Recent Advances in Heavy Oil Hydroprocessing Technologies

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Abstract: Urgent demand for light oils and strict laws of environmental protection make it important for refiners to convert heavier oils into lighter and more valuable products efficiently. Hydroprocessing technology is one of the major residue upgrading processes and it is performed with a series of reactors, each with different catalyst for different function. Depending on the residue properties, the reactors in the hydroprocessing unit may be fixed-bed, moving-bed, ebullated-bed, slurry-bed or a combination. The present article discussed the useful patents in the field of heavy oil hydroprocessing technologies. The latest development and application of hydroprocessing technologies were reviewed. Comparison of catalysts used in the processes such as solid powder catalysts and homogeneous dispersed catalysts were also examined. There is not a general rule that can give a solution to all refineries, and the final choice should be made by comprehensive consideration of feed property, product demand and economic benefit.

Keywords: Heavy oil, hydroprocessing, catalyst, reactor.

1. INTRODUCTION

It is well accepted that the crude oils available to refineries are becoming heavier. Meanwhile, the demand for high value products such as gasoline and middle distillates is increasing. The trend towards heavy feedstock and urgent demand for high quality products as well as tightening fuel regulations are presenting new challenges for refineries. Among them, how to improve product quality and maximize returns from the bottom-of-the-barrel is significant [1, 2].

To meet these challenges, a lot of efforts have been committed and a number of heavy oil upgrading technologies have been developed by leading petroleum research institutions. Among all these commercially applied options, catalytic hydroprocessing is one of the most promising technologies for conversion of heavy oils. The process can convert heavy oils into high-value products with simultaneous hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodemetallization (HDM) and Conradson Carbon Removal (HDCCR) and asphaltene conversion in the presence of catalysts and hydrogen under high pressure condition. Nowadays, the hydroprocessing technology is well established and has been extensively practiced in refineries worldwide.

Various residue hydroconversion processes are now commercially employed using fixed bed, moving bed, ebullated bed, slurry bed or a combination. These processes are different from one another in terms of method, feedstocks and products [3]. The typical operating conditions of the four types of reactors are summarized in Table **1** [4]. The choice of process type depends mainly on the amount of metals and asphaltenes in the feed and on the levels of conversion required. By the time of March 2003, there were total 73 residue hydroprocessing units operating in the world, of which 60 (82%) had fixed bed reactors, 12 (16%) were moving beds (including ebullated bed reactors) and 1 (1%) was a slurry reactor.

Advances in residue hydroprocessing are a combination of reactor design and catalyst development. Catalysts play a vital important role in the heavy oils upgrading process, and research and development related to catalysts have attracted increasing attention internationally. The catalysts used in residue hydroprocessing technology are usually composed of oxides of Mo, Co, Ni, and W on a matrix or carrier of alumina, silica, silica/alumina. In fixed bed processing, some leading guard beds which contain catalysts with high pore diameter and pore volume and high capacity for asphaltenes and metals are used to pretreat the refractory feedstocks. Compared to fixed bed technology, catalysts used in ebullated bed process are the same active metal components supported on alumina, and the obvious difference is that extrudated catalyst are used in ebullated reactor while cylindrical, trilobal, quadrolobe or quincunx shaped catalysts are used in fixed bed reactor. Additionally, the physical properties including particle size and mechanical strength are also different. The moving bed reactor catalysts can be replaced continuously and the shape is designed to reduce abrasion and particle strength is greater. Catalysts for slurry bed are much different from the three mentioned above, all of them are unsupported. In the early times, heterogeneous solid powder catalysts such as red mud, natural ore were used widely. In order to improve the conversion, homogeneous dispersed catalysts with high catalytic activity and good performance are developed.

