# MAXIMIZING CYCLE LENGTH OF VACUUM RESIDUE HYDRODESULFURIZATION UNIT

S. Kressmann [1], V. Harlé [2], S. Kasztelan [2], I. Guibard [1], P. Tromeur [3], F. Morel [1]

IFP,
[1] Centre d'Études et de Développement Industriel "René Navarre",
B.P. 3, 69390 Vernaison, France.
[2] Division Cinétique et Catalyse, 92852 Rueil-Malmaison Cedex, France.
[3] Division Industrielle, 92852 Rueil-Malmaison Cedex, France.

## ABSTRACT

Achievement of long cycle length is an important objective for the refiner operating a vacuum residue hydrodesulfurization unit. The fixed bed technology generally used for this purpose requires a specific design such as swing/permutable reactors as well as the use of sophisticated associations of catalysts to reach a long cycle length and constant low sulfur content in the products. In particular, it is shown that the stability of the refining catalyst is a key parameter to improve the run length while keeping a high level of hydrodesulfurization. An efficient HDS catalyst has been designed to respond to this demand and also recommendations to conduct the operation of the VRDS unit have been mentioned.

## INTRODUCTION

Atmospheric residue (AR) and vacuum residue (VR) are the most difficult feed to be treated catalytically under hydrogen pressure because they contain all the impurities present in the crude oil and among them, asphaltens and metals (1-3).

The hydrodesulfurization of vacuum residue is nowadays carried out with well-established upgrading process using usually fixed bed technology (4-6). The objectives of the refiner are mainly to desulfurize and to convert the vacuum residue in order to produce a stable low sulfur fuel oil (LSFO) according to the specifications of the market. This objective is driven by an increasing demand for LSFO, residue FCC feed and an increasing needs for clean transportation fuels (gasoline and diesel).

One main aim of the refiner is to maintain cycle length of the Vacuum Residue DeSulfurization (VRDS) unit as long as possible. This is a major challenge for fixed bed technology because, as it is well known, the asphaltens and metals are concentrated in the still bottom and therefore the deactivation of conventional hydrotreating catalysts is strongly enhanced during the treatment of vacuum residue.

Several process technologies have been introduced to improve cycle length of VRDS units such as the moving bed technology (7-8), ebullated bed technology (11) and Swing/Permutable fixed bed reactors (4-6, 9). To increase the cycle length on vacuum residue and improve the protection of downstream HDS catalyst, a concept of fixed bed VRDS process including a permutable-swing guard reactors system has been developed by IFP (HYVAHL process, Figure 1, see also reference 9) and is industrially proven. The process scheme includes permutable fixed bed guard reactors that can be switched in operation allowing the possibility to isolate temporally one reactor for change out of the guard HDM catalyst.

However, in order to maximize the HDM and HDS performances of the unit and to maintain the stability, it is now well recognized that associations of several catalysts with different functions are also mandatory (9). One typical association comprises three types of catalysts :

- a HDM catalyst for the metal removals in front of the unit,
- a HDM/HDS catalyst with balanced HDS and HDM activities,
- a very active and stable HDS catalyst in the last section.

The HDM catalyst has the objective to remove the metals contained in the feed and as a consequence to protect the downstream catalysts from metal deposits. A special porous structure designed for this purpose is the so-called "chestnut-burr" structure (10) in which the porosity has been adjusted to allow access of the heavy molecules to the active phase and to get a high porous volume to accommodate metals deposits accumulated during a minimum of one year of operation. In addition, the coke deposit due to the conversion of asphaltens and resins is minimized by using a low acidity alumina base (10) The stability of this system has been already

reported (5, 6, 10) and can maintain during a long period a good HDM activity on vacuum residue (4-5).

The aim of the second HDM/HDS catalyst is to continue with the demetallization and to begin the desulfurization step. It is in general a large mesoporous monomodal catalyst. The HDS catalyst located in the third and last section is the catalyst for deep refining which remove the sulfur content in the effluent.

In this paper we shall discuss the need for a specifically designed HDS and also the optimum way to carry out this catalyst for improving the cycle length of VRDS unit.

