Asphaltenes and Asphalts, 2. Developments in Petroleum Science, 40 B
edited by T.F. Yen and G.V. Chilingarian

Chapter 7

ASPHALTENE HYDROCONVERSION

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INTRODUCTION

Around 1972, when oil prices began to increase, there were high economic incentives to convert low-value asphaltenes into more valuable white products. Price differentials between diesel oil and fuel No. 6 were over US$ 25 per barrel and this was the main driving force to develop technology for asphaltene hydroconversion. At that time, asphaltene conversion technology was almost limited to thermal processes such as visbreaking, delay coking, fluid coking and flexicoking. Nowadays, the driving force for new developments in this area are new environmental regulations aimed to control SO_x, NO_x and CO_2 emissions. Both in Europe and the U.S. burning asphaltenes requires significant investments to meet air pollution standards. On the other hand, asphaltene conversion using conventional coking processes is not environmentally sound considering the large amount of coke that has to be disposed of. Other technologies such as asphaltene pyrolysis, gasification or partial oxidation have also been proposed to eliminate asphaltene. Asphaltene gasification is perhaps the most promising technology providing that investment costs could be reduced and the synthesis gas could be integrated into a petrochemical complex. Power co-generation through asphaltene gasification has not yet been proven to be economically attractive, especially with the existing low-energy prices.

Asphaltene hydroconversion is an environmentally acceptable solution to transform asphaltenes with high sulfur, nitrogen and metals into clean fuels, leaving no byproducts to be disposed of. However, the existing technology is capital intensive and this has limited further applications. In the case of Venezuela, which has vast reserves of heavy oil with a high asphaltene content, there has been a permanent interest in developing new technologies that will improve asphaltene conversion. Following the world trend to develop new technologies to produce clean products, INTEVEP, S.A. (the research branch of Petróleos de Venezuela) has conducted intensive research in the area of asphaltene conversion for more than 10 years. This chapter summarizes some of the most important developments made by INTEVEP, S.A., as compared to some other existing or emerging technologies that are able to transform asphaltenes by hydrogen addition. This review includes an analysis of the type of technology that is available for asphaltene conversion both from the process point of view (reactor type), as well as the catalyst type, and the relationship between asphaltene reactivity and chemical composition.

ASPHALTENE HYDROCONVERSION PROCESSES

There are many type of processes that could be applied to destroy asphaltene molecules by adding hydrogen and avoiding coke formation. All these processes operate at high pressure (70 to 300 atm) and high temperature (390 to 480°C) and they are mainly differentiated by the reactor type and catalyst used in the process. The analysis of the available technology is made according to the type of reactor used as follows:

Coil and soaker hydrovisbreaking reactor

Coil and soaker hydrovisbreaking reactor technology is an extension of the well known visbreaking technology that has been widely used in petroleum refinery operations for conversion of resins at low pressure without hydrogen addition. Companies have adapted this technology to operate at high pressure in the presence of hydrogen. The most advanced process is the Super Oil Cracking (SOC) developed by Asahi Chemical Industry together with Nippon Mining and Chiyoda [1]. The SOC process employs a tubular reactor without soaker, operating at 220 atm, temperature between 470 and 490°C and 1 h residence time. A dispersed catalyst is used to avoid coke formation. It is claimed to be a highly active disposable catalyst that can be disposed together with the unconverted vacuum residue which could be used as boiler fuel, in hydrogen production or as coker feed. The process can reach 90% conversion of the 520°C$^+$ fraction with 1.3% coke production. The process yields about 8% C_1–C_4, 64% gas oil, 28% VGO and 10% vacuum residue when processing heavy Arabian short residue.

The SOC process has been demonstrated in a 3500 BPD plant in Mizushima, Japan, that was in operation for two years. The unit was shut down in 1989 and no commercial plant has yet been built.

ASVAHL, an association of French companies comprising ELF, Total and IFP has developed the TERVAHL process [2]. In this process the residual oil and hydrogen-rich stream are heated using heat recovery techniques, fired heater and passed through the soaking drum. The gas and oil from the soaking drum effluent are mixed with recycled hydrogen and separated in a hot separator where the gas is cooled, passed through a separator and recycled to the heater and soaking drum effluent. This process has been demonstrated in a 4 t/h development plant at Lyons, France, using Boscan Venezuelan crude oil with very high metal and asphaltene contents. Conversion of the 500°C$^+$ fractions have been reported to be about 30 to 35%, while still yielding a very stable syncrude of very low viscosity (122 cSt at 50°C) that can be transported or stored. The TERVAHL technology is based on the experience gained by IFP in licensing more than twelve visbreaking plants all around the world.

From 1978 to 1982, INTEVEP also developed its own process concept on hydrovisbreaking. This process concept is called SHH [4]. The SHH process can convert heavy residues into distillate products by means of a thermal treatment in a low-residence time tubular reactor, and a second thermal stage in a bubbling column reactor (soaker) operating at the same pressure and temperature. The reaction products are separated under high pressure and temperature and the light fraction is hydrotreated to reach final product specifications. The heavy fraction is deasphalted with a heavy solvent (C_5/C_6)

and water. The deasphalted oil is recycled back to the second hydrovisbreaking reactor. This reactor uses up to 10% water in the feedstock and 500 to 1000 ppm molybdenum additive. This additive, as well as most of the metals, is recovered from the solid by precipitation after deasphalting. The operating temperature of the first reactor is between 400 and 460°C and the operating pressure is between 130 and 150 atm with residence times between 10 and 25 min.

The SHH process produces 13.5% gasoline, 43.6% diesel, 37.5% gas oil and 5.4% residue to be disposed. Asphaltene conversion is in the order of 90%. Two patents were issued to INTEVEP in 1986 regarding this process [3,5]; however, the process has not been scaled-up.

At this point, it is worth mentioning the HSC process developed by TOYO ENGINEERING [6]. This is a non-conventional visbreaking technology without hydrogen addition and able to reach moderate conversion higher than visbreaking, but lower than coking. In this process, thermal cracking in the heater tube is minimized and a relatively large soaking drum is used for both thermal cracking and simultaneous deepsteam stripping nearly at atmospheric pressure. The stripping steam functions also to make homogeneous enforced turbulence in the liquid phase; thus, coke-free operation of the soaking drum is achieved. Conversion of the 500°C$^+$ fraction between 40 and 50% has been reported in pilot plant work with some crude oils. A commercial plant of 14,000 BPSD has been operating successfully at the PCK refinery in Germany since 1988.

Hydrovisbreaking technology has the advantage of low investment and can be readily scaled-up based on well-known practices of visbreaking. The HSC process that requires minor scale-up investment is a good example.

The main disadvantage of the hydrovisbreaking processes operating at high conversion is the highly sophisticated control system needed to avoid runaway conditions with highly exothermic reactions. Although the technology is rather conventional, it has never been applied at a commercial scale at high level of conversion, except by the demonstration done by Asahi at Mizushima and IFP at Lyon at a rather small scale.

The coil and soaker technology, when operating at high conversion, tends to produce unstable unconverted residues that cannot be incorporated as fuel oil components. The SHH and HSC processes have solved this problem by combining the conversion step with deasphalting to get rid of the polyaromatic compounds. This solution, however, gives rise to environmental shortcomings due to the need for asphaltene disposal. This type of technology is recommended for use only when moderate asphaltene conversion is targeted (between 30 and 40%); therefore, a rather low-investment, low-risk process can be implemented to produce stable fuel oil components. If this is the case, the TERVAHL and HSC processes should be carefully considered as valuable technological options that are environmentally safe.