In a word, the catalyst activity, selectivity, particle size and shape, pore size and distribution, as well as the type of the reactor, have to be optimized according to the properties of the heavy oils and to the desired purification and conversion levels. So far, a variety of improvements have been made in the last decades. The fixed-bed, moving-bed, ebullated-bed technologies have gained maturity while the slurry bed technology is still in the development phase, thus more emphasis will be placed on the slurry bed processes in

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Table 1. Comparison of Different Hydroprocessing Reactor Types [4]

	Fixed Bed	Moving Bed	Ebullated Bed	Slurry Bed
Maximum (Ni+V) in feed, ppm	50 - 250	50 - 400	100 - 600	>300
Tolerance for impurities	Low	Low	Average	High
Max. conversion to 550°C, wt%	50	50	80	95
Unit operability	Good	Difficult	Difficult	Difficult

this paper. Specifically, the following aspects are included in this thesis: Catalysts grading scheme, onstream catalyst replacement systems, slurry bed hydroprocessing technology. With the increasing trend towards heavy oil and residua processing, the presented hydroprocessing technology will have a broader prospect in view of future development.

2. FIXED BED PROCESS

The fixed-bed process technology is applied extensively and has the highest presence industrial applications due to its technical maturity, lower cost, stable and reliable performance in the world. This processing can treat sour and high-sulfur crude oil. However, in order to prevent a too fast and uneconomic deactivation of hydroprocessing catalysts, the percentage of metals in the feedstock are strictly limited: (Ni+V) <250 ppm.

The major goal of fixed bed hydroprocessing is hydrotreatment of heavy fractions with simultaneous HDS, HDN, HDM and asphaltene conversion. The hydrocracking activity remains moderate. This process can reduce the level of the impurities present in the feed and provide additional quantities of high quality feedstocks for FCC (Fluid Catalytic Cracking) and RFCC (Resid Fluid Catalytic Cracking) processes.

Heavy oil or residue feeds usually have a fair amount of metals and coke precursors. These impurities can deposit on the surface of catalyst during the reaction and lead to deactivation of catalyst. Therefore, how to inhibit metal depositing on the catalysts and prevent bed plugging to prolong the run length is an important challenge in fixed bed technology.

Recently, the catalyst grading scheme has been developed to solve this problem. To meet the different requirements of the products, this grading technology involves different kinds of catalysts and each type has its specific objectives. The general principal of catalyst grading scheme for fixed bed technology is shown in Table **2** [5].

As it can be seen, there are mainly three types of catalysts used in fixed bed hydroprocessing: for HDM, HDS or HDN. The HDM catalyst is used to remove the metals as well as convert parts of resid and asphaltenes present in the feed, while the other two play a major role in removing compounds containing sulfur and nitrogen plus Conradson carbon. Based on the physical characteristics such as particle size and catalytic function, catalysts are loaded in the reactor in sequence. In the multicatalyst system, the first bed or catalyst layer is always designed to perform HDM function, the second provides some HDM but mostly HDS and the third is responsible for deep hydrotreatment as well as HDS and HDN. The first layer contains a large pore catalyst while in the second and third beds catalysts with smaller pores and larger surface areas are required. The characteristics of some typical catalyst grading schemes are shown in Table **3** [6-8].

All the schemes have something in common, the first layer is loaded with high HDM activity and metal uptake

Table 2. The Catalyst Grading Scheme for the Fixed Bed Residue Hydrotreatment [5]

Catalyst	Pore Size	Specific Surface Area	Activity	Position in the Reactor	Function
A	Big	Small	Low	Upper	HDM
B	↑	↓	↓		HDM
C					HDM+HDS
D					HDM+HDS
E				Middle	HDS+HDM
F					HDS+HDM
G	Small	Big	High	Lower	HDS+HDN
H					HDS+HDN
I					HDS+HDN

Table 3. Typical Catalyst Grading Scheme for the Fixed Bed Residue Hydrotreatment [6-8]

