A New Generation of Hydroconversion and Hydrodesulfurization Catalysts

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Prepared for
14th Annual Symposium
Catalysis in Petroleum Refining & Petrochemicals
King Fahd University of Petroleum & Minerals-KFUPM
The Research Institute, Dhahran, Saudi Arabia
December 5th-6th, 2004

Session Petroleum Refining: Residue Upgrading
Abstract

Desulfurization and residue upgrading processes are becoming important in the world today as the residual fuel oil demand continues to decline, with increasing demand for low sulfur fuel oils. This market is driven by legislation to produce clean low-sulfur fuels. EU legislation and requires users to lower SOx emissions in Power Plants and to use non-polluting marine fuels. The profitability of investment in residue conversion capacity is a strong function of product values. With current high oil prices there are favorable economics for investment in residue conversion and upgrading. The combination of high prices and dwindling supplies of light crude oil has also created a strong interest in upgrading heavy crude oil as high sulfur crude oil.

The HYVAHL™ and H-Oil® Process are commercially proven technologies respectively for deep desulfurization and conversion of petroleum residue heavy oils. The HYVAHL Process uses the catalytic fixed technology reactor developed by Axens using permutable fixed bed technology. The H-Oil® Process uses the catalytic ebullated-bed reactor. The H-Oil® Process operates at high severity and utilizes a daily replacement of catalyst to maintain a constant catalyst activity level. This broad commercial experience coupled with a dedicated, full-time research and development team at the IFP Research Center in Lyon, France has given Axens the in depth knowledge necessary to optimize catalyst in residue upgrading either in the Hyvaahl or H-Oil® processes over a wide range of processing objectives. This paper will describe advances accomplished in catalyst development for the different Hyvaahl configurations to obtain very low sulfur content down to 0.3 % wt in the fuel. A new generation of catalysts has been developed either for HDM and HDS section, which have a higher activity than the last generation. The new catalysts developed for several H-Oil® process configurations are more related to the hydroconversion of vacuum residue feed with relatively high CCR and contaminant metals associated with good control of the fuel stability produced at the outlet. Two catalysts have been developed and will be used depending on the feed quality and objectives being pursued by the refineries.
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Introduction

Market Highlights:

Around 500 Million tons of fuel are produced in refineries every year and a strong demand for very low sulfur fuel oil (LSFO - 1 wt %) has been requested by the market. This is mainly due to the evolution of the regulations on SOx emissions for power plants, refineries (bubble concept in EU) and on sulfur content in marine fuels and bunker fuel used by ships in order to limit the pollution. This limitation could be very severe in restricted area like the Baltic Sea, North Sea and Channel (concept of SECA: SOx Emission Control Areas). Atmospheric Residue (AR) and Vacuum Residue (VR) are the most difficult feeds to desulfurize and to convert catalytically because they concentrate impurities like sulfur, nitrogen, asphaltenes and metals (essentially nickel and vanadium).

Consequently, the market demand is for residue upgrading by the reduction of the sulfur content and in some case the conversion of this residue. The forecast will increase the demand for distillates and clean fuels versus heavy residues as the world consumption demand strongly increases, namely in Asia and China. The other incentives are the differentials of price between HSFO and either the LSFO (in the range of 10-20 $/ton) or either the diesel and gasoline products (differential around 80 $/ton). Another solution for the refiners is to purchase light and low sulfur crude oils to reduce the amount of HSFO produced. Again, the economics are driven by the differential price between these two types of crude and the differential is substantial and not stable (around 2 $/bbl for several years, now over 5 $/bbl). The availability of heavy and sour crude oils could give incentive for the oil producer to directly refine them and consequently boost the price of this sour oil. Concerning the fuel market, some particular cases can be evidenced in Asia and Japan, the investment in desulphurization units (44 units) enables the refiner to market LSFO (1 wt %) and even ULSFO (0.3 to 0.5 wt %). In this case, the differential
between the two types of fuel could be around 50 $/ton, giving a strong incentive to the refiner to upgrade the fuel oil. The possibility to combine these fixed bed desulphurization units with residue catalytic cracking units also offers the possibility to have full conversion of the fuel produced and cope with the trend of the market (cf. Figure 1). The conversion offers more return due to the strong difference between the gasoline and fuel prices. The demand for gasoline as shown in Figure 1 and the fuel demand will be constant, so full conversion of bottom of the barrel will be requested. Consequently, considering the economics of the product demand and prices, evolution of the regulations on emissions in power plants and ships’ fuel are going to be more drastic in the near future (2005-2007), these will require definitely more hyd roprocessing of residues. A strong initiative for the refiner will be to upgrade the fuel and the technologies are available to respond to this incentive depending on the quality of feed to be processed.

