

# CONSIDER NEW TECHNOLOGY TO PRODUCE 'CLEAN' DIESEL

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# Consider new technology to produce 'clean' diesel

## Advances in catalysts enable cracking gasoils at moderate pressures

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**D**emand for diesel and jet fuel is expected to grow, and many refiners are actively focused on the shifting demand from motor gasoline to diesel. While still analyzing possible options, some refining projects will require significant capital investment. The future of diesel fuel is a topic of much speculation. In markets dominated by fluid catalytic cracking (FCC)-based refineries, the need to increase distillate production has taken on a new dimension, posing interesting challenges, while presenting some unique opportunities. In addition, following the European and US regulation trends, regulatory decisions have substantially reduced sulfur levels in fuels. Much attention on the possibility of tighter specifications for aromatics, density, boiling range and cetane number can be expected.

Therefore, European refiners are faced with the challenge of supplying this incrementally increasing demand for diesel and jet fuels while meeting tough new regulations on the quality for all products. All of this must be accomplished within a business climate that mandates applying low-cost technical solutions while optimizing the use of existing refinery resources.

New technologies are being developed to address these challenges. For example, a commercialized moderate-pressure hydrocracking (MPHC) suite of technologies can provide an economic solution to desulfurize heavy gasoils (HGO) with options to convert part of the feed into valuable higher-quality distillate products.

MPHC uses a lower pressure, once-through, lower-cost approach that is well suited for partial conversion of a variety of feedstocks at lower costs as compared to other hydrocracking technologies. These processing methods are also highly reliable and can handle difficult feeds from FCCs, visbreakers, cokers, solvent deasphalters and deep-cut fractionators. It offers refiners a very efficient and economical hydroprocessing option.

A single-stage MPHC unit is highly economical for up to 65% conversion of HGOs to low-sulfur distillates while producing a highly upgraded unconverted oil stream. The unconverted MPHC bottom product is an excellent FCC feedstock and can significantly improve the economics of the FCC operation with better yields and lower environmental emissions.

For conversion levels greater than 65%, an integrated two-stage MPHC method is a commercially proven approach that will allow refiners to selectively hydrocrack vacuum gasoil (VGO) and to maximize production of high-quality Jet A1 and diesel products. This unique technology option uses a proprietary catalyst system and takes advantage of two different chemistries, i.e., hydrocracking as well as selective hydroisomerization hydrocracking, both at moderate pressures, to achieve up to 85% once-through conversion. The technology was first applied at the Mobil Jurong refinery in 1990.

In either the single- or two-stage case configuration, the unit will operate at moderate pressure (about 100 bar) and achieve good selectivity to diesel and jet products, while providing the refiner with the processing flexibility to make ultra-high-quality premium distillates. Operating at lower pressure significantly lowers capital investment and substantially reduces hydrogen consumption and compression energy, thus making this method a very attractive technology option for European refiners.

Furthermore, the processing requirements for the MPHC unit is within the range of many existing VGO or FCC feed desulfurization units and provides opportunities to economically convert these units to provide additional conversion. Several examples highlight the technical and economic features of one- and two-stage MPHC technologies and provide comparisons with conventional high-pressure (HP) hydrocracking units.

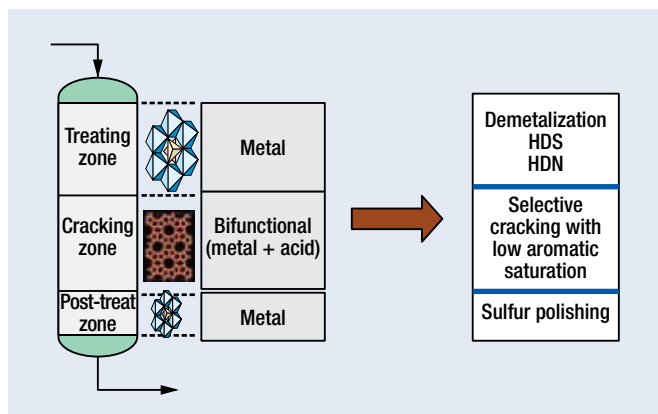
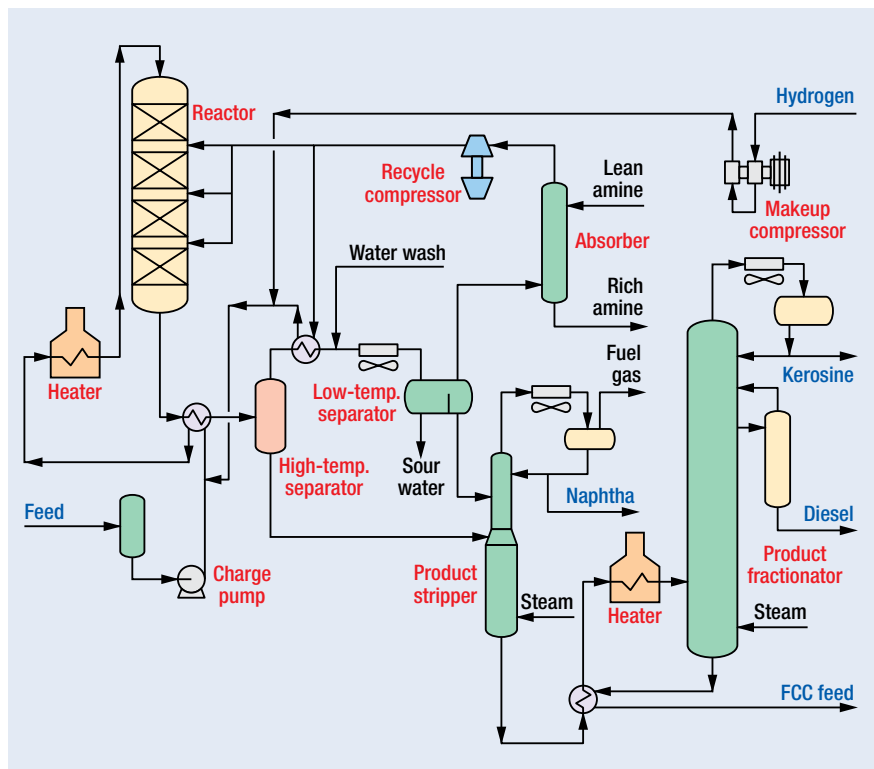
**Single-stage moderate pressure hydrocracking.** In the 1960s and 1970s, the most common hydrocracking application was the conversion of distillate boiling range materials for maximum naphtha production and, finally, to make gasoline. As demand for middle distillate products increased and gasoline demand leveled off, hydrocracking processes that maximized conversion of VGO to jet and diesel fuel gained in importance.

