

## Hydrocracking: converting Vacuum Residue in Naphta and Diesel

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### 1. Theme description

In the refinery sector, both the fuel and the feedstock market as well as the more stringent environmental regulations are exacerbating the need of maximizing the residue conversion to distillates. In particular, while the distillate fuel demand (gasoline, diesel) is still increasing, the demand of residue fuel oils is about to fall sharply.

Compared with traditional technologies, the present refineries face several challenges because of the presence of crude oils characterized by high content of aromatics, acids, metals and nitrogen, therefore putting more pressure on the hydrocracking and hydrotreating processes that have to handle a low quality feedstock without significant loss of yield or efficiency<sup>1</sup>.

The Hydrocracking (HC) process is able to remove the undesirable aromatic compounds from petroleum stocks producing cleaner fuels and more effective lubricants. In other words, the main application is to upgrade vacuum gas oil alone or blended with other feedstocks (light-cycle oil, deasphalted oil, visbreaker or coker-gas oil) producing intermediate distillates (naphta, jet and diesel fuels), low-sulfur oil and extra-quality FCC feed. HC works by the addition of hydrogen and by promoting the cracking of the heavy fractions in lighter products. With reference to Figure 1, HC globally involves the catalytic cracking (end other micsplitting of a C-C bond) and the addition of hydrogen to the C = C bond (exothermic)

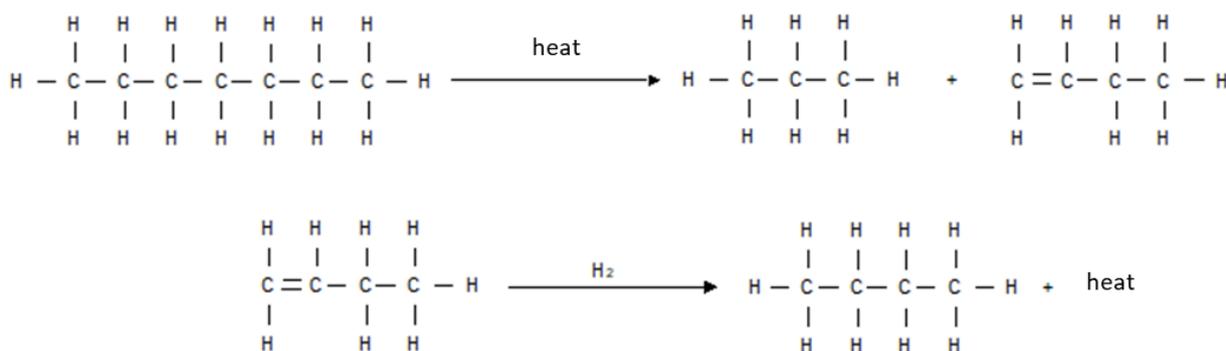


Figure 1: Reactions of cracking and hydrogen addition during hydrocracking

<sup>1</sup>Shell Global SolutionsNEXT-LEVEL HYDROCRACKER FLEXIBILITY UNLOCKING HIGH PERFORMANCE IN TODAY'S TURBULENT MARKETS. [www.shell.com/globalsolutions](http://www.shell.com/globalsolutions)

The hydrocracking process is overall exothermic, it is necessary to control this surplus of energy through quenching of cold hydrogen in the reactor. With reference to Figure 2, main reactions (as hydrogenation of an aromatic and isomerization to generate the olefin-based products) taking place in the system with related  $\Delta h$  of reaction are reported. The removal of hetero-atoms requires a hydrogenation catalyst, while the cracking reactions (through carbonium ions) need an acid catalyst. These reactions need a refining catalyst, mixed metal sulfides (mainly NiS / MoS<sub>2</sub> and Ni / WS<sub>2</sub>) to provide the hydrogenation function followed by hydrocracking catalyst, for example a silica-alumina, and, more frequently, zeolites (acid support).

