hydrocarbon feeds that contain high quantities of metals and solids and still achieve run lengths of three years and more.

To date, there are nine LC-FINING units in operation worldwide and three in various stages of design and construction.

The Shell Scotford LC-FINING Unit

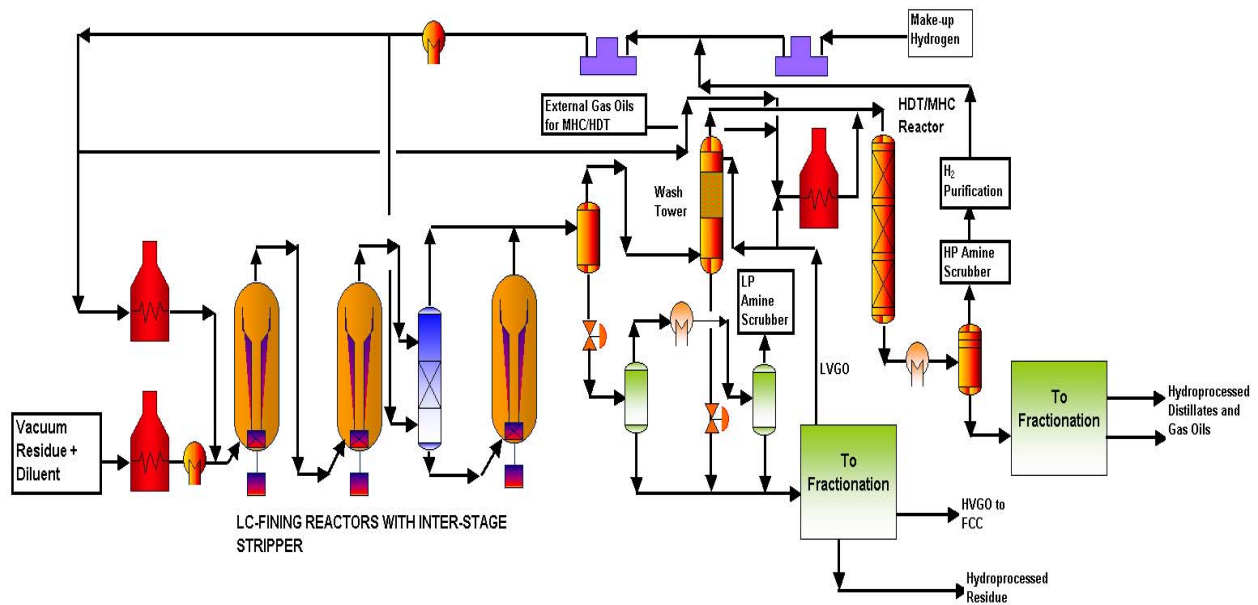
Shell Scotford, Canada is processing very heavy vacuum residuum which is derived from Athabasca bitumen. This bitumen, which is obtained by open pit mining of tar sands, contains a high amount of metals, sulfur and asphaltenes. Shell selected CLG's LC-FINING technology for upgrading bitumen derived residuum oil into white products. The unit processes 80,000 BPSD of

heavy vacuum residuum. It started up in 2003 and has since been operating successfully above design capacity.

The unit has a design capacity of 80,000 BPSD and is built with two parallel reactor trains, each having capacity of 40,000 BPSD. The design conversion is 77 wt % of the vacuum residuum. The integrated hydrotreater has a design capacity of 105,000 BPSD, of which 53% is LC-FINING distillates and 47% are external distillate streams in the refinery.

The Shell Scotford design is unique since it is the first LC-FINING unit that is integrated with a close-coupled hydrotreater.

Figure 2: Schematic Representation of Shell Scotford LC-FINING Unit



Integrated Hydrotreating

The close-coupled hydrotreater processes the distillates that are produced in the LC-FINING unit, and it also treats external distillate feeds from the refinery. The hydrotreater utilizes the excess hydrogen that is present in the LC-FINING effluent so there is no additional burden on the recycle gas compressor. This also makes this processing scheme attractive in a revamp scenario.

The heat of reaction formed by hydrotreating is quenched by a combination of gas and liquid coming from the Integrated HDT effluent.

The reaction section piece count for the integrated hydrotreater is 50% less than that of a stand-alone unit. There is no need for an additional recycle gas compressor since both the LC-FINING and Integrated HDT reactors share the same high-pressure hydrogen loop. Also some distillate fractionation is common for both sections and the unit can be designed in a very energy-efficient manner because of increased heat integration opportunities between both sections. Typical properties of the products coming from the integrated hydrotreater are shown below.