## EXPERIMENTAL

HDS Catalyst has been tested in a pilot unit using a demetallized feedstock obtained after the demetallization section and the equilibrium HDM/HDS catalyst section. The pilot unit is a one-liter reactor working in isothermal configuration. The average temperature is calculated from the temperature measurements made in the catalyst bed.

The Arabian vacuum residue (Table 1) previously demetallized contain 3.6 wt% of sulfur and 100 wt ppm of Ni+V. Different severities have been applied to this primary feed in order to obtain three level of demetallization. The analyses of these three demetallized feeds are shown in Table 1 (references : charges 1, 2 and 3). The metals content are ranging from 9.3 to 16.5 wppm and the sulfur content varies from 0.98 to 1.8 wt % depending of the severity of the HDM and equilibrium HDM/HDS section.

The demetallized feeds (charges 2 and 3) with high sulfur and metals content was used to age quickly the HDS catalyst. Dimethyl disulfide was added to the demetallized feeds to generate $H_2S$ in order to be representative of the gas phase composition at the outlet of the previous reactors.

The sulfur compounds of the demetallized feeds are mainly present in asphaltens and aromatics and are therefore very difficult to be desulfurized. Thus, the residence time of the HDS section is around twice more important than in HDM and HDM/HDS section (Figure 2). This residence time of the HDS section must be optimized depending of the HDS done in the two first sections. Thus, for HDS section, we have carried out some variations of LHSV for kinetic studies. The catalyst deactivation for HDS has been evaluated by a correction of LHSV using a kinetic order of reaction. Moreover, for each change of demetallized feeds, we have checked the catalyst activity by using the same Arabian light straight run atmospheric residue feed. The temperature was adjusted in order to maintain on A.L. A.R. a minimum of 90 % of HDS. This procedure was done all along the test and also has the aim to evaluate the reactivity of each demetallized vacuum residue.

## RESULTS AND DISCUSSION

HDS catalysts are often based on high specific surface area carriers with monomodal pore size distribution. It has been found that monomodal catalysts have different selectivities for the HDM and HDS functions depending on the size of the mesopores (HDM=60 %, HDS=90 % on A.L. A.R. for HDS catalyst). An increase of the mean average mesopore diameter leads to a decrease of the HDS and an increase of the HDM performance (HDM=77, HDS=85 %, on A.L. A.R.). This change HDS vs. HDM activity results from the variation of BET surface area and also the change in the level of diffusional limitations. In addition, as the mean average mesopores increases, the penetration of resins, which contain metals, is more important leading to an increase of HDM and therefore a higher rate of deactivation of HDS function. A compromise in term of mean mesopore diameter has to be found between high activity and high diffusional limitations. This has be done to develop a specific HDS catalyst. Performances on demetallized vacuum residue that can be reached with this catalyst are developed in the following.

In Figure 3, the sulfur content of the product from the HDS reactor is plotted versus hours on stream (HOS). The reactor temperature increase is also plotted in Figure 3 showing the deactivation of the HDS catalyst. We have tried during the run to maintain the severity of the HDS section to reach a sulfur content at the reactor outlet around 0.4 to 0.5 wt %. For the first 2000 hours and also during 75% (in hours) of the test, the LHSV is the same than the base. By consequent, 25 % of the points had to be corrected for the LHSV variation.

In Figure 3, we have indicated when we have switched on A.L. A.R. in order to check the catalyst activity for the temperature adjustment if necessary. The total HOS using demetallized feeds from vacuum residue can be evaluated to around 5600 hr, so 75 % of the overall H.O.S.

The overall deactivation of the HDS catalyst on demetallized feed can be estimated if we compare the activity on the same charge (charge 1) from the end of run to the start of run. We begin at 360°C and finish at 390°C for 5600 hours of run on demetallized vacuum residue. The behavior of this HDS catalyst is in line with the expected cycle length of an industrial unit. The end of run temperature of an industrial unit is usually around 415°C. So, the HDS catalyst could reach at least one year of cycle length on pure A.L. V.R.
The use of charges 2 and 3 (metals content around 16 wppm) shows that the slope of deactivation for HDS catalyst doesn't increase even during 4000 HOS on these charges. The HDS catalyst achieves this task because of its monomodal structure protecting the catalyst sites for HDS. This system demonstrates its flexibility in case of problem in HDM section.