Scheme	Catalyst Type	Functions and Characteristics	Position in the Reactor
A	HDM	Remove Fe, Ca, Na	Upper
		Remove Ni, V	
	HDS+HDM	HDS, HDM and remove CCR	Middle
	HDS+HDN	HDS, HDN, MHC	Lower
B	HDM	High HDM activity and metal uptake capacity	Upper
	HDM+HDS +HDN+HDCCR	High HDM activity and good HDS, HDN and CCR removal activities	Middle
	HDS+HDN +HDCCR	Very high HDS, HDN and CCR removal activities	Lower
	MHC	High MHC activity	Lowest
C	HDM	High HDM activity and metal uptake capacity	Upper
	HDM+HDAs	High HDM activity	Upper
	HDM+HDS	Middle HDM and HDS activity	Middle
	HDS	High HDS activity	Lower
	HDN+HDS +HDCCR	Remove N, S and CCR	Lowest
	HDN+HDS+ HDCCR+MHC	Remove N, S and CCR and MHC	

HDAs: hydrodeasphaltenization.
CCR: conradson carbon residue.
MHC: mild hydrocracking.

capacity, the difference is that in scheme C, the upper catalyst can also convert parts of asphaltene and the different types of catalysts are loaded with more layers and each catalyst functions as certain specific objective. The HDM catalysts have different activity level and the activity increases with the increase of layers, this can not only obtain the objective of metal removal but also prolong the life circle of catalysts. Scheme A also has some other guard catalysts in order to remove the impurities such as particles and salts.

Figure **1** [9] is a schematic of the typical fixed bed reactor configuration including feed distributor, guard bed, catalyst bed and a catalyst support. The multicatalyst system can be tailored according to the nature of the feeds and the target products. In the process, HDM catalysts with high metal uptake capacity and good activities for metal removal and asphaltene conversion are used in the guard bed reactor. Downstream of the demetallization stage, HDS and HDN catalysts are used to obtain a better hydroconversion. Nowadays, this technology has been widely used to improve the efficiency of catalyst and decrease pressure drop in the reactor in residue hydroprocessing.

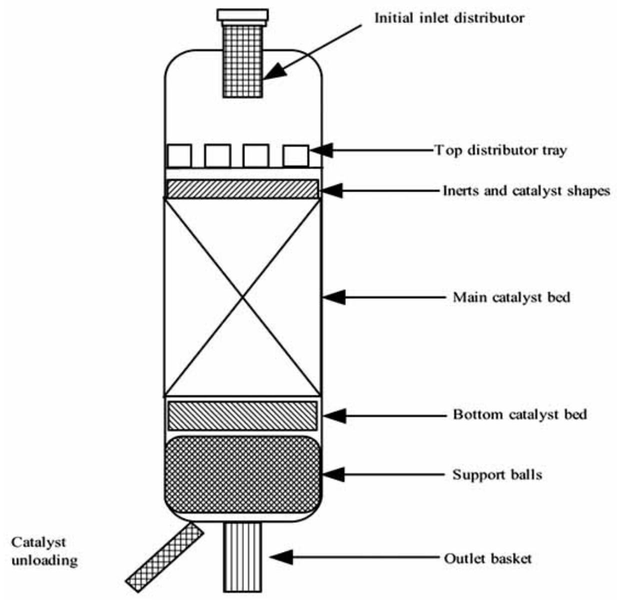

Fig. (1). Typical fixed bed reactor configuration [9].

3. MOVING BED PROCESS

As discussed above, a major limitation of the fixed bed technology is that it can only handle feed with metal levels

(Ni+V) <250 ppm. However, the refineries are faced with drastic changes in petroleum feed properties (such as increases in asphaltenes, sulfur, metals, and nitrogen contents) due to the growing volume of heavy crudes. To solve the problem, moving bed technology have been developed.

Generally, the moving bed is usually used as the front reactor before the fixed bed to prolong the operating cycle. In the process, one or more moving bed reactors precede conventional fixed bed reactors, and its major goal is to remove contaminants which lead to plugging or fouling of the main reactors with periodic replacement of the catalyst and keep the main reactors online.