Residue upgrading technology:

While several kinds of residue upgrading processes are now commercially proven, such as fixed bed, moving bed (1) and ebullated bed processes(2), the fixed bed processes are still the main process used to remove sulfur from residues (34,6,14). The hydrodesulphurization of residue in fixed bed processes is a well established residue upgrading process which requires specific catalysts designed to desulfurize the feed and to remove contaminants (Nickel and Vanadium). IFP has developed a fixed bed residue upgrading process using several fixed bed reactors in series, the HYVAHL™ process (4,6,7,14). As we'll describe later, this technology utilizes:
- the use of either a "by-pass" guard reactor or either a permutable reactor system (PRS) in front of the classical fixed bed,
- the design of catalyst packages optimized for various residues feedstocks and process objectives.

But even these technology options are available for fixed bed technology, the residue upgrading depends on the difficulty of the feed to be processed, whether it is atmospheric (AR) or vacuum residue (VR), and whether the metal content is high, as we can sometimes observe in heavy crude oil (API > 10). Fixed bed technologies also have some limitations to handle the conventional feeds at high conversion level (over 30-40 %). IFP summarizes these phenomena in Figure 2 in order to select the appropriate technologies versus the objectives and quality of the feed. Ebullated bed technology, such as H-Oil®, is more suitable for feeds with high metals content and when moderation to high conversion is desired. The ebullated bed technology offers the added advantage of not having the run length limits that conventional fixed-bed reactors have. This is because the catalyst bed is expanded giving the possibility to be withdrawn from and added to the unit. The cycle length becomes the period between refinery turnaround. But the level of desulphurization of ebullated bed technology is a little bit lower (70 to 85 wt %) compared to fixed bed (85 to 95 wt %).

These options are able to cover the entire range of residue feeds by employing unique combinations of commercially proven operating modes and well-adapted graded catalyst systems that we are describing in the paper. We’ll focus our paper’s objective on the
fixed and ebullated bed technologies and new developments carried out for residue hydrotreating catalysts. The fixed bed technology HYVAHL (Figure 3) employs a new graded combination of HDM catalysts (HMC845) and HDS catalysts (HT438) with the objective of producing ultra-low-sulfur fuel oil (ULSFO - 0.3 % wt). Eventually, LSFO can be produced, having an objective sulfur content ranging from 0.5 to 1.0 wt% which could be used as a feed pretreating of residue fluidized catalytic cracker unit, producing “zero” fuel oil.

The catalyst development of the H-Oil® technology developed two new types of catalyst, one (HOC845) dedicated to convert the heaviest feed in the world containing high content of metals (from 300 to 1200 wppm of Ni+V). A second catalyst (HOC458) corresponding to the standard H-Oil® catalyst in order to be used for moderate conversion of the residue in H-Oil® ebullated bed technology while maintaining constant product quality and a good stability of the converted fuel.

Figure 2: Technology selection
Fixed Bed Technology: Hyvahl Process and New Catalysts Development:

The upgrading of AR or VR implies a large deactivation of the catalysts by coke formation and metal sulfides deposition \((10,11,12,13)\). Therefore, several kinds of catalysts are generally used, each of them playing a specific and complementary role to achieve the following main functions:

- Disaggregation of large asphaltenes molecules \((8)\) to enable removal of nickel and vanadium and reduction of asphaltenes content.
- Hydrogenation and hydrogenolysis reactions for sulfur and nitrogen removal, and Conradson Carbon reduction.

The first major function to perform is the hydrodemetallization (HDM) and the HDM catalyst must convert as much asphaltenes as possible into lighter compounds and remove as much metals (Ni and V) as possible from their host molecules. The second major function, the refining one, needs refining catalysts located after the HDM ones to desulfurize the already deeply transformed feed.

A high hydrogen pressure is also useful in these conditions for preventing polycondensation reactions leading to coke formation. An increase of the hydrogen partial pressure has also a tremendous impact on the quality of the products. In addition, deep hydrogenation and hydrodenitrogenation is more and more requested to meet the product specifications notably for FCC pretreatment. However, the high temperatures needed \((350^\circ\text{C}-410^\circ\text{C})\) are generally not favorable to these reactions because of thermodynamic limitations. In some cases the possibility to associate a Fixed bed and cracking catalytic process, such as Axens Hyvahl\textsuperscript{TM} process, associated with the R2R\textsuperscript{TM}, a residue fluidized catalytic cracker (RFCC) is employed to afford high conversions to middle distillates and gasoline having attractive sulfur levels and cetane numbers.