Hydrocracking has since achieved widespread use in petroleum refining for converting various petroleum fractions to lighter and more valuable products, especially distillates such as jet fuels, diesel oils and heating oils. Mild hydrocracking is

**TABLE 1. Typical single-stage MPHC operating conditions as a function of conversion**

|   |    |     |     |     |
|---|----|-----|-----|-----|
| Conversion, wt%   | 30 | 50  | 50  | 70  |
| H <sub>2</sub> pressure, bar                                | 55 | 55  | 84  | 100 |
| H <sub>2</sub> consumption, Nm <sup>3</sup> /m <sup>3</sup> | 90 | 115 | 160 | 219 |
| Kerosine properties   |    |     |     |     |
| Sulfur, wppm  | 30 | 10  | 5   | <5  |
| Smoke point, mm   | 13 | 14  | 17  | 22  |
| Diesel properties   |    |     |     |     |
| Sulfur, wppm  | 50 | 30  | 10  | 5   |
| Cetane no.  | 43 | 45  | 50  | 55  |
| Aromatics, wt%  | 50 | 55  | 35  | 25  |
| Polyaromatics, wt%  | 18 | 20  | 7   | 5   |

Note: Middle East VGO feedstock

**FIG. 1** Moderate-pressure hydrocracking reaction zones and reaction processes.**FIG. 2** Moderate-pressure hydrocracking using a single-stage processing design.

widely practiced in Europe as an efficient route for incremental conversion of HGO to distillate products.

The MPHC technology was first developed and commercialized in the early 1980s for VGO conversion (Fig. 1). The single-stage MPHC technology extends the reach of mild hydrocracking to higher conversions and longer operating cycles on increasingly heavier feedstocks. It has since been improved. Current research and commercial operating experience has extended the processing capabilities of MPHC to include deep-cut VGO, heavy coker gasoil (KGO), catalytic cycle oils and deasphalted oil (DAO). The optimal specification of MPHC design depends on the optimization of product quality requirements, yield and operating cycle objectives, and investment and operating costs.

This processing method is generally carried out in conjunction with an initial hydrotreating step in which the heteroatom-containing impurities in the feed are hydrogenated without a significant degree of boiling point conversion. During this initial step, the heteroatoms, principally nitrogen and sulfur, are converted to inorganic form (ammonia, hydrogen sulfide) prior to the subsequent hydrocracking step in a stacked-bed reactor system, as shown in Fig. 1.

In the second catalytic step, the hydrotreated feedstock is contacted with a bifunctional hydrocracking catalyst, which possesses both acidic and hydrogenation/dehydrogenation functionality. In this step, the characteristic hydrocracking reactions occur in the presence of the catalyst. Polycyclic aromatics in the feed are hydrogenated, and ring opening of aromatic and naphthenic rings occurs together with dealkylation. Further hydrogenation may take place upon opening of the aromatic rings. Depending upon the severity of reaction conditions, the polycyclic aromatics in the feed will be hydrocracked into paraffinic materials or, under less severe conditions, to monocyclic aromatics as well as paraffins. Naphthenic and aromatic rings may be present in the lighter products, and as substituted naphthenes and substituted polycyclic aromatics in the higher boiling products, depending upon the operational severity.

The single-pass MPHC process is not subject to fouling or high catalyst deactivation rates that can result from the buildup of polynuclear aromatics (PNAs) in the recycle oil stream. The kinetic impact of lower hydrogen pressure is compensated by lower conversion level and by lowering liquid hourly space velocity (LHSV) if necessary. The naphtha and bottoms products are not over-saturated, and hydrogen consumption is minimized.

Designing an MPHC unit for single-pass partial conversion operation mitigates the need for high operating pressures. The required operating pressure level is usually less than 100 bar and is determined by a complex relationship between feed properties, desired conversion level, catalyst life and product quality constraints. In general, heavier, higher end-point feedstocks will require higher design pressures for a given conversion level and catalyst life. Also, the aromaticity of the hydrocracked products will be directly proportional to hydrogen partial pressure. Table 1 summarizes the typical operating parameters for a single-stage MPHC unit.

The primary conversion mechanism in the moderate pressure regime involves selective saturation of the aromatic rings, ring opening and dealkylation of the resultant intermediate species to produce diesel and jet boiling range components. Little paraffin conversion is realized at these pressures, thus preserving these molecules for more favorable conversion in the FCC unit. Relative installed costs inside battery limits (ISBL) and operating costs based on curve-type estimates for an HP hydrocracker and the MPH unit operating at the same conversion level is summarized in Table 2.

For example, a grassroots MPH unit that utilizes available refinery hydrogen will require 20% less capital investment and 40% less hydrogen consumption than an equivalent high-pressure hydrocracker (HPC) at a similar capacity and conversion. In a refinery system that includes an existing FCC unit, installing a full-conversion HP hydrocracker to improve distillate to gasoline production ratio is often uneconomical.