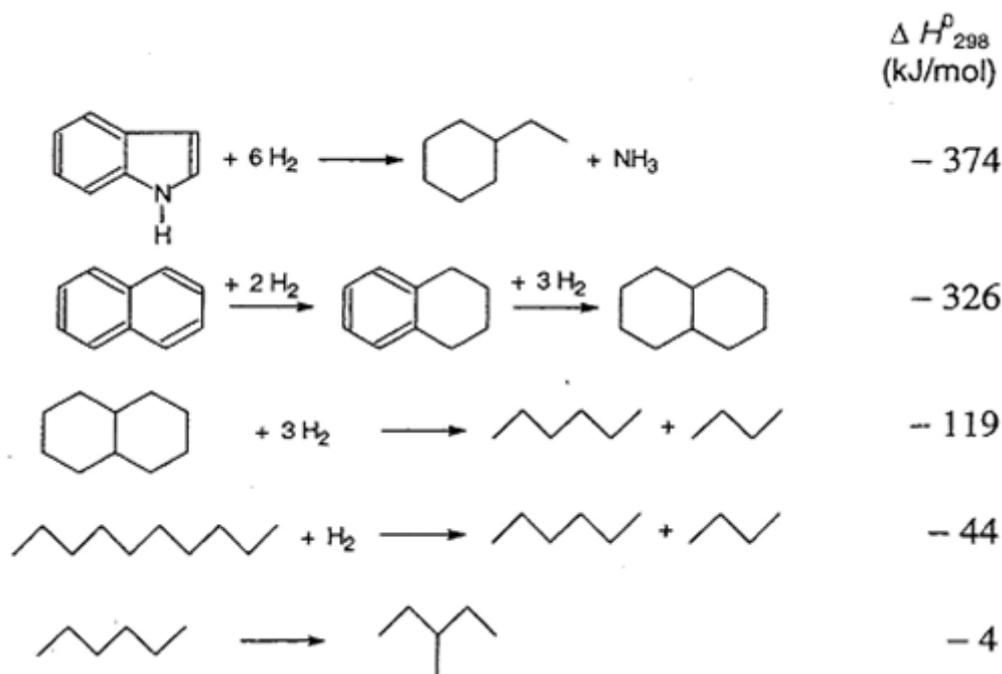


Figure 2: Main reaction mechanisms and standard heat of reaction<sup>2</sup>.

The process can be realized in one-step and two steps configuration. The main units (as depicted in Figure 3) consists of reaction sections, gas separation (& recirculation), stripping, product fractioning. Global operating conditions are reported in Table 1. Elkilani and Fahim proposed a process analysis to maximize the Diesel production from vacuum gas oil (VGO) in a two-stage hydrocracker. They tested several operating parameters (temperature, pressure and partial pressure of H<sub>2</sub>) and concluded that that reactions of VGO to diesel have the highest effect on catalyst deactivation<sup>3</sup>

<sup>2</sup> R.A. Mayers. Handbook of Petroleum Refining Processes. McGraw Hills. 2003

<sup>3</sup>A. Elkilani & M. Fahim (2014) Maximizing Diesel Production From Vacuum GasOil Using a Two Stage Hydrocracker, Petroleum Science and Technology, 32:19, 2303-2311, DOI:10.1080/10916466.2012.762017

