

UPGRADING RESIDUES TO MAXIMIZE DISTILLATE YIELDS

Dan Gillis, Mark VanWees, Paul Zimmerman

UOP LLC, A Honeywell Company
Des Plaines, Illinois, U.S.A.

INTRODUCTION

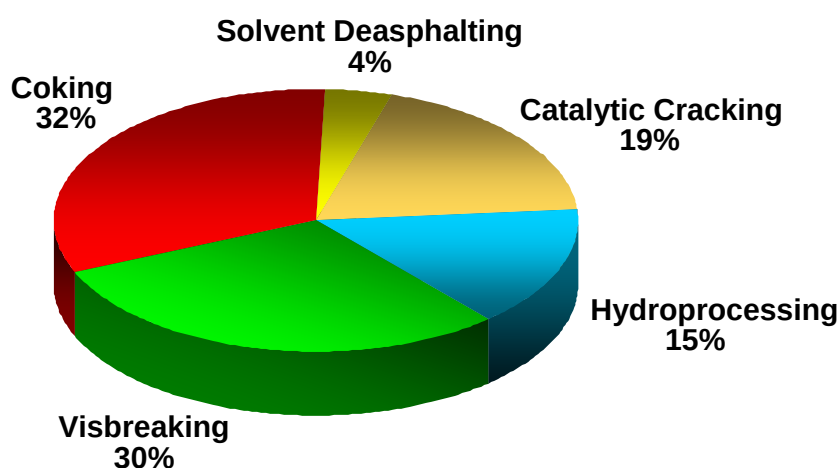
Never before have refiners faced the challenges caused by dramatic changes in crude prices and refinery margins. However some worldwide trends have not changed, such as the need to shift refinery product distributions to a more diesel-oriented slate and to reduce residue fuel oil production. The required shift from gasoline to distillate fuels cannot be accomplished solely by modifications to current hydrocracking or FCC operations. New technologies will be required that achieve higher non-distillable conversion and increased selectivity to distillate-range products. Ideally, these technologies should be both cost-effective and commercially proven.

UOP has responded to the needs for increased distillate yield and non-distillable conversion with the introduction of its latest residue upgrading technology offering, the UOP UniflexTM Process. This high-conversion slurry hydrocracking technology contains elements of a commercially-proven slurry reaction system and the UOP UnicrackingTM and UnionfiningTM technologies. The Uniflex Process can achieve non-distillable conversion levels in excess of 90 wt% with distillate yield over 50 vol%. This paper discusses the features of the Uniflex Process technology, its yield and economic advantages over conventional residue upgrading technologies, and other applications of the technology.

EXISTING RESIDUE CONVERSION SOLUTIONS

Conventional residue conversion solutions are well developed and, for the most part, operate efficiently within their technical constraints. Figure 1 illustrates the worldwide distribution of the major residue conversion technologies which refiners have installed. Thermal technologies such as visbreaking and coking account for approximately two-thirds of this installed capacity, with hydroprocessing, RFCC and solvent deasphalting, to a lesser extent, making up the remainder.

Figure 1: Historical Worldwide Residue Conversion Selection



Visbreaking and Delayed Coking

Visbreaking is the oldest of all residue upgrading technologies. The large number of installed visbreakers reflects refiners' needs to minimize residue fuel oil cutter stocks. Few new visbreaking projects are being considered primarily because a visbreaker's major product is residue fuel oil for which demand is not increasing.

A significant number of recent projects have selected delayed coking due to the technology's ability to fully convert non-distillables. The product yields, consisting of light ends, naphtha, distillates, heavy coker gas oil (HCGO), and the byproduct coke are dependant on the feedstock qualities. The HCGO product is suitable for feedstock to downstream hydroprocessing, hydrocracking, and FCC units. For these reasons, the majority of recent grass root and major refinery expansion projects have selected the combination of delayed coking and hydrocracking to maximize distillate yields. While delayed coking technology continues to be improved from operational and reliability perspectives, only minor improvements in reduced coke yield and increased liquid yields have been obtained.

Residue Hydroprocessing

Hydroprocessing, including fixed bed residue hydrotreating and ebullated-bed residue hydrocracking, has seen limited commercial application. Typically, fixed-bed residue hydrotreating processes, such as the UOP RCD UnionfiningTM Process, are used in conjunction with RFCC-type units to address gasoline-focused markets. This is due to the hydrotreating unit's ability to obtain very high residue contaminant removal, Conradson Carbon (CCR) reduction and hydrogen addition.

Ebullated-bed residue hydrocracking can obtain conversion levels equivalent to or even higher than delayed coking. However, it produces a low-to-medium quality liquid residue product which is usually only suitable for fuel oil applications.

Solvent Deasphalting

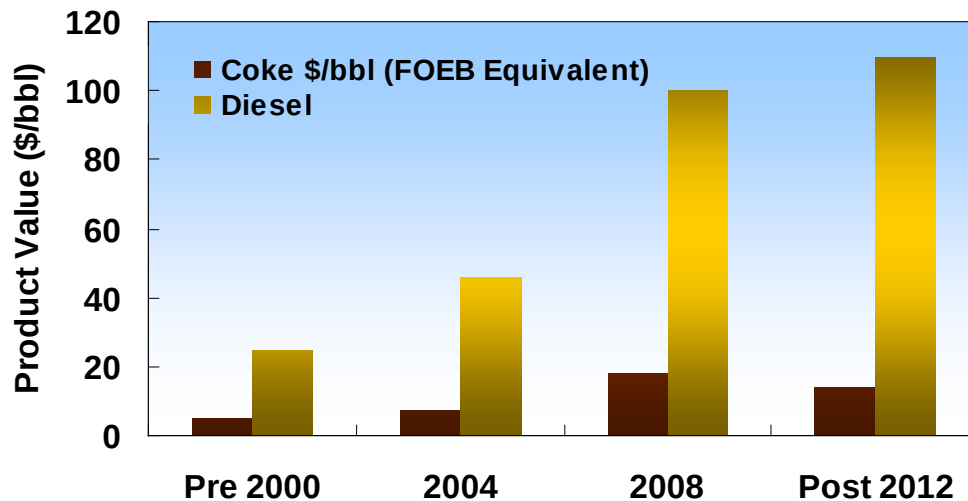
Similar to residue hydrotreating, solvent deasphalting applications have been limited. Recently, however, interest in the combination of solvent deasphalting and conversion technologies to obtain higher vacuum residue conversion has increased. Solvent deasphalting applications are typically limited by both the ability of the downstream conversion unit to process the recovered deasphalted oil and the limited uses for its large volume of pitch byproduct.