The MPH process can be a low-cost route to produce high-quality distillates while substantially upgrading FCC feedstock quality. The combination of MPH and FCC also provides excellent flexibility for a refiner to adjust gasoline and diesel balance in response to market needs. The refinery will also see the added benefit of improved FCC yields, substantially lower sulfur levels in the FCC gasoline and cycle oil products, and a significant reduction in emissions of sulfur and nitrogen oxides from the FCC regenerator. Fig. 2 is a simplified flow scheme for a single-stage MPH unit.

It is also possible to revamp existing low- and moderate-pressure VGO hydrotreaters to achieve conversion levels of 30% to 65%. In such situations, the capital investment will be substantially below that stated in Table 2. The Mobil Chiba unit and the OMV HDS-3 unit at Schwechat, Austria, represent prototypical applications for the economic conversion of low-pressure cat-feed hydrotreater units (70 barg) to partial conversion units operating at 35–40% conversion while substantially improving the quality of FCC feed and FCC unit performance.

**TABLE 2. Single-stage partial conversion hydrocracker—comparison of pressures**

| Unit                 | MPHC  | HPHC       |
|----------------------|-------|------------|
| Conversion, %        | 50    | 50         |
| Pressure, bar        | 100   | 165        |
| Installed cost, US\$ | Base  | Base + 20  |
| Diesel properties    |       |            |
| Sulfur               | <50   | <10        |
| Cetane index         | 45–55 | 55–65      |
| Polyaromatics        | 5–10  | <1         |
| Hydrogen demand      | Base  | Base x 1.4 |

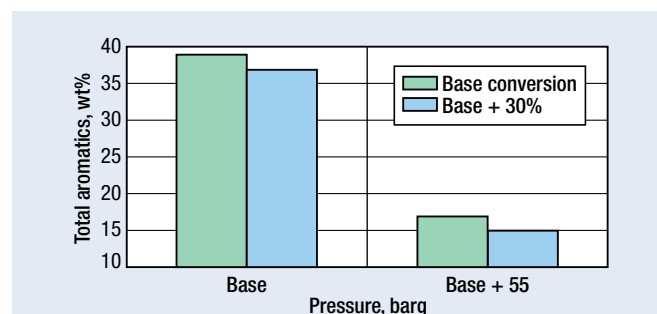
**TABLE 3. Single-stage MPH with PTU—comparison of pressures**

| Unit                 | MPHC  | MPHC/PTU   | HPHC       |
|----------------------|-------|------------|------------|
| Conversion, %        | 50    | 50         | 50         |
| Pressure, barg       | 100   | 100        | 165        |
| Installed cost, US\$ | Base  | Base + 15  | Base + 20  |
| Diesel properties    |       |            |            |
| Sulfur               | <50   | <10        | <10        |
| Cetane index         | 50–55 | 55–65      | 55–65      |
| Polyaromatics        | 5–10  | <1         | <1         |
| Hydrogen demand      | Base  | Base x 1.2 | Base x 1.4 |

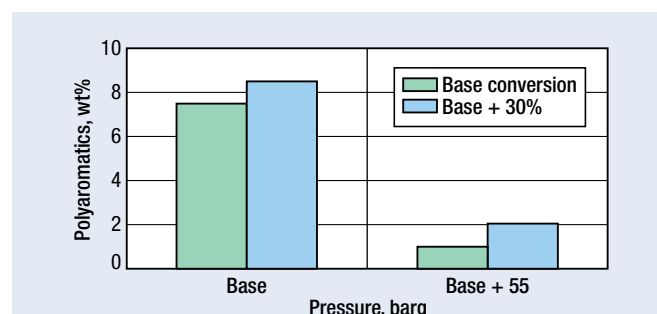
**Limitations of single-stage hydrocrackers.** The principle process variables that influence the quality of middle distillates produced by hydrocracking are hydrogen partial pressure and conversion. The primary reaction pathway for most conventional hydrocracking catalysts is selective conversion of aromatics and naphthenes, resulting in a high concentration of ring compounds in hydrocracked naphtha and distillate products.

Extensive pilot plant investigations to examine the effects of pressure and conversion on hydrocracker performance covering most refinery heavy feedstocks have been conducted (Fig. 3). As would be expected, **both** product density and cetane number improve significantly as pressure and conversion are increased. The data also reveal that the improvement of density and cetane with increased conversion is greater at higher operating pressure.

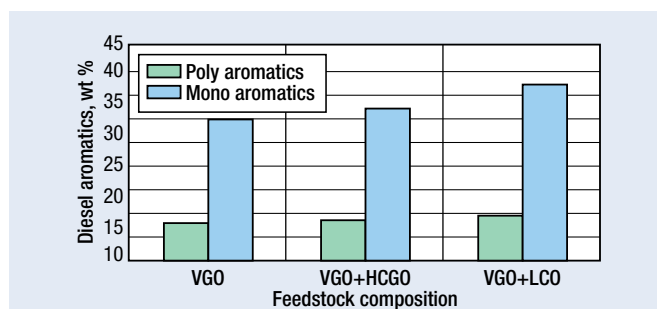
The effect of pressure and conversion on product total aromatics is similar. However, there is a notable difference with respect to polyaromatics. Polyaromatics in the diesel product actually increase as conversion increases, even at elevated hydrogen pressures (Fig. 4). This observation can have significant bearing on the



**FIG. 3** Effect of pressure on total aromatics and percent conversion.



**FIG. 4** Effect of pressure on diesel polyaromatics and percent conversion.



**FIG. 5** Effect of pressure on percent conversion with varying feedstock types.

design of new hydrocracking facilities to meet the requirements for possible future product specifications.