Table 1

	Naphtha	Diesel	VGO
	C₅-165°C	170-360°C	360°C+
Specific Gravity	0.705	0.858	0.900
Nitrogen	<1 wppm	<10 wppm	<100 wppm
Sulfur	<30 wppm	<100 wppm	<200 wppm
Cetane Index		45	

After the successful startup of the unit in 2003, the unit has been operating at 10% above design capacity and has met or exceeded all expectations.

Expansion Project

As part of Shell's expansion plans to ultimately process up to 500,000 BPSD of Athabasca bitumen, Shell announced in April 2005 a growth strategy that would expand the Athabasca Oil Sands Project (AOSP) into three blocks of 100,000 BPSD each. The first building block will include an expansion of the mine and an expansion of the Scotford upgrader including the LC-FINING unit. As a result, an additional LC-FINING + Integrated HDT train will be added increasing the total LC-FINING operating capacity to 135,000 BPSD, making this the largest ebullating bed residue hydroprocessing complex in the world. The basic design of the revamp

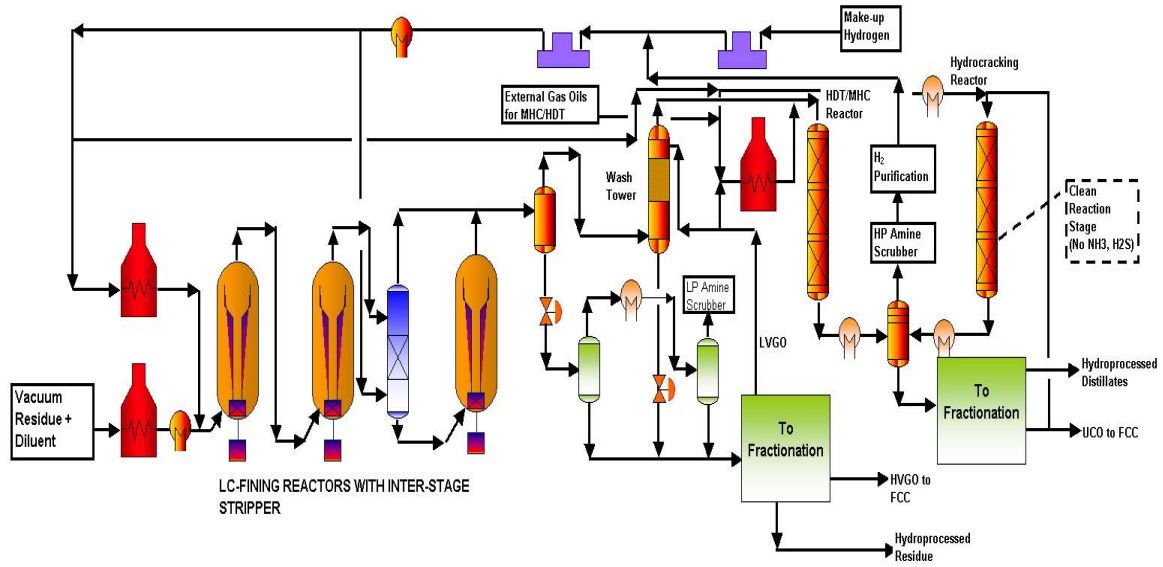
has been completed and a final investment decision will be taken by Shell in 2006. Also the major contractors have been selected for the mine and upgrader expansions.

The product quality of the hydrotreated naphtha and diesel fractions are the same as for the base plant, while the VGO fraction is expected to contain 1000 wt ppm sulfur and 200 wt ppm nitrogen.

Integrated Hydrocracking

Following the successful commercialization of the integrated hydrotreater at Shell Canada, CLG extended the concept to integrated hydrocracking for a large refiner in Europe. The 40,000 BPSD LC-FINING unit is close coupled with a 35,000 BPSD ISOCRACKING unit capable of converting upwards of 65% of the VGO derived from the LC-FINING unit to diesel and lighter materials. All of the gas oils and lighter products from the LC-FINING unit are upgraded within the same high pressure loop to Euro diesel, naphtha reformer feed and very high quality FCC feed. The unit is capable of processing a significant quantity of external straight-run VGO instead of or in addition to LC-FINING VGO. Detailed cost estimates done during project execution indicated that because of the reduced piece count capital cost reductions were of the order of 30-40% compared to a stand-alone hydrocracker. Parallel pilot plant studies conducted as part of the design phase at Chevron's Richmond Technology Center has provided very valuable insights into the peculiarities and processing challenges of hydrocracking LC-FINING VGO. While the desulfurization, denitrification, and subsequent hydrocracking of the lighter products from the LC-FINING unit were relatively simple, the hydrocracking of the vacuum gas oils require very careful selection of catalysts and operating parameters.