Figure 4 shows the calculated temperature to obtain a constant sulfur content (0.45 wt %) of the reactor outlet effluent from HDS section. This temperature was calculated by assuming a constant activation energy along the test.

After 2000 hours, the HDS catalyst is more stabilized and the deactivation becomes lower. An interpretation could be that the A.L. A.R. washes the catalyst by removing one part of the coke. In Figure 4, we have observed that we recovered the slope of HDS deactivation on demetallized vacuum residue after only 200 hour. This effect has been observed at 3000 HOS and 4000 HOS. Thus, we expect to extent the cycle length of the HDS catalyst by suggesting to work in block operation (switch between A.R. and V.R.). We also observed that the slope of desactivation for HDS is lower after this washing period than during S.O.R. This observation confirms also that overall deactivation of HDS catalyst must be calculated only on demetallized vacuum feeds (75 % HOS of the run).

## CONCLUSION

The upgrading of vacuum residue to obtain a constant fuel oil quality can be improved by using a complex association of catalysts with particle size, pore size distribution and activity grading. The improvements come from a better optimization of each catalyst and the association of different selectivity in term of HDM/HDS. The synergy effect has been demonstrated and two commercial units are running under this concept. The use of adapted design HDM catalysts and monomodal catalysts for HDS objective insure the stability of the system. Monomodal catalysts for HDS section permit to achieve the goal of a constant sulfur in fuel oil with a run length cycle of at least one-year on Arabian vacuum residue feedstock. The possibility for the refiner to work by block operation (switch between A.R. and V.R.). has certainly a good impact for increase the cycle length.

## REFERENCES


1. T. Ohtsuka, Catal. Rev. Sci. Eng., 16, 291, (1977).
2. W.I. Beaton; R.J. Bertolacini, Catal. Rev. Sci. Eng., 33, 281, (1991).
3. H. Koyama, E. Nagai, H. Torii, H. Kumagai, Stud. Surf. Sci. Catal., 100, 147, (1996).
4. F. Morel, S. Kressmann, V. Harlé, S. Kasztelan, Stud Surf. Sci. Catal., 106, 1, (1997).
5. A. Billon, J.P. Peries, M. Espeillac, T. des Courrieres, NPRA 89th Annual Meeting, San Antonio, March 17-19, 1991.
6. A. Billon, G. Henrich, A. Hennico, Pétrole et Techniques, n°388, mai-juin 1994.
7. B.E. Reynolds, J.L. Rogers, R.A. Broussard, NPRA Annual Meeting, San Antonio, March 16-18, 1997.
8. B. Scheffer, K.W. Robschlager, F.C. de Boks, Preprints of ACS San Francisco CA, April 13-17, 1997, 347-350
9. S. Kressmann, F. Morel, V. Harlé, S. Kasztelan, Catalysis Today, 43, 1998, 203-215
10. H. Toulhoat, R. Szymansky, J.C. Plumail, Catal. Today, 7, 1990, 531.
11. S. Kressmann, J. Colyar, E. Peer, A. Billon, F. Morel, 7th Unitar Conference, Beijing, China, October 27-30, 1998, 857-866