Conventional thinking will suggest that, to improve the diesel and kerosene qualities, the operating pressure and conversion level must be increased to enhance the level of aromatics saturation of these fractions. This improvement in product quality is achieved at the expense of higher hydrogen consumption and operating costs.

However, a key factor to note is that, at a given pressure and conversion level, product quality is highly dependent on feedstock composition. As would be expected, more aromatic feedstocks produce higher aromatics diesel at constant conversion and hydrogen partial pressure. Processing jet and diesel fractions with low aromatics content becomes increasingly difficult even at elevated pressures and higher chemical hydrogen consumption, when processing heavy-cracked components in the hydrocracker feed.

As refiners switch to lower hydrogen-containing opportunity crudes and install additional bottom-of-the-barrel processing capacities, the hydrocracker will see an increase in cracked feedstock components. The ability to produce Euro IV grade premium

distillates over the entire operating cycle then becomes increasingly difficult even at very high pressures.

As pressure and conversion are increased to compensate for these hydrogen-deficient feeds, the resulting chemical hydrogen demand also increases substantially. At some point, improving product quality by using higher operating pressures and increased conversion becomes impractical, as hydrogen and operating costs, as well as the direct investment required, become prohibitive (Fig. 5).

This is clearly evident in hydrocracking of highly aromatic Canadian bitumen-derived feedstocks in which operating pressures exceed 200 barg and have been found to be insufficient. Escalation in project costs and a resultant decline in project economics have contributed to the shelving of several large-scale grassroots projects.

### Integration of MPHC with distillate post-treating.

With the advent of incremental volumes of hydrogen-deficient feeds, while the single-stage hydrocracker will continue to yield a high-quality FCC feed, the diesel fuel component cetane and density may not meet Euro IV ULSD and the kerosene fraction may not independently meet aviation turbine fuel specifications. In some refining situations, the kerosene and diesel cuts will be suitable for blending into the refinery product pool. In most other situations, the distillate products must be reprocessed for incremental aromatic saturation utilizing the option for conversion at moderate pressure and selectively limiting the hydrogen uptake to the fractions that matter the most, i.e., jet and diesel, make economic sense.

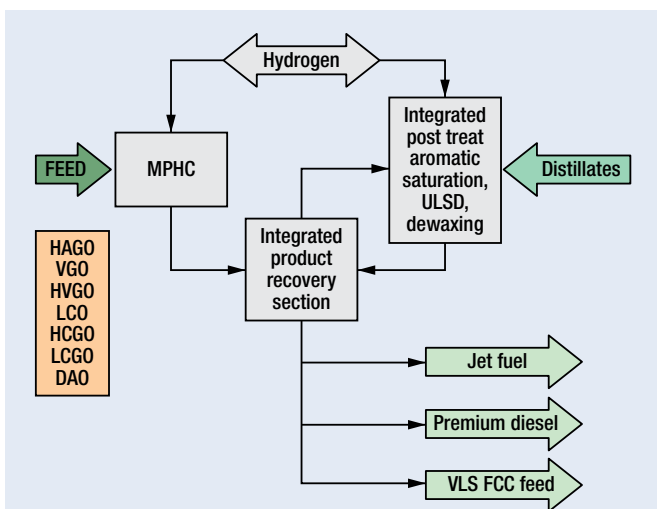
Integrating an advanced distillate post-treating unit (PTU) within the MPHC process can extend the capability of moderate-pressure hydrocracking to process diesel fuel with an ultra-low sulfur, low-aromatics and high-cetane number. Kerosene fractions suitable for aviation turbine fuel blending can also be economically produced.

A highly flexible process scheme to integrate diesel upgrading and hydroconversion was first conceived in the 1990s and implemented in the OMV Schwechat refinery post-2001.<sup>1</sup> In an MPHC and PTU processing configuration, each reaction block, as shown in Fig. 6, can be built independently or retrofit from existing hydrotreating units. Also, the blocks can be integrated together into multistage units with common process facilities.

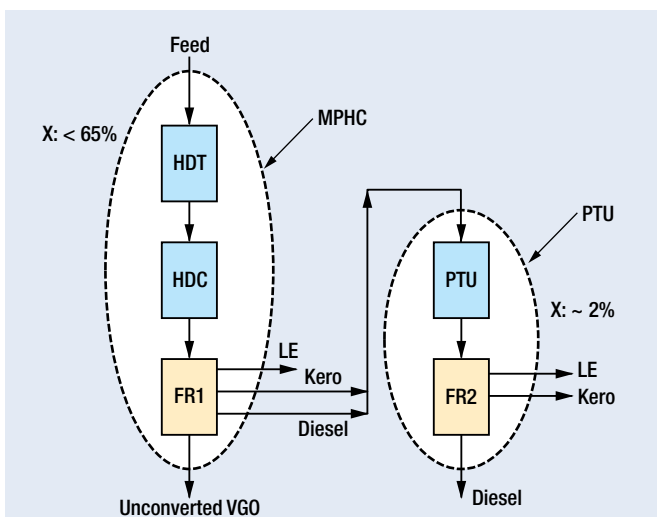
In an MPCH and PTU processing configuration, the integrated PTU option allows the refiner to selectively upgrade the jet and diesel fractions produced from the MPHC unit to produce premium distillate products. The operating conditions and catalyst systems for the PTU are flexible enough to allow the refiner to custom select the catalyst system to meet the processing objectives—traditional hydrotreating catalysts to produce Euro IV ULSD and Jet A, isomerization dewaxing catalyst for cold-flow property improvement or aromatic saturation catalysts for higher saturation and low aromatics. In summary, the two independent reaction environments offer the flexibility to optimally upgrade all key jet and diesel properties with maximum yield and minimum hydrogen consumption.