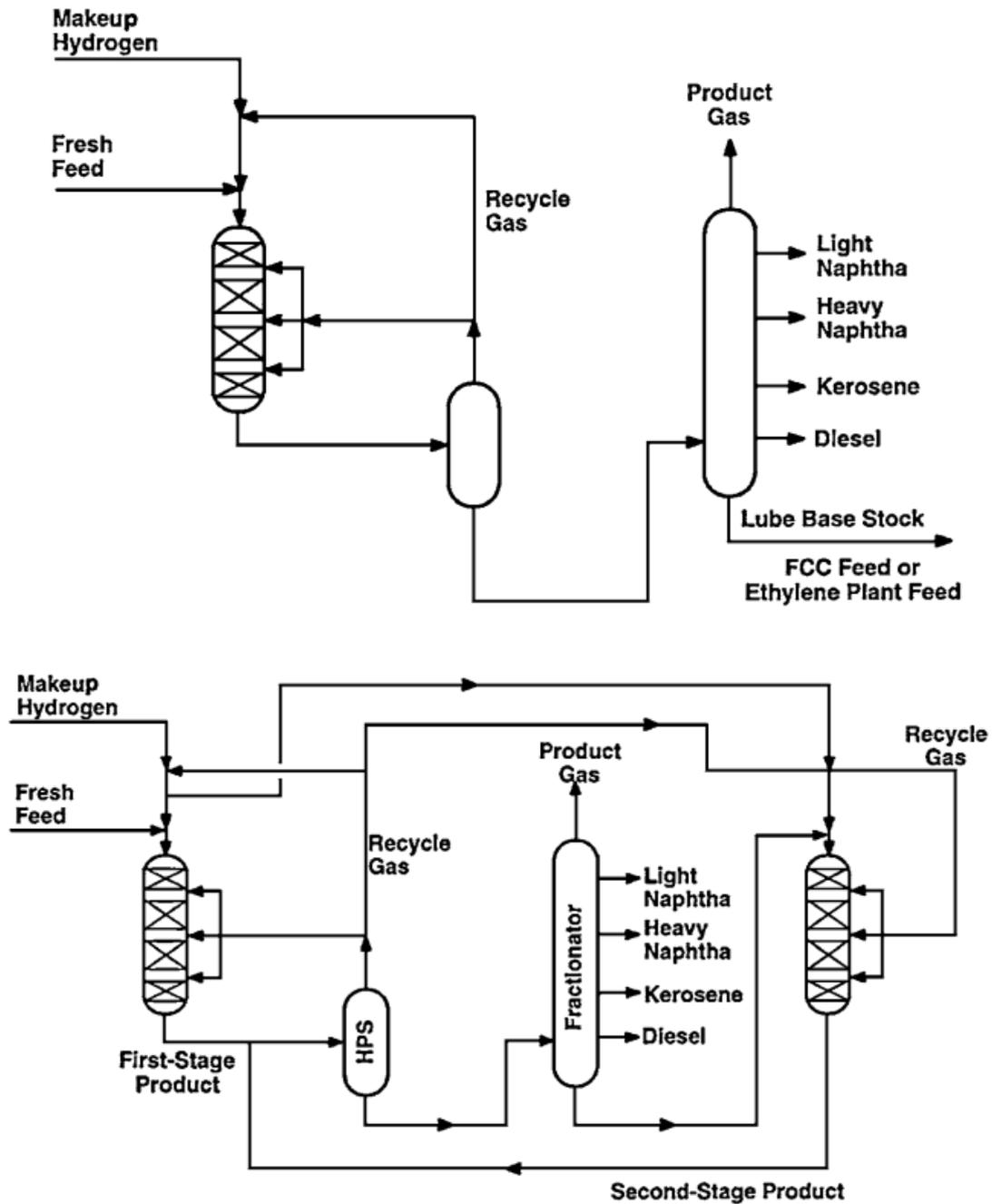


Figure 3. Single Stage Once Through (SSOT) and Two-Stage to produce transportation fuels, middle distillates, and naphtha<sup>4</sup>.

<sup>4</sup> R.A. Mayers. Handbook of Petroleum Refining Processes. McGraw Hills. 2003

**Table 1. HC operative conditions**

	Single/first stage	Second stage
T (K)	610 – 710	530 – 650
P <sub>H2</sub> (bar)	80 – 130	80 – 130
P (bar)	100 - 150	100 – 150
Catalyst	Ni/Mo/S/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> + P	Ni/W/S/USY zeolite

## 2. Recent Advances

In the Refinery sector, the current trend will continue to require new technologies which are able to convert heavier and heavier feed stocks into high quality transportation fuels, putting even more pressure on the HC, one of the most critical catalytic conversion units to provide valuable feedstock and product slate flexibility. Only the hydrogen addition route allows to reach high conversion, high diesel selectivity and Euro V grade products. In this framework, several proprietary technologies, cited in the following, have appeared from the recent advanced in R&D. These solutions are based on fixed bed, moving bed slurry phase and ebullated-bed configurations<sup>5</sup>.

