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Recent developments in fixed-bed catalytic residue upgrading

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Abstract

Atmospheric or vacuum residue can be converted into valuable distillates in fixed-bed hydroprocessing units using high reaction temperature, high hydrogen pressure and low contact time. This paper discusses some recent developments made to improve the desulfurization level, denitrogenation level, the run length and the conversion level of fixed-bed hydroprocessing units, both from the process and catalyst points of view. These improvements include the development of a multiple swing-reactor system as well as of complex associations of guard-bed materials and catalysts with particle-size, activity, pore-size and shape gradings. Synergy between fixed-bed operation and other conversion units has been studied and revealed that fixed-bed residue upgrading technologies will play a key role in future refinery schemes in order to establish new specifications on gasoline, diesel and fuel. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Hydrodesulfurization of residues in fixed-bed processes is a well-established residue upgrading process which requires specific catalysts designed to desulfurize the feed and to remove contaminants [1–3]. Until recently, the aim of these processes were mainly to produce fuel and distillates satisfying the specifications imposed by regulations, notably for SO_x emissions of power plants.

Recently, new regulations have been implemented in EEC and, more generally, worldwide for SO_x emissions of new power plants, and for fuel oil and diesel qualities. These specifications are going to be even more drastic in the near future (Table 1) and will require more severe hydroprocessing of residues. In parallel, one can note a decreasing demand for heavy

fuel oil, an increasing demand for low sulfur fuel oil (LSFO) and an increasing need for clean transportation fuels (gasoline and diesel) worldwide.

The increasing severity of the products specifications as well as the change in the demand of products will lead to a shift of the main objective of residue upgrading processes from hydrodesulfurization (HDS) to conversion. In addition, improvement of hydrodenitrogenation (HDN), aromatics hydrogenation (HDA) and Conradson carbon reduction (HDCCR) performances will be sought after in order to produce better feeds for residue catalytic cracking units (RCC).

HDS of residue is usually associated with some degree of conversion of the feed; however, to achieve a deep HDS together with a high conversion level will be very difficult. Therefore, higher severity will be required and, in particular, higher reaction temperature and residence time. The level of severity will be

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Table 1 EEC sulfur specifications on fuel oil and powerplant or refinery emissions

	Current	Future (year 2000) under discussion	SO_x	Powerplant/ new unit
	S wt%	S wt%	mg/Nm ³	
Heating oil	< 0.2	<0.1		
LSFO	<2	<0.25	400 1000 ^a	>500 MWth (95)
HSFO	<4	<1 b	1700	<300 MWth (95)

^a Under discussion for old and new powerplants, equivalent in sulfur: 0.6 wt%, to be applicable from 1 Jan, 2000.

strongly dependent on the feedstock and the fuel specifications. This trend will lead to the revamping of older residue hydroprocessing units and the building of new ones.

While several kinds of residue upgrading processes are now commercially proven, such as the fixed-bed, moving-bed and ebullated-bed processes, fixed-bed processes are still the main process used [4]. IFP has developed a fixed-bed residue upgrading process using several fixed-bed reactors in series, the HYVAHL-F process [5]. Recently, two major developments in this residue hydroprocessing technology have been made, namely:

 the use of a 'by-pass' guard reactor or a swingreactor system (SRS) in the HYVAHL-S process (Figs. 1 and 2), the design of catalyst packages optimized for various feedstocks and process objectives.

These developments lead to a family of heavy feedstocks upgrading technologies licensed by IFP, specially designed to be very flexible.

In this paper, the recent improvements of IFP's fixed-bed residue hydroprocessing technology and the major developments of IFP-PROCATALYSE catalysts will be reviewed.

2. Fixed-bed residue hydroconversion processes

2.1. HYVAHL residue hydroconversion processes

Atmospheric residue (AR) and vacuum residue (VR) are the most difficult feeds to convert catalyti-

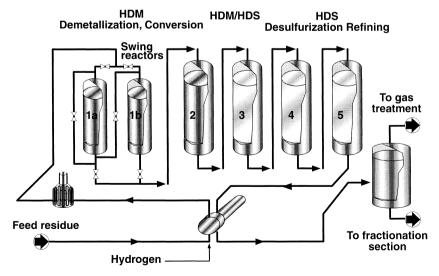


Fig. 1. Simplified scheme of HYVAHL-S hydroconversion process.