During 1993–98, INTEVEP developed a new hydrovisbreaking technology that uses a dual catalyst system to achieve higher conversion levels, lower asphaltene and Conradson carbon contents, and more stabilised residue than conventional visbreaking technologies [41]. Pilot plant tests by INTEVEP, S.A. and commercial tests of the new AQUACONVERSION™ process at Refinery ISLA, Curaçao S.A. Emmastad, Curaçao refinery, confirm these advantages.

In the AQUACONVERSION technology the residue is heated in the presence of steam and a novel oil-soluble dual catalyst system. Thermal cracking occurs both in the heater and soaker drum together with mild hydrogenation of the free radicals formed. This hydrogenation is achieved by the hydrogen transfer from the water to the oil. The reaction products are separated in a fractionation column to yield naphtha, middle distillates and gas oil. The stream from the bottom of the fractionater is sent to a catalyst recovery unit to partially recover the catalyst that is reused. The process reaction sequence proceeds by the unique interaction between the non-noble metal components of the catalyst. The first catalyst component facilitates the formation of hydrogen and oxygen free radicals from water. The highly reactive hydrogen free radicals that are formed concurrently with the thermal cracking of the components of the feedstock, saturate the resulting thermal hydrocarbon free radicals. The catalyst also reduces the condensation reactions by promoting selective addition of hydrogen to the aromatic free radicals. The result is, like a typical partial steam reforming, the formation of a smaller hydrocarbon component, as well as additional hydrogen free radicals and carbon dioxide. This entire reaction sequence effectively retards and competes with the undesirable aromatic-condensation reactions so the refiner can benefit from the increased viscosity reduction associated with the higher conversion and still produce a stable converted product.

AQUACONVERSION™ is currently being offered by PDVAS–INTEVEP, UOP and Foster Wheeler as a commercial alternative both for refinery and wellhead applications. The first commercial revamp of an existing visbreaking unit is now in the basic engineering phase and is scheduled for start-up in the year 2001 at the ISLA Refinery. In addition, development programs are under-way at the three companies to extend the technology's range of feedstocks and investigate its applicability to a wide range of other refining applications. AQUACONVERSION™ has proved to be a very competitive option for the transportation of heavy crude oil in wellhead applications. Its economic advantages are due to increase in volumetric yields and low capital costs. Also, it improved the API gravity and viscosity of the crude allowing transportation without the need for additional dilution. This application is also ready to enter into the basic engineering phase in January 2000 after PDVSA's definition of a 40 TBPD production project based on AQUACONVERSION™ to produce a transportable crude oil from the Morichal area.

Fixed-bed reactors

There are many commercial fixed-bed processes that are able to convert the asphaltenes contained in atmospheric or vacuum oil residues. The best known commercial processes are: CHEVRON RDS/VRDS [7], UNICRACKING/HDS [8] and EXXON RESIDFINING [9]. Other processes with less commercial experience are: HYVAHL F licensed by IFP [10], RCD UNIBON of UOP [11], R-HYC [12] from Idemitsu, and the ABC process licensed by Chiyoda [13].

All these fixed-bed, catalytic processes for the hydrotreating of residual oils have very similar process schemes. The feed and hydrogen-rich recycle gas are preheated, mixed and introduced into a guard chamber, which removes particulate matter, residual salts and a fraction of the metals from the feed. The effluent from the guard chamber flows down through the main reactors, where it contacts one or more catalysts designed to remove metals and sulfur, to convert a substantial fraction of the 500°C^+ material into vacuum gas oil. The product from the reactors is cooled, separated from the hydrogen-rich recycle gas and fractionated to produce distillate fuels, upgraded vacuum gas oil and vacuum residue. Recycle gas, after hydrogen sulfide removal, is combined with makeup gas and returned to the guard chamber and main reactors.

These types of processes usually operate at 130 bar of hydrogen partial pressure. The space velocity changes according to the feedstock characteristics, but typical values are between 0.1 and 0.25 h^{-1}. The typical start of run temperature is 365°C up to a maximum of 415°C at the end of run.

The fixed bed process can only provide up to 60% conversion of the 500°C^+ fraction depending on the asphaltene content in this fraction. Degree of desulfurization (HDS) and demetallization (HDM) is within 70 and 90%. Typical yields from Arabian Heavy vacuum residue are: 5% gasoline, 10% diesel, 25% VGO and 63% of unconverted residue with lower sulfhur and metal content.

Fixed-bed reactors have the advantage of being a well-proven and reliable technology. Nevertheless, its economy is extremely sensitive to feedstock properties. Most fixed-bed processes consist of two swing reactors acting as guard chambers and four main reactors as illustrated in Fig. 7-1. Despite this high equipment investment, these processes are restricted to process only feedstocks with no more than 200 ppm of metals.

For feedstocks with higher metal and very high asphaltene contents, process economy is shattered by a short life cycle and a high catalyst consumption. Recently, Idemitsu Kosan Co. [12] has reported the operation of existing resid conversion units with a feedstock containing between 9 and 11% of asphaltene. Moderate asphaltene conversion (40%) was reported with low-coke deposition using proprietary catalysts. Also, IFP [8] and Chiyoda [13] offer proprietary catalysts that can tolerate higher metal and asphaltene contents.

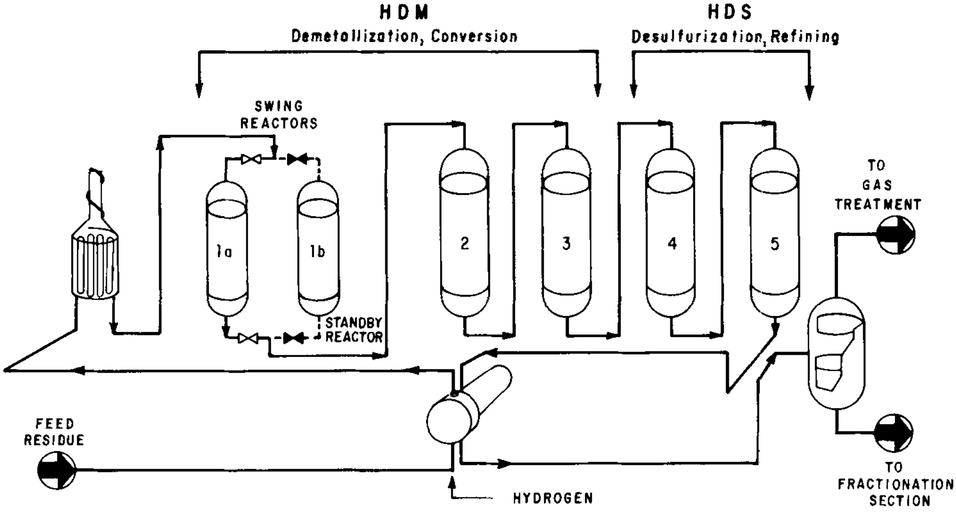

Fig. 7-1. Fixed-bed process flow scheme.

A typical value for catalyst consumption is approximately 0.5 ton for 1000 tons of feedstock containing 200 ppm of metals. This means that the metal retention capacity of the catalyst is about 40%. Some catalysts are reported to have up to 100% capacity to retain metals, but they are also affected by the asphaltene and carbon content (Conradson) in the feedstock due to coke deposition.