**Table 1**

| FEEDS : | S.R. Arabian A.R. | SR Arabian V.R. | Charge 1 | Charge 2 | Charge 3 |
|---|---|---|---|---|---|
| Specific gravity | 0.959 | 1.017 | 0.967 | 0.980 | 0.982 |
| Sulfur (wt %) | 3.34 | 3.68 | 0.98 | 1.23 | 1.80 |
| Nitrogen (wppm) | 2075 | 3610 | 3305 | 3200 | 3000.0 |
| Hydrogen (wt %) | 11.20 | 10.48 | 11.32 | 11.36 | 11.23 |
| Nickel (wppm) | 9.3 | 20.0 | 5.5 | 7.8 | 7.7 |
| Vanadium (wppm) | 35.0 | 80.0 | 3.8 | 8.7 | 8.1 |
| Total of metals (wppm) | 44.3 | 100.0 | 9.3 | 16.5 | 15.8 |
| | | | | | |
| Viscosity @ 100°C | 25.6 | 1028 | 90.6 | 182 | 138 |
| Conradson carbon (wt %) | 9.5 | 19.8 | 11.3 | 13.2 | 13.0 |
| Asphaltens C5 (wt %) | 5.6 | 12.9 | 4.3 | 5.4 | 5.6 |
| Asphaltens C7 (wt %) | 3.1 | 6.2 | 1.6 | 1.5 | 1.8 |
| | | | | | |
| Saturates (wt %) | 30.7 | 10.2 | 22.4 | 18.1 | 18.2 |
| Aromatics (wt %) | 47.5 | 45.8 | 47.8 | 51.2 | 50.4 |
| Resins (wt %) | 17.6 | 34.6 | 22.9 | 26.0 | 25.4 |
| ASTM D2887 | | | | | |
| IBP (°C) | 300 | 385 | 182 | 223 | 234 |
| T(°C) for 5 wt % | 325 | 533 | 330 | 433 | 403 |
| T(°C) for 10 wt % | 358 | 554 | 426 | 498 | 468 |
| T(°C) for 20 wt % | 404 | 580 | 514 | 546 | 518 |
| T(°C) for 30 wt % | 436 | | 553 | 572 | 547 |
| T(°C) for 40 wt % | 468 | | 577 | 594 | 572 |
| T(°C) for 50 wt % | 503 | | 602 | | 596 |
| EBP (°C) | 720 | 600 | 620 | 613 | 614 |
| wt % EBP | 92 | 25 | 58 | 49 | 57 |

Figure 1

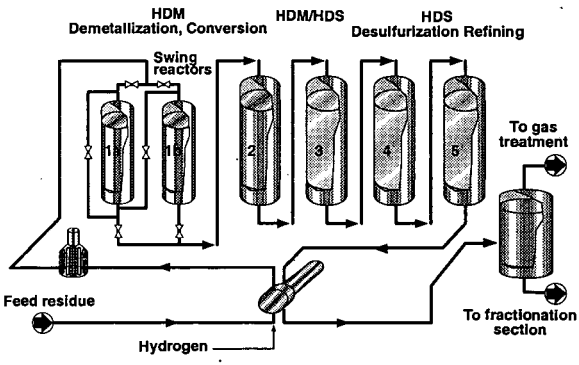


Figure 2

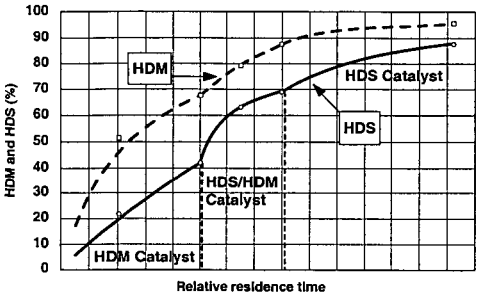
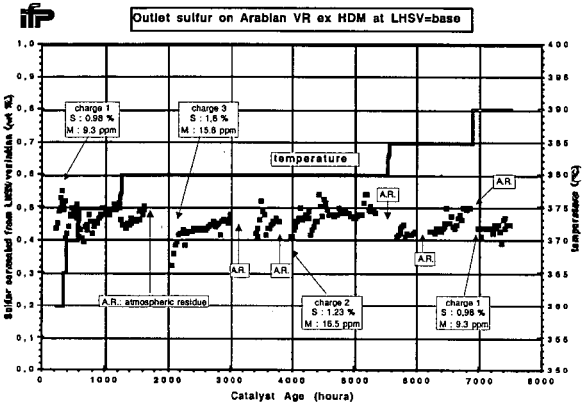



Figure 3



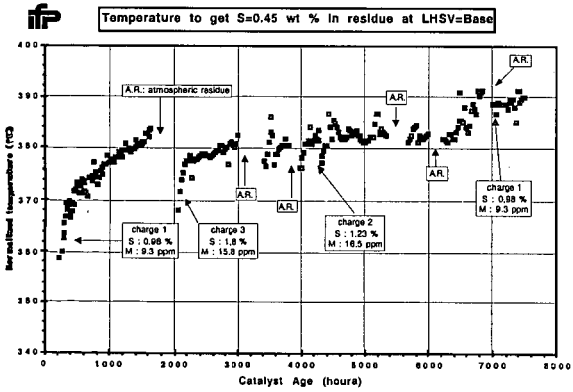


Figure 4