SLURRY HYDROCRACKING ALTERNATIVE

As the world's leader in refinery and petrochemical technology licensing, UOP understands the unique benefits and limitations associated with each of the above residue conversion technologies. UOP also realizes that the need for both high conversion and high distillate yields requires the development of more-selective vacuum residue conversion processes, as illustrated by the price differential trends shown in Figure 2.

For these reasons, UOP evaluated alternate residue conversion technologies, concluding that slurry hydrocracking technology has the highest potential of meeting these requirements. Although not well known to most refiners, slurry hydrocracking is actually one of the industry's oldest residue conversion technologies. It involves the processing of a mixture of residue and fine particulate catalyst in an upflow reactor in a hydrogen-rich environment. This reaction environment facilitates very high conversion of residue to liquid products, particularly distillate boiling-range components.

Figure 2: Diesel and Coke Prices



Reference: 2008 FACTS Global Energy

The first slurry processes were developed in the 1920-1930's to liquefy coal to produce low quality distillates. These first processes utilized extremely high pressures and were hampered by high costs and by operational issues. Eventually, slurry hydrocracking was recognized as a potential solution for the conversion of difficult vacuum residues to transportation fuels. The strong presence of processes such as delayed coking and residue hydrotreating, however, limited its application. It was not until the development of heavy and extra-heavy crude oil projects in the late-1970's and early-1980's that interest in slurry hydrocracking reemerged. However, the collapse of heavy-to-light crude price differentials in the late-1980's severely curtailed the need for a high conversion technology such as slurry hydrocracking.

In the early-2000's UOP began the evaluation of several options focused on providing a commercially-viable slurry hydrocracking technology offering to the market. It was concluded that the most efficient approach involved Natural Resources Canada's (NRCan) CANMET Hydrocracking Process.

In 2006 UOP began work with NRCan to evaluate and improve their CANMET Hydrocracking Process technology package. Pilot plant testing was conducted, as well as detailed reviews of engineering design and operations. UOP acquired the exclusive worldwide rights to license the CANMET Hydrocracking Process in 2007. Continuing work has resulted in the development of the UOP Uniflex Process, which includes a combination of elements from the commercially proven CANMET Hydrocracking Process reactor section and UOP's Unicracking and Unionfining Process technologies.

UOP UNIFLEX PROCESS

Background

The CANMET Hydrocracking Process was developed in the mid-1970's at the Energy Research Laboratories of the Canada Centre for Minerals and Energy Technology (CANMET). The technology was designed to convert vacuum residue into salable products at moderate operating severities through the use of an inexpensive coke-inhibiting catalyst that was not poisoned by coke or by high feed organometallic contents.

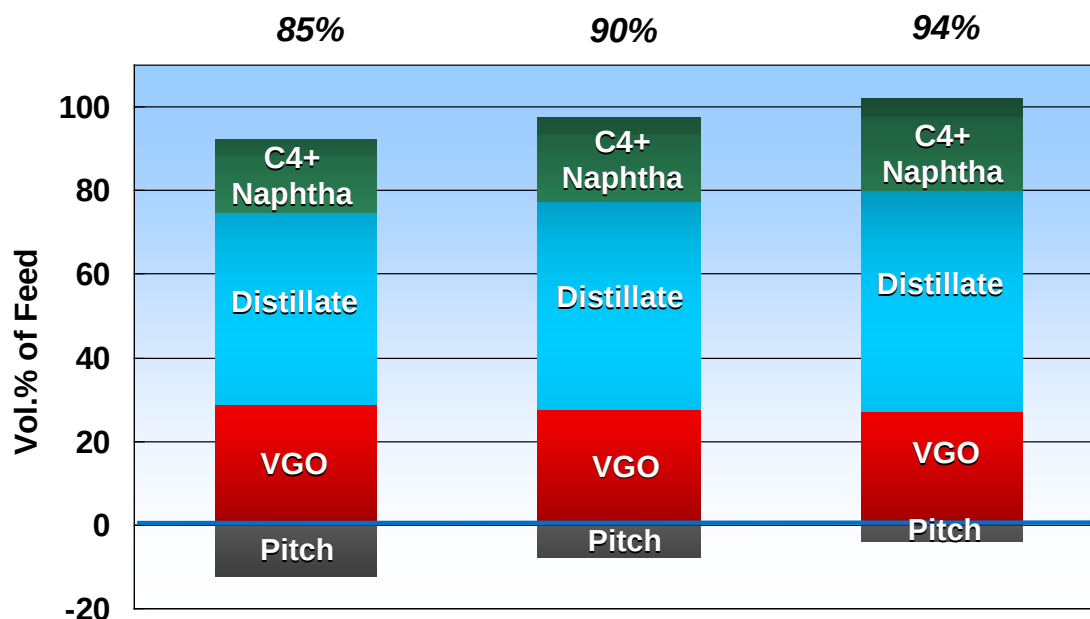
After extensive research and development work, the decision was made in 1979 to commercialize the CANMET Hydrocracking Process technology. A 5,000 BPD CANMET Hydrocracking Process demonstration unit was designed and built for Petro-Canada's Montreal Refinery. This unit was commissioned in 1985 and was used to verify the reactor design parameters, the accuracy of performance prediction models and the suitability of materials of construction. The first five years of operations achieved:

- Validation of commercially measured hydrodynamics, feedstock conversion, yields and product qualities against pilot plant results and design models,
- Verification of the operability, flexibility and reliability of the process,
- Improvements in catalyst formulations,
- Improvements in control systems, interlocks and procedures, and
- Development of reactor monitoring and optimization techniques.