Moving bed catalysts are similar to the fixed bed catalysts except that a catalyst shape is chosen which reduces abrasion and provides better particle strength. During the process, the catalyst bed slowly moves down the reactor as catalyst is withdrawn from the bottom and make-up catalyst added at the top. The back mixing of catalysts and feedstock is so slight that the efficiency of the process is higher than that of an ebullated bed reactor, and the quality of products is better. On the whole, moving bed processing can handle a feedstock with metal content of up to 400 ppm and Conradson carbon residue (CCR) <20wt%.

Nowadays, there are five commercial units worldwide in operation since the start up of the first commercial unit was introduced in the 1990’s. Three typical kinds of moving bed technology are reviewed in detail in the following: Chevron Lumus Global's onstream catalyst replacement (OCR) system, Shell's Bunker type reactor (Hycon) system and IFP's Hyvahl swing reactor system.

3.1. Chevron's OCR System

Chevron's Onstream Catalyst Replacement process is a counter-current, moving bed reactor that enables refiners to significantly increase capacity or improve product quality from a fixed bed RDS reactor. Figure **2** is a simplified schematic of the OCR system. An up-flow reactor is employed as a guard bed preceding the fixed bed reactor. The heavy oil feed is combined with H_2 and flows upward through the guard reactor, at the same time, the catalyst flows downward. Therefore, the catalyst beds have a slight expansion which avoids caking and plugging and reduces the pressure drop of the system. The catalyst can be replaced while the unit is on-stream at a rate of 2 to 8% per week depending on the feed metals content. OCR was first commercialized in 1992 at Idemitsu Kosan Company (IKC) Ltd.'s Aichi Refinery. By adding an OCR reactor in front of their existing RDS unit, IKC was able to switch feeds from 100% Arabian Light to a less expensive blend of 50% Arabian Light and 50% Arabian Heavy. Nowadays, the OCR technology is used in three commercial units in Japan.

As a developed technology, some advantages over other technologies are: processing higher metal feeds, producing ultra-low sulfur fuel, preparing feed for the RFCC, retrofit or grassroots OCR improves production economics.

Kramer *et al.* disclosed a method for hydroprocessing heavy oil feed through a single onstream reactor having a mixture of two different catalysts. The first one is a HDM catalyst, and the second one is a HDN catalyst. Based on the difference in replacement interval, they can be used under optimal conditions [10].

Gibson *et al.* disclosed an improved catalyst adopted for on-stream catalyst replacement in upflow processing units. It is characterized by a smaller peak pore diameter than general hydrotreating catalysts. The catalyst particles have a uniform density and a low proportion of macropores [11].

Trimble *et al.* and Stangeland et al. improved the OCR system and in the process, the feedstock and hydrogen are distributed uniformly and flow across a densely packed catalyst bed in alternate annual rings. At the desired flow rate, the catalyst continuously flows in a plug-like manner