Larger shifts in boiling point are better accomplished in the MPHC unit to avoid over-cracking of the diesel feed. Controlling final product quality in the second stage ensures meeting the tightest possible specifications (less than 10-ppm sulfur, for instance) while avoiding excess naphtha production. As is the case with one refinery in Europe, it was demonstrated that the PTU can be closely integrated with MPHC to give a process that achieves the same objectives as HP hydrocracking units but at significantly lower cost.

Based on achieving the same diesel density and cetane number as that produced at high pressure, the post-treatment results in



**FIG. 6** Flow diagram applying an integrated moderate-pressure hydrocracking process with post-treating unit.



**FIG. 7** Block diagram of an integrated moderate-pressure hydrocracking process with post-treating unit.

lower total and polyaromatics as well as lower sulfur content (less than 10 wppm) in the diesel fraction (see Table 3).

Accordingly with the integral PTU approach, there is added flexibility to produce “near-zero” diesel sulfur and very low aromatics content if future regulations become even tougher than now envisioned.

This analysis also indicates that the integrated MPHC–PTU process results in a lower total installed cost as compared to a single-stage HP hydrocracker while meeting the same stringent diesel quality specifications. Because the integrated MPHC–PTU process adds hydrogen selectively to the distillate streams, the chemical hydrogen consumption is also reduced by about 20%.

Due to the lower compression energy requirements, utility consumption for the integrated MPHC–PTU process, particularly power demand, is lower than that for the corresponding HP unit. Therefore, the MPHC–PTU process generates substantially better total revenue with a significantly lower capital investment. Also of significance is that the investment in diesel post-treating can be staged until such time as future regulations require further upgrading.

There is also the added benefit of bringing in additional volumes of external distillate feed streams directly to the PTU. This approach allows eliminating dedicated distillate hydrotreater units.

Several versions of the integrated PTU system exist, including once-through hydrogen systems, parallel units and hydrocracker/PTU reactor systems in series. All these versions have been licensed, and some are in operation.

Figs. 7 and 8 are simplified flow sketches illustrating the MPHC process with an integral PTU in one such configuration. As is shown in Fig. 8, including the integrated PTU can typically be accomplished by adding nine pieces of new equipment. The substantial synergy that exists between the two stages is clearly apparent and includes using common HP equipment and heat integration. The simplicity of the low-pressure section result in significant capital cost savings. The addition of the PTU is accomplished without the additional compression or fired-heater equipment. In summary, the MPHC–PTU process is a low-cost route to produce high-quality distillates while substantially upgrading FCC feedstock quality.

### Two stage-MPHC—high conversion.

The full conversion of HGOs to diesel and lighter products typically requires applying hydrocracking units designed for high operating pressures (150–200 barg) and involves two stages of reaction and product recycle. Capital costs for both stages of HP hydrocracking equipment with capacity to recycle and with the incremental hydrogen consumption have made such facilities difficult to justify within increasingly capital constrained operating environments.

Operating at marginally less than total conversion can open up opportunities to optimize the relationship between pressure, conversion, catalyst life, hydrogen consumption and product quality, thus leading to substantially reduced capital investment and highly profitable returns.

Several technology options can be considered to meet the high-conversion process-

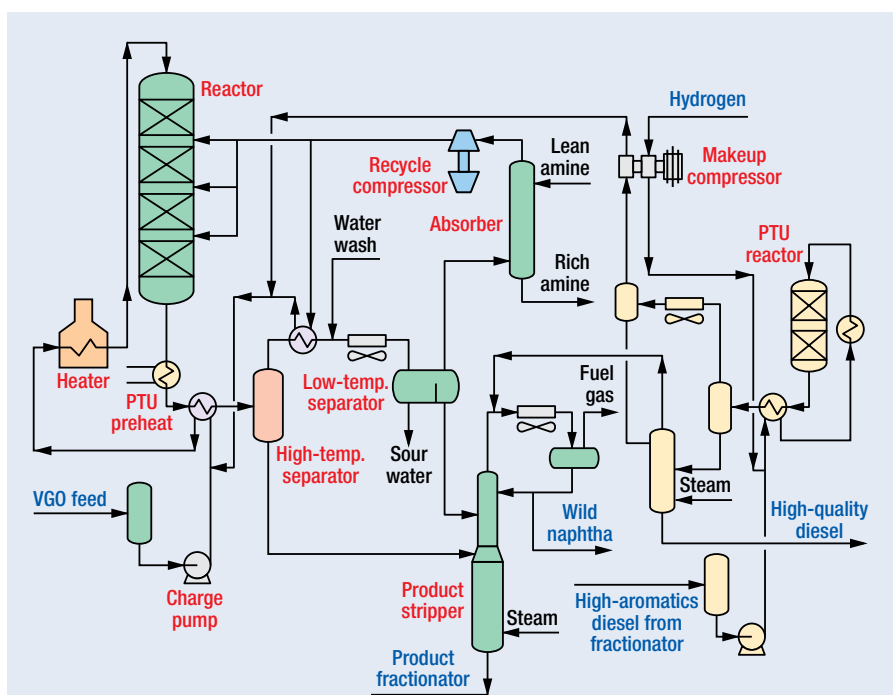
ing objectives. The challenge is to develop a technically attractive lower-cost technology option that will meet or exceed all processing objectives. Yet, the process must be flexible enough to meet future challenges. In addition, due to the current market conditions for delivery of materials and fabrication, technology selection has a very significant impact on project implementation schedules.

**Jurong refinery.** Following the successful demonstration of MPHC technology in the KPI refinery, a second grassroots MPHC unit to convert HGO was installed in the Jurong, Singapore refinery. This unit was started up in 1990 with a 60% first-stage conversion and a second-stage hydroisomerization hydrocracking unit to increase the once-through conversion levels to 75%–80%. The unconverted bottoms may serve as FCC feed or used for base-oil production. This unique two-stage MPHC option offered a lower cost alternative for HGO conversions up to 85%, which meets or exceeds all Euro IV distillate specifications (Fig. 9).