The ability of the CANMET Hydrocracking Process to achieve high levels of residue conversion at high distillate selectivity is best illustrated by a long-term demonstration test run conducted in the Petro-Canada Montreal unit with Cold Lake bitumen vacuum residue. Figure 3 summarizes the yields from this test at three different conversion levels. At the most severe processing conditions, the unit achieved nearly 94 wt% 975°F+ conversion. At this conversion, C₄ – 975°F yield was slightly more than 102 vol% of feed and the distillate yield was 53 vol%.

Having met their objectives, Petro-Canada shut down the CANMET demonstration unit in 1989. In 1992 the plant was restarted due to increased heavy-to-light crude price differentials. In the last five years of operation the average on-stream efficiency was 97%. During this period, the unit processed a wide range of crudes from Venezuelan, Mexican and Middle Eastern sources. Process improvements allowed the co-processing of other refinery streams including FCC slurry oil, CANMET VGO, visbroken vacuum residue and CANMET unconverted pitch.

Figure 3: Impact of Vacuum Residue (975°F+) Conversion on Yields



Uniflex Process Flow Scheme

The typical Uniflex Process flow scheme is shown in Figure 4. As this figure illustrates, the flow scheme is similar to that of a conventional UOP Unicracking Process unit. Liquid feed and recycle gas are heated to temperature in separate heaters, with a small portion of the recycle gas stream and the required amount of catalyst being routed through the oil heater. The outlet streams from both heaters are fed to the bottom of the slurry reactor.

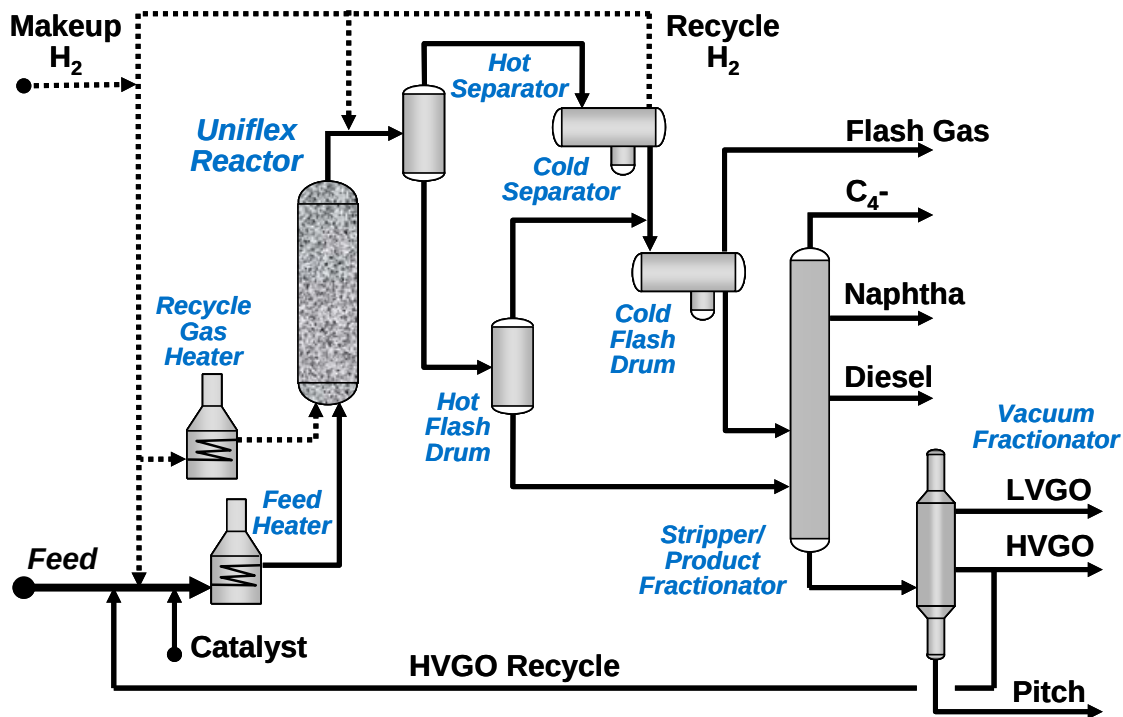
The reactor effluent is quenched at the reactor outlet to terminate reactions and then flows to a series of separators with gas being recycled back to the reactor. Liquids flow to the unit's fractionation section for recovery of light ends, naphtha, diesel, vacuum gas oils and unconverted feed (pitch). Heavy vacuum gas oil (HVGO) is partially recycled to the reactor for further conversion.

Reactor Design and Performance

The heart of the Uniflex Process is its upflow reactor that operates at moderate temperature and pressure (815–880°F and 2000 psi, respectively). The reactor's feed distributor, in combination with optimized process variables, promotes intense backmixing in the reactor without the need for reactor internals or liquid recycle ebullating pumps. Because this backmixing provides near-isothermal reactor conditions, the entire reactor can operate at the higher temperatures required to maximize vacuum residue conversion. Reactor conditions also allow the majority of the products to vaporize and quickly leave the reactor, thereby maximizing the residence time of the feed's heavier

components and minimizing any undesirable secondary cracking reactions which would produce lower-valued products and increase hydrogen consumption.