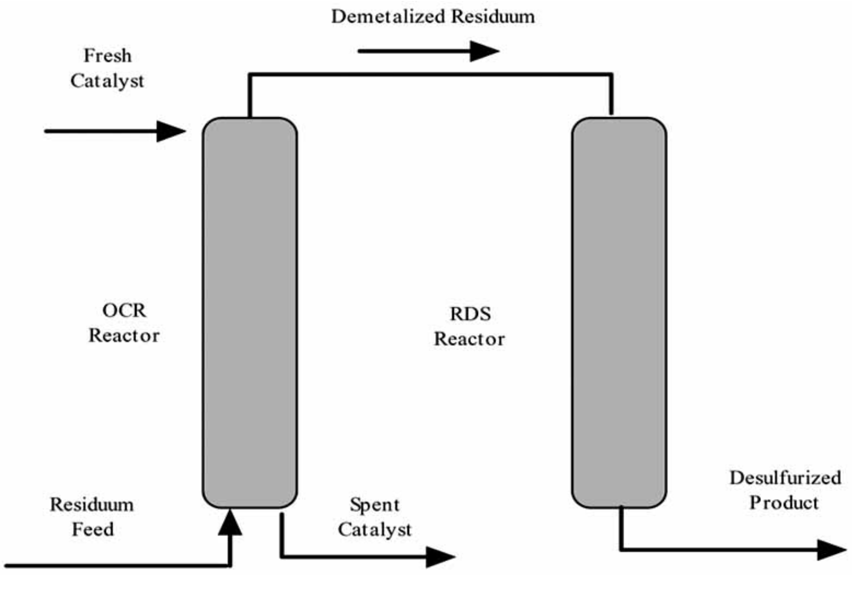

Fig. (2). A simplified schematic of Chevron's OCR system [9].

downwardly through the vessel by introducing fresh catalyst at the top of the bed and the spent catalyst is removed in a liquid stream out of the bottom of the bed [12-15].

Trimble *et al.* also developed a system which used multistage fixed catalyst beds contained in a single onstream reactor with a separate catalyst addition and a separate withdrawal system. The upper fixed bed functions as a guard bed for removing the contaminants in order to extend the life of the other beds, the catalysts particles are withdrawn from the fixed bed by slurrying the particles in a container disposed within the reactor [16].

Bachtel *et al.* developed a light-weight catalyst support structure which is formed in a cone-like shape and comprises a shell-like support member, a first mesh layer and a second mesh layer. The structure has capabilities for uniformly distributing hydrogen and feedstock and facilitates removal of catalyst from the reactor [17].

Krantz *et al.* developed the OCR reactor having a cone at the bottom to support the catalyst. The catalyst stream enters at the top of the reactor counter-current to the flow of the hydrogen and feedstocks which enters at the bottom. The contaminated catalyst particles become heavier and move downward through the reactor and are finally withdrawn at the bottom of the reactor. The extracted catalysts can either be reintroduced at the top of the reactor, or mixed with fresh catalyst. The process enables the reactor to run a longer time without downtime for catalyst change-out [18].

Leung *et al.* provided a method for presulfiding catalysts in order to reduce catalyst fouling rate and extend the life of the catalyst bed employed in the OCR process. The pretreatment zone comprises one or more vessels which are separate from the hydroconversion reaction zone contained in the reactor and are part of the equipment used to transfer the catalyst to the reaction zones from storage in the catalyst hopper [19].

3.2. Shell's Hycon System

Shell's Hycon system consists of five bunker reactors. The first three reactors are bunker demetallisation (HDM) reactors. The last two reactors are fixed bed desulfurization and conversion (HCON) reactors. A simplified flow scheme is shown in Fig. (**3**) [20]. In this process, the residue feedstock and catalyst flow downwards through the HDM reactor. The demetallized products pass to the fixed bed HCON section, which contains highly active desulphurisation and conversion catalysts. Downstream fractionation provides distillate fractions, vacuum distillate and converted vacuum residue. The deactivated catalyst is replaced from the bottom at a rate of 0.5 to 2.0% of the total catalysts to insure a steady operation. Shell’s first moving bed reactor was successfully applied in Pernis in 1989.

After improvement of catalyst and modification of operating conditions, the Arabian and Iranian vacuum residue could be handled and the treatment capacity is 1.25 Mt/a. The quality of the products is good and the typical distillate conversion is 65-70%. Recently, Shell has announced that they have developed a type of catalyst with a high metal uptake capacity for processing of feeds with very high metal contents (>500 ppm) [21].