^b Directive proposed for EEC.

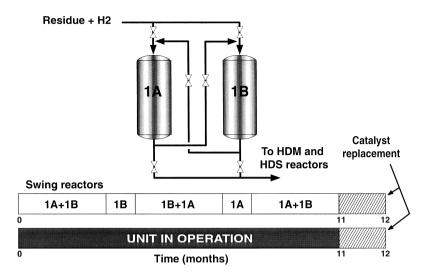


Fig. 2. Swing-reactor system of the HYVAHL-S process: Improved cycle length.

cally because they contain concentrated impurities like sulfur, nitrogen, asphaltenes and metals (essentially nickel and vanadium).

To achieve deep refining and conversion of AR or VR, fixed-bed desulfurization processes are generally composed of several large reactors in series and sometimes a few trains of several reactors in series [4,5]. IFP has developed several kinds of fixed-bed processes under the name HYVAHL. The HYVAHL-F process is a classical fixed-bed process using several reactors in series and the HYVAHL-S process – a fixed-bed process using a 'by-pass' guard reactor or a swing-reactor system (SRS) in front of several fixed-bed reactors in series.

The upgrading of AR or VR implies a large deactivation of the catalysts by coke formation and metal sulfides deposition. 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 asphaltene molecules to enable removal of nickel and vanadium and reduction of asphaltene content.
- Hydrogenation and hydrogenolysis reactions for sulfur and nitrogen removal, and Conradson carbon reduction (CCR).

The first major function to perform is the hydrodemetallization (HDM) and the HDM cata-

lyst must convert as much asphaltene 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.

In addition to refining reactions, mainly hydrodemetallization and hydrodesulfurization, a substantial conversion of the residues is generally requested. Reaction temperatures in the 400-420°C range are, therefore, applied on the first catalyst, which results in an enhanced rate of deactivation. In this temperature range, both catalytic and thermal conversions occur, the proportion of each depending mainly on the reaction temperature, on the nature of the catalyst and on the hydrogen partial pressure. 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 to achieve high conversion are generally not favorable to these reactions because of thermodynamic limitations.

2.2. HYVAHL-S process

In conventional hydrotreating units, fixed-bed reactors use liquid and gas phases, flowing co-currently downstream in a trickle flow regime [4]. In AR and VR hydroprocessing, large amounts of metal sulfides (VS_x and NiS_v) 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 [6-10]. 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 buildup 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 offers two solutions to increase the cycle length of the process depending on the nature of the feedstock and the performances required. The first one is the installation of a guard reactor of relatively small size that can be by-passed during the run. When, for instance, a pressure drop appears on the guard reactor, this reactor is by-passed and the unit remains onstream with the other reactors in operation. During that time, the guard reactor is standing by while waiting for the shutdown of the unit. By optimizing the catalysts properties, the residence time, pressure and temperature on each catalysts, a three years continuous operation is obtained if the metals content in the feed is <100-120 wt ppm. A 26000 BPSD unit based on this concept and developed by IFP is in operation in the USA.

The second possibility is to use a swing-reactor system (SRS) containing two reactors in series which can be switched alternatively in operation (permutable reactors), allowing to operate continuously the unit for at least one year. Such process development has been made possible by using special high-pressure switching valves. The process scheme includes, therefore, the SRS followed by several fixed-bed reactors in series. The swing reactors are single fixed-bed reactors with simple internals that allow easy catalyst loading and unloading.

The SRS operating procedure follows two major steps (Fig. 2):

- i) when the catalyst contained in the first swing reactor (1A) is deactivated or when the pressure drop is too high, a suitable procedure and technology allow for a fast switching off of this reactor while the second reactor (1B) remains on-stream, thus avoiding any production loss. Fast, reliable and safe switch off operation is achieved by
- a proper catalyst conditioning package,
- adapted operating conditions, and
- the selection of special high-pressure valves tested and qualified at representative conditions for switching the guard reactors. In addition, special devices such as interlocks and suitable procedures are used.
- ii) the switched off reactor (1A) is then unloaded and reloaded with fresh catalyst. The catalyst is then sulfided and the reactor (1A) is put back in operation in the second position after the swing reactor (1B) in less than one week (see Fig. 2). During this operation, the unit is still running onstream with the second reactor (1B) now in the first position.