![Figure 3: Hyvahl process flow diagram with PRS feature](image-url)

In AR and VR hydroprocessing, high amounts of metal sulfides \((\text{VS}_x\text{ and Ni}_y)\) and coke are deposited on the catalyst. The amount of metal sulfides deposited on the catalyst varies greatly along the reactor, the rate of deposition being highest at the top of the reactor. After a certain period of time the catalyst, at the top of the bed, has reached its maximum uptake capacity with its pores completely plugged and has lost its activity.
Thereafter the metals deposition phenomena will move further down the fixed bed, eventually it leads to the termination of the run due to a pressure drop build up at the top of the first reactor. This causes the incomplete use of a large proportion of the catalytic mass. To replace the catalyst of the first reactor, the complete shut down of the unit is needed. This operation of several days is complex and uneconomical. IFP-Axens offers to increase the cycle length of the process by using the PRS system. This arrangement facilitates reaction section temperature control as well as the loading and unloading catalyst from the reactors. During the run, both the pressure drop and the quantity of metals removed in the lead (permutable) reactor increases. When one of these reaches its threshold value, a switch occurs. With the PRS technology, the HDS catalyst is well protected from premature deactivation because the PRS ensures a reduced and constant level of contaminants throughout the cycle. When, for instance, pressure drop appears on the guard reactor, this reactor is by-passed and the unit remains on stream with the other reactors. The by-pass provides the possibility to unload and reload with new HDM catalysts. By optimizing the catalyst properties, the residence time, pressure and temperature on each catalyst, the cycle length could be maximized. These advantages of the PRS system provide:

- no operational problems due to attrition common to moving beds technologies and causing plugging in subsequent fixed beds protection of the downstream reactors of the process
- prevents accidental plugging by sediments and unusually high coke deposits related to a temperature run-a-way of furnace, reactor, even up-stream units such as a vacuum tower distillation unit. This protection is obtained from the high level of HDM, of asphaltenes removal protected by guard materials in the guard reactors.

The first catalyst used is the HDM. It must have a high capacity for metal retention and be stable as long as possible while carrying out the bulk conversion. This is obtained by optimizing the HDM activity, pore structure and acidity of the catalyst. This kind of catalyst is therefore designed to achieve a high rate of HDM. Due to the deactivation by metal deposits, the HDS performances of this kind of catalyst are limited. The main features of a good HDM catalyst are therefore a large pore volume to store as much metal deposits as possible and a large amount of macropores to allow resins and asphaltenes to diffuse deep inside the grain and be cracked.

The refining catalyst located after the HDM catalysts, must desulfurize the already deeply demetallized and transformed feed and reduce Conradson Carbon. The refining catalyst has a greater HDS function than the HDM. These catalysts have a porous texture specially designed for these reactions and a large specific surface area but a low metal retention capacity. The refining catalysts must also have a very low acidity as well as a good hydrogenation activity to limit deactivation by coking. The pore size distribution of this kind of catalysts is generally monomodal. According to the Ni+V content of the already deeply demetallized feed to be desulphurized by this catalyst, different mesopore size can be chosen.
New Catalysts for HYVAHL Process

**HDM Catalyst: HMC845**

HMC845 is the new high capacity hydrodemetallization (HDM) catalyst. The key combination of this catalyst is its enormous metal retention capacity due to a "chestnut bur" porous structure and its excellent initial performances in HDM, HDAsC₇, HDCCR, and HDN due to a very powerful hydrogenation function. This catalyst has a spherical shape and it is available with different diameter ranges to manage pressure drop.

The carrier of HMC845 catalyst is characterized by a "chestnut bur" porous structure as shown in the picture of Figure 4. This type of structure, which was the feature of the HMC841 previous-generation catalyst (15), is specially designed to increase the accessibility of the large molecules. The macroporosity which is provided by the interstices between the burs allows asphaltenes and resins to move quickly through the grain mass and access to a maximum active surface area. The active surface is in the mesoporosity of alumina acicular platelets which are agglomerated in the “chestnut bur” structure. This type of structure, which is characterized by a continuous pore distribution between macropores and mesopores (Figure 5), enables a homothetic deposition of metals in the mesopores contrary to conventional structures (Figure 6). Therefore, a high metal retention capacity, up to 100g Ni+V/100 g (based on fresh catalyst) is reached depending on the feed and operating conditions as well as process objectives. The metal retention capacities of the conventional structures which are characterized by a bimodal porosity are significantly lower because of the “pores mouth plugging” phenomenon. Indeed, these structures are constituted by the agglomeration of alumina mesoporous particles and the macroporosity results from the inter-particle free spaces. In this case, the peripheral pores of particles plug faster than the central pores. The access to the nearly unmodified internal porosity of the particles is then closed to the reactants (Figure 6) and the catalyst prematurely deactivates.

![Fig. 4: Scanning electron microscopy picture of a typical "chestnut bur" residue catalyst](image)

![Fig. 5: multimodal and bimodal pore size distributions for HDM catalysts](image)
Nevertheless, multimodal catalysts have the drawback to be less active in initial activity than the bimodal catalysts on HDM, HDAC7 (Asphaltenes definition are the insoluble in n-heptane), HDCCR (reduction of Conradson Carbon) functions because of their smallest active surface. This criterion of the initial activity is today primordial for the fixed-bed residues hydrotreatment to obtain very low sulfur content down to 0.3% wt in the fuel. Indeed, these functions must be maximized to protect the downstream HDS catalysts from the inhibition by asphaltenes and organic nitrogen species and from metal and coke deposits.