3.3. Axens/IFP's Hyvahl System

The Hyvahl system was developed by IFP and is licensed by Axens. It uses two HDM reactors in series as guard bed which can be switched alternatively in the processing. It is a process using a permutable reactor section to remove the bulk of the metals and asphaltenes. Fig. (**4**) [22] is a simplified scheme of HYVAHL-S hydroconversion process. When the catalyst in the first reactor deactivates, the reactor can be removed from service for catalyst replacement, meanwhile, the entire unit can be kept running because the other one is still in service. During this pretreatment process, half of the metals are removed from the feed in the guard

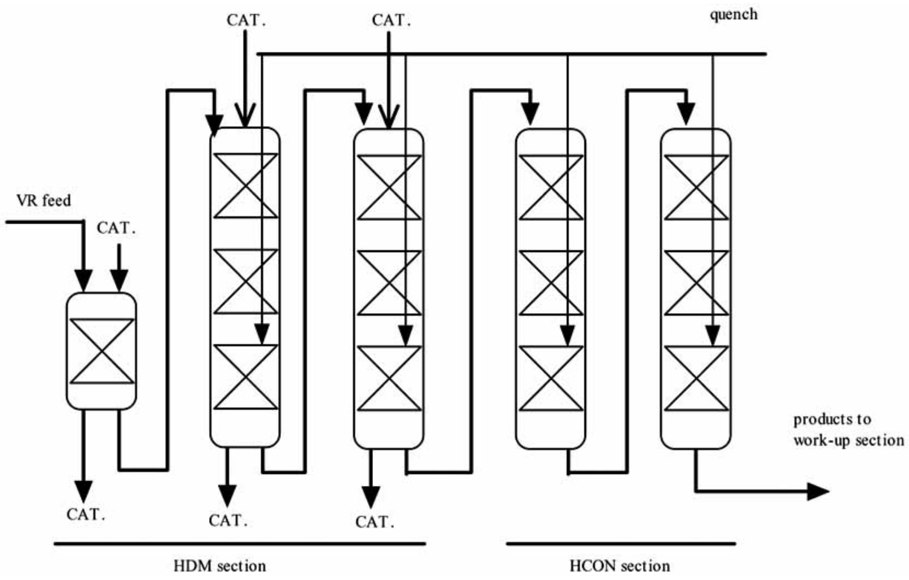

Fig. (3). Process flow scheme of the HYCON Pernis unit [20].

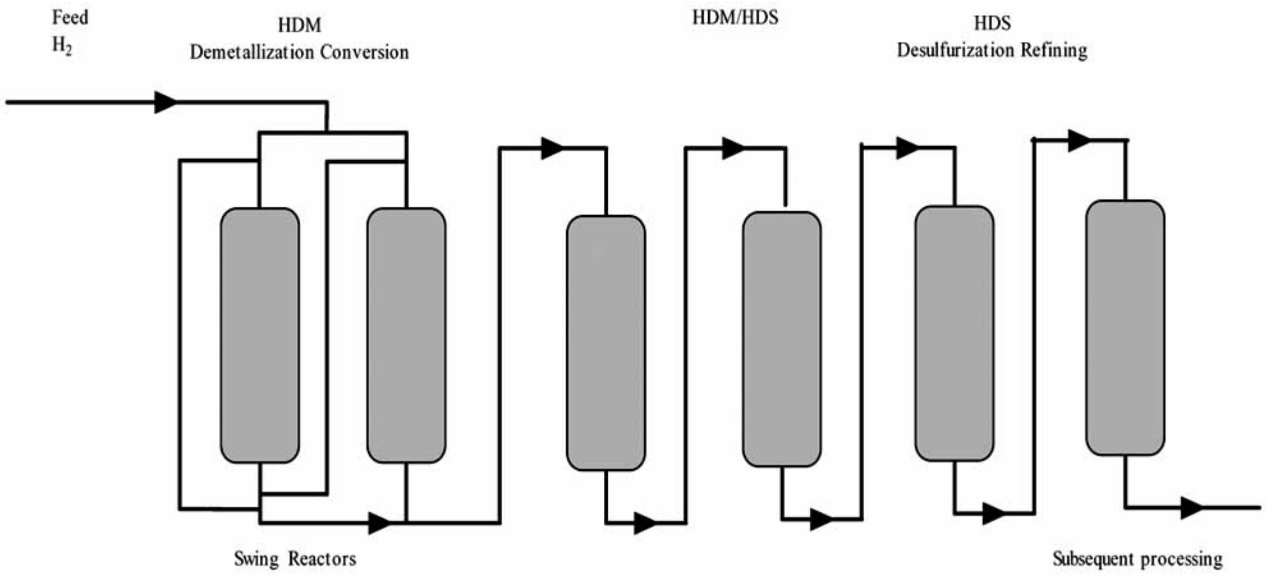

Fig. (4). Simplified scheme of HYVAHL-S hydroconversion process [22].