Recently, Chevron has introduced its Onstream Catalyst Replacement (OCR) system that provides enhanced flexibility to residue hydrotreaters [14]. The advantage of OCR is the more efficient use of catalyst and the ability to remove spent catalyst while continuing to operate. OCR is a technology that allows catalyst removal from a proprietary OCR reactor in a safe and reliable way, while the unit continues to operate. An OCR reactor differs from a normal fixed-bed reactor in that it operates with the feed upflow and contains the internals to allow addition and withdrawal of the catalysts. Fresh catalyst is added at the top of the reactor and spent catalyst is withdrawn from the bottom. The OCR reactor could be used as a guard reactor to minimize the amount of metals that contacts the downstream hydroconversion fixed-bed reactor. This could significantly increase the catalyst cycle life in the conventional fixed-bed system. The first commercial application of OCR technology went into operation on May 1992 at the Idemitsu Kosan Company's Aichi Refinery in Japan. A 50-MBPD two-train resid hydrotreater designed by Gulf Oil Co. was retrofitted with two new OCR reactors. This retrofit allows the Aichi refinery to process heavier feedstocks, while at the same time extending the run length of the existing fixed-bed from one year to two years. This technology is commercially proven, and opens new possibilities for asphaltene conversion using fixed-bed processes.

INTEVEP, S.A. has also done extensive research on fixed-bed processing of high-metal feedstocks. As a result of this effort, a deasphalting and hydrodesulfurization process was developed (DHDS) [15]. The process is based on a deep crude or residue deasphalting stage followed by hydrotreatment of the deasphalted oil. Deasphalting is done with heavy solvents (C_6^+ cut) and asphaltene separation is carried out in a solid phase, with a very high yield of deasphalted oil (87%). Once the solvent is recovered, the deasphalted product obtained from the centrifugal separator is treated in two hydrotreatment stages. The first one is a hydrodemetallization stage, whereas the second stage is the hydrodesulfurization. The catalyst in the first stage is a proprietary catalyst INT-R1 developed by INTEVEP [16] and produced by KETJEN. The hydrodesulfurization stage uses a conventional catalyst. Typical yield is: 12.4% gasoline, 31.9% diesel, 28% vacuum gas oil, and 11.6% of 500°C$^+$ residues. Asphaltene yield is 13% by weight. The solid asphaltenes could be further converted using the LR coker technology that was jointly developed by Lurgi and INTEVEP [17]. This process is commercially available, but no plant has yet been installed.

A second version of the same process uses a preliminary stage of hydrovisbreaking, which improves yields and reduces the metal content in the deasphalted product [18]. The process operates at a pressure of 100 bar and temperatures between 400 and 460°C, with a residence time of several minutes. This route was jointly developed by INTEVEP and ASVAHL, and demonstration was performed in the ASVAHL's heavy oil platform pilot plant of 400 BPD capacity. No commercial plant has yet been built, but the process is commercially available from IFP.

INTEVEP, S.A. also demonstrated the advantages of the upflow reactor with the catalyst added from the top and removed from the bottom, similar to the OCR's reactor [19]. The studies done at INTEVEP, S.A. confirmed that a higher liquid hold-up in the reactor improves the hydrocarbon–catalyst contact and, therefore, increases demetallization, as compared with the traditional operation with a downstream flow. INTEVEP, S.A. has not yet commercialized this type of reactor.

Fixed-bed technology is a reliable technology for moderate conversion of asphaltenes (40 to 50%) from feedstocks with metal contents lower than 200 ppm. It is capital-intensive, however, and operating costs could skyrocket if the metal content in the feedstock increases. This technology is not recommended to convert high-metal, high-asphaltene feedstocks, but it could become an attractive alternative to process low-quality deasphalted oil or petroleum resid with a metal content less than 200 ppm. The outcome of OCR technology developed by Chevron could widen the range of application of fixed-bed reactors to convert heavier resids containing asphaltenes with higher metal concentrations. The actual potential of this innovative technology is now being evaluated and is promising.

Mobile fixed-bed reactor

The mobile fixed-bed reactor is a variation of the conventional fixed-bed reactor where the catalyst is added from the top and removed from the bottom in a periodical way. The feed and the hydrogen flow down. The best known mobile-bed process is the Shell HYCON process that went commercial three years ago at the Shell Nederland Refinery in Pernis, The Netherlands. This novel moving-bed reactor allows addition and withdrawal of the demetallization catalyst under normal operating pressure (160 bar) and high temperature (420–445°C) and is better known as the Shell bunker reactor. The special internal construction in the reactor includes screens that separate the catalyst and the process stream before these leave the reactor. A fully automated catalyst handling system, containing high-pressure slices, special rotary star valves and slurry transport loops, is used for catalyst loading and unloading. This system allows plug flow of the catalyst during the bunker operation concurrently with the process stream.

The mobile-bunker reactor makes it possible to replace the catalyst as required to maintain a high catalytic activity and avoid catalyst bed plugging. In this way, high-metal feedstocks can eventually be processed without frequent stops or guard reactor utilization.

The Pernis plant consists of two parallel trains of 12500 BPD capacity each with five reactors in series. The first three reactors of each train are bunker reactors filled with spherical silica-based hydrodemetallization catalysts. The last two reactors in the train are of the fixed-bed type filled with a standard hydroconversion catalyst. The unit was designed to operate with Maya vacuum residue containing 760 ppm of metals, but the actual start-up operation was done with Arabian Heavy vacuum residue with a significantly lower metal content. In the first cycle of operation, 7700 h were achieved, in which the longest period without interruption was 3700 h. Total conversion was 66–68% by weight with 95% of demetallization and 92% of desulfhurization [20].

From the start up and during the first cycle many problems were encountered. Improperly positioned internals created catalyst sealing problems right after the start-up

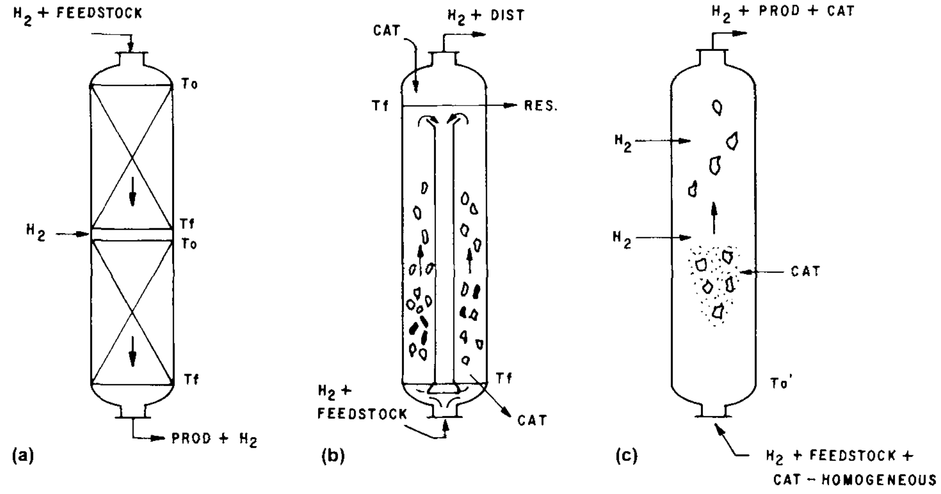

Fig. 7-2. Reactor configurations: (a) fixed bed, (b) ebullated bed and (c) slurry bed.

that required the opening of the second reactors to rectify the internals. Later on, fouling and plugging developed in the third reactor of each train. This caused serious liquid maldistribution in the catalyst bed which occasioned unscheduled shutdown. Shell has attributed the plugging to the deposition of iron particles in the catalyst bed that were introduced with the feed. After implementing the necessary modifications, the plant was restarted in November of 1992 and is currently running well.

IFP has also developed its own version of the mobile fixed-bed reactor, but no commercial application has been reported. IFP tested the periodical loading and unloading cycles in the ASHVAL platform.