The innovative technology of the HYVAHL-S swing-reactor system provides the following benefits to the refiner:

- the high efficiency of fixed-bed catalysts;
- no operational problems due to catalyst attrition common to moving-bed technologies and causing plugging in the following fixed beds; and
- protection of the downstream reactors of the process from accidental plugging by sediments and from unusually high coke deposits related to a temperature run-a-way on furnace or reactor (this protection is obtained from the high level of HDM, of asphaltenes removal and conversion in the guard reactors).

The reactor volumes of the SRS are optimized to minimize the loss of activity during this operation. Therefore, assuming that less than one month is needed for the replacement of the whole catalyst inventory of the unit, a high stream factor of 0.92 per year is achieved when the metal content in the feed is up to 350 ppm (Fig. 2).

In the case of VR AH feeds, the life cycle of the HDM catalyst located in the swing reactors ranges from 3 to 6 months, whereas the typical life cycle of the other catalysts used in the downstream reactors of the unit is more than 11 months.

Thus, when comparing the swing-reactor system with the by-pass reactor, it can be seen that the swing reactor allows the unit to run for a duration of 11 months with all of the reactors in operation and in series.

With appropriate catalyst, metal retention can reach up to 80 wt% in the swing reactors. This concept has been developed by IFP to achieve a minimum of one year of continuous operation with feedstock from most available crude oils containing up to 250–400 wt ppm Ni+V. A 32 000 BPSD HYVAHL-S unit on AL VR using this concept is in operation in Asia (Fig. 1).

2.3. Integration of the HYVAHL units and performances

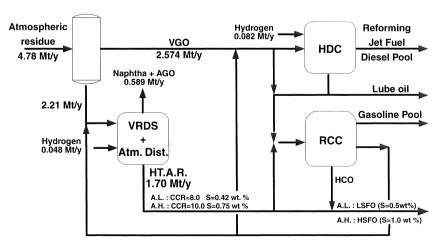
The HYVAHL unit can be used in the refinery in two major schemes as discussed in previous papers [4,7]:

- the direct conversion scheme
- the semi-direct conversion scheme

The objective of the direct conversion scheme is to convert AR or VR residues into a maximum amount of middle distillates. Figs. 3 and 4 give examples of the

direct conversion scheme for AL and AH feeds. Upgrading an Arabian Light (AL) VR with a direct conversion scheme using HYVAHL processes produces a very good 375°C+fraction (S ca. 0.4 wt% and CCR ca. 8, see Table 2) which can be used as LSFO or as a feedstock for a RCC unit such as the R2R-FCC. The large reduction of Conradson carbon and of metal contents in the hydrotreated residue allow to maximize the gasoline yield and to prevent rapid deactivation of the RCC catalyst, thereby limiting catalyst consumption. In addition, the deep desulfurization of the residue reduces SO_x emissions and sulfur content of the liquid products, namely gasoline. The diesel cut, obtained by the HYVAHL-S process (Table 2), has a very low sulfur content, but the nitrogen content is relatively high, and the cetane index is a little bit low to be used directly as diesel feed. However, it is a very good blending cut for diesel pool. The various distillates obtained from residue hydroconversion processes may, therefore, require further hydroprocessing to reach cetane number and low aromatic content for jet fuel, for example. This can be obtained by the association of downstream hydrotreating units.

In the case of VR AH feeds, the still bottom of the HYVAHL unit can be sent to an RCC unit after blending with either an SR VGO or the still bottom of a hydrocraking unit (HDC). Another option is to associate a solvent deasphalting unit (SDA) as shown



* basis: Arabian Heavy Crude (8 Mt/y)

Fig. 3. Residue upgrading by association of HDC, VRDS and RCC units.

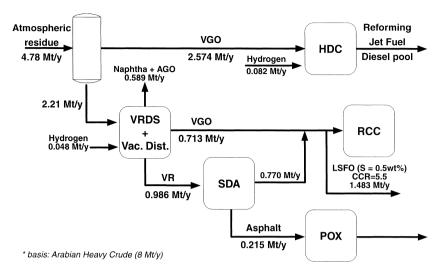


Fig. 4. Residue upgrading by association of HDC, VRDS, RCC, SDA and POX units.

in Fig. 4. This configuration permits to increase conversion by minimizing fuel oil production. Also, the blend of DAO and VGO of conversion easily meets the specification of RCC feed. However, this association is more economic if the refiner adds a partial oxidation (POX) unit of the asphalt in order to produce hydrogen.