**Shell Global Solutions** show some of the new paradigms in the shift towards more flexible HC. In particular, they discuss the main strategies and issues in the HC implementation: i) integration between vacuum distillation unit (VDU)–hydrocracker (Figure 4); ii) optimization of the Coker–hydrocracker line-up with the former enabling to handle the more difficult residue and the HC processing the higher nitrogen and more aromatic feed; iii) combination of SDA and de-asphalted oil (DAO) hydrocracking. They also reports same case studies including hydrocrackers with high feed and product slate flexibility<sup>6</sup>.

<sup>5</sup>R.M.Eccles Residue hydroprocessing using ebullated-bed reactors. Fuel Processing Technology Volume 35, Issues 1–2, September 1993, Pages 21-38

<sup>6</sup>Shell Global SolutionsNEXT-LEVEL HYDROCRACKER FLEXIBILITY UNLOCKING HIGH PERFORMANCE IN TODAY’S TURBULENT MARKETS. [www.shell.com/globalsolutions](http://www.shell.com/globalsolutions)



Figure 4. High Vacuum distillation unit (Shell)<sup>7</sup>

Conventional HC (e.g. based on fixed and ebullated bed technologies) can be applied to a limited number of feedstocks (in terms of quality) and suffers of residue stability issues. These latter limit the maximum conversion and increase the O&M costs. Slurry Technology has been implemented to process a large variety of feed stocks (e.g. extra-heavy oils, bitumen, de-asphalter bottoms, visbroken tars, coal liquids) showing high flexibility and resistance to the contamination (e.g. from metals, asphaltenes, sulphur, nitrogen)<sup>8</sup>. The slurry phase hydrocracking of vacuum residue was investigated by Kim et al<sup>9</sup>. The experimental conditions varied in a wide range of temperature, pressure, and reaction time, in the presence of dispersed MoS<sub>2</sub> catalyst. Their main findings are: i) Dispersed catalyst enhanced HC with liquid oils to over 90%; ii) the HC follows parallel reaction pathways to form liquid oils, gas, and coke; iii) the oil-soluble Mo precursor is transformed into a nano-MoS<sub>2</sub> catalyst. Several homogeneous and heterogeneous catalysts are reviewed and compared in the work of Sahu et al<sup>10</sup>. They also reported the reaction mechanisms and the main strategies to choice the technology by considering the feed properties, the product demand as well as economic and environmental considerations.

To answer the need to shift refinery product distributions to a more diesel-oriented slate and to reduce residue fuel oil production, **UOP** has presented a residue upgrading technology offering, the UOP Uniflex™ Process, based on the slurry hydrocracking technology. Their revamp option allows to obtain a high conversion of vacuum residues and a longer catalyst life in the RCD reactors<sup>11</sup>. One of the key advantages of the UOP

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<sup>7</sup> <https://www.shell.com/business-customers/global-solutions/refinery-technology-licensing/distillation-and-separation-technologies.html>

<sup>8</sup> EST - eni Slurry Technology. [https://www.eni.com/docs/en\\_IT/enicom/publications-archive/company/operations-strategies/refining-marketing/eni\\_EST\\_esecutivo.pdf](https://www.eni.com/docs/en_IT/enicom/publications-archive/company/operations-strategies/refining-marketing/eni_EST_esecutivo.pdf)

<sup>9</sup> Sung-HoKim, Ki-DukKim, Yong-KulLee, Effects of dispersed MoS<sub>2</sub> catalysts and reaction conditions on slurry phase hydrocracking of vacuum residue. *Journal of Catalysis* Volume 347, March 2017, Pages 127-137

<sup>10</sup> RamakantaSahu, ByungJinSong, Ji SunIm, Young-PyoJeon, ChulWeeLee, A review of recent advances in catalytic hydrocracking of heavy residues. *Journal of Industrial and Engineering Chemistry* Volume 27, 25 July 2015, Pages 12-24

<sup>11</sup> Dan Gillis, Mark VanWees, Paul Zimmerman UPGRADING RESIDUES TO MAXIMIZE DISTILLATE YIELDS UOP LLC, A Honeywell Company Des Plaines, Illinois, U.S.A.

