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The shell residue hydroconversion process: development and achievements

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Abstract

The Shell HYCON process converts high sulphur, high metal content vacuum residues into atmospheric and vacuum distillates. The HYCON process is equipped with catalyst bunkering facilities that make on-line catalyst replacement possible. The first unit was built at the Shell Pernis refinery and was started in 1989. The process performance (in terms of sulphur/metals removal and conversion into distillates) is in line with predictions, and the catalyst bunkering system works well. During the start-up phase of the Pernis unit, equipment and materials problems were encountered. These problems were solved by repairs and replacement of the affected equipment. At present, the throughput has been increased to well above design value and a high conversion of vacuum residue into distillates has been consistently achieved. © 1998 Shell International Oil Products B.V. Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

The challenges facing the refining industry are presently larger then ever. The emphasis on the conversion of less valuable streams into transportation fuels continues to grow, while the environmental demands on the processes and products become more stringent.

The residue hydroprocessing units form the backbone in the refiners strategy to residue disposal. Most common process duties are to convert part of the residues into distillates and to produce low-sulphur fuel oil blending components or feed for residue cat cracker units. Several different technologies are now in commercial use, based on fixed bed, moving bed, ebullating bed or slurry phase reactor configurations. Typical feeds for these units are atmospheric residues (80% of total installed capacity), vacuum residues (16% of capacity) or deasphalted oils (4% of the capacity). Fig. 1 illustrates the relative positions of the various technologies in processing atmospheric and vacuum residues.

As illustrated, most existing residue hydroprocessing units are based on fixed bed reactor systems. Advantage of the use of fixed bed technology over, for example, the use of ebullating bed or slurry phase technologies is that much better product qualities can be obtained.

Shell has been actively developing residue hydroprocessing for more than 20 years [1,2]. Examples of the Shell technology are:

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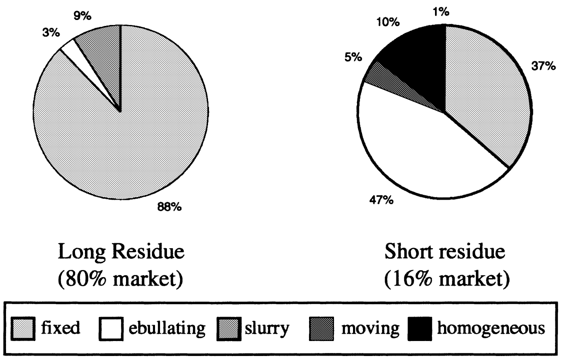

Fig. 1. Share of the various residue hydroprocessing technologies in upgrading of atmospheric and vacuum residues, respectively.

The atmospheric residue HDS (LR-HDS) unit of Seibu Oil (Japan) came on stream in 1976. This LR-HDS produces low-sulphur fuel and FCC feedstock. In 1981, the unit was extended with two HDM reactors, which resulted in an increase in cycle length and higher desulphurisation. Since then, the performance of the unit has steadily improved further by the application of improved internals and better catalysts. The development of LR-HDS technology has also enabled the processing of heavier and higher metal sour feeds without requiring hardware changes. As an example, the increase in metal content of the feed in recent years is shown in Fig. 2.

In 1995, a Shell licensed LR-HDS came on stream in Italy. This unit converts residues from local and Middle-East crudes into low-sulphur fuels. This unit concluded its first cycle and is now operating above design throughput in its second cycle.

In 1996, the LR-HDS in the Showa Yokkaichi Sekiyu refinery (Japan) was started-up. Due to its advanced design, this unit benefits from lower investment and low energy costs. The unit consists of four world scale reactors in a single string design. The feed to the Yokkaichi unit is heavier than the Seibu Oil feedstock and contains the highest level of metals that can be economically processed in fixed bed units. All the treated residue is routed to the new Shell designed R-FCC unit. The start-up went smoothly and the unit has since been running according to design. The LR-HDS and the R-FCC units now form the backbone of the residue conversion capacity in this refinery.