Although the mobile-bunker reactor can be considered at the commercial level, its relative advantage over the existing fixed bed or ebullating bed have to be fully demonstrated in a long-term commercial run. Still there are many questions to be answered to establish a fully proven bunker technology. Process reliability and on-stream factors are still matters of concern regarding mechanical performance. From the process point of view, only a limited increase in conversion has been demonstrated as compared to the fixed-bed, and operation with high-metal feedstocks is still to be proven to be economical. Low space velocity is also detrimental to this type of technology.

Ebullating-bed reactor

In the ebullating-bed reactor, the solid catalyst is suspended and perfectly agitated due to the dynamic pressure of the liquid coming from the bottom and leaving at the top of reactor. This pressure is generated by an internal or external recirculation pump. The catalyst can be removed from the bottom of the reactor and added from the top as shown in Fig. 7-2 [26]. Catalyst particle size ranges from 0.5 to 1 mm. There are two well-known commercial processes for resid hydroconversion that use this type of reactor. H-oil from HRI Inc. a subsidary of IFC and LC-fining from ABB Lummus Crest Inc., Amoco Oil

Co. and Cities Services Co. Both processes have similar flowsheets. Oil and hydrogen are heated separately and then passed into the hydrocracking reactor in upflow, through an expanded bed of catalyst. A reactor recycle pump is used to maintain the solids suspended in the liquid, while continuously being recycled through an internal circulating channel. The mixed vapor–liquid effluent from the reaction section flows to the high-pressure, high-temperature separator. Vapor effluent from the separator after reduction in pressure goes through the condensate remover and gas purification section. The hydrogen-rich gas is recycled in the reactor and the condensates are removed as light products.

The liquid from the bottom of the hot separator is let down in pressure and stripped of light components. In both processes, the unconverted bottom can be optionally recycled back to the reactor or disposed of as a fuel oil component. In the LC-fining process, the unconverted bottom can be pumped through a coke precursor removal step to stabilize it before recycling to the reactor [21]. The H-oil process uses the patented vacuum bottoms recycle (VBR) mode of operation if recycling is needed to increase asphaltene conversion [22].

The LC-fining process has three commercial units in operation with an average capacity of 50,000 BPD, whereas H-oil has seven units of 30,000 BPD average capacity. All these units operate at a conversion level of the 520°C$^+$ fraction between 55 and 65%. Typical volumetric yields at this conversion level are: 15.5% gasoline, 22.1% diesel, 34.1% vacuum gas oil, and 32.2% of unconverted bottom which at this conversion level is stable and can be used as a fuel oil component. Operating pressure is between 130 and 160 bar and temperatures are in the range of 430 to 460°C, with a space velocity of 0.5 h^{-1}.

Both H-oil and LC-fining claim to be able to operate at higher conversion (up to 90%), although no commercial unit is normally being operated at high conversion. HRI and Texaco have disclosed a two-month operation of the Convent unit in Louisiana [23] at 80% conversion. The unconverted bottom was fed to the Texaco gasifier to produce hydrogen. Lummus has also reported short-time commercial demonstration using the asphaltene recycle mode of operation in Amoco's Texas refinery.

Ebullating-bed reactors have several important advantages over the fixed-bed reactors. The reactor conditions are near isothermal, exhibiting little temperature gradient across the bed because the heat of reaction is absorbed immediately by the cold feed oil and the hydrogen entering the reactor due to intensive mixing regime. The catalyst in the reactor behaves like an homogeneous fluid phase, which enables it to be added to and withdrawn from the reactor onstream. Units can run for 24 to 36 months between turnarounds, depending on the type of feedstock.

The dynamic backmixing characteristic of the ebullated-bed, as opposed to the static conditions of the fixed-bed reactors, reduces the possibility of plugging or increase in pressure drop from a buildup of coke or sediment in the system. Ebullated-bed reactors allow the processing of heavy feedstocks with higher metal, sulfur and nitrogen contents. Periodical removal of spent catalyst avoid catalyst deactivation as opposed to fixed-bed operation.

The main drawback of the ebullated-bed technology is the complex system required to maintain a stable expanded bed, including the speed driver of the recirculation pump and the sophisticated proprietary internals to assure proper gas and liquid distribution.

Solid handling for the onstream catalyst addition and withdrawal requires complex control systems that have to be operated by well experienced operators. After many years of commercial operation, the technology is well established and a reliable performance can be expected. Scale-up of this type of reactor is very sensitive to the type of feedstock. Most of the new units have required intensive troubleshooting during start-up. The last LC-fining unit installed by Syncrude, Canada, for example, had some problems related to the let-down valve due to a 1% entrained solid content in the feedstock, that reduced significantly the life cycle of the same valve proven in other applications.

Another limitation of the H-oil and LC-fining processes is the high consumption of catalyst when high metal feedstocks are processed. These are synthetic catalysts with a cost of approx. 7 to 10 US$/kg. For feedstocks with metal contents over 500 ppm, catalyst consumption most likely will have a significant impact on the process economy by increasing the operating costs. Normal catalyst consumption for a low-metal feedstock (less than 200 ppm) is 0.50 US$/bbl of fresh feed. This cost could approach 1 US$/bbl if the metal content is 500 ppm. In the future, there could also arise the problem of catalyst disposal due to environmental restrictions for transportation.

Although the ebullated-bed technology could increase total conversion up to 90% by recycling the unconverted bottom, this product becomes unstable and cannot be disposed of as fuel oil component. High conversion operation of these processes will require additional investment to dispose of the unstable pitch. If a gasifier or a coker is available, this could be the best way to dispose of this unstable byproduct.

To overcome some of these problems, EXXON Research and Engineering has developed the Microcat-RC (MRC) process for asphaltene conversion [24]. This is a hydroconversion process operating with a uniformly dispersed catalyst throughout an ebullating-bed reactor. The novel catalyst containing molybdenum sulfide in a carbonaceous matrix has a very small particle size (10^4 Å in diameter). In this case, the catalyst flows homogeneously with the liquid phase and leaves the reactor with the unconverted bottom. Only a small amount of molybdenum is required (parts per millions (wt) over the feedstock) making it economically feasible to dispose the wasted catalyst on a once-through basis. Process conversion can be as high as 95% of the vacuum residue with 17.2% volume yield of naphtha, 63.6% of distillates, 21.9% of gas oil, and 3 to 4% by weight of unconverted bottoms. Operating conditions are in the same range as the existing ebullating-bed processes. EXXON claims that the uncovered bottom is stable and could be disposed of as a fuel oil component or as a coker feedstock.

The MRC process is still under development and has not been commercially proven. Nevertheless, EXXON has considered that the process is ready to be scaled-up to a commercial plant based on the wide experience accumulated during the demonstration of the EDS (Exxon Donor Solvent) process for coal liquefaction in a 2500-BPD demonstration unit. The MRC reactor would operate at similar hydrodynamic conditions as does the EDS reactor [25].

INTEVEP, S.A. also explored the route of the ebullating-bed reactors, but using a bauxite-based catalyst. A process concept was developed consisting of two hydrocracking stages in series. In the first step, the feedstock is hydrocracked in an ebullated bed using a MoP/bauxite catalyst, followed by a second fixed-bed hydrocracking stage using a NiMo/Al catalyst developed by INTEVEP. This process concept was tested at bench scale at INTEVEP, S.A. and later on further tests were done in a 3-BPCD ebullating-bed pilot plant at ABB-Lummus using the INTEVEP's bauxite catalyst. The results showed conversion of the 530°C$^+$ fraction between 80 and 85%. Product slate at the lowest conversion was approximately 10% gasoline, 25% diesel, 40% vacuum gas oil, and 25% residue.