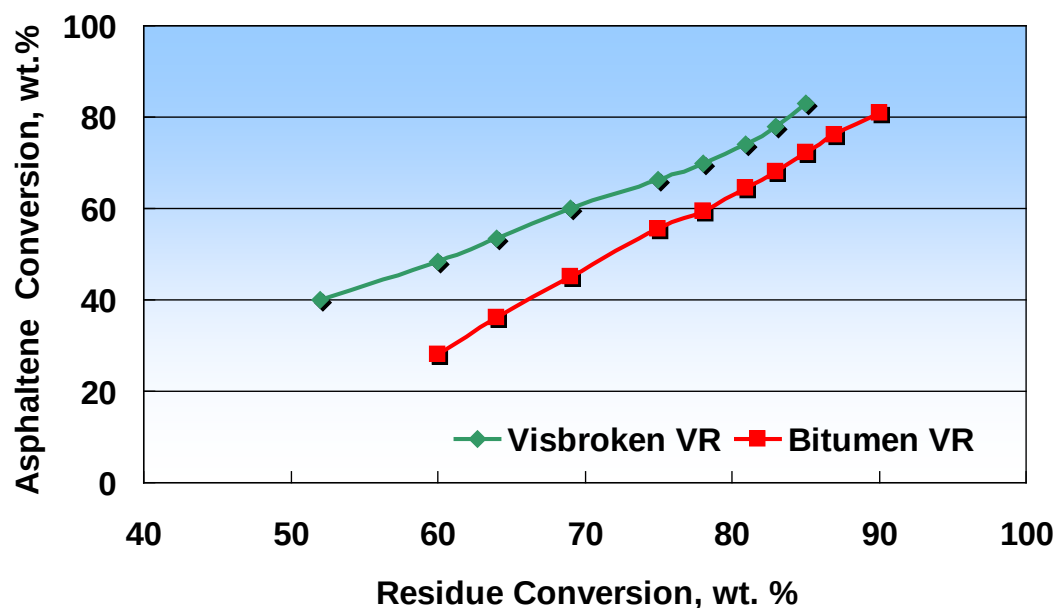
Figure 4: Uniflex Process Flow Scheme



Catalyst

The Uniflex Process employs a proprietary, nano-sized solid catalyst which is blended with the feed to maximize conversion of heavy components and inhibit coke formation. Specific catalyst requirements depend on feedstock quality and the required severity of operation. The catalyst is dual functional, with its primary function being to impart mild hydrogenation activity for the stabilization of cracked products while also limiting the saturation of aromatic rings. As can be seen in Figure 5, this permits the reactor to operate at both very high asphaltene and non-distillable conversion levels.

Figure 5: Uniflex Process Asphaltene Conversion



The Uniflex Process catalyst also decouples the relationship between conversion and a feed's CCR content. This is distinct from delayed coking where a higher feed CCR content produces proportionally higher coke yields. As a result, the Uniflex Process provides significantly more feedstock flexibility than delayed coking. The large catalyst surface area hinders the coalescence of pre-coke material, including toluene insolubles and mesophase, aiding in their conversion to lower molecular weight products. The dual functionality of the Uniflex Process catalyst provides stable operations at very high conversion levels under both normal operating and upset conditions.

Technology Improvements

Since acquiring the rights to license the CANMET Hydrocracking Process, UOP has invested significant effort in improving catalyst performance, engineering design and feedstock processing flexibility. This work has been carried out with financial support and strategic input from the Alberta Energy Research Institute (AERI) as part of its Hydrocarbon Upgrading Demonstration Program. This program is aimed at developing and demonstrating commercially viable advanced technologies that convert bitumen and bitumen-derived products into higher-valued products with reduced environmental footprints.

The Uniflex Process catalyst costs are lower relative to other slurry hydrocracking technologies because expensive catalytic materials, such as molybdenum, are not required. Operating costs will be further reduced by UOP's on-going development of a second-generation catalyst that will reduce catalyst consumption by over 50% while also providing improved catalytic performance.

UOP's engineering efforts have included the development of an updated and improved engineering design. This new design reduces capital and operating costs and allows for customization for specific refinery applications.

UOP pilot plants are able to confirm the design basis for new applications. This is possible because UOP and NRCan have over 100,000 hours of cumulative pilot plant experience with the Uniflex Process technology. Performance of these pilot plants has been validated against the Petro-Canada demonstration unit.

UOP can offer several integration opportunities because the Uniflex Process operates at hydrogen partial pressures suitable for hydroprocessing and hydrocracking of its products. The type of integration depends on the specific circumstances of the existing refinery and project. Depending on the level of integration, significant reduction in equipment count and capital investment can be obtained.

The Uniflex Process typically produces a pitch product which represents around 10 wt% of the unit's incoming feed. This pitch is a viable, low-cost substitution fuel for conventional boilers, fluidized bed boilers, gasification, cement kilns and other applications. In fact, for many years the Petro-Canada Montreal refinery sold pitch in liquid form to a local cement manufacturer. UOP is developing a pitch solidification process so that the pitch may be transported as a solid to distant markets.

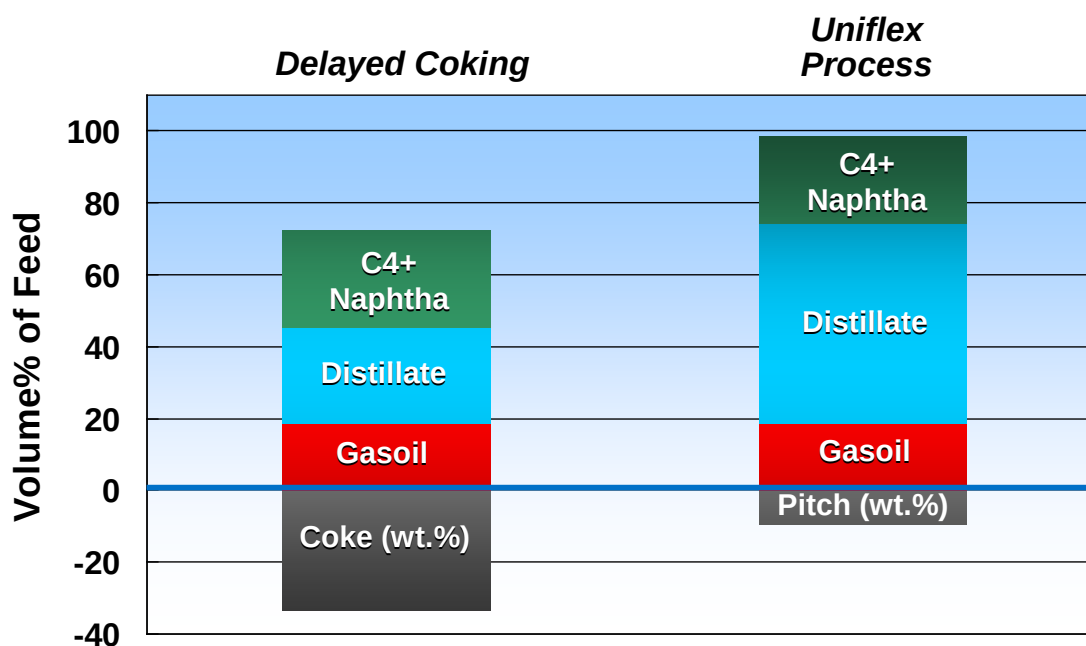
TECHNOLOGY COMPARISONS

Product Yields: Delayed Coking and the Uniflex Process

The ability of the Uniflex Process to increase the conversion of residues to valuable products, particularly distillates, relative to other technologies can best be illustrated by a comparison of the yields produced from the Uniflex and delayed coking processes when processing a typical sour residue. This comparison, which is shown in Figure 6, indicates the Uniflex Process relative to delayed coking provides refiners:

- One third the yield of lower-valued residue byproduct,
- More than 25% increase in total liquid yield, and
- Twice the distillate yield.