If the feedstock contains higher metal contents (e.g. vacuum residue), fixed bed operation is no longer attractive because of the short cycle length. This paper deals with the development and

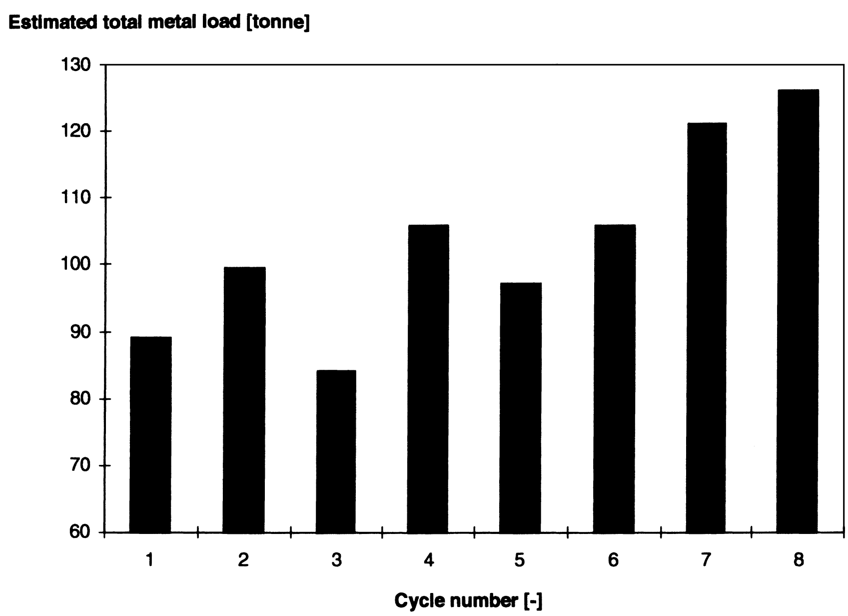

Fig. 2. Increase in total amount of metals processed per cycle in a SIOP designed LR-HDS unit.

progress of the Shell HYCON process which was designed to process these heavy feeds.

Through the conversion of heavy residue into low-sulphur fuels and the application of the bottom product of the HYCON process as low-sulphur refinery fuel, the refinery is thus able to meet stringent limits on sulphur emissions while still processing high-sulphur crudes. The first commercial HYCON unit was constructed in 1989 [3]. It represents the first full-scale application of the moving bed technology.

2. Description of the HYCON process

The feedstocks can range from conventional residues, heavy oils to tar sands derived bitumen. In the Shell refinery in Pernis, the HYCON process converts high-metal vacuum residues into atmospheric and vacuum flashed distillates and a low-sulphur residue. A typical feed is shown in Table 1.

The HYCON process consists of the reactors, catalyst handling facilities and a work-up section [4,5]. The reactors operate at high pressure and relatively high temperatures. The HYCON unit in the Shell Pernis refinery (Rotterdam, The Netherlands) was designed to process 4000 ton vacuum residue per day.

A HYCON reactor train in the Pernis refinery consists of five reactors. The first three reactors are bunker demetallisation (HDM) reactors. The last two reactors are fixed bed desulphurisation and conversion (HCON) reactors. A simplified flow scheme is shown in Fig. 3. The feedstock is fed to the HDM section. The catalysts in the HDM reactors flow concurrently downward. The demetallised products pass to the fixed bed HCON section, which contain highly active desulphurisation and conversion catalysts. Downstream fractionation provides distillable fractions, vacuum distillate (FCC or hydrocracking feedstock) and converted vacuum residue.

Table 1
Typical HYCON feedstock

Feed type	Vacuum residue
Density	1.03 kg/m^3
Sulphur content	4.6 wt.%
Metals (V+Ni)	250 ppm wt.%
Boiling above 52°C	95 wt.%

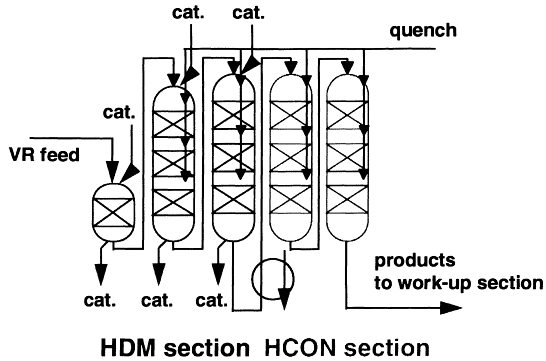

Fig. 3. Process flow scheme of the HYCON Pernis unit.

3. Products

More than 60% of the feedstock is converted into lighter products with low-sulphur content. A typical product breakdown of the HYCON process is shown in Fig. 4. The product breakdown can be adjusted by the selection of alternative catalysts. The distillates form valuable low-sulphur fuel components. The vacuum distillate is routed to a FCC unit. The remaining bottom product is deeply desulphurised and constitutes an excellent refinery fuel and a low density component of commercial fuel oil.

4. Bunker reactor design

With high metal feedstocks even HDM catalysts have a relatively short life, and frequent catalyst replacement is necessary. The Shell HYCON process employs bunker flow-moving bed technology to replace the HDM catalysts continuously on-line [4,5].