For this direct conversion scheme, the investment costs are important because they need the full

HYVAHL unit (HDM and HDS sections) and an RCC unit. Hydrocraking can be an option. Currently, two refineries have the configuration of Fig. 3, except one which has no hydrocraking unit (HDC).

In order to minimize investment cost, IFP suggest the semi-direct conversion scheme as shown in Fig. 5. The objective of the semi direct conversion scheme is the preparation of feedstock suitable for existent downstream conversion processes, such as the FCC

Table 2
Properties of effluents from Arabian Light vacuum residue HDS

Feed or product		VR ^a -AL ^b feed	VRDS ^c -AL ^b product	VRDS ^c -AL ^b product
boiling range		530°C ⁺	150–375°C	375°C ⁺
Specific gravity		1.014	0.870	0.958
°API		8.1	31.1	16.2
Viscosity at 100°C	(cst)	650		87
Sulfur	(wt%)	4.14	0.014	0.42
Nitrogen	(wppm)	3000	250	2100
Hydrogen	(%)	10.4	12.7	12.0
Nickel	(ppm)	15		3.5
Vanadium	(ppm)	80		2.8
Molecular weight	(g)	940		700
Asphaltenes/C7	(%)	6.6		0.8
Carbon Conradson	(wt %)	19.8		8.0
Cetane number	· · ·		42	
NMR CA	(% atm.)	30.5	20.6	20.4

^a Vacuum residue.

^b Arabian Light.

^c Vacuum residue after desulfurization.

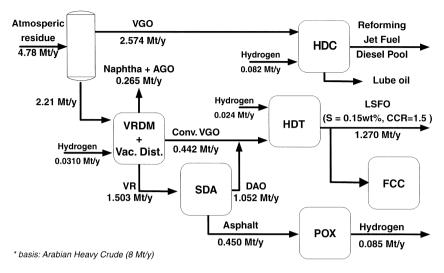


Fig. 5. Residue upgrading by association of HDC, VRDM, SDA, HDT, FCC and POX units.

process. This last scheme (Fig. 5) also involves an SDA unit and has been already discussed in previous papers [4,7]. The interest of this configuration is the low investment cost, namely on VR AH feedstock, because the HYVAHL unit is reduced to its first HDM step. The heavy distillate produced by the HYVAHL unit and the DAO produced by the SDA unit have to be mixed and hydrotreated in a conventional unit in order to adjust CCR and sulfur and to have the possibility to be processed through conventional FCC unit. This scheme is able to treat VRs which have a CCR between 25 and 35. From an AH feed, this scheme offers the possibility to produce a very low sulfur fuel oil: S=0.15 wt%, CCR ca. 1.5. In this case, one can achieve the most stringent specifications on sulfur fuel oil with the use of low-pressure pretreatment of the FCC unit. Asphalt produced by this route can be sent to a POX unit in order to produce hydrogen for hydrotreating units.

3. Fixed-bed residue upgrading catalysts

Fixed-bed residue upgrading processes, in general, use an association of several catalysts and guard-bed materials within the guard reactor and the downstream reactors of the unit. The concepts driving these associations are the particle size, activity and pore size gradings (Fig. 6). A recent study reports that the cycle

length can be increased by >50% by selecting the good grading of catalysts in fixed-bed processes [8] and an association of up to 10 catalysts has been claimed in the literature [9].

In addition to catalyst deactivation by coke and metal deposit, vacuum residue HDS in fixed-bed reactors involves typical problems such as hot spot occurrence and pressure drop buildup. According to a recent paper, a hot spot could occur in a local region of low liquid flow, generally originated from an initial poor distribution of the liquid flow. The use of good liquid distributor is therefore necessary but unfortunately the effect of this good distribution is limited to a certain depth of the bed, which varies with catalyst particle shape and size. In addition, the flowing of the liquid phase is related to the orientation of the catalysts particles in the reactor. The loading method is therefore an important parameter in order to control this orientation. Moreover, the shape of the catalyst is of importance, the beads leading to the more homogeneous liquid flow. IFP has chosen to develop its residue upgrading catalysts in various sizes and shapes and, in particular, in the shape of beads and cylinders.