Figure 6: Product Yields from Delayed Coking and the Uniflex Process



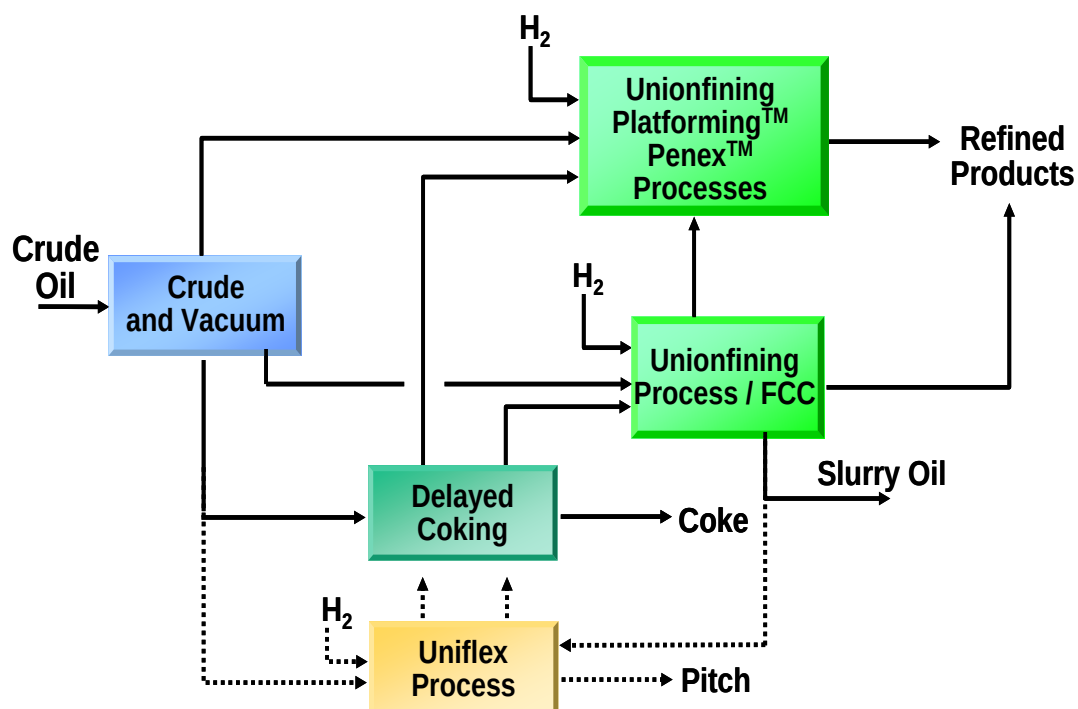
Not evident in this comparison, the Uniflex Process also produces higher quality products than those from delayed coking due to the hydrogenation function of the catalyst. Additionally, the Uniflex Process vacuum gas oil product is further improved by recycling the heavy vacuum gas oil product back to the reactor section so it can be further converted. This reduces the amount of the vacuum gas oil's high boiling point components, thereby increasing the distillate and, to a lesser extent, naphtha yields from the Uniflex Process unit. Conversely, the process of maximizing liquid yields from a delayed coking unit results in an increase in the HCGO's end point. With this increased end point, there is a significant increase in the amount of contaminants and multi-ring aromatic components in the HCGO that increase catalyst deactivation in the required downstream hydroprocessing units.

Overall Refinery Impacts

To fully understand the economic impact of the Uniflex Process, UOP developed an LP model of a typical full-conversion North American refinery employing FCC and delayed coking conversion technologies. This configuration, which is illustrated in Figure 7, assumes the FCC feed hydrotreater can be operated in a high-conversion, mild hydrocracking mode and includes typical distillate and naphtha hydrotreating process units, as well as heavy naphtha reforming and light naphtha isomerization units. UOP's evaluation has assumed a mid-range refinery capacity of 150,000 BPD crude throughput.

For comparison, the Uniflex-based configuration would replace the delayed coking unit with a Uniflex Process unit. In addition to processing vacuum residue, the Uniflex Process unit would also process the slurry oil produced in the FCC.

Figure 7: Refinery Configuration



The major crude and product prices summarized in Table 1 reflect longer-term, stable production and demand structures. UOP’s evaluation considered the processing of the two different crude blends shown in Table 2 to allow the impact of feed quality on refinery economics to be determined.

Table 1: Refinery Evaluation Study – Price Assumptions

<i>Purchases:</i>	<i>\$/Bbl</i>
West Texas Intermediate	82.68
Arab Medium	74.94
Western Canadian Select	59.11
<i>Major Product Sales:</i>	<i>\$/Bbl</i>
Regular Gasoline	93.77
Low Sulfur Diesel (Future Price)	106.50
FCC Slurry Oil	64.50
Petroleum Coke/Pitch, \$/MT	15.32

Table 2: Refinery Evaluation Study – Crude Blends

Crude Blend:	Medium	Heavy
West Texas Intermediate	38%	19%
Arab Medium	50%	53%
Western Canadian Select	12%	28%

Yields

Table 3 contains a summary of the results of UOP's evaluation. As this table indicates, the capacity of the conversion unit, be it a delayed coking or Uniflex Process unit, varies from 27,600 BPD to 34,100 BPD depending upon the crude blend.

When processing the medium crude blend, the delayed coking-based refinery configuration achieves a total refinery liquid product yield of 105 vol% of the incoming crude, with approximately equal amounts of gasoline and distillate products being produced. Because the refinery objective involved maximizing distillate production, the LP chose to operate the FCC pretreating unit in a high-conversion mode which resulted in approximately 40% conversion of the pretreater's feed into distillate-and-lighter products.