Catalysts are transported through a slurry transport system. The rate of catalyst replacement is controlled in accordance with the rate of metal deposition. Special screens separate the catalysts from the process fluids before leaving the reactor. Sluice systems are present at the top and the bottom of the reactor to enable catalyst addition and withdrawl. Valves are used to regulate the amount of catalyst to be transported. Proper fluid flow and quenching is required to make full use of a catalyst's particular properties. Each reactor is, therefore, equipped with proprietary internals that optimise the distribution of fluid throughout

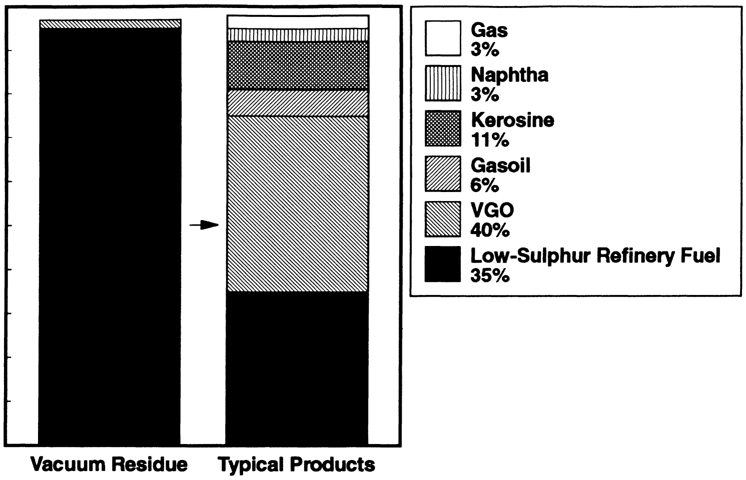

Fig. 4. Typical properties of HYCON feed and products.

the reactor, while also allowing the flow of the catalyst during bunkering. In each reactor (except the first), several catalyst beds are present. After each bed, the fluids are redistributed. This results in better temperature control and a wider operating window than for a reactor with a single bed. Thus, the available reactor volume (at high pressure and temperature) is optimally exploited. In this way, the bunker reactor technology combines the advantages of fixed-bed operation, that is, plug-flow, with easy catalyst replacement.

5. HCON section

The demetallised product from the bunker reactor section is further upgraded in the HCON section. This section consists of two fixed-bed reactors in series that contain catalysts that are highly active for sulphur removal and conversion. These reactors are also equipped with advanced internals to ensure an optimal flow and temperature control.

6. Development of the HYCON process

The process was developed in Shell's Amsterdam laboratories in the 1970s. It originated from research on the desulphurisation of residues into low-sulphur fuel oil. Due to the changes in the economic driving forces, the development was redirected towards the conversion of vacuum residues into transportation fuels. Compared to distillate desulphurisation, the process is much more difficult, because the feedstocks contain large amounts of coke precursors and metals. These can poison the catalysts rapidly. The coke deposition is controlled by applying high hydrogen pressures. The deposition of metals on the catalyst is controlled through multiple catalysts systems, with demetallisation (HDM) catalysts protecting the desulphurisation (HDS) or conversion (HCON) catalysts. Catalysts play a key role in improvements in residue hydroprocessing. The pore volume, pore size distribution, particle size and shape of the catalysts are the aspects of paramount importance in obtaining an optimum catalyst activity and stability.

6.1. Demonstration of the bunker reactors

The feasibility of the bunker operation and catalyst handling section was first tested in Shell's Gothenburg refinery in 1977–1978. This demonstration unit consisted of a single bunker reactor followed by two fixed-bed reactors.

The next step in the development was the construction of HDM complex in Maraven's Cardon refinery. The complex consisted of four HDM reactors in a series (intake 400 tpsd). It processed Venezuelan residues with vanadium contents upto 640 ppm. This complex demonstrated the operation of the HDM bunker section and the catalyst handling system.

6.2. First full-scale application

In the first cycle of the HYCON unit in the Pernis refinery, the catalyst performance was satisfactory. A wide variety of feeds was converted with high severity and at design throughput.

During the start-up phase of the Pernis unit, equipment and materials problems were encountered; the sealing in the bunker reactors internals was not fully effective and essential valves did not function properly. These problems were solved by repairs and replacement of the affected equipment.

When the plant was shut-down and inspected for the first time, it became clear that the proper flow of catalysts had not been maintained and that maldistribution of the feed had occurred in the bunker reactors. This was due to more severe fouling in the reactors than was expected. After extensive investigations the fouling was combated by several measures:

- Adaptation of the catalyst replacement rate in the bunker reactors to remove foulants and installation of fouling resistant internals.
- More attention to housekeeping: desalting operation and filtration of the vacuum residue at high temperatures.