Nevertheless, HMC845 catalyst exhibits a very strong hydrogenation function which enables it to have excellent initial performances in hydroprocessing of residues. The HDM, HDAsC7, HDCCR and HDN performances of HMC845 are so comparable to the ones of bimodal catalysts. HMC845 presents the advantages of HMC841 and bimodal catalysts without the drawbacks.

Table 1 shows the highest activity of HMC845 in hydrogenation of toluene with respect to HMC841 catalyst. For the same volume of catalyst, an increase of 50 % in HYD activity is observed with the new active phase of HMC845 which contains less molybdenum. This activity gain is not due to a modification of acido-basic properties of the carrier (the activity in isomerization of cyclohexane does not change) but only an increase of the dispersion of the Ni-Mo-S initial active phase. This improvement is achieved by a better control of the genesis of the oxide phase which is a precursor of the initial active phase.

![Figure 6: pore plugging by metal sulfides deposition: comparison between "chestnut bur" and conventional](image_url)

Table 1: catalytic performances of HDM catalysts in hydrogenation of toluene and isomerization of cyclohexane
The impact of the improvement of the metallic dispersion on the performances of HMC catalysts in hydroprocessing of residue is illustrated Figures 7 to 10. The experiments were performed in a up-flow trickle-bed reactor during 300 hours at high total pressure and a constant reaction temperature using Arabian Light Atmospheric Residue (AL AR) that contains 45 ppm metals (Ni+V), 3.2 %wt sulfur, 3 %wt asphaltenes, 9.8 %wt CCR and 0.4 %wt nitrogen. The HDM, HDCCR and HDN functions are significantly improved on HCM845 whereas the HDS function does not change. After 300 hours, HMC845 is more active by 5°C for HDM and by 10°C for HDCCR and HDN. On the other hand, the asphaltenes content in the effluent is two times as low with HMC845 (0.6 %wt (±0.06) at 300 hours for HMC845 against 1.2 %wt (± 0.12) for HMC841) corresponding to an activity difference of at least 10°C. We can also show that the HDCCR function of HMC845 is extremely stable in accordance with its strong hydrogenation function. All these initial performances combined with an enormous metal retention capacity make this catalyst highly suitable for residue HDM.

Lastly, the spherical shape (bead) of HMC845 leads to a more homogeneous liquid flow. It generates less of an initial pressure drop allowing an increase of the catalyst life cycle. The beads also enable a discharging of the catalyst more easily because of a lower inter-granular plugging. On the other hand, the Grain-size grading is easy to implement and allow a decrease of the pressure drop of a fixed-bed while keeping a high metal retention capacity.
1.2. HDS catalysts

The HT438 is a new generation of tail-end catalysts. The active phase, the catalyst shape, the diameter of extrudates and the porosity have been optimized to maximize the HDS activity but keeping an excellent stability. When compared to the previous-generation catalytic system (HT318 and HT328 used in series), HT438 shows a much higher HDS activity than HT318 and combines excellent properties in hydrogenation, midway between HT318 and HT328.

Table 2 presents the typical properties of the HT438 catalyst compared to the HT318 and HT328 catalysts. A new generation alumina has been perfect to achieve the features of porosity and surface of this new catalyst. The “pores diameter - size of 3-lobe extrudates” couple has been optimized to ensure a more efficient utilization of the active surface, a better stability and to reduce pressure drops. A NiCoMo active phase type has also been perfect to boost the hydrogenation properties of the CoMo phase without modification of the acid properties of the alumina carrier.

The Figures 11 to 15 illustrate the performances of HT438 in hydroprocessing of demetallized vacuum residue compared to the HT318 and HT328 catalysts. The experiments were performed in an up-flow trickle-bed reactor during 350 hours at high total pressure and a constant reaction temperature using demetallized vacuum residue (VR) that contains 21 wppm metals (Ni+V), 1.1 wt % sulfur, 1.8 wt % asphaltenes, 10.3 wt % CCR and 0.3 wt % nitrogen.
<table>
<thead>
<tr>
<th>Shape extrudates</th>
<th>Previous generation catalytic System</th>
<th>New catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HT318</td>
<td>HT328</td>
</tr>
<tr>
<td>Active phase</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type</td>
<td>Cylinder</td>
<td>Cylinder</td>
</tr>
<tr>
<td>Content</td>
<td>CoMo base</td>
<td>NiMo Higher</td>
</tr>
<tr>
<td>Surface Area</td>
<td>Base</td>
<td>Base</td>
</tr>
<tr>
<td>Pore volume</td>
<td>Base</td>
<td>Base</td>
</tr>
<tr>
<td>Pore diameter</td>
<td>Base</td>
<td>Base</td>
</tr>
<tr>
<td>k HYD (volume)</td>
<td>Base</td>
<td>Base × 2</td>
</tr>
<tr>
<td>k ISOM (volume)</td>
<td>Base</td>
<td>Base</td>
</tr>
</tbody>
</table>