The ebullating-bed technology is an appropriate choice if moderate asphaltene conversion (less than 70%) is required to process feedstocks with no more than 500 ppm of metal content. A conversion higher than 70% tends to produce unstable unconverted bottoms that have to be further processed in a coker or a gasifier. A metal content of over 500 ppm in most cases penalizes process economy due to high catalyst consumption. Otherwise, the technology is well proven and provides an environmentally safe solution to asphaltene conversion, considering that waste catalyst can be safely disposed to metal recovery companies. Nevertheless, this type of technology requires high investments, and the process economy strongly depends on the oil price differentials.

Slurry reactors

During the last twelve years, there has been significant progress in the development of slurry reactor technology to achieve high asphaltene conversion. In this type of reactor, the catalyst is in a powder form suspended in a mixture of gas and liquid that flow from the bottom to the top of reactor. The catalyst is transported through the reactor due to gas dynamic pressure generating a significant degree of mixing. The solid concentration inside the reactor can be higher than in the feedstock, but the outlet stream has the same solid inlet concentration without solid accumulation. This is usually known as a three-phase, bubbling column-type reactor.

The slurry reactor has not yet been commercially used for asphaltene conversion, except for the Bergius Pier process utilized during the Second World War for the conversion of coal operating at a pressure of 700 bar, and during the period of 1950 to 1954 for the conversion of residual oil. Veba Oel has developed a modern version of this process that can be applied to the asphaltene conversion. The process is called VCC (Veba Combi Cracking) and operates within a pressure range of 220 to 300 bar with fine particles of carbonaceous material as an additive [26].

This process integrates a liquid phase hydrogenation (LPH) slurry reactor system directly coupled with a fixed-bed gas-phase hydrogenation (GPH) reactor system. The feedstock is mixed with 1 to 3% of finely grounded additive and hydrogen before preheating. This hot mixture is fed to the LPH reactors that operate at temperatures between 465 and 480°C. The slurry from the LPH reactors is routed to a hot separator (HS), where gases and vaporized products are separated from nonconverted residue. The HS top product enters the GPH reactors that operate at a temperature between 370 and 420°C and at the same pressure as the LPH reactors and contain a fixed bed of commercial hydrotreating catalyst.

Distillates from the HS bottom product are recovered by a vacuum flash and the unconverted bottom is fed to a low-temperature carbonization unit (LTC) to produce more distillate and a small amount of coke. This is a continuous coking process patented by Veba Oel.

Typical yields from the process with Arabian Heavy vacuum residue at 95% conversion are as follows: 26.9% naphtha, 36.5% middle distillates, and 19.9% gas oil. Total hydrogen consumption is 395 N m^3/t and coke production is between 2 to 3% of the feedstock. The VCC process has a demonstration unit with a capacity of 3500 BPD in operation since 1988 at Bottrop, Germany. No commercial plant has yet been built, although the VCC process was selected to process approximately 80,000 BPD of Athabasca bitumen for the Oslo project in western Canada and 25,000 BPD for the Karlsruhe refinery of Ruhr Oel in Germany, but these plants were not built.

Petro-Canada has developed the CANMET process for oil residue and asphaltene conversion. In this process, the feedstock is mixed with a small portion of recycled hydrogen and 2 to 5% by weight of a solid additive before heating. The recycled hydrogen is heated separately. Both streams are mixed before entering the slurry reactor. The CANMET process uses only one vertical reactor where the solid additive particles are suspended in the liquid hydrocarbon phase, through which the hydrogen and product gases flow rapidly in a bubble form. [27]. The reactor exit stream is quenched with cold recycle hydrogen prior to the high-pressure separator. The heavy liquids are further reduced in pressure to a hot medium-pressure separator and from there to fractionation. The spent additive leaves with the heavy fraction and remains in the unconverted vacuum residue to be disposed of. The process uses an additive of iron sulfhate, with temperatures ranging from 460 to 475°C and pressures from 140 to 170 bar. Typical yields using Cold Lake vacuum residue with 15.5% asphaltene are as follows: 19.8% naphtha, 33.5% distillates, 28.5% vacuum gas oil, and 4.5% pitch. Hydrogen consumption is 2.5% by weight of feedstock.

The CANMET process has been demonstrated in a 5000-BPD pioneer plant designed and constructed by the Partec Lavalin Inc. in the Pointe-aux-Tembles refinery, Montreal, Canada. A conversion of approximately 85% was reported using only one reactor in this unit. More recently, Petro-Canada and Unocal, now UDP, have joined efforts to combine the CANMET process with UDP's technology for hydrotreating at high pressure. This combined technology is called U-CAN and integrates hydrotreating of the vapor product from the CANMET hot separator directly into the high-pressure UDP reactors. This process scheme is similar to the VCC process. However, U-CAN is said to include a proprietary design to completely avoid solid entrainment into the downstream fixed-bed hydrotreaters. This new technology will eventually be demonstrated in the 5000-BPD unit in Montreal [28].

The MRH process (Mild Resid Hydrocracking) is a three-phase reactor technology developed by Idemitsu Kosan Co. and the M.W. Kellogg [29]. In this process, a slurry consisting of heavy oil feedstock and fine powder catalyst is preheated in a furnace and fed into the reactor vessel. Hydrogen is introduced from the bottom of the reactor and flows upward through the reaction mixture, maintaining the catalyst suspended in the reaction mixture. The reactor has special internals to operate at mild pressure between 60 and 80 bar. Spent FCC catalyst could be used as powder catalyst although a proprietary catalyst is also being offered by Idemitsu. At the upper part of the reactor, vapor is disengaged from the slurry and sent to a high-pressure separator to remove light gases and hydrogen. The condensed overhead vapor is fractioned and each fraction hydrotreated separately.

From the lower section of the reactors, the bottom slurry which contains catalyst, uncracked bottom oil and a small amount of vacuum gas oil fraction are withdrawn and sent to the catalyst separation section. Here, the vacuum gas oil is recovered and the catalyst and coke are separated and fed to a catalyst regenerator. The catalyst is recycled and a purge stream is taken out of the process. Coke produced in the reactor is deposited on the catalyst and burned in the regenerator. A large amount of catalyst (approximately 20%) is mixed with the feedstock. Typical product distribution using Arabian Heavy vacuum residue as feedstock is as follows: 8.2% naphtha, 29.2% middle distillates, 31.7% vacuum gas oil, 17.5% vacuum residue, and 5.5% coke. The MRH process, due to the moderate pressure, operates in a conversion range between 70 and 80%.

INTEVEP, S.A. has done intensive research and development on heavy oil and asphaltene conversion using slurry reactors during the last ten years. The result has been the development of the HDH process (Hydrocracking, Distillation, Hydrotreatment) which is ready for commercial application [30]. The HDH process diagram is shown in Fig. 7-3. A slurry of resid and fine catalyst is prepared and heated up to the reactor inlet temperature separately from the H_2 stream. This slurry of resid and catalyst is contacted with H_2 in three slurry reactors in series. In these up-flow three-phase reactors, conversion and hydrogenation of the resid to lighter product take place. The reaction products are flashed in a high-pressure hot separator and the distillates recovered at the top are condensed and fractionated to be processed in separate hydrotreating units so as to meet product specifications. The slurry of spent catalyst and unconverted resid recovered at the bottom of the hot separator is fed to the catalyst separation unit. A stable and solid-free resid, which can be either recycled to the reactors or incorporated in the fuel-oil pool, is obtained. The separated spent catalyst is incinerated to enable its use in the metallurgical industry. The gases from the incinerator are desulfurized to produce a fertilizer. The HDH process is able to reach high conversion (90 to 92%) operating at moderate pressure (130 bar of H_2 partial pressure) and temperatures between 465 and 475°C, under the once-through mode of operation. This conversion can be increased up to 97% in the recycle mode under similar operating conditions. Space velocity is 0.5 1/h and catalyst addition is between 2 and 4% of the feedstock. The catalyst is a cheap naturally occurring mineral that can be easily prepared through a simple grinding and classification step. The use of this low-cost but quite effective natural catalyst efficiently controls the coke and gas formation, which results in high liquid yield and moderate H_2 consumption.