Since these measures were implemented, the performance of the unit has been very satisfactory and is steadily improving further. At first, an intermediate clean-out stop was required during a cycle. Due to the improvements in equipment and control, this intermediate stop was no longer required in the recent cycles.

Over the past cycles significant progress has been made to reduce length of the HYCON turnaround, also. A reduction of 30% in turnaround days has been achieved by:

- Build-up of expertise and ownership by the different contractors. This was achieved by dedicated training, multidisciplinary stopmanagement and contract strategy.
- Development of dedicated equipment and tools to enable efficient cleaning.
- Hardware modifications to achieve easy access and dismantling of internals.

7. Current operation of HYCON

The HYCON process in the Shell Nederland Pernis refinery is now in its fifth cycle. The bunker reactor operation and catalyst handling are very successful. The technical performance in the last cycles has been very satisfactory and the unit operates now routinely above design throughput. Both the higher throughput levels and the reduction in shut-down duration have contributed significantly to the increase in capacity utilisation as is illustrated in Fig. 5.

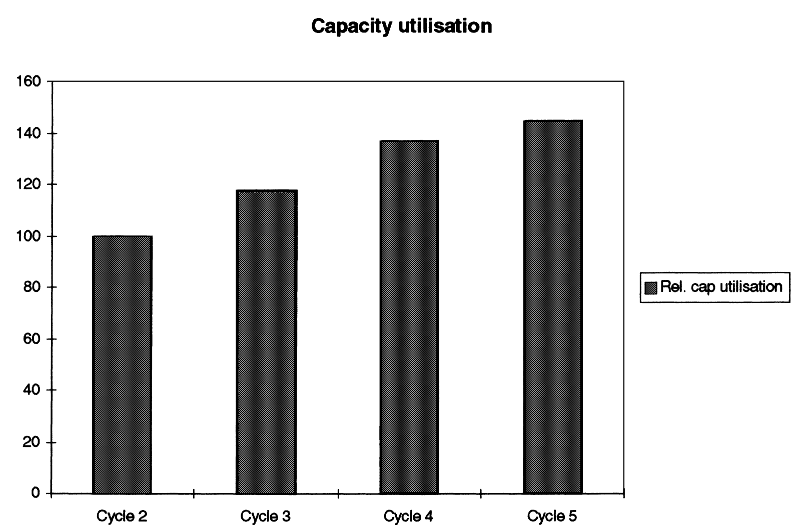

Fig. 5. Capacity utilisation of HYCON Pernis.

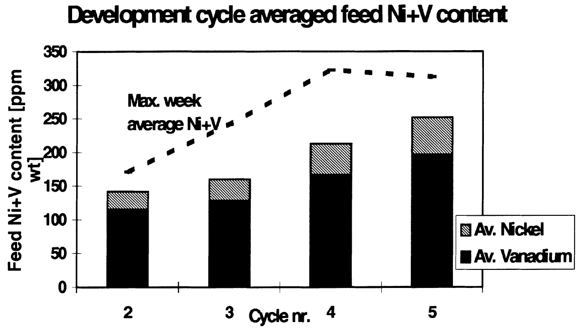

Fig. 6. Metal content of HYCON feed.

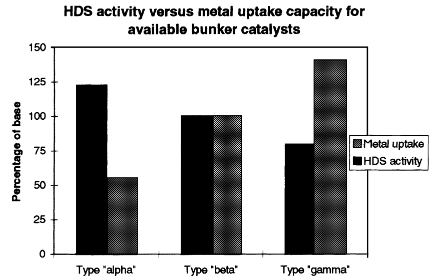

Fig. 7. Characteristics of the catalysts in the bunker catalyst range.

The feed diet has been extended steadily to take full advantage of the capabilities of the HYCON process. The increase in average metal content of the feed is illustrated in Fig. 6. Weekly average metal contents above 300 ppm wt are achieved on a routine basis, since the economic incentives to process such high metal vacuum residue have significantly increased over the past 2 years.

While the metal content of the feed and relative capacity utilisation were increased, the sulphur removal was maintained and the conversion into lighter fractions was even increased.