Table 2: typical properties of HDS catalysts

(k HYD, k ISOM : rate constants obtained during the hydrogenation of toluene and isomerization of cyclohexane respectively)

At 350 hours, HT438 is more active by 10°C for HDS than the previous generation catalysts. Concerning the HDM performance, it is as active as HT318 and more active than HT328. HT438 shows the same HDM/HDS selectivity as HT328 but at a higher activity level, as shown in the figure 10. Lastly, its HDCCR and HDN functions are comparable to the ones of HT328 in accordance with its strong efficiency in hydrogenation.

Figure 11: HDS level on demetallized VR
Figure 12: HDM level on demetallized VR
The new HDS catalyst has absolute proof in activity and stability that it performs accordingly, based on results from pilot plant trials. The catalyst is performing just as well as predicted: a 10°C lower SOR temperature and a significant cycle length increase is currently estimated to be three to four months compared to a conventional catalyst’s performance. In conclusion, HT438 is a NiCoMo type catalyst, used for the hydrotreatment of demetallized heavy cuts like atmospheric and vacuum residues. HT438 combines the advantage of a high desulphurization and a higher denitrification rate than CoMo catalyst with a unique stability to process the heavy cuts. It should be used after HMC series catalysts in order to get maximum activity and protection against metal toxicities.
contamination. The relative proportion of HMC845 and HT438 catalyst has to be optimized according to the feed quality, the operating conditions and the required yields and product quality.

**Ebullated Bed Technology: H-Oil Process and New Catalysts Development:**

Like a fixed-bed reactor, the ebullated-bed reactor (Figure 16) is used to contact hydrocarbon feedstock, hydrogen and a bed of hydrogenation catalyst. The innovation of the ebullated-bed reactor (1617,18RENVRENV), however, was to maintain the individual catalyst particles is a state of constant motion or fluidized state, by recycling an internal liquid stream. This simple concept solved all of the technical problems that a fixed-bed reactor had for high severity processing of poor quality feedstocks.

![Figure 16 H-Oil ebullated bed reactor](image)

The internal liquid recycle stream is obtained from an internal vapor/liquid separation device (recycle cup) which provides suction to the ebuliating pump. The recycle liquid relative to the fresh feed provides for a back mixed system and the inherent advantages of a back-mixed bed are excellent temperature control and low constant pressure drop. Fresh catalyst can be added and spent catalyst withdrawn to control the level of catalyst activity in the reactor. The capability of the daily addition of a small quantity of catalyst is a key feature of the ebullated-bed reactor and results in constant product quality over time. The run length for the ebullated-bed reactor system is therefore not a function of catalyst activity or bed plugging, as in a fixed-bed system. A complete listing of commercial units is provided in Table 3.

There are seven Axens licensed H-Oil® units operating worldwide. In addition to the H-Oil® Process for processing of petroleum residues, ebullated bed technology has been extended to processing heavy vacuum gas oils and deasphalted oils in the T-Star™ Process. Two T-Star units have been licensed. The first T-Star unit has just started operation at the Lukoil refinery in Perm, Russia. The combined processing capacity of all of the licensed ebullated-bed units is 370,000 barrels of oil per day. Axens ebullated-bed
technology now has more than 35 years of commercial design and operating experience. This broad commercial experience coupled with a dedicated, full-time ebullated-bed research and development team at the IFP research center in Lyon, France has given Axens in depth knowledge to optimize residue conversion in the H-Oil® process over a wide range of processing objectives.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Licensee</th>
<th>Location</th>
<th>Design Capacity, BPSD</th>
<th>Start-up</th>
<th>Feedstock</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Oil</td>
<td>KNPC</td>
<td>Shuaiba, Kuwait</td>
<td>28,000</td>
<td>1968</td>
<td>Refinery Vacuum Residue</td>
</tr>
<tr>
<td>H-Oil</td>
<td>PEMEX</td>
<td>Salamanca, Mexico</td>
<td>18,500</td>
<td>1972</td>
<td>Refinery Vacuum Residue</td>
</tr>
<tr>
<td>H-Oil</td>
<td>Motiva</td>
<td>Convent, LAUSA</td>
<td>43,000</td>
<td>1984</td>
<td>Refinery Vacuum Residue</td>
</tr>
<tr>
<td>H-Oil</td>
<td>Husky</td>
<td>Lloydminster, Canada</td>
<td>32,000</td>
<td>1992</td>
<td>Heavy Crude</td>
</tr>
<tr>
<td>H-Oil</td>
<td>TONEN</td>
<td>Kawasaki, Japan</td>
<td>25,000</td>
<td>1997</td>
<td>Refinery Vacuum Residue</td>
</tr>
<tr>
<td>H-Oil</td>
<td>PEMEX</td>
<td>Tula, Mexico</td>
<td>50,000</td>
<td>1997</td>
<td>Refinery Vacuum Residue</td>
</tr>
<tr>
<td>H-Oil</td>
<td>PKN</td>
<td>Plock, Poland</td>
<td>34,000</td>
<td>1999</td>
<td>Refinery Vacuum Residue</td>
</tr>
<tr>
<td>T-Star</td>
<td>Lukoil</td>
<td>Perm, Russia</td>
<td>70,000</td>
<td>2004</td>
<td>Vacuum Gas Oil</td>
</tr>
<tr>
<td>T-Star</td>
<td>Shenhua</td>
<td>Inner Mongolia, China</td>
<td>69,500</td>
<td>2007</td>
<td>Coal Derived Liquids</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>370,000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3 – Commercial Ebullated-Bed Units