Table 3: Refinery Evaluation Study – Yields

	Medium Crude Delayed Coking	Medium Crude Uniflex Process	Heavy Crude Delayed Coking	Heavy Crude Uniflex Process
Conversion Unit Size, BPD	27,600	28,200*	33,350	34,100*
Coke Yield, MTD	1,199	444	1,627	544
Yields, volume% of crude feed				
Total Liquids**	105	108	105	110
Gasoline	48	47	50	48
Distillate	50	55	49	55
Gasoline-to-Distillate Ratio	0.96	0.86	1.01	0.88

* Includes FCC slurry oil

** Includes LPG's and Fuel Oil

Table 3 indicates substitution of a Uniflex Process unit for the delayed coking unit increases refinery total liquid yield to 108 vol% of crude. This increase is reflected by a 63% reduction in the yield of lower-valued residue byproduct. Equally as important, the product distributions indicate the Uniflex configuration increases the refinery's yield of distillate product to 55 vol% of crude, a

10% increase in distillate production. The Uniflex Process represents a step change in the ability of a refinery to maximize distillate yields.

The Uniflex Process has additional benefits when processing heavier crudes. With the heavy crude blend, the Uniflex Process total liquid yield increases to 110 vol%, 5 vol% higher than delayed coking. When processing the heavy crude there is an additional 2 vol% yield of total liquid relative to the medium crude Uniflex Process operation. This demonstrates how the Uniflex Process increases feedstock flexibility.

Another exciting benefit of the Uniflex Process is that the FCC unit can be optimized to further increase distillate yields. Operating the FCC unit in a maximum-diesel mode will increase the production of low-value slurry oil. Now, with the Uniflex Process, this slurry oil can be converted to high-value products, especially distillates. This results in an additional 1 vol% increase in refinery distillate yield.

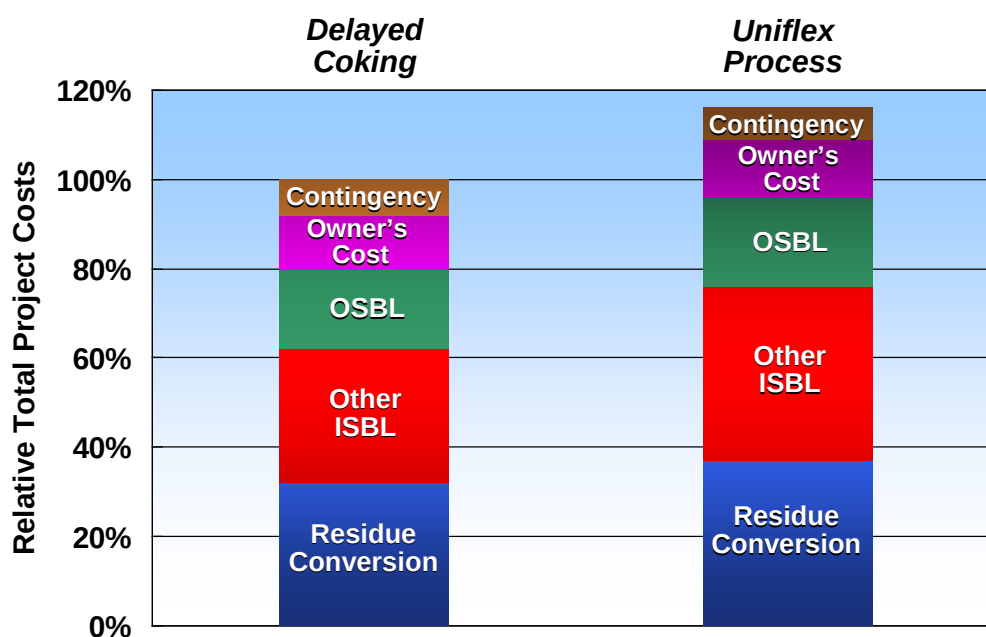
Relative Capital Costs

In order to fairly compare capital costs, the entire residue upgrading complex needs to be considered. The total cost needs to include:

- The residue upgrading unit,
- Other process units required to support the residue upgrading unit,
- Outside battery limits (OSBL) facilities,
- Owner's costs, and
- Contingency costs.

To baseline these costs, UOP provided detailed Uniflex Process equipment information to a major US contractor who also developed costs for the equipment items required for the delayed coking unit. As Figure 8 indicates, the total ISBL cost is higher for the Uniflex Process configuration relative to the delayed coking configuration primarily due to the larger product treating, hydrogen plant and sulfur recovery requirements. As OSBL requirements and Owner's costs are expected to be similar for both processing configurations, the total relative project costs are within 10 to 20% of each other.

Figure 8: Relative Capital Costs



Refinery Margins

Table 4 shows that the Uniflex Process configuration significantly increases refinery revenue relative to the delayed coking configuration. For the medium crude operation, inclusion of the Uniflex Process unit increases refinery margins by \$128 million per year, or a \$2.60/bbl increase in refinery margin on a crude oil basis over the delayed coking configuration.

Refinery margins increase even further when the Uniflex Process unit processes the heavy crude as a result of the lower crude price and the increased product yields. The margin advantage of the heavy crude, Uniflex Process configuration relative to the medium crude, delayed coking configuration increases to \$384 million per year, or a \$7.70/bbl increase in refinery margin on a crude oil basis.

As the investment in a Uniflex Process configuration is only slightly higher than the delayed coking configuration, the payback for the incremental investment is typically 1 year or even less. Additionally, the relatively high refinery margins provided by the Uniflex Process provide a refinery with robust economics and protects against downside scenarios of low crude and product prices.