While the considerations presented here apply mostly to fuel hydrocracking processes, they will also be relevant in greater or lesser measure to lube hydrocracking. Much of the understanding of the base chemistry is also derived from the rich and varied experience in lubes production.

In the two-stage MPHC process, an initial hydrocracking step is done under moderate pressure in the presence of a bifunctional catalyst that affects partial saturation and ring opening of the aromatic components, present in the feed. As discussed earlier, the economic conversion level for the first stage of the MPHC process is limited to about 65% before substantial overcracking, loss of distillate yields and a proportionally higher naphtha make can occur.

The bottoms from the first-stage hydrocracking step that are paraffinic in character, include components with a relatively high pour point that need to be hydrocracked in the dewaxing step. The second-stage isomerization and dewaxing process is a low-pressure, once-through, single-stage technology that is well-suited



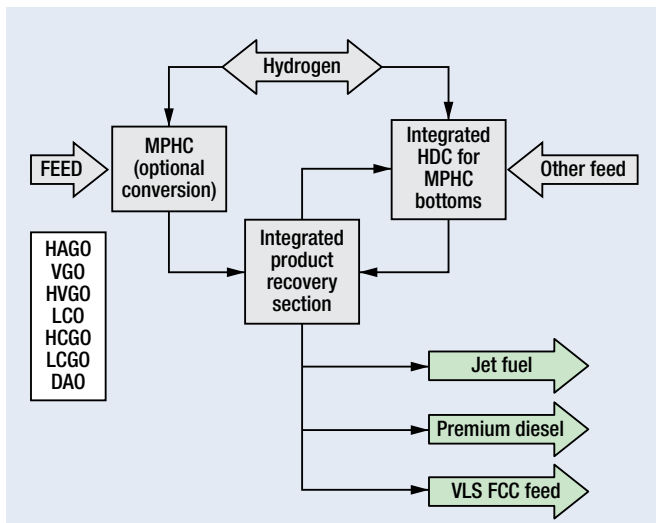
**FIG. 8** Flowsheet of applying an integrated moderate-pressure hydrocracking process with a post-treating unit.

for partial conversion of paraffinic streams such as that derived from the MPHC bottoms. Conventional hydrocracking catalysts find it difficult to crack this stream. Similar to lubes, where hydrocracked products are subjected to dewaxing to reach the target pour point, the paraffin hydroisomerization and cracking mechanism is used in the second stage to produce high-quality distillates.

A new process uses a unique isomerization and dewaxing process catalyst system for conversion (Fig. 10). The second-stage catalyst is zeolitic and bifunctional, and includes a hydrogenation-dehydrogenation component to the catalyst. Metals having a strong hydrogenation function are preferred, especially noble metals; although other metals are capable of acting as a hydrogenation component and may also be used. The catalyst may be treated by conventional pre-sulfiding treatments, e.g., by heating in the presence of hydrogen sulfide, to convert oxide forms of the metal components to their corresponding sulfides. The catalyst may also be treated with gases, such as hydrogen and nitrogen, at elevated temperatures prior to contacting with feed to improve catalyst activity.

In the isomerization and dewaxing step, the feedstock is contacted with the proprietary catalyst in the presence of hydrogen under hydrocracking conditions of elevated temperature and moderate pressure. Conditions of temperature, pressure, space velocity, hydrogen to feedstock ratio and hydrogen partial pressures are very similar to those used in conventional hydrocracking operations and can conveniently be applied. The operating conditions are advantageously selected to provide conversion levels of 20 wt% to 70 wt%.

The conversion products in the second stage are selective to middle distillates (jet and diesel), are highly paraffinic or isoparaffinic, and result in extraordinary product properties. The commercial properties from the distillate material derived from the Jurong unit operating at less than 55 bar total pressure is illustrated in Table 4. The lower operating pressure was necessitated by the revamp limitations of an available low-pressure distillate unit. For a grassroots, high-conversion unit, a higher pressure (70–100 bar) is more in line with the MPHC operations and can be used to limit overcracking and is more optimal for the proposed conversion levels of 50–70% and even higher product quality.



**FIG. 9** Block diagram of applying an integrated moderate-pressure hydrocracking unit with isomerization/dewaxing unit.

**Case study—High-conversion hydrocracker.** This case history compares the alternative schemes for a grassroots hydrocracker where the principle objectives are to process a VGO feed and selectively convert 80 wt% of the feed to distillate and lighter products. The project economics are dictated by maximizing middle distillates, and a large incentive exists to produce premium jet product that meets Jet A1 quality specifications of 25 mm smoke point minimum and  $-47^{\circ}\text{C}$  freeze point. The ultra-low-sulfur diesel product is expected to meet Euro IV plus specifications, i.e., cetane index greater than 55, total aromatics less than 15 wt% and PNA less than 2 wt%. The light- and heavy-naphtha products will be suitable for feeding an isomerization unit and reformer respectively. The unconverted bottoms will be fed to an existing FCC unit. Finally, the unit is expected to operate for two cycles between turnarounds.

The feed to the hydrocracking unit consist of the VGO directly from the crude and vacuum towers. This case study feed is similar to Arabian heavy crudes that are currently being processed in ExxonMobil's worldwide refinery system and specifically in two of the running MPHC units. The low nitrogen, asphaltenes, metals and Conradson carbon residue (CCR) content of the feed makes it easier to process at lower pressures. The feed and processing objectives for two different configurations were evaluated: a traditional HP configuration and the integrated MPHC configuration.

**HP hydrocracker.** The combination of a once-through, high-conversion requirement and the need for high-quality distillate products would intuitively suggest an HP hydrocracker unit. A single-stage HP hydrocracking unit typically operating at 150–200 bar pressure can meet these conversion requirements and the requisite product specifications. This unit can be designed to be flexible and operate at 75% to 85% conversion at a reasonable space velocity, and the total catalyst volumes and costs will be low.