End-of-run conditions can arise due to an increase in pressure drop above the maximum design conditions. Combining catalysts with different sizes and shapes in the first reactor can limit the rate of pressure drop buildup (Fig. 6). In that case, the control and dispersion of inorganic solid deposits throughout the

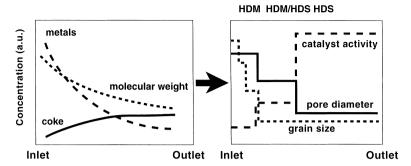


Fig. 6. Grain-size, pore-diameter, activity gradings of catalysts in fixed-bed residue hydroconversion process.

bed is obtained. On top of the first catalyst bed, guardbed materials are frequently used. They are mainly used to trap solid particles remaining in the feed such as coke particles coming from heating tubes, iron scales from corrosion, dissolved impurities such as iron, arsenic, calcium-containing compounds, sodium chloride, silicon contained in upstream additives, etc. The guard-bed materials also improve fluid distribution over the entire radial section of the reactor. We have developed new guard-bed materials which have very low surface area with an ultra-large macroporosity (Table 3). This porosity increases the void space in the guard bed compared to filled alumina balls. Such a material traps iron much more efficiently than a conventional HDM catalyst as shown in Table 4. This is due to the fact that iron compounds are highly reactive and are trapped in the external surface of the catalyst grains. Therefore, an ultra-large macroporosity provides a larger external surface and, hence, a higher amount of iron is trapped. These materials are commercialized by procatalyse under the brand name FEREXSPHERE®.

Table 4
Analysis of used HDM catalyst and guard-bed material

Metal (wt%)	Guard material	HDM catalysts
V	3.9	11.7
Fe	2.0	0.1

Activity and pore-size gradings are both needed to improve metal storage capacity, HDS activity, conversion level and run length. In any case, a specific loading method has to be employed. This optimization is closely connected to the choice of the operating parameters (hydrogen partial pressure, liquid hourly spatial velocity, hydrogen/hydrocarbon ratio, temperature) and the nature of the feed. To design the residue upgrading catalysts association, IFP has studied a lot of catalysts of different shapes, activities and pore-size distribution. A large variation of HDS and HDM activities and Ni+V uptake capacities can be achieved. From this, a typical association of catalysts can be designed. It is generally a combination of an HDM, a balanced HDM/HDS and an HDS catalyst

Table 3
Typical properties of fixed-bed catalysts

Shape	Guard material sphere/pellets	HDM catalysts sphere/Extrudate	HDS/HDM catalysts sphere/Extrudate	HDS catalysts Extrudate
Size (mm)	3–10	1.2–6	0.8–1.6	0.8-1.6
Active phase	no	Mo/NiMo	NiMo/CoMo	CoMo/NiMo
Surface area (m ² /g)	<1	80–180	150-220	180-250
Pore volume (cm^3/g)	< 0.15	0.7-1.2	0.5-0.8	0.4-0.7
MPD (nm)	10–100 μm	20–100	10–20	8-12
Ni+V (wt% fresh cat.)	-	>50	30–40	10-20
Catalyst load (%vol)	<5	30-60	10–40	30-60

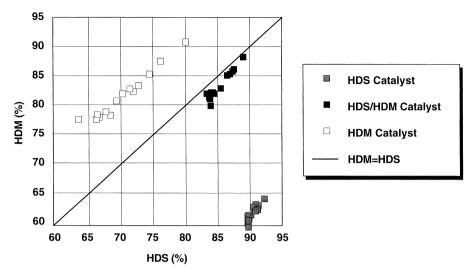


Fig. 7. HDS and HDM performances on Arabian Light atmospheric residue.

with a guard-bed material on top of the first bed (Table 4 and Fig. 7). Fig. 8 shows an optimization done for AL-VR in order to produce LSFO. The kinetic constants of the HDS reaction are different for each catalyst. This is explained by the nature of the sulfur compounds which are more and more difficult to be desulfurized as the HDS level increases. This result shows that a synergy effect can be obtained with several catalysts in series. However, kinetic modeling and experimental work have to be done on each

catalyst to optimize the association of catalysts. Moreover, the proportion of the different catalysts needs to be determined according to the nature of the feedstock, the performances required and the operating conditions such as hydrogen partial pressure and the rate of feedstock to be treated.