Uniflex process is its simple integration into most existing refineries, minimizing the level of new investment CAPEX required<sup>12</sup>.

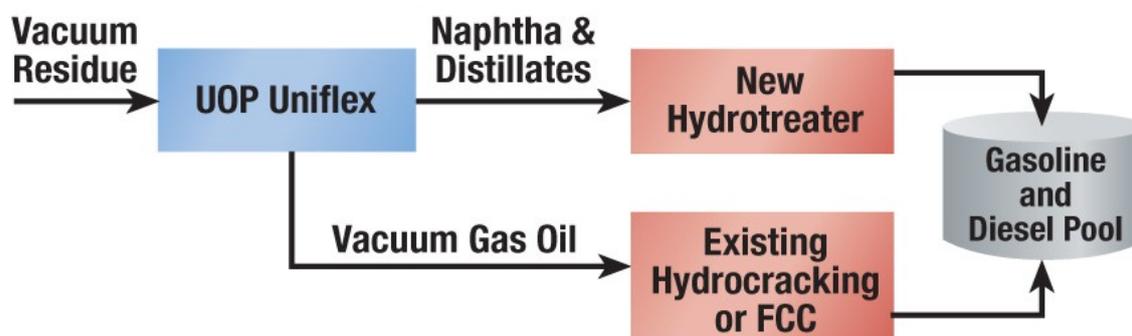


Figure 5 - UOP Uniflex Process block diagram<sup>5</sup>.

Catalysis for the slurry-phase HC of heavy oil is based on heterogeneous solid powder catalysts and homogeneous dispersed catalysts (with better performances). There is an ongoing search for a low cost catalyst with good catalytic performance for industrialized applications<sup>13</sup>.

An other slurry phase HC by the **Kellogg Brown & Root (KBR)** is the Veba Combi-Cracker (VCC™), operating with two stage and obtaining very high conversion with several feed stocks ranging from refining residue to coal and a mixture of oil and coal<sup>14</sup>. John Petry from **Honeywell/UOP** described the overall process of the NWR Sturgeon refinery, which implements Ebullated bed hydrocracking to converts the vacuum residue into intermediates, to realize a full conversion of bitumen<sup>15</sup>.

**ENI** Slurry Technology, EST incorporates a dispersed slurry catalyst to promote the upgrading reactions and to reduce the coke formation<sup>16</sup>. The EST recirculating system (see Figure 6) requires only a small purge amount to limit the build-up of metals (Ni and V). Both pilot and demonstration units showed the excellent flexibility of EST and some advantages in terms of H<sub>2</sub> utilization and catalyst life. The first industrial application (23,000 BPD), realized with an extensive use of the pre-assembly (both of large structures and process heaters), is located in the Sannazzaro de' Burgondi refinery, allowing the conversion of bottom-of-the-barrel into Euro V diesel (as well as minor streams of LPG and naphtha)<sup>16</sup>. Also Chevron has developed a new technology for the catalyst replacement without shutting down the hydrotreater. It is named On-stream Catalyst Replacement (OCR) and is allowing to work with a wide range of residuum and catalysts and to handle a very high metal content<sup>17</sup>.

<sup>12</sup> <https://www.uop.com/return-investment/>

<sup>13</sup> Chinh Nguyen-Huyet et al., Slurry-phase hydrocracking of vacuum residue with a disposable redmud catalyst. *Applied Catalysis A: General* 447– 448 (2012) 186– 192

<sup>14</sup> <http://www.gulfoilandgas.com/webpro1/prod1/services.asp?id=214>

<sup>15</sup> John Petri Honeywell/UOP. Full conversion of bitumen. [www.digitalrefining.com/article/1001433](http://www.digitalrefining.com/article/1001433)