**TABLE 4. Isomerization and dewaxing product properties—commercial unit at 55 bar total pressure**

|                   | Feedstock | Naphtha             | Kerosine | Diesel   | LSHFO    |
|-------------------|-----------|---------------------|----------|----------|----------|
| Boiling range, °C | 350–510   | C <sub>5</sub> –150 | 150–255  | 255–388  | 388+     |
| Yield, vol%       | 100.0     | 22.9                | 21.5     | 19.2     | 36.8     |
| Gravity, °API     | 32.0      | 73.0                | 49.5     | 34.7     | 29.5     |
| Sulfur, ppmw      | 260       | <1                  | 2        | 20       | 40       |
| Smoke point, mm   | –         | –                   | 32       | –        | –        |
| Freeze point, °C  | –         | –                   | <–54     | –        | –        |
| Pour point, °C    | >38       | –                   | –        | –43      | <–7      |
| Cetane index      | –         | –                   | 52       | 56       | –        |
| P/N/A, wt%        | 44/39/17  | –                   | –/–/10   | 45/31/24 | 36/42/22 |

**TABLE 5. Operating conditions for the integrated MPHC/isomerization and dewaxing unit**

|   | MPHC | Isomerization/<br>dewaxing | Combined |
|---|------|----------------------------|----------|
| Conversion, wt%   | 55   | 55                         | 80       |
| Feed, %   | 100  | 45                         |          |
| H <sub>2</sub> consumption (max), Nm <sup>3</sup> /m <sup>3</sup> |      |                            | 280      |
| Reactor inlet pressure, barg                                      | 100  | 100                        |          |
| Minimum cycle length, months                                      | 24   | 48                         |          |

However, the severity of conventional single-stage operation required to meet the distillate product specifications of low aromatics (smoke point, total aromatics, polyaromatics) and high-quality fluidity properties (freeze point and cloud point) will result in significant over cracking and loss of yield while incurring higher capital and operating costs.

Initial estimates of a once-through, high-conversion hydrocracker at 150–160 bar pressure showed that, although the production of high-quality Euro IV diesel was feasible, the aromatics content at end of run (EOR) conditions was not meeting the required product specifications. Thus, a further increase in total pressure to a higher level or a substantial increase in the catalyst volume, expanding the installed and operating cost of the unit would be required. As a result, and for the additional reasons listed below, the HP option was dropped from further consideration:

- For the single-stage 75–85% conversion case, substantial overcracking will occur, the distillate (jet+diesel) selectivity will be lower and the total distillate yields will be lower.
- Due to the higher operating pressure, the capital cost for the unit will be higher. Due to the higher hydrogen consumption and greater compression energy requirements, operating and utility costs are expected to be significantly higher than equivalent lower-pressure hydrocrackers.
- The required wall thickness for these vessels will be well in excess of 200 mms requiring forged cans for fabricating these vessels. In 2007, the anticipated delivery of these reactor vessels is in excess of 36 months as opposed to 24 months for vessels that can be rolled from plates (<20-cm thickness).
- When processing high total acid number (TAN) feeds, the

**TABLE 6. Estimated hydrocracker products (SOR)**

|                       | Bottoms | Diesel | Jet   |
|-----------------------|---------|--------|-------|
| Yields, wt%           | 20      | 20     | 31    |
| SG @ 60°F             | 0.850   | 0.837  | 0.802 |
| Total sulfur, ppmw    | <10     | <6     | <2    |
| Cloud point, °C       |         | -18    |       |
| Smoke point, mm       |         |        | 25    |
| Freeze point, °C      |         |        | -50   |
| Total aromatics, wt%  |         | 12.2   | 10    |
| PNA, wt%              |         | 1.6    | 0.1   |
| CI D976-80            |         | 56     |       |
| CI D4737              |         | 66     |       |
| Hydrogen content, wt% | >14     |        |       |

**TABLE 7. Comparison of technology options**

|                       | Two-stage MPHC | One-stage HPHC | Two-stage HPHC with recycle |
|-----------------------|----------------|----------------|-----------------------------|
| Conversion            | 85%            | 75–85%         | >95%                        |
| Capital Investment    | Base           | Base +/- 5%    | Base + >50%                 |
| Hydrogen Consumption  | Base           | Base+ 20%      | Base + 30%                  |
| Distillate yield      | Base           | Base -2%       | Base + 6%                   |
| Reactor fabrication   | Rolled plates  | Forging        | Forging                     |
| Reactor delivery 2007 | 24–26 months   | 36–40 months   | 36–40 months                |
| Project schedule      | 32 months      | 44 months      | 44 months                   |

metallurgy of the hot section of the feed system must be upgraded to TAN-resistant metallurgy (SS317L). At higher pressures, the piping specifications will require 2,500-lb flange ratings. While this is technically feasible, this design will be expensive and hard to procure. It will require special fabrication, installation, and maintenance, and introduces safety risks.

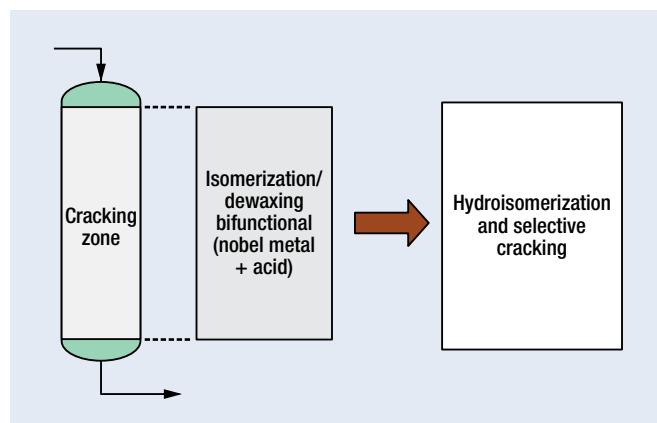
- Due to higher hydrogen consumption and compression ratios, the size of makeup gas compressors will be larger and will require three stages of compression. This will also result in large frame sizes. Depending on the size of the unit, the delivery of these compressors can be almost as long as the reactors themselves.