Typical yield of the HDH process operating with a Venezuelan oil vacuum residue (Morichal 5°API) at 92% conversion is as follows: naphtha 27.5%, middle distillates 40.4%, vacuum gas oil 27.7% and unconverted resid 5.5% by volume.

Hydrogen consumption is 258 N m^3/t of feedstock. All the products obtained after hydrotreatment are of high quality and can be mixed with the main product streams from the refinery. The naphtha goes to the catalytic reformer to produce high-octane gasoline and the middle distillates are directly sent to the diesel pool. Vacuum gas oil is used as feedstock to the FCC unit to increase the gasoline and diesel production. The small amount of unconverted bottom product has very low metal (10 ppm) and sulfur contents (1.2%) and it can be incorporated in the fuel-oil pool due to its high stability generated in the catalyst separation section. This catalyst separation unit is a unique

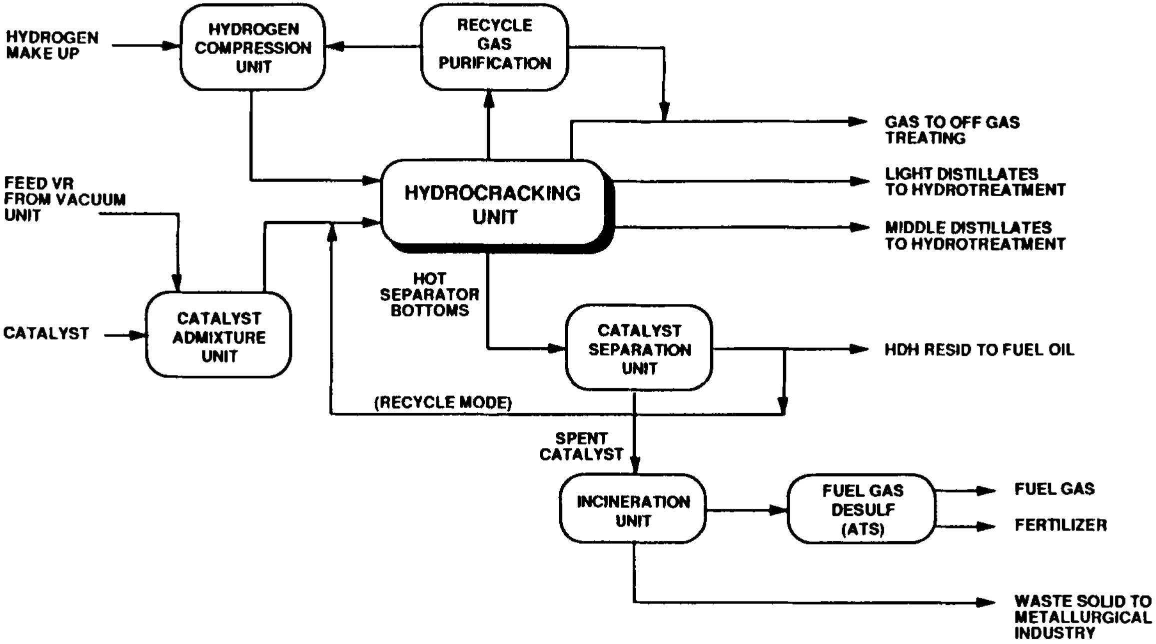

Fig. 7-3. HDH^{TM} simplified process block diagram.

feature of the process that enables the operation of recycle mode by removal of the coke precursors from unconverted resid. If the recycle mode of operation is used, it is possible to completely eliminate the unconverted bottom stream leaving no hydrocarbon resid.

The HDH process has been successfully demonstrated in a 150-BPD pilot plant located in the Ruhr Oel refinery at Scholven, Germany. In this large pilot plant, the demonstration program accumulated over 7000 h of operation. Detail engineering design for a 15,000-BPD pioneer plant to be installed in the Cardon refinery of MARAVEN, S.A., Venezuela, was completed in 1997, but construction was deferred until the year 2001. In the last year, INTEVEP S.A. has developed an improved version of the process called HDH™ PLUS. The main changes introduced include the use of a coke-based catalyst instead of the natural catalyst and the replacement of the catalyst separation unit, the incineration unit and the fuel gas desulfurization unit by a vacuum tower and a flaker. These changes reduced significantly the investment costs [43].

It is clear that the slurry reactor is the frontier technology in asphaltene conversion. Extremely high conversion can be achieved using this type of reactor, practically eliminating production of unconverted bottom. Although this type of technology is environmentally clean, its commercial application has not yet crystallized due to the high capital investment required. Economics of the slurry-reactor technology at high conversion and with high product quality is strongly related to price differentials between middle distillates and No. 6 fuel oil. As a rule of thumb, it can be concluded that this type of process is economically attractive if this price differential is over 16 US$/barrel. In the last years, the market has shown lower price differentials jeopardizing the possibility of installing the first commercial slurry reactor for asphaltene conversion. Future trends would tend to improve process economics due to the increasing difficulties in allocating high-sulfur resid in the fuel market. Environmental regulations will increase commercial opportunities for the high-conversion slurry process, improving its economics. Slurry reactors still have to be proven in reliable commercial operation using large-diameter reactors (over 2.5 m). Once the first commercial unit is on stream, this technology should become the preferred option for high-asphaltene conversion in a scenario where environmental concern is the primary issue. Future developments in this area shall be oriented to reducing investment costs, mainly by reducing the operating pressure and catalyst downstream processing. Otherwise, this is the technology that fits better with the future needs to transform low-value asphaltene into clean fuels without environmental impact.

CATALYSTS

The type of hydroconversion catalysts used depends on the type of technology. Fixed-bed catalysts have a different structure from ebullated-bed and slurry-reactor catalysts. Most of the commercial catalysts used in a fixed bed or moving bed for petroleum resid hydrotreating consist of Mo on alumina with Co or Ni promoters. Their properties are also related to the type of feedstock. The high contents of asphaltenes and carbon (Conradson) with a wide distribution of molecular weights in the feedstock require the catalyst to have a wide distribution of pore size as well as a high contribution of micropores. The macroporous structure must facilitate the diffusion of the large asphaltene molecules to the active centers. Likewise, a high hydrogenation activity will control the formation of coke, which is favored by the presence of asphaltene and a high content of carbon (Conradson). The presence of a high content of contaminants in the feedstock (sulfur, nitrogen and metals) requires catalysts to have a hydrogenolysis activity and a high capacity to store metals without detriment to their catalytic functionality.

Fan [31] has summarized the composition and properties of several hydrotreating catalysts for petroleum resids currently used in commercial applications. The catalyst bulk density ranges from 0.4 to 1 g/cm^3, average pore volume from 0.2 to 0.8 cm^3/g, specific surface area from 100 to over 300 m^2/g, and pore size from 40 to 200 Å. It has been demonstrated that the selection of a suitable pore size distribution makes it possible to penetrate heavy molecules inside the pores, where they react at active sites, giving a good vanadium and nickel dispersion along the radius of the particle. These metals are deposited inside the particles, at active sites or nearby, decreasing the number of active sites and the effective diffusion of the reactants due to reduction of pore size. Active sites in these catalysts are provided by the acidic nature of the support and Mo–Co interactions.