Figure 2A: Schematic Representation of LC-FINING and Integrated ISOCRACKING



The heavier portion of the Vacuum Gas Oil is very rich in highly condensed heavy polynuclear aromatics that are so refractory in nature that operating conditions tend to be severe in order to achieve reasonable conversion levels. Catalyst deactivation is far more pronounced than for straight run or other cracked stocks.

CLG designed the unit as a two-stage hydrocracker with partial recycle. The first stage is close coupled with the LC-FINING reactors and utilizes the excess hydrogen and heat from the upstream LC-FINING section. The second stage is incorporated in the same gas loop and recycle gas requirement for the overall unit, is minimized. A membrane-based hydrogen purification system is used to reduce power consumption significantly. One of the most important elements of the design was addressing safety issues, emergency procedures, upset conditions, control issues, and minimization of downtime. These were considered to be at least as important as the process integration. An interesting feature of the design is the capability to run the hydrocracking unit should the LC-FINING section be out of commission for any reason.

Case Study:

Integrating a 35,000 BPSD hydrocracking unit with a 40,000 BPSD LC-FINING unit.

Feed (from LC-FINING unit):

VGO - 46%

Diesel - 40%

Naphtha - 14%

Blended Feed Properties:

API - 29

Nitrogen - 2900 wt ppm

Sulfur - 0.25 wt %

Conversion: 60 – 70%

Product Quality Requirements:

Diesel - <10 wt ppm Sulfur, 51 Cetane

Desulfurized VGO (FCC Feed) - <50 wt ppm Sulfur, <100 wt ppm nitrogen

Naphtha (Reformer Feed) - < 0.5 wt ppm Sulfur, <0.5 wt ppm nitrogen

Incremental Investment: US Gulf Coast, Third Quarter 2005 basis

Total Equipment (ISBL): US \$25 million

Total Investment Cost (ISBL): \$75 million

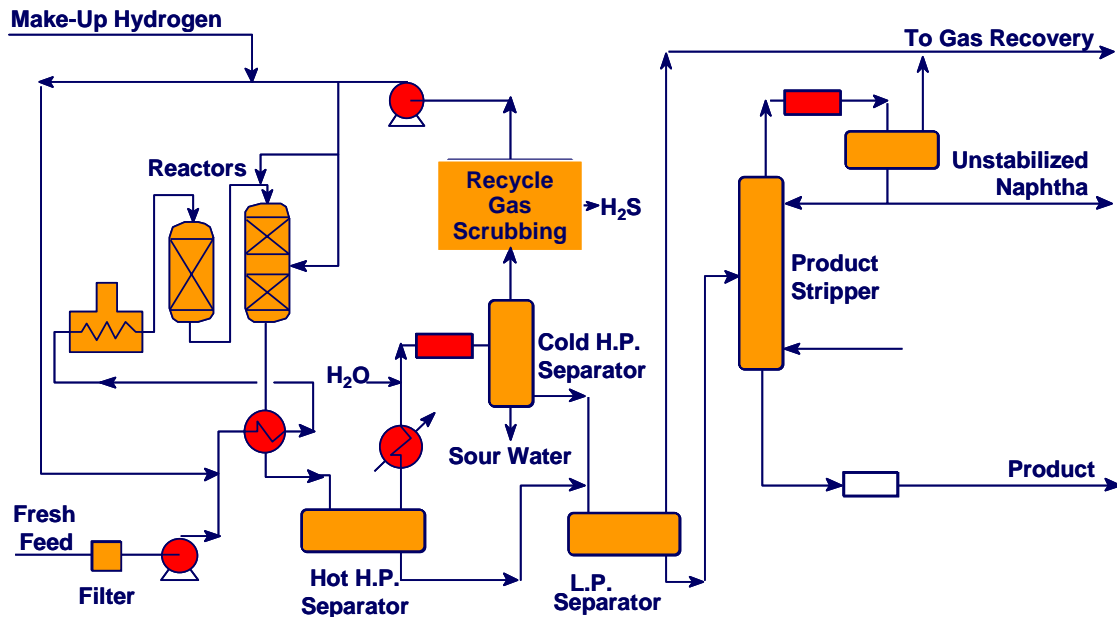
A stand-alone hydrocracking unit will cost ~ \$115 million on the same basis, representing a savings of approximately \$40 million.