The first catalyst used is the HDM one. 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,

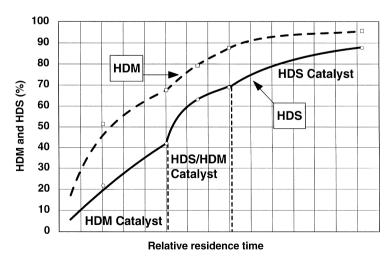


Fig. 8. Typical performances (HDM and HDS) on AL-VR for one association of residue HDT catalysts of HYVAHL-S process.

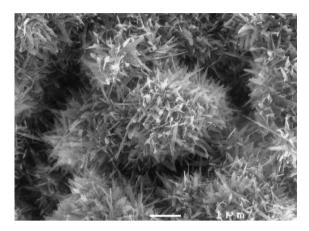


Fig. 9. Scanning electron microscopic picture of a typical "chestnut burr" residue HDM catalyst.

pore structure and acidity of the catalyst. This kind of catalyst is, therefore, designed to achieve a high rate of HDM as illustrated in Fig. 7. Due to the deactivation by metal deposit, the HDS performance of this kind of catalyst is 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 (Table 3). A significant example of HDM catalyst structure is the 'chestnut burr' type [4,10] as shown in the picture of Fig. 9. This type of catalyst allows to obtain a uniform distribution of metals deposited in the grain. Therefore, a high metal retention capacity, up to 100g Ni+V/100g, of fresh catalyst is reached depending on the feed and operating conditions as well as process objectives.

To improve HDS and HDC performances of fixed-bed processes, a catalyst with balanced HDM/HDS activity is generally employed after the HDM catalysts. Its main function is to desulfurize the demetallized feed even if traces of the metal are still present in the feed (30–60 ppm wt). This catalyst has a porosity specially designed to accumulate a significant amount of metal and to provide more HDS activity than the HDM catalyst (Table 3 and Figs. 7 and 8). The capacity for metal retention of this kind of catalyst is generally ca. 30–40 wt%.

The refining catalyst located after the HDM and the HDS/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 function, as indicated in Fig. 7. These catalysts have a porous texture specially designed for these reactions and a large specific surface area but a low metal retention capacity (Table 3). 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 desulfurized by this catalyst, different mesopore sizes can be chosen. Fig. 10(a and b) indicates that a decrease of the mesopore size leads to an increase of the HDS activity and a decrease of the HDM activity and metal-retention capacity. This behavior is linked to the depth of penetration of the asphaltenes in the grain which decreases when the pore size is diminished.

The HDS/HDM selectivity of a catalyst can, therefore, be adjusted by parameters such as the pore-size distribution, the particle shape, the particle size and the nature of the active phase. For each kind of catalyst, the HDN level is usually relatively low. We have developed an improved catalyst able to achieve a high level of HDN on these kinds of feed-stock compared to an older generation of HDS catalysts (Fig. 11).

The nature and type of feedstock is a very important parameter. We have compared four catalysts (Fig. 12): two monomodal catalysts (a small and a large mesopore size), a multimodal catalyst and a bimodal catalyst of which the mean mesopore diameter is very small. When the feedstock is changed, the HDM performance of the very-small mesopores bimodal catalyst sharply increases. The same behavior is observed for the small mesopore diameter monomodal catalyst, even if to a lesser extent. On the contrary, the HDM performances of the two other catalysts are nearly stable. Properties of the feedstocks, such as asphaltenes content, asphaltene-to-resins ratio, metallic impurities level and size of asphaltenes are of importance. The extent of variation of the catalysts activities is closely linked to the properties of the catalyst. Fortunately, general tendencies have been observed for all of the catalysts with different poresize distributions, obtained when some parameters are modified. For example, Fig. 13 indicates that a large decrease of the HDS and HDM performances is

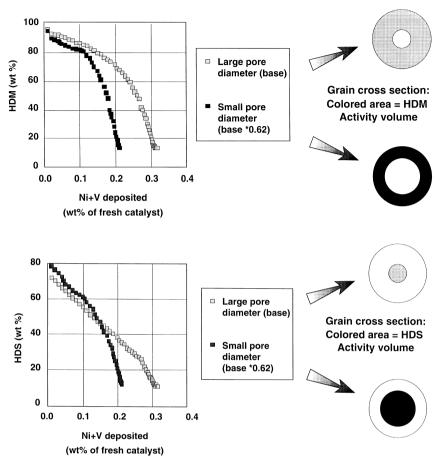


Fig. 10. Influence of pore diameter for different types of catalyst on (a) HDM and (b) HDS.