Most of the fixed-bed processes use the synthetic Mo–Co catalyst on alumina. Among the newest catalysts available on the market are the catalysts developed by IFP (Procatalyse), Chevron (OCR process), IDEMITSU and the ABC catalyst from CHIYODA. IFP has developed the catalysts HMC 895 and HMC 841 with a high capacity to retain metals. IFP claims that these catalysts can retain more than 100% by weight of metal without loosing activity. The IFP catalyst has been used in the Nattreff refinery in South Africa, with a live cycle of five to six months processing a feedstock with 180 ppm of vanadium. Two new units are being designed to use the IFP catalyst in Korea. Idemitsu has been successfully using a new catalyst to treat feedstocks with high asphaltene content between 8 and 10% with nine-month cycles. Chiyoda has also developed a catalyst that is able to tolerate high metal and asphaltene contents with live cycles of six months or more.

The principle behind these metal-resistant catalysts lies in the pore size distribution that allows for a smooth metal distribution in the used catalyst particle. For example, a bimodal pore size distribution allows greater access to the internal pore structure and a more complete penetration by the metal complexes. In these catalysts, the metals (Ni and V) deposit more uniformly on the pore walls.

INTEVEP's approach to hydroconversion catalyst development was two-fold. INTEVEP started the development of hydrocracking catalysts by selecting and activating natural material available in Venezuela. The route of synthetic supports impregnated with active metals, however, was also followed. Natural catalysts were developed mainly to be used in bubbling or slurry reactors, whereas synthetic catalyst development was oriented to the fixed-bed hydrodemetallization and hydroconversion.

INTEVEP developed a line of synthetic demetallization catalysts with a high metal retention capacity. Catalyst INT-R1 was developed for the demetallization of residues and deasphalted oils. This catalyst is based on a commercial alumina support impregnated with molybdenum and nickel. Distribution of pore sizes was adjusted to a bimodal system with pore diameters ranging from 30 to 300 Å. The INT-R1 catalyst is currently being commercialized by KETJEN-AKZO [32]. Later on, a second catalyst, INT-R7, was developed. This catalyst still has a bimodal pore size distribution, but the macropores have a larger diameter to allow for the access of vanadium molecules. The metal dispersion ratios are: Mo/Al = 4.5 to 7.5 and Ni/Al = 3 to 6. There is a higher number of intermediate acidity sites than in the INT-R1 catalyst. Both catalysts proved to have good stability in long-duration tests with a Venezuelan vacuum residue having high metal and asphaltene contents [32]. During these studies, it was demonstrated that basic asphaltene compounds such as porphyrins were adsorbed preferentially in the molybdenum sulfides, through the interaction of vanadium with these sulfides.

Deactivated catalysts were grinded and used again. They exhibited 50% of the initial activity, indicating that plugging of the structure in the pore throats is the cause of premature deactivation. These experiments demonstrated that highly reactive molecules tend to demetallize at the pore's entrance, whereas low-reactivity molecules need to diffuse inside the pores to react. This is the reason why most of the processes use graduated catalyst beds with different pore size distributions and activity to treat feedstocks containing asphaltene molecules with diverse chemical structure and reactivity.

INTEVEP's main objective in developing natural hydroconversion catalysts has been to produce low-cost catalysts that could be safely disposed of. The aim is to use naturally existing minerals that, upon going through a minimum pretreatment, yield cheap but active catalysts. Many iron-containing minerals were tested as catalyst sources including: ferruginous and nickel laterites, limonite, siderite, clay, bauxite, pyrite, iron monosulfate, hematite and magnetite. These natural minerals underwent thermal and/or hydrothermal pretreatment to produce catalytic materials with active surface areas ranging from 2 to 80 m^2/g, pore volumes from 0.02 to 0.5 cm^3/g, and average pore radii from 50 to 160 Å. Hydroconversion test results showed that some of these natural catalysts were able to convert more than 70% of asphaltene [33]. After optimization, three main catalysts were finally developed for commercial use in bubbling and slurry reactors.

A low-cost catalyst known as INT-BHC-1 was developed for hydrodemetallization and hydrocracking in an ebullated-bed process. This catalyst was prepared from bauxite with a high iron content and three types of additives: promoter, hardener, and pore developer. Phosphoric acid was used as a hardener and starch as a pore developer. The catalyst contained Fe, Mo, Al, Si, Ti and P. Surface composition is as follows: Mo/Al = 0.04 to 0.07, Fe/Al = 0.08 to 0.12, Si/Al = 0.10 to 0.20, Ti/Al = 0.01 to 0.02, and P/Al = 0.15 to 0.50.

Surface area is between 90 and 250 m^2/g and pore volume is between 0.25 and 0.55 cm^3/g, 50% of the pores were larger than 200 Å and 30% were larger than 1000 Å. The pellet mechanical strength can be as high as 12 k. This catalyst was tested in the ebullated-bed pilot plant of Lummus in New Jersey, U.S.A. [34], with Cerro Negro crude as the feedstock. The results showed high conversion of asphaltene, with high demetallization and catalyst stability in a 20-day period.

In addition to bauxite-based natural catalysts, two laterite-based catalysts were developed. The INT-LHC-1 catalyst consists of nickel-containing laterite impregnated with molybdenum and extruded with a macroporous alumina [35]. This catalyst contains 5 wt% molybdenum and 42 wt% alumina. Surface area is between 150 and 170 m^2/g, pore volume, 0.60 and 0.07 cm^3/g, and average pore diameter, 160 to 180 Å. The catalyst has a layered structure, high macroporosity, and an adequate substitution of magnesium for other ions to create the required acidity for asphaltene hydrocracking. Magnesium silicates with laminar-type structures, such as serpentines, provide an adequate support material for impregnation with hydrogenation metals. Both the iron and silicate particles are of vital importance for the reactions of hydrocracking of asphaltenes. A mixture of these materials yields a meso-macrosupport that allows the asphaltene molecules to diffuse into the pore system.

The INT-LHC-1 catalyst was tested in a fixed-bed pilot plant at INTEVEP, S.A., using a very refractory type of feedstock (Tia Juana short residue) at 415°C, 140 atm, and LHSV of 0.5 h^{-1}. The catalyst exhibited a good stability for a period of 1000 h with high asphaltene conversion and vanadium removal (83%). These two natural catalysts could be used either in ebullating-bed or fixed-bed reactors. These catalysts were thoroughly analyzed after the reaction was completed. The analysis showed that 40% of the metal sulfide surface had been eliminated by coke and vanadium deposition with a 60% reduction of mesopores and practically most of the micropores. Coke was responsible for 20% of deactivation, whereas vanadium exhibited only 7 wt% loss of activity.

A third hydroconversion catalyst has been specifically developed to be used in slurry reactors. This is also an iron-based catalyst with a very wide particle size distribution. Particle size is less than 500 μm. The catalyst is prepared from a cheap iron oxide mineral with different impurities, such as aluminum (1%), silica (0.5%), and phosphorus (0.2%). Surface area is 20 m^2/g and pore volume is between 0.2 and 0.6 cm^3/g. Catalyst preparation is done through a very simple procedure of grinding, drying and classification yielding a low-cost catalyst [36].

The slurry-reactor catalyst, used as a fine powder, helps to achieve cracking and to provide metal sites to promote hydrogenation. Although coke formation cannot be completely avoided during asphaltene hydroconversion, it can be minimized by ensuring that there is less dependence on hydrogen transfer reactions. The INTEVEP catalyst helps to consume the hydrogen more efficiently. In the presence of this inexpensive catalyst in the reactor, the hydrogen molecules preferentially hydrogenate aromatic and polyaromatic compounds, thereby avoiding thermal dehydrogenation reactions that create condensed ring systems, unavoidably the precursors to coke formation. The INTEVEP slurry catalyst has been fully tested in the operation of the 150-BPD pilot plant. During these tests, two independent feed systems for two catalyst streams with different catalyst particle sizes were employed. One of these feed systems is employed to provide the high-activity catalyst fraction using a fine particle size, whereas the second feed stream introduces a less active catalyst with a larger particle size [37]. These demonstration tests clearly proved that larger particles are able to diminish the amount of foam inside the slurry reactors for gas velocities in use at the commercial scale, thereby increasing the liquid-phase reaction volume, which achieves the desired high conversion of the asphaltenic fraction at lower temperatures. This catalyst can also be regenerated and reused or eventually disposed of due to its low cost.