RDS / VRDS Technology

Chevron and Gulf pioneered in the development and commercialization of fixed bed residuum hydrotreating (RDS) in the 1960s and 1970s. Chevron built the world's first modern residuum boiling range hydrotreating unit in its Richmond Refinery in 1966 to process deasphalted oil for partial conversion to distillate fuels and to prepare the unconverted material as an FCC feedstock. The crude source of this feedstock was California San Joaquin Heavy which contained high concentrations of iron naphthenate.

Processing this material provided Chevron with substantial commercial incentive to develop catalyst concepts such as catalyst size, shape, and activity grading, to mitigate the impact of reactive and particulate feed metals on fixed bed pressure drop build-up long before these concepts were adopted by other hydroprocessing licensors in the industry

Figure 3: Typical RDS Flow Scheme



Gulf licensed several of the earliest commercial RDS units in Japan to desulfurize Kuwait atmospheric residuum for power plant fuel oil. Gulf licensed a total of nine residuum desulfurization units before the technology was merged with Chevron’s technology in the 1985 merger between Gulf and Standard Oil of California (now Chevron) operations.

Chevron extended the residuum processing technology to process all vacuum residuum (VRDS) and built the world’s first unit designed to process vacuum residuum in its El Segundo (near Los Angeles) refinery in 1972. Subsequently Chevron licensed VRDS units to Nippon Petroleum Refining Company in Japan, SINOPEC in China and Yukong Ltd in Korea. Chevron remains the only licensor to have ever designed and commercially operated fixed-bed hydroprocessing units for processing 100% vacuum residuum.

CLG is the only licensor that operates its own RDS unit. In 1983, Chevron started the world's largest RDS unit in its Pascagoula Refinery in Mississippi. It was designed to process Arabian Heavy Atmospheric Residuum in a three module plant at a rate of 96,000 BPSD.

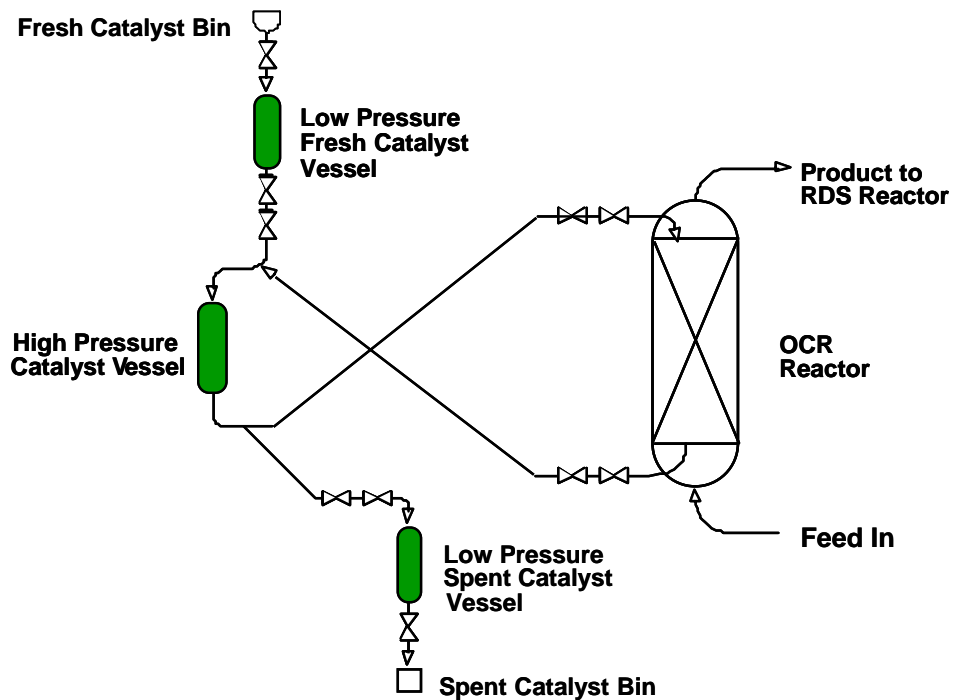
The modular design of the unit permitted a relatively short cycle life of 6 months by allowing one module to be brought offline each alternate month for catalyst change out while the other two modules ran at a rate of 80,000 BPSD. On alternate months, in which all three modules operated, the plant processed 112,000 BPSD. The modular approach kept the unit on-stream at no less than 83% of design capacity all of the time, minimized the tankage, impact on maintenance scheduling and the large amount of simultaneous catalyst movement that would have resulted from a single unit design. Chevron's 20 years of operating this modular plant resulted in valuable lessons learned and best practices development that can be shared with licensees, should their process needs be served by a large modular residuum plant design.