The maintaining of constant product properties during long cycles achieves the objective of fitting FCC operation periods. The latest H-Oil® unit to start up was at the PKN Orlen’s Plock refinery in Poland (Figure 17). This 250,000 BPSD refinery is located about 100 km north of Warsaw. PKN Orlen was required to meet new sulfur emissions standards in its 250 MW power plant by 2000. This LVGO and HVGO are sent to the FCC unit producing gasoline and providing more return.

Figure 17: Refinery block flow diagram at high conversion level

The conversion level of the 538°C + residue into distillates varies up to 65 vol. % to meet seasonal fuel oil demand. The main difficulty with this feed is to reach the conversion and product quality levels while maintaining product stability by minimizing sedimentation. Various process and design solutions are available in the H-Oil® unit.
including catalyst and operating conditions. The sulfur content in the residue is maintained below 1.0 wt% for both conversion levels and sediment formation and fouling are reduced. A process solution is to inject FCC slurry oil at a key point in the process. This highly aromatic oil peptizes the otherwise unconverted asphaltenes resulting in reduced fouling rates that are characteristic of high conversions. In this way, the refiner is able to upgrade low value slurry oil into high quality distillate.

**Advances in H-Oil Process Configuration**

A new development in H-Oil® process technology is inter-stage separation for a two-stage unit design (Figure 18). In this configuration, an additional vessel is fed the first stage reactor effluent (mixed phase) and separates it into vapor and liquid products. The inter-stage liquid is fed to the second stage reactor and the vapor to the overhead of the hot high-pressure separator located after the second stage reactor.

![Conventional Two-Stage Unit](image1.png)

![Inter-Stage Separation](image2.png)

**Figure 18 – Inter-Stage Separation**

With inter-stage separation, off loading of the first-stage reactor gas results in improved reaction kinetics in the second stage reactor since the amount of gas hold-up in the reactor is greatly reduced and increasing liquid hold-up enables greater conversion of the heaviest part of the residue. Alternatively, the second-stage reactor size can be reduced to decrease the plant investment. Inter-stage separation also allows for optimization of the treat gas rates to the individual reactors providing an operating cost savings. The studies have indicated that the inter-stage separation is best applied to the following situations:

- High feed rate applications where the specification of the inter-stage vessel would allow H-Oil® processing in a single train reactor system
- Applications where the H-Oil® Reactor size is limited by shipping, weight or plot
restrictions
• For revamping of an existing H-Oil® Unit with objective of increased feedstock throughput
• High conversion applications where the hydrogen consumption high

The use of inter-stage separation technology in single-train capacity provides a doubling of the throughput depending on conversion level and operating conditions. At a typical residue conversion level of 65 %, a single train capacity can be increased from about 45,000 BPSD to almost 80,000 BPSD

Hydroconversion catalyst used in H-Oil process

Two catalysts have been developed and will be used depending on the feed quality and objectives being pursued by the refiners. HOC458 catalyst has been specifically designed for the ebullated bed such as H-Oil® process and exhibits high conversion performance associated with exceptional stability of the fuels produced. It is used for hydroconversion of residue and extra-heavy crudes in ebullated bed units working under very high hydrogen partial pressure and very high temperature in order to achieve high levels of conversion of heavy oil into distillates, associated with a very good stability of unconverted residue of fuel. The special design of HOC458, small cylindrical extrudates and specific bimodal pore distribution achieves this purpose:
• the particle size distribution is controlled to ensure optimal fluidization properties in ebullated bed, keeping very high attrition resistance.
• the macroporous volume allows high metal retention and the bimodal distribution protects the active sites which provide the good desulphurization performance.

The performance of HOC458 catalyst have been compared to a standard catalyst in a Robinson-Mahoney unit (two stage of operation) on VR Safaniyah and Bench unit on AR Lloydminster (one stage). In this paper, we present the results on AH VR obtained in an R/M unit with two reactors of 1.2 liter. This unit has been specifically designed to benchmark the catalyst. These perfect reactors are running 24 hours on stream and can rank the catalyst in ten days very precisely. The feedstock used is an Arabian Heavy Vacuum Residue Safaniyah (standard reference feed) deeply cut to the vacuum tower, the main petroleum properties are reported in Table 4.