Very recently INTEVEP S.A. has developed a coke-based catalyst that is manufactured by partial oxidation of delayed coke (shot coke) to generate macroporosity. This catalyst is used as very fine particles in slurry reactors together with submicronic particles of active metals incorporated using a similar technique as in the AQUACONVERSION™ process [41,43].

ASPHALTENE REACTIVITY

Amerik and Hadjiev [38] have pointed out that selection of the most efficient technology for upgrading heavy residues is directly connected with the amount of available data on the physical–chemical properties of asphaltenes. These authors indicated five main characteristics related to the macromolecular nature of the asphaltenes that may influence reactivity when hydrocracked. These properties are the following:

(1) Asphaltene-analogous transformations. Like polymer-analogous transformations, the fragments, which compose asphaltene, actively enter into condensation, halogenation, nitration, sulfhonation and oxidation reactions.

(2) Asphaltene molecules display the highest activity in crosslinking reactions, which are determined by the molecular weights of asphaltenes.

(3) The presence of polyconjugated structures in asphaltenes is responsible for their tendency to form coke precursors, such as carbenes and carboids. Asphaltene properties like paramagnetism, low ionization potential and high electron affinity are related to their high reactivity and their tendency towards associate formation.

(4) Asphaltenes show a high tendency to adsorb on solid surfaces. In catalytic hydrocracking, this property plays a critical role in increasing reaction rates by the presence of metallic surfaces.

(5) The mesomorphic pile-shape structure of the aromatic fragments of asphaltene molecules allows the segregation of aromatic and paraffinic–napthenic fragments during thermal treatment.

These asphaltene properties may cause significant differences in the behavior of different type of feedstocks in a hydrocracking process. The above-mentioned parameters, however, are still too broad to enable the prediction of the performance of a given feedstock when subjected to the thermal or hydrothermal catalytic processes. In recent years, INTEVEP, S.A. has been investigating more specific correlations between feedstock properties and their reactivity. The results from these extensive research on asphaltene reactivity are summarized by Izquierdo et al. [39]. In this publication, the authors have been able to establish well-defined correlations between physical and chemical properties that can vary from one feed to another and their influence on hydrocracking processability.

Feedstock reactivity and processability depend mainly on the following parameters.

Geologic age. The maturity index expressed as the DPEP/ETIO porphyrin ratio is a commonly used parameter to determine the maturity of crude oils. In general, it has been observed that more mature crude oils (maturity index between 20 to 30) are less reactive than the youngest crude oils (maturity index around 50). The application of

TABLE 7-1

Structural characteristics of asphaltenes (A, B, and C) with different reactivities

Feedstock/properties		A	B	C
C	% wt	82.24	83.71	86.16
H	% wt	7.84	7.37	7.29
Sulfur	% wt	4.72	3.87	2.73
C aromatic	% wt	48.25	55.46	53.27
C satured	% wt	51.75	44.54	46.73
C naphthenic	% wt	7.97	6.87	7.82
C paraffinic	% wt	47.79	37.67	38.91
C non-bridging	% wt	15.45	20.49	12.54
C Bridging	% wt	32.80	35.00	40.70
CI/C_I	ratio	2.12	1.71	3.25

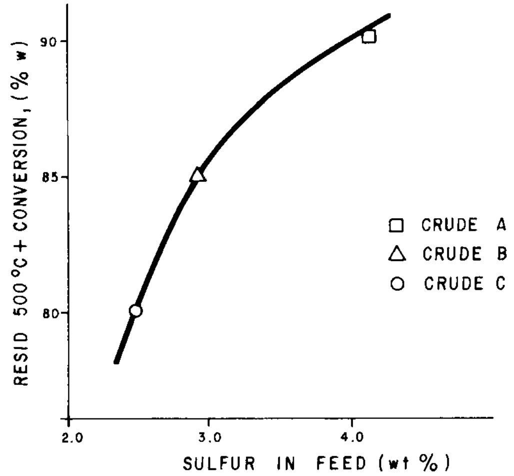

Fig. 7-4. Effect of sulfur in feedstock on asphaltene conversion at similar operating conditions.

these criteria should also take into account the origin of the crude oil and whether or not the asphaltenes have been previously submitted to pretreatment.

Aromaticity. Asphaltenes with high polycondensate aromatic molecules tend to produce more coke, and due to its high degree of condensation, hydrogenation becomes more difficult. Table 7-1 shows the main structural characteristics of three types of asphaltenes with different reactivity. Asphaltenes A are more reactive than asphaltenes B and C. The parameter CI/C_I, defined as the ratio of bridging or internal aromatic carbons to non-bridging or peripheral carbons, is a critical variable to predict reactivity. These values are obtained from the HNMR spectra. A high value of CI/C_I (over 3) means that the average asphaltene molecule has a more compact aromatic core and, therefore, should be more difficult to process. On the other hand, a lower value of CI/C_I (between 1.5 and 2) is characteristic of more reactive asphaltene feedstocks.

Sulfur content. The amount of sulfur in the feedstock is a critical parameter used to define reactivity in hydroconversion catalytic processes. Fig. 7-4 shows that as the sulfur content in the feedstock increases, a lower thermal level is required to achieve the same conversion as compared to the asphaltenes with lower sulfur content. This behavior is due to the fact that it is easier to break the sulfur–carbon bonds than the carbon–carbon bonds.

Asphaltene polarity. By means of SARA analysis by TLC-FID it is possible to differentiate between the polar and nonpolar asphaltenes according to the way they are retained on the silica rods. A correlation has been observed between the nonpolar/polar asphaltene ratio and the behavior of feeds during hydrocracking. Feedstocks with a higher concentration of polar asphaltenes (ratio of 0.3) have a lower reactivity than nonpolar asphaltene (ratio of 0.7). This is probably due to the higher concentration of heteroatoms and the type of polyaromatic units.

CONCLUSIONS

Selection of the asphaltene conversion process involves many variables in addition to technological and economic issues, including: crude oil source, product specifications, environmental restrictions, secondary conversion requirements, integration with existing units, disposal of by-products, and the state of development of technology [40].

Economic comparison of different types of technologies available for resid conversion is not an easy task due to many economic factors such as: scenario of application, price of raw material, type of feedstock, scale economy, market price of final products, product quality, by-product prices, environmental investment, percent of local component, financing schemes, tax policy and data base, and the methodology. The selection of hydroconversion technology is usually limited by the amount of metals in asphaltenes. As a general rule, for metal contents higher than 300 ppm, the fixed-bed technology will not pay-out. The economy of the ebullating-bed technology is limited to 500 to 550 ppm of metals in the feedstock due to the high catalyst cost. Slurry reactor technology is not limited by the metal content in the feed, but usually requires a price differential (between No. 6 fuel oil and diesel) of over 16 US$/bbl to yield a reasonable return on investment.

In general, it could be concluded that hydrocracking technologies are moving fast into a mature stage of development to offer an environmentally sound clean fuel production from heavy asphaltenes. New developments resulting from research activity and use of cheap catalysts and/or additives could substantially improve the economy of hydrocracking processes, balancing requirements for large capital investments.

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