The commercial experience at Pascagoula also gave Chevron incentive to pioneer new directions in RDS catalyst technology. The first bimodal structure demetallation (HDM) catalysts, shaped HDM and RDS catalysts, and the concept of tailoring different catalysts for different reaction zones were first practiced at the Pascagoula refinery.

UFR and OCR

The need to process extremely high metal content feeds, to run high severity operations in RDS units or to extend cycle length and throughput via retrofits to plants already constructed led Chevron to the concept of replacing the catalyst while the unit is on-stream. Chevron was the first, and to date, only licensor to commercially design and practice liquid filled UpFlow Reactor (UFR) technology with On-stream Catalyst Replacement (OCR). This concept has the catalyst moving in counter-current flow direction of the reactor mix of residuum and hydrogen, thus ensuring maximum utilization of the catalyst. The most deactivated catalyst sees the most reactive feed at the reactor (bottom) inlet, and spent catalyst is withdrawn from the bottom. The least reactive feed sees the freshest catalyst at the reactor exit (top), the point at which fresh catalyst is introduced during the online catalyst replacement cycle.

Figure 4: OCR Catalyst Withdrawal / Addition System



This novel process was first commercialized with Idemitsu Kosan Company in Japan in 1992 as retrofit to an existing RDS unit.

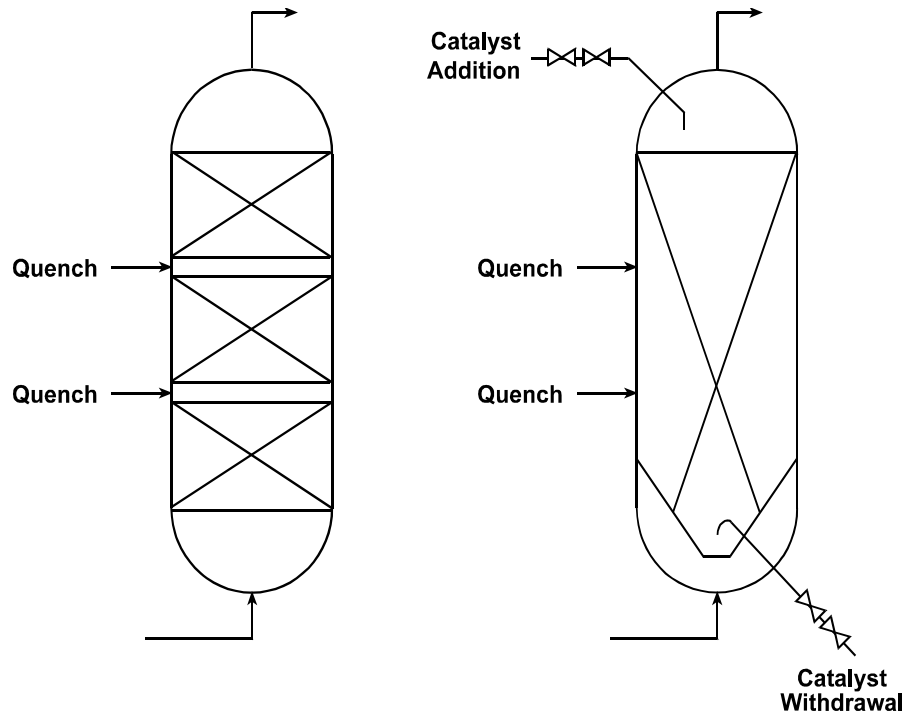
The counter-current moving bed catalyst replacement concept was especially well suited and the most economic choice for revamping an existing RDS unit to get maximum increase in throughput, feed difficulty (high metals), or fixed bed cycle life. However, CLG learned from the development of the design of liquid filled upflow reactor technology that substantial benefits could be obtained from the upflow reactor concept regardless of employing the catalyst handling system that permitted the online catalyst replacements.