<table>
<thead>
<tr>
<th>Properties of the feed</th>
<th>Units</th>
<th>Vacuum residue Arabian Heavy Saf.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>wt %</td>
<td>1.046</td>
</tr>
<tr>
<td>Sulfur</td>
<td>Wppm</td>
<td>5.4</td>
</tr>
<tr>
<td>Nickel</td>
<td>Wppm</td>
<td>50</td>
</tr>
<tr>
<td>Vanadium</td>
<td>Wppm</td>
<td>163</td>
</tr>
<tr>
<td>Viscosity @ 100°C</td>
<td>cSt</td>
<td>5110</td>
</tr>
<tr>
<td>ASTM-D1160 10 % vol.</td>
<td>°C</td>
<td>558</td>
</tr>
<tr>
<td>Asphaltenes</td>
<td>wt %</td>
<td>14.5</td>
</tr>
<tr>
<td>CCR</td>
<td>wt %</td>
<td>24.0</td>
</tr>
<tr>
<td>« Mérite »</td>
<td>0/10</td>
<td>3</td>
</tr>
</tbody>
</table>
Figures 19 through 23 present respectively conversion, HDM (hydrodemetallization), HDS (hydrodesulphurization) and HDAC7, as a function of catalyst age for the HOC 458 and the standard catalyst. The catalyst age is defined as the number of barrels reported on weight of fresh catalyst. Figure 23 illustrates the stability of the fuel obtained during the test. The stability is measured by an IFP method called 'Mérite' which is a test of flocculation threshold of the asphaltenes in the fuel. The method uses a mixture of xylene and isoctane in different proportions (ranging from 0 to 100%) as solvent and anti-solvent. Using a spot test, "Mérite" is determined by the detection of transition between flocculation of asphaltenes in the spot and a uniform spot for the different xylene/isoctane ratio in the solvent. "Mérite" is equal to the xylene concentration at the transition divided by 10. From IFP experience, "Mérite" must be below 7 to have a good export quality fuel.

All these results confirm very good performances of HOC458 catalyst compared to standard catalyst. The nickel content of the active phase provides a good hydrogenation activity and good product stability. The conversion is enhanced by 4-5 points due to the new structure of macro porosity. Consequently the asphaltenes conversion is not inhibited by the coke lay down on the catalyst which generally plugs the porosity and induces a diffusion problem as the run is progressing. The catalyst hydrogenation function is decreasing versus time and explains why the performances (HDS, conversion, HDM) dropped; this phenomenon corresponds to the normal deactivation of the catalyst. On the industrial unit, this is compensated by the daily addition of the catalyst. The slope of deactivation measured during the run directly gives the catalyst replacement rate (pounds of catalyst to be added versus the cumulative number of barrels processed).

The commercial HOC458 is a very good candidate for higher residue conversion at given feed rate and temperature. The high stability of fuel allows higher conversion level. Moreover the attrition level (below 3 wt %) of the catalyst is very low giving low hard sediment production in the fuel.
Fig. 20: HDM level

Fig. 21: HDS level

Fig. 22: HDAC7 level

Fig. 23: Evolution of 'Mérite'
The second catalyst developed by IFP is the HOC845. It is advantageously used to convert heavy residue containing very high metal content. This application case is dedicated to the heavy crude oil and the objective is to remove the metals in order to protect the subsequent conversion catalysts. Conventional catalyst has the main drawback of having a low retention power and the catalyst consumption is very high, insinuating high operating cost. The industrial catalyst consumption of this “Demet” catalyst (HDM) must be minimized by maintaining a constant activity inside the reactor. Therefore the retention capacity is very important to advantageously convert residue with high metal content.

The catalyst HOC845 exists in the shape of spheres with different diameter range and with a very specific porous structure designed to increase the accessibility of the large molecules. Its development is based on twenty years of experience in fixed bed reactors and benefit from a chestnut bur porous structure previously described in this paper allowing an enormous metal retention capacity. IFP-Axens has developed a high porous volume and sufficiently solid and strong structure to be used in ebullated bed reactors. The attrition test shows values below to 3 wt % of generated fines. This catalyst can uptake up to 100 wt % of Ni+V. Consequently, a relatively small replacement rate can be estimated. We have evaluated this catalyst using the same procedure as the HOC458. Figures 24 and 25 show the evolution of net conversion on VR AH and asphaltenes conversion.

![Fig. 24: Evolution of net conversion (565C+ cut)](image)
Fig. 24: Evolution of net conversion (565C+ cut)

![Fig. 25: Conversion of the asphaltenes versus catalyst age](image)
Fig. 25: Conversion of the asphaltenes versus catalyst age
The performances of HOC845 in a Robinson Mahoney unit using the same operating conditions as previously described are compared with a standard catalyst. The level of conversion is equivalent. Conversion of asphaltenes is even higher at the early catalyst age. These results confirm the great affinity of this catalyst for hydroconversion of residue with high metals content.