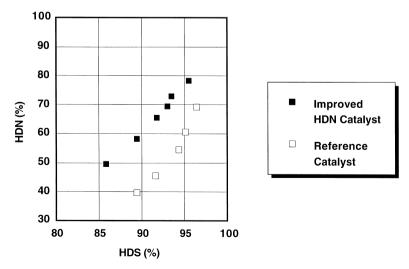


Fig. 11. Relation between HDS and HDN of two different generations of catalyst.

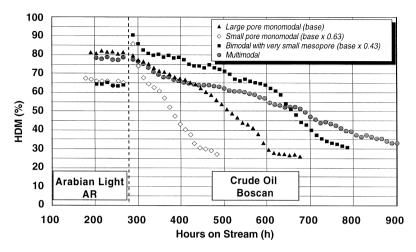


Fig. 12. Influence of feedstock on HDM performance for various type of catalysts.

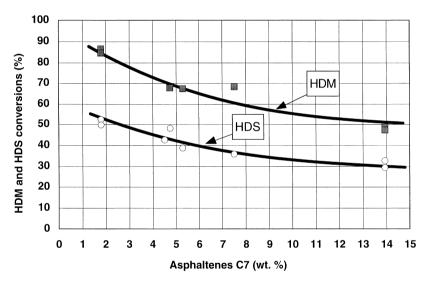


Fig. 13. Influence of asphaltenes content on HDS and HDM performances for HDM catalyst.

observed when the asphaltenes content of the feed increases.

4. Conclusion

In recent years, IFP has developed three different processes for the VRDS treatment: a classical fixed-bed VRDS process (HYVAHL-F), a fixed bed-process with by-passed guard-bed reactor and a fixed-bed process with a swing-reactor system (HYVAHL-S).

These HYVAHL processes use specific and adapted catalyst packages developed by IFP. These catalyst packages feature guard-bed materials, complex association of catalysts with particle-size, pore-size distributions and activity grading. These catalyst packages have been implemented in order to obtain higher levels of conversion, better products qualities and increased run length while maintaining residual fuel stability. The performances of these catalyst packages have been demonstrated on bench-scale pilot units and the concepts of the various HYVAHL

processes have been tested for different crude types (high asphaltenes and metal contents, as well as high sulfur and nitrogen contents). By using an optimized catalyst package and proper operating conditions, HYVAHL processes can achieve 95 wt% hydrodemetallization and 92 wt% hydrodesulfurization as well as a good conversion level of Arabian Light or Arabian Heavy Vacuum residues with a 1-year continuous operation.

The choice between the various HYVAHL processes strongly depends on the amount of contaminants contained in the feed. The by-passed guard-bed and HYVAHL-S processes have been industrially proven. A first 26 000-BPSD unit is running in the USA and a second 32 000 BPSD unit using the SRS is in operation in Asia. Both units allowed for the plant to run a 1-year continuous operation.

References

- [1] T. Ohtsuka, Catal. Rev. Sci. Eng. 16 (1977) 291.
- [2] W.I. Beaton, R.J. Bertolacini, Catal. Rev. Sci. Eng. 33 (1991) 281
- [3] H. Koyama, E. Nagai, H. Torii, H. Kumagai, Stud. Surf. Sci. Catal. 100 (1996) 147.
- [4] F. Morel, S. Kressmann, V. Harlé, S. Kasztelan, Stud. Surf. Sci. Catal. 106 (1997) 1.
- [5] A. Billon, J.P. Peries, M. Espeillac, T. des Courrieres, NPRA 89th Annual Meeting, San Antonio, March 17–19, 1991.
- [6] T.H. Fleisch, B.L. Meyers, J.B. Hall, G.L. Ott, J. Catal. 86 (1984) 147.
- [7] A. Billon, G. Henrich, A. Hennico, Pétrole et Techniques, No. 388, mai-juin 1994.
- [8] P.W. Tamm, H.F. Harsberger, A.G. Bridge, Ind. Eng. Chem. Proc. Des. Dev. 20 (1981) 262.
- [9] D.S. Thakur, M.G. Thomas, Ind. Eng. Chem. Prod. Des. Dev. 23 (1984) 349.
- [10] H. Toulhoat, R. Szymansky, J.C. Plumail, Catal. Today 7 (1990) 531.