CLG learned that the slightly expanded bed in a liquid filled upflow reactor eliminates the potential for reactor plugging at the reactor inlet, even when the UFR reactor is followed by a trickle bed downflow reactor. The particulate matter is carried upward through the expanded bed. When it enters the downflow reactor, the feed is much less reactive, thus removing the

opportunity for feed metals to react on these particulate surfaces or the catalyst pellet exterior. Thus, most of the particulate matter carries through the trickle bed downflow reactor or is distributed throughout the bed length instead of crusting across the top of the reactor.

The UFR reactor design is essentially the same as an OCR reactor with the exception that there is no on-line catalyst replacement. Thus, the use of the UFR reactor provides a future opportunity to increase plant capacity of RDS catalyst life with a relatively low cost revamp without adding the catalyst replacement equipment.

Figure 5: UFR Versus OCR



While the UFR reactor technology cannot provide all the demetallation benefit of an OCR, the UFR is able to add utility in other ways. Because it is not a moving bed, multiple beds of different catalysts can be used, including combinations of HDM and HDS catalysts. By far, the greatest attribute of the UFR (as well as the OCR) is its very low pressure-drop. This avoids typical limitations in the recycle compressor and therefore, revamping an existing (V)RDS unit suddenly becomes not only feasible but economically very attractive. This was one of the main

reasons for the Shengli Refinery of Sinopec's Qilu Petrochemical Corp., in China to select CLG's UFR technology.

Qilu's original VRDS Unit was licensed by Chevron with FCC feedstock and fuel oil being the main products. In order to meet company strategies, it was necessary for this refinery to feed high-sulfur imported crude, while increasing the VRDS capacity. CLG's innovation, the UFR process, gave Qilu the capability to process Mid-East crudes at 43% increased capacity at one-fifth the cost of building a new unit to achieve the same objective. Qilu started up the UFR in late-2000 and its performance was demonstrated in December (Table 2 below).

Table 2. Evaluation of Catalyst Performances – Qilu UFR

	SOR (Design)	SOR (Actual)	Dec. 2000
S Remove Ratio, %	88.7	90.6	84.4
N Remove Ratio, %	34.4	46.9	34.9
Metal Remove Ratio, %	87.6	83.2	87.6
CR Remove Ratio, %	60.0	58.7	58.3
Conversion Ratio, 538°C+, %	33.5	36.0	35.2
Chemical Hydrogen Consumption, Nm ³ /m ⁻³	176	140	110

KNPC OCR Project

Since the first OCR start-up in 1992, OCR reactors have been licensed to three other refiners including KNPC's Mina Abdullah (MAB) Refinery. With minimal modifications and limited tie-in works the MAB OCR/ARDS unit achieves a 25% feed increase from its original design and 25% increase in catalyst run length while meeting the same product quality objectives. The OCR retrofit work was completed in fall of 2004 and the OCR/ARDS was started up successfully in October 2004.

The KNPC OCR test run showed that by adding one OCR reactor in the high-pressure reactor loop, the unit feed rate could be increased from 66,000 BPSD to 84,000 BPSD. This could be

achieved because the OCR reactor has a very low pressure drop and at the same time makes the feed easier for the fixed-bed reactors. During the test run the unit produced fuel oil with 0.63 wt% sulfur and 19 wt ppm metals. The OCR reactor provided more than 40% of the overall unit desulfurization and 55-65% of the overall unit demetallation.

KNPC was pleased that the unit passed all the performance guarantees, and the computerized catalyst transfer system continues to work safely and reliably. In December 2005, the fixed bed catalyst successfully achieved 15 months on stream, resulting in significant savings in unit downtime and fixed bed catalyst costs.

Interest in OCR/UFR is currently picking up, as evidenced by the KNPC OCR. Another UFR design is currently under construction for ENI in Taranto, Italy, with startup scheduled for April 2006.

KNPC RDS Project

Earlier this year, KNPC has awarded CLG the world's largest residuum hydrotreater complex to be built anywhere in the world. This hydrotreater complex is part of the New Refinery Project (NRP) in Kuwait. This 600,000 BPSD refinery will supplement KNPC's existing refineries at Mina-Al Ahmadi, Mina Abdullah and the Shuaiba Refinery. The objective of the New Refinery Project is to meet Low Sulfur Fuel Oil (less than 1 wt% sulfur) demand for domestic power production. During the planning stage of the new refinery project, KNPC selected fixed bed residuum hydrotreating as process for producing fuel oil in order to meet the desired fuel oil qualities – 0.5 wt% sulfur, and 15 ppm metals. CLG has extensive experience with designing units at this level of sophistication. Several of these RDS units are producing high quality low sulfur fuel oil with very low sediments throughout the runlife. Others are used as RFCC pretreaters.