8. HYCON catalyst developments

In order to allow tailoring of the HYCON moving bed 'bunker' technology to specific applications or to changing refinery economic environments, different bunker catalysts have been developed. A 'type α' regenerable catalyst with high metal uptake capacity was designed, which is specially suited to process very high metal vacuum residues. The regeneration of this 'type α' catalyst has been carried out on commercial scale in the eighties as part of the operation of the SIOP designed Maraven, Cardon 400 tpsd demo-plant. The HYCON Pernis unit has been started-up on this catalyst, but regeneration of the spent HYCON catalyst has never been economic as catalyst consumption rates were only moderate as a result of the moderate metal contents of the feed. As the 'type α' bunker catalyst has a high metal uptake capacity, is very stable at high temperature operation and is regenerable, it is ideally suited for economic processing of very high metal feeds (more than 500 ppm wt metals). A 'type γ' bunker catalyst has more recently been developed which has a higher activity for desulphurisation, but a lower metal uptake capacity. This catalyst is designed to be used in atmospheric and vacuum residue hydroprocessing of feeds having metal contents upto 400 ppm wt.

The bunker catalyst range is completed by the intermediate 'type β' catalyst, which demonstrates a metal uptake capacity and activity level in between the 'type α' and 'type γ' catalysts. The relative characteristics of the catalyst in the bunker catalyst range are shown in Fig. 7.

The SIOP moving bed bunker technology allows change-over from one catalyst system to the other during the cycle without temporary plant upgrading losses or increased catalyst consumption rates. This flexibility allows the refiner operating a bunker system to take maximum advantage of crude price differentials and to respond to changing product quality demands. The possibility of on-stream switching-over has been demonstrated in the Pernis HYCON unit, which has switched from 'type α' catalyst to operation on 'type γ' catalyst. The more active 'type γ' catalyst allows, at equal feed heaviness and conversion levels, to operate at lower reactor temperatures. The actual inlet temperature trend on one of the six bunker reactors in the Pernis HYCON unit during the transition is shown in Fig. 8.

The feed compositions and rates were constant during the transition, that is, the feed consisted of 4300 tpsd vacuum residue containing 95 wt.% material boiling above 520°C and on average 300 ppm wt metals.

Also new tail-end catalysts have become available. After extensive testing at Shell's Amsterdam labora-

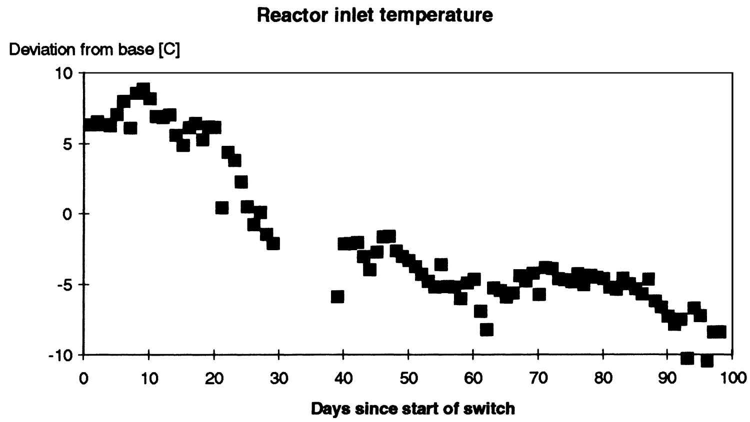

Fig. 8. Moving bed reactor inlet temperature reduction (activity gain) as a result of the on-stream switch from 'type α' to 'type γ' bunker catalyst.

tories, these catalysts have been implemented and the Pernis HYCON process now uses new catalysts in both the HDM and HDS sections. The experience with the catalysts is excellent and represents important economic benefits.

9. Conclusion

The SIOP moving bed bunker technology has been demonstrated successfully in operation of the Pernis HYCON unit for processing of very high metal vacuum residue feeds. The initial hardware problems were solved by repairs and replacement after the start-up of the unit. A range of bunker catalysts is available and has been commercially applied. The variety of catalysts available allow tailoring of the catalyst system to meet the economic challenges faced by the refiner. The SIOP bunker technology allows on-stream replacement of one catalyst system with the other, which further enhances the refiners flexibility.

The process performance in terms of demetallisation, desulphurisation and distillate production make HYCON a valuable asset in the Pernis refinery. With the HYCON unit, the Pernis refinery is able to remove most of the sulphur from crudes, even when processing heavy, high-sulphur crudes. The application of a HYCON unit thus increases the flexibility in the crude diet of the refinery in terms of sulphur content and heaviness, while reducing fuel oil make and meeting more stringent limits on SO_2 emission.

10. Outlook

Based on the HYCON technology, Shell has the option to retrofit existing LR-HDS units with a guard bunker reactor. Application of a small bunker reactor in front of an (existing) residue unit allows to process heavier feeds in longer cycles. Because of the high uptake capacity and high metal removal activity of the catalysts, the size of these bunker reactors is relatively small and the additional investment limited. The moving bed retrofit option for existing fixed bed residue hydroprocessing units becomes even more attractive to refiners as the light sour/heavy sour crude differential increases.

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