Table 4: Refinery Evaluation Study - Margins

	<i>Medium Crude Delayed Coking</i>	<i>Medium Crude Uniflex Process</i>	<i>Heavy Crude Delayed Coking</i>	<i>Heavy Crude Uniflex Process</i>
<i>Delta Margins, MM\$/year</i>				
Uniflex Process - Delayed Coking	Base	128		207
Heavy Crude - Medium Crude			173	384
Incremental Margin \$ per VR Bbl	Base	13.8		18.5
Incremental Margin \$ per crude Bbl	Base	2.6	3.4	7.7
Simple Payback, years		1.3		0.8

* 335 operating days per year

UNIFLEX PROCESS SYNERGIES WITH OTHER PROCESSES

Refineries with existing residue conversion units such as Delayed Coking, Solvent Deasphalting, and Residue Hydrotreaters can take advantage of the addition of a Uniflex Process. There are 2 main scenarios where this is attractive:

- 1) With crude capacity increases and or shifts to heavier crude diets resulting in a larger quantity of vacuum residue to process.
- 2) Desire to increase distillate yields with existing crude rates.

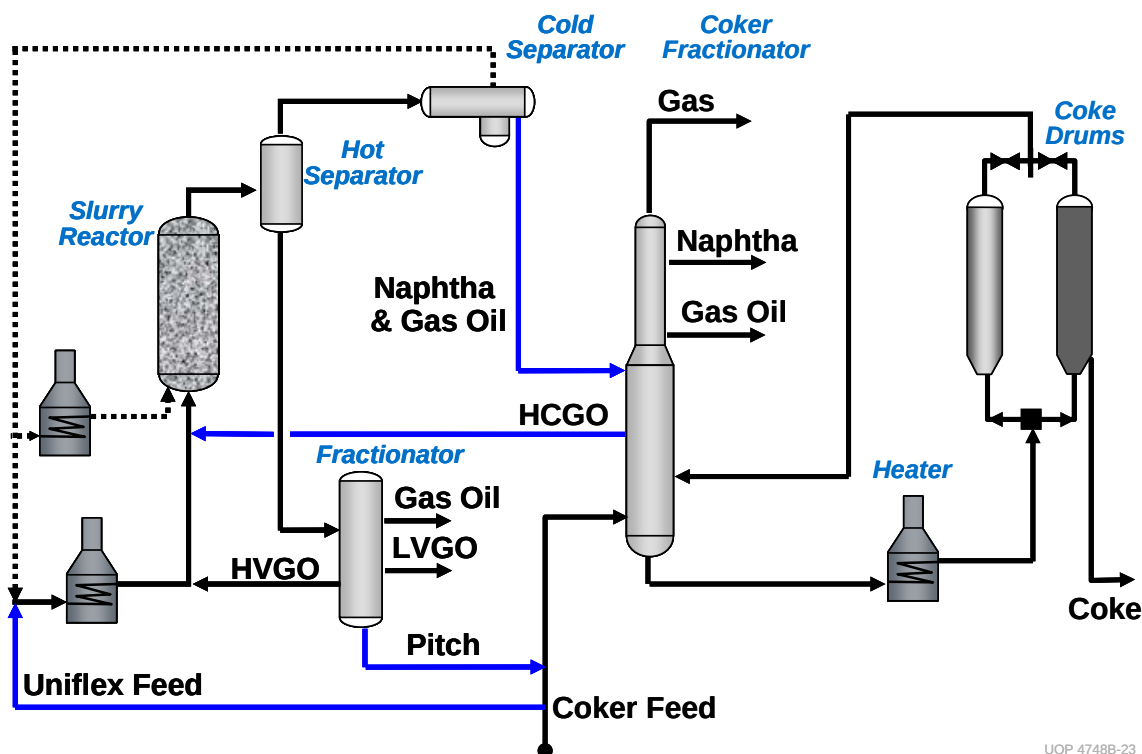
Synergies with existing Delayed Coking Units

Although the Uniflex process is a significantly different process than delayed coking, it can be efficiently integrated into a refinery with an existing delayed coking process. This integration would predominately be via selective routing of each unit's streams to the other unit and sharing of infrastructure and light-ends fractionation systems.

In this integration scenario, the vacuum residue is split with part of it directed to the Uniflex Process and the remainder to an existing delayed coking process. The Pitch stream from the Uniflex Process is combined with the remaining vacuum residue and directed to the Delayed Coker. Heavy coker gas oil (HCGO) is now routed to the Uniflex Process feed along with the Uniflex HVGO recycle stream. Both processes products are sent to common fractionation.

Figure 9 shows one possible integration between the Uniflex Process and delayed coking.

Figure 9
Uniflex Process Integrated with Delayed Coking



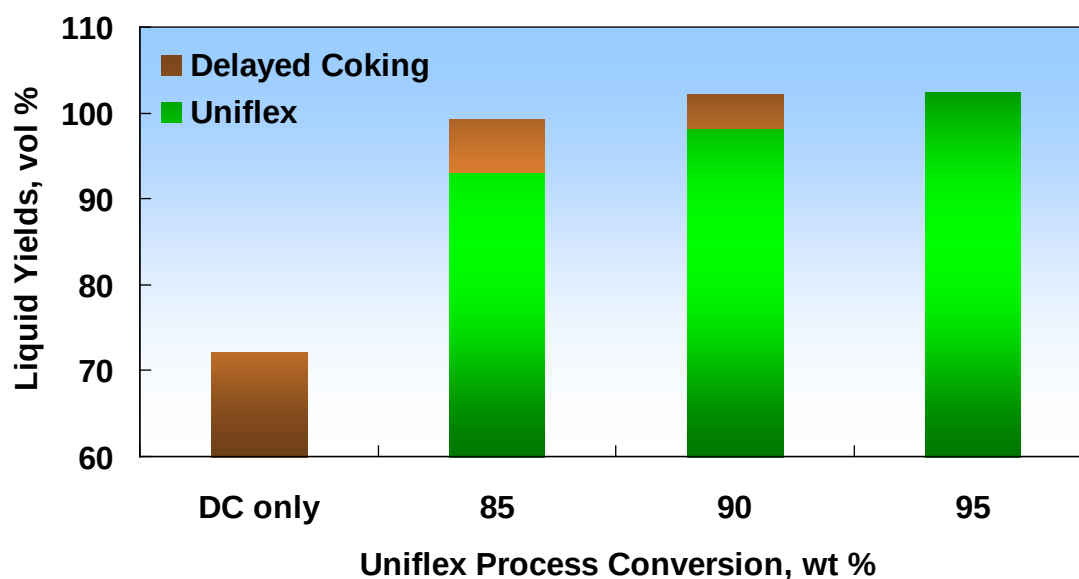
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The processing of vacuum residue in the Uniflex Process before the delayed coking process results in both significant increases in product yields and reductions in net coke yield. The degree to which this occurs depends on the selected conversion level in the Uniflex Process. Figure 10 shows how the liquid yields are increased.