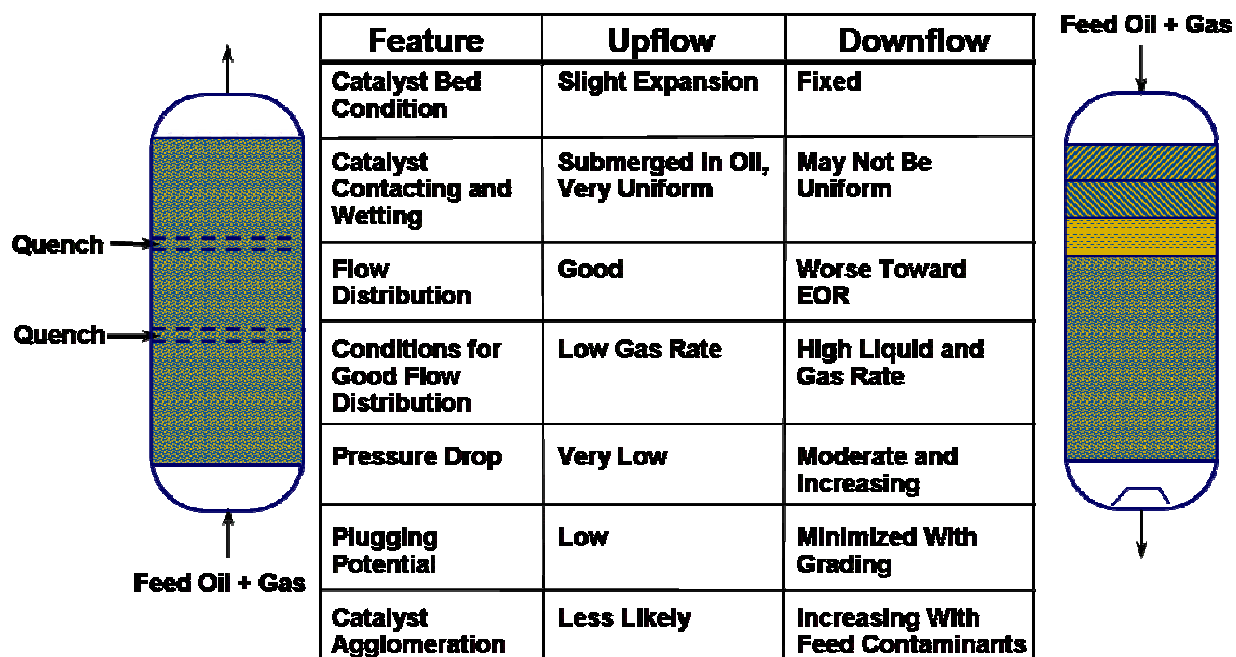
The design capacity of the ARDS complex is 330,000 BPSD which is by far the largest heavy oil hydrotreater in the world! Because of equipment size and weight limitations and to provide additional operational flexibility, KNPC has decided to build three RDS units, each processing

110,000 BPSD atmospheric residue feed. In addition each unit will have two independent high pressure reactor loops with a common fractionation section. To avoid pressure drop build-up during the run, the units are designed with an UFR as guard reactor.

Clearly such a large scale project needs to be carefully planned. In an early stage the manufacturing schedule of the reactors and catalyst will be coordinated with the reactor and catalyst manufacturers, to ensure that they will fit in the overall project schedule. The basic design for this ARDS unit is underway; the unit is scheduled to start-up in 2010.

CLG strongly believes that for processing heavy feeds, the UFR technology is much more economical in assuring that cycle life will be determined by catalyst deactivation rather than by fixed bed guard zones of reactors. The benefits of upflow relative to fixed-bed downflow reactors are shown in Figure 6.