Figure 26: HDM versus catalyst age

Figure 26 presents the HDM performance obtained and metal (Ni+V wt %) uptake on the catalyst using a Venezuelan feed in order to accelerate the aging of the catalyst and reduce test duration. HDM performance is quite similar to the standard catalyst on VR Safaniyah and lower on Venezuelan feed. The duration run was longer using multimodal HOC-845 catalyst compared to the bimodal standard catalyst. The standard catalyst has a low porous volume and HDM performance decrease when the porosity is saturated, achieving no more than 65 % of metal uptake on the catalysis. HOC-845 has an important porous volume and open porous structure which enables it to store the metals and keep a good activity. Consequently, the activity will be maintained longer in a commercial unit than the standard catalyst which is generally limited to an overall retention of Ni+V up to 40 wt %. The catalyst replacement rate will be considerably reduced and the operating cost will be minimized.

CONCLUSION

In recent years, IFP and Axens have developed the ARDS and VRDS processes through the use of classical fixed beds and implemented the concept of permutable reactors. These processes use specific and adapted catalyst packages developed for deep
refining and conversion of various residues. Among the main developments made in recent years, two new series of catalysts have been issued: HMC845 and HT438. HMC845 is a new multimodal catalyst for feed hydrometallization. It is able to overcome diffusion problems of the asphaltenes and convert them. The HDM grading is performed with different particle size to overcome the pressure-drop management, and still maximize the activity of subsequent HDS catalyst by achieving a good asphaltenes removal associated with the production of a stable fuel. HT438 is a new HDS catalyst. The NiCoMo type catalyst is used for the post-treatment of demetallized atmospheric and vacuum residues. HT438 combines the advantage of a high desulphurization and a higher denitrification rate than CoMo catalyst with a unique stability to process the heavy cuts. It should be used after HMC series catalysts in order to achieve maximum activity and protection against metal contamination. These new features are also good news for refiners having existing fixed-bed HDS processes for the catalyst replacement market.

Depending on the markets needs, the conversion of crude oils can be achieved using H-Oil® technology into valuable distillate products associated with the production of residual low sulfur fuel oil. Residue conversion and hydro treatment units such as H-Oil® or a combination of Hyvahl VRDS and RFCC are powerful tools that refiners can use to meet future market demands and product specifications. These tools offer solutions to address major challenges such as the decreasing heavy fuel demand, the need for low sulfur heavy fuels, reduced sulfur emissions, reduced sulfur content in gasoline, and the increasing diesel-to-gasoline ratio.

Major improvements and development in H-Oil® process technology is inter-stage separation for a two-stage unit design. In this configuration, the inter-stage vessel would allow just about double the H-Oil® throughput in a single train reactor system. For a typical residue conversion level of 65 %, a single train capacity can be increased from about 45,000 BPSD to almost 80,000 BPSD.

Axens ebullated-bed technology now has more than 35 years of commercial design and operating experience. This broad commercial experience coupled with a dedicated, full-time ebullated-bed and fixed bed research and development team at the IFP research center in Lyon, France has given Axens in depth knowledge to optimize residue conversion in the H-Oil® process over a wide range of processing objectives. New ebullated bed catalysts have been presented in this paper, including:

HOC458 catalyst has been specifically designed for the Axens H-Oil® process and exhibits high conversion performance associated with exceptional stability of the fuels produced.

HOC845 catalyst has been issued to be a “demet” catalyst providing a strong reduction of the catalysis operating cost. It has a powerful aptitude to remove metal and to convert the heavy residue containing very high metal content. This application case is dedicated to the hydroconversion of heavy crude oil and the objective is to remove the metals in order to protect the subsequent conversion catalysts.
Years of research and development in the field of residue Hydroconversion catalysis for both ebullated and fixed bed processes allowed Axens to create a real breakthrough and to bring forward a new best-in-class catalytic system that pushes back the limitations of residue upgrading processes. In residue hydroconversion and hydrodesulfurization, a one catalyst solution does not exist. Each problem required a specific activity grading. The combination of new catalysts can be foreseen and a tailor made catalyst system can be designed by Axens. A catalyst solution is optimized by taking into account the objectives of the client and maximizing run length while constantly maintaining the performance to produce good fuel stability. The performance of the previous catalyst fixed bed unit packages has been demonstrated on commercial units and should be applied to the new packages. By using an optimized catalyst package and proper operating conditions, HYVAHL processes can achieve LSFO target as ULSFO, H-Oil® processes can achieve Hydroconversion and stable LSFO target.

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Acknowledgement
The authors would like to acknowledge the contributions of Sebastien Gachadouat of IFP-Rueil for his work on economic study of the fuel market.