As was discussed in the previous section it was shown that directionally the relative economic attractiveness of the Uniflex Process versus delayed coking increases with the level of conversion in the Uniflex process. This economic advantage is to a certain extent maintained at lower conversion levels in the Uniflex Process. This is because of the additional processing of the Pitch stream in the delayed coking process resulting in some additional liquid yields. This then provides the opportunity to optimize the level of conversion in the Uniflex process depending on several factors such as:

- Availability and cost of Hydrogen
- Existing delayed coker coke drum capacities
- Other refinery processing unit's limitations and costs of expansions

Figure 10
Liquid Yields from Uniflex Process Residue Processed in Delayed Coking
 (Arab Light Residue)



Synergies with Solvent Deasphalting and Residue Hydrotreating

The Uniflex Process also has synergies with other conventional conversion units such as with solvent deasphalting (SDA) and residue hydrotreating.

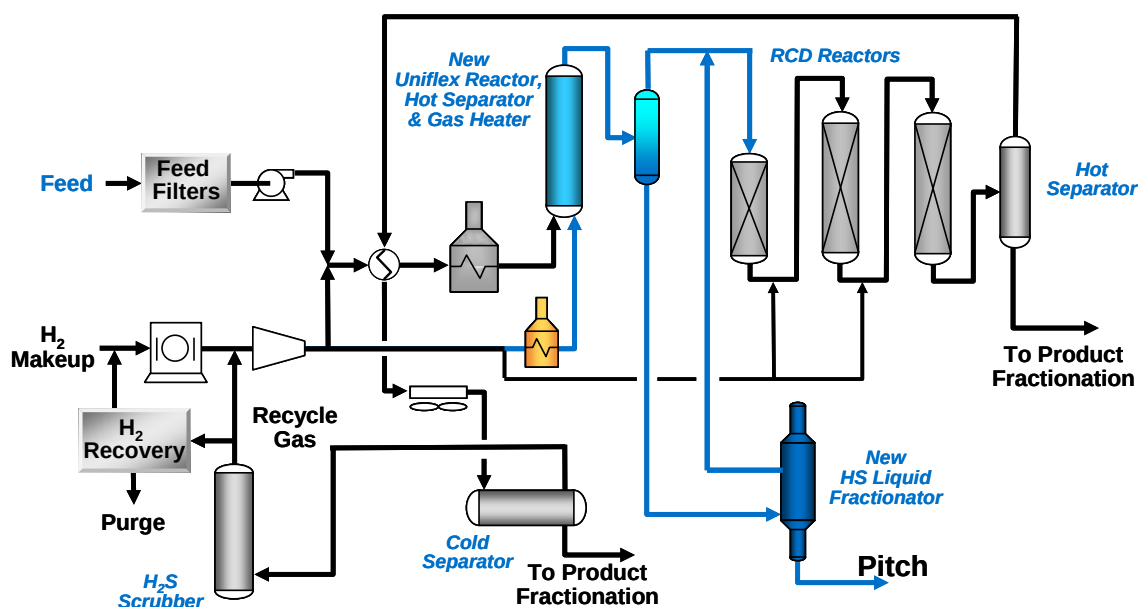
For light residues that contain a large percentage of low contaminant level saturated compounds the installation of a Solvent Deasphalting Process up front of the Uniflex Process will allow capturing of high-quality deasphalted oil (DAO) for downstream processing in FCC or hydrocracking units. The feed to the Uniflex Process would then start to resemble the residue from a medium to heavy crude. Refineries with an existing SDA process would probably find this to be an attractive option.

Refiners with existing residue hydrotreating processes (RCD) have a unique opportunity to add a Uniflex Reactor up front of the fixed bed reactors. This results in an integrated Uniflex-RCD Process with the benefits of both technologies. Beside the addition of the Uniflex Process reactor there would be the requirement for some additional fractionation equipment to separate the Pitch stream from the other Uniflex products before they are processed in the main RCD reactors. The investment cost for this approach would be significantly less than the cost of a delayed coking process and possibly competitive with the cost of a new SDA process.

This revamp option provides a refiner with an existing RCD process the following opportunities:

- Very high conversions of vacuum residue to desired product, especially Diesel,
- Obtain very long catalyst life in the RCD reactors
- Produce much higher quality of RCD products for downstream processing
- Obtain additional conversion of the Vacuum Gas Oil components by middle hydrocracking in the RCD reactors.

Figure 11
Residue Hydrotreater Converted to an Integrated Uniflex Process Unit



CONCLUSIONS

The Uniflex Process includes elements of UOP's hydroprocessing expertise and a commercially proven slurry hydrocracking reactor system that demonstrate very high residue conversions with a reliable operating history. UOP's Uniflex Process maximizes distillate and gasoline yields from vacuum residues. Distillate yields from vacuum residue feed can be more than double those obtainable with existing conversion technologies. The yield advantages with the Uniflex Process increases with heavier, high-CCR residues. This demonstrates the greater feedstock flexibility with the Uniflex Process compared to other residue upgrading processes including delayed coking.

The Uniflex Process will significantly increase refinery margins. The margin advantage is two-fifty to eight U.S. dollars per barrel of crude higher than the refinery margin with other residue

upgrading processes. As the Uniflex Process complex capital investment is only slightly higher than the capital investment for a delayed coking complex, the payback for the incremental investment is typically one year or less. These advantages result in the Uniflex Process providing very attractive rates of return, even with modest crude and product prices.

Opportunities for integration of the Uniflex Process with existing refinery residue conversion units enable a refiner to utilize existing assets and take advantage of the Uniflex capabilities at significantly lower investment costs.

The Uniflex Process provides refiners with a unique opportunity to maximize distillate yields and refinery margins from vacuum residue.

UOP LLC
25 East Algonquin Road
Des Plaines, IL 60017-5017
Tel: 847.391.2000
www.uop.com

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