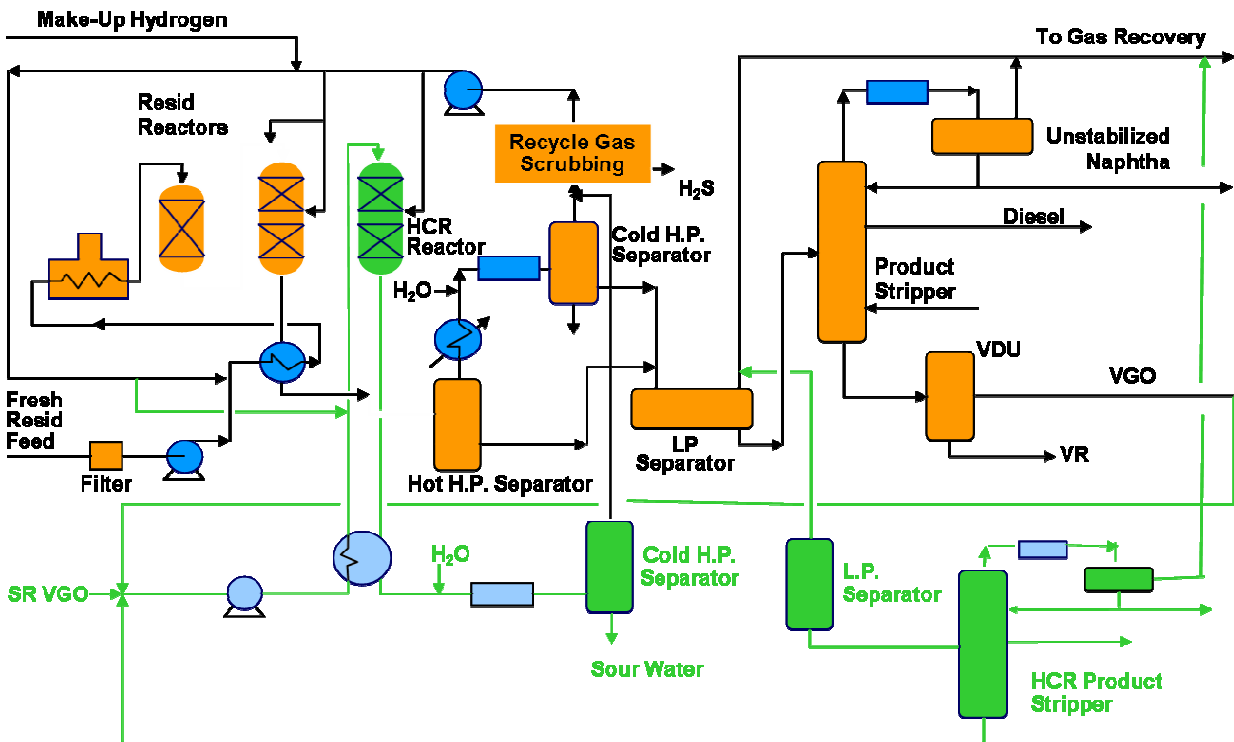
Figure 6: Upflow Versus Downflow Reactors



Hydrocracking Integrated with an RDS Unit

Applying the concept of integrated hydrotreating, CLG has designed a HCR integrated in a VRDS unit (24 MBPSD) for a European refinery. In this case the last of five resid reactors is converted to a hydrocracking reactor by installing new internals. The single-stage hydrocracker using CLG's ISOCRACKING technology is designed for 19 MBPSD – a combination of treated VGO from the resid product fractionator and some SR VGO. The hydrocracker is sharing a common recycle loop with the VRDS. New separators and fractionators will be installed to separate the high value ultra low sulfur diesel. Overall 50 LV% of the VRDS feed will be converted to diesel. The unit is currently in the detailed design phase and start-up is expected end of 2007.

Figure 7: CLG RDS/HCR Flow Diagram



Summary and Conclusion

The incentive for refiners to process heavier, high-sulfur crudes is greater than ever before due to the large differentials between sweet and sour crudes. Processing less expensive, heavier crudes that contain more sulfur to begin with makes it even more urgent to invest in bottom of the barrel upgrading to meet the new specifications and to maximize refinery margins. Residue upgrading technologies from CLG are selected by more refiners worldwide, in comparison to other technologies, when the refiner has decided on hydrogen addition as the preferred route.

CLG is the market leader in residue hydroprocessing technologies, which are mature and well proven. We continue to develop these technologies further together with refineries. One example is the integration of LC-FINING with a close-coupled hydrotreater that has been in operation at Shell Canada for three years. The concept has been extended to integrated LC-FINING and hydrocracking. Integration of LC-FINING and hydrotreating or hydrocracking is an advantageous and elegant solution to meet also the ULSD requirements at a significantly lower investment cost than two stand-alone units.

Other examples are the OCR technology that has been started up successfully at KNPC, and the UFR reactors that are integrated in the 330,000 RDS unit for KNPC as part of KNPC's New Refinery Project that will start-up in 2010. The combination of UFR and RDS technology resulted in the economically most attractive solution for KNPC for production of low-sulfur fuel oil.