**Integrated MPHC/isomerization/dewaxing unit.** To achieve the stated objectives, MPHC technology, in combination with isomerization dewaxing at a nominal reactor pressure of 100 barg, was considered (Fig. 11). The optimization exercise resulted in an integrated MPHC unit operating at 50% to 60% conversion, followed by an isomerization/dewaxing unit that further cracks the MPHC bottoms (higher paraffin content than the feed) into distillates and lighter using a selective hydrocracking. This combination allows for a more flexible design to maximize jet fuel production without overcracking by co-processing more heavy MPHC diesel in the isomerization/dewaxing reactor while ensuring that all product properties are met over the entire cycle at a much lower pressure.

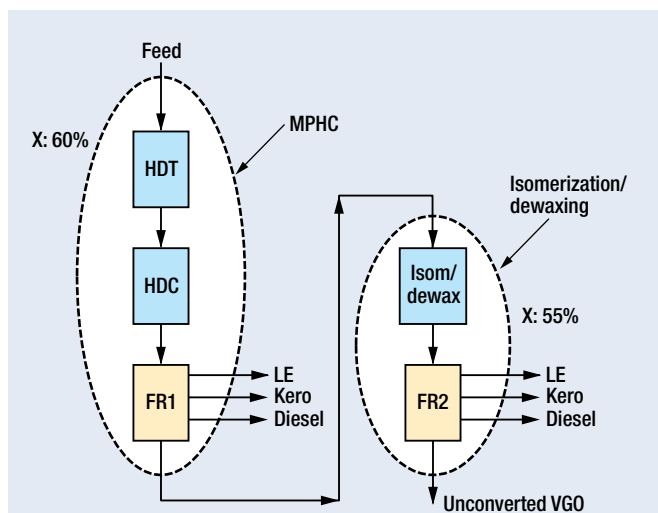
The operating conditions for the integrated MPHC unit with the isomerization/dewaxing reactor are listed in Table 5. In this case, both MPHC and isomerization/dewaxing operations were run as once-through operations at reactor inlet pressure of 100 barg and at 55% conversion. The two-stage configuration allows for custom optimization of the product quantity and quality requirements after a full understanding of the specific economic drivers for the particular application is realized.

Table 6 summarizes the expected yields and the product qualities for the two stages combined. The isomerization/dewaxing unconverted bottoms from the integrated unit have excellent quality and can be used as FCC feed or other applications including petrochemical feed, lubes production, steam-cracker feed, etc. If desired, the yields of jet and diesel can be easily adjusted over a wide range by changing the catalyst and operating conditions.

The diesel product is a high-quality Euro IV diesel. At the start of run (SOR), the combined diesel from MPHC and



**FIG. 10** Two-stage reaction zone with an integrated moderate-pressure hydrocracking unit with an isomerization/dewaxing unit.



**FIG. 11** Flowsheet of applying an integrated moderate-pressure hydrocracking unit with isomerization/dewaxing unit.

isomerization/dewaxing will meet the more stringent aromatics and polyaromatics specifications. The jet product will meet Jet A1 specifications. One can further increase the jet make by increasing the jet endpoint closer to 300°C, without having to be concerned about the jet freeze point. As mentioned earlier, the isomerization/dewaxing catalyst will selectively hydroisomerize and crack the normal paraffins (the primary cause for freeze point problems) into lighter boiling range product and/or hydroisomerize them into iso-paraffins with a much lower freeze point.

Conversion above 80% is possible with the integrated MPHC/ isomerization/dewaxing scheme without significant loss of diesel selectivity. Conversions above 85% will yield proportionally higher naphtha make.

One of the options available with the integrated MPHC/ isomerization/dewaxing unit is to recycle some of the naphtha product back to the isomerization/dewaxing reactor. Keeping the same amount of catalyst from the base case, the effect of running light or heavy naphtha through the isomerization/dewaxing reactor along with the unconverted bottoms from the MPHC unit was examined. The total heavy naphtha make can be reduced by more than 25%, and it can increase LPG production by about 35%–40%.

The integrated two-stage flowsheet closely resembles the MPHC-PTU unit flowsheet included as Fig. 6, and is available in several configurations. The fractionator system for the two stages can be separate or integrated for cost savings and has the provision to separately produce distinctly different distillate streams from each of the two stages. One version of the fractionator configuration offered includes a proprietary divided-wall column option as well.

**Comparison of technology options.** A comparison of the high-conversion MPHC unit with single-stage high-conversion HP hydrocracker and the two-stage, full-conversion HP hydrocracker is summarized in Table 7.

In addition to the technical issues highlighted throughout this article, project implementation issues have taken on a serious dimension in the current market. The availability of alloy materials and the requirement to use forged vessels makes the delivery of reactors a major impediment to project schedules. In the case

of the MPHC unit, this obstacle is substantially reduced, and a 12-month project schedule saving can easily be realized.

It is clear that Europe is shifting to cleaner burning diesel fuel. In addressing cleaner fuels production and specifications, refiners must significantly increase production and improve diesel quality with cost-effective technologies. **HP**

#### ACKNOWLEDGMENT

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#### LITERATURE CITED

<sup>1</sup> Danzinger, et al., "Diesel Maximization Asset Optimization-Life Cycle Cost Minimization," ERTC 2006.

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