<sup>16</sup> EST - eni Slurry Technology. [https://www.eni.com/docs/en\\_IT/enicom/publications-archive/company/operations-strategies/refining-marketing/eni\\_EST\\_esecutivo.pdf](https://www.eni.com/docs/en_IT/enicom/publications-archive/company/operations-strategies/refining-marketing/eni_EST_esecutivo.pdf)

<sup>17</sup> G.L.Scheuerman et al. Advances in Chevron RDS technology for heavy oil upgrading flexibility. *Fuel Processing Technology* 35, 1–2, 1993, 39-54

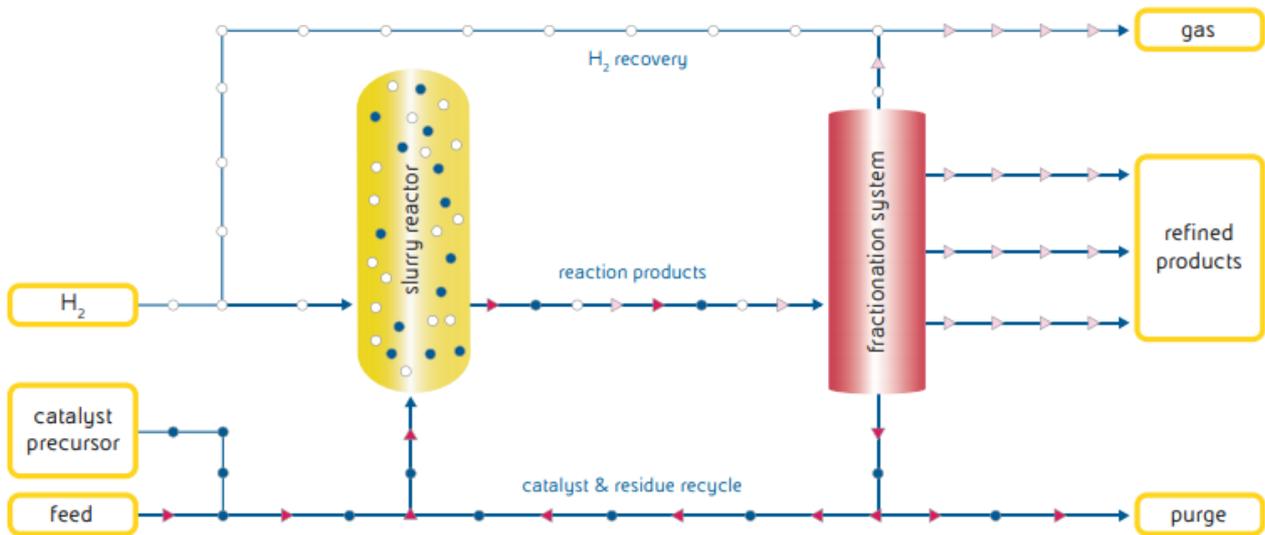


Figure 6–Process block diagram of the ENI slurry technology (EST)<sup>18</sup>

### 3. Conclusions

Conversion of residues into valuable distillates is a key factor for the sustainability and profitability of the new oil refineries: the reduction of the residues outputs leads to an increase of marketable products, a higher plant profitability and a lower environmental foot prints of refineries operation.

As above described, many industries and R&D groups are working on innovative solutions to solve the problems of residues generation in refineries, developing new concepts for hydrocracking and hydrotreating processes. An innovative solutions will be implemented in industrial environment only if the following targets are achieved:

- 1- low CAPEX and OPEX, economic and financial benefits (the increased fix and operating costs are balanced by the increase of revenues due to the maximization of distillate products);
- 2- reduced environmental impact, which means that the balance between the residue outputs reduction and the increase of impact due to the installation of a more complex unit is environmentally positive;
- 3- easiness in retrofit installation in operating plants.

<sup>18</sup> EST - eni Slurry Technology. [https://www.eni.com/docs/en\\_IT/enicom/publications-archive/company/operations-strategies/refining-marketing/eni\\_EST\\_eseutivo.pdf](https://www.eni.com/docs/en_IT/enicom/publications-archive/company/operations-strategies/refining-marketing/eni_EST_eseutivo.pdf)