reactors. The reconditioning of the catalyst takes less than two weeks. Compared with other technology, the swing-reactor system has many advantages: High efficiency of catalysts, no operational problems due to catalyst attrition, protection of the downstream reactors of the process. So far, there are two commercial units in operation in South Korea. The effluent from the units is used as feed for residue fluid catalytic cracking unit but the conversion of heavy oil is limited [9, 23].

4. EBULLATED BED PROCESS

As mentioned above, fixed-bed technologies have many problems in treating particularly heavy feeds with high heteroatom, metal and asphaltene contents. One solution to the problems is to use several fixed-bed reactors connected in series to achieve a relatively high conversion of such heavy feedstock, however, such designs would be costly, and for certain feedstock, commercially impractical. Therefore, ebullated-bed technologies have been developed with numerous advantages in performance and efficiency, particularly with heavy crudes.

In the process, the feed and H_2 mixture enters the bottom of the reactor and flows upward through a catalyst bed, expanding and backmixing the bed, minimizing bed plugging. The catalysts are not fixed and maintained in an ebullient or fluidized condition with upflowing feed. The reaction involves a three-phase system: gas, liquid and solid (catalyst) with good mass and heat transfer. The ebullated bed process is able to convert most of the refractory heavy oil feedstock to either distillate products or low sulfur fuel oils [3].

The most important feature of the ebullated-bed process is its capability to periodically withdraw and add the catalyst to the reactor without interrupting operation. This is important for hydroprocessing of high asphaltene and metal feeds. The bed design ensures ample free space between particles allowing entrained solids to pass through the bed without accumulation, plugging or increased pressure drop. This allows utilization of catalyst particles having a diameter smaller than 1 mm and results in a considerable increase of reaction rate. The process is flexible and can be operated either in a high conversion or low conversion mode.

As far as the catalyst is concerned, catalysts used in the ebullated bed are chemically similar to those used in the fixed bed and both are supported type catalysts. Such supported catalysts may be beads or extrudates containing small amounts of one or more active promoter metals such as cobalt, molybdenum or nickel deposited on an inert support material such as alumina or silica. There are a few differences in the physical properties: Particle size, mechanical strength and shape. Ebullated-bed catalysts are made of pellets or grains that are 1-1.5 mm in size to facilitate suspension by the liquid phase in the reactor. The mechanical strength of the catalyst is even stronger than the fixed bed catalyst to sustain its operability [24-27].

In general, there are two important ebullated bed processes: the H-Oil process and the LC-Fining process. Among all the ebullated-bed processes in commercial service, 7 operating units are H-Oil process, and 9 are LC-Fining process. Basically, H-OIL$_{DC}$ and LC-fining processes are technically quite similar.

4.1. H-Oil$_{DC}$ Process

The H-Oil$_{DC}$ process was initially developed by Hydrocarbon Research Corp and Cities Service R&D and first commercialized in 1963. It is now developed by IFP and licensed by Axens. Fig. (**5**) is a schematic of the ebullated bed reactor of the H-OilDC Process. In the process, the feed mixed with H_2 and recycle vacuum residue are fed into the bottom of the reactor and flow upwards through the catalyst bed. The small extruded particle size catalysts used in the reaction provide efficient contact among gas, liquid and solid. Due to the movement of catalysts, deposition of tar and coke is minimized. The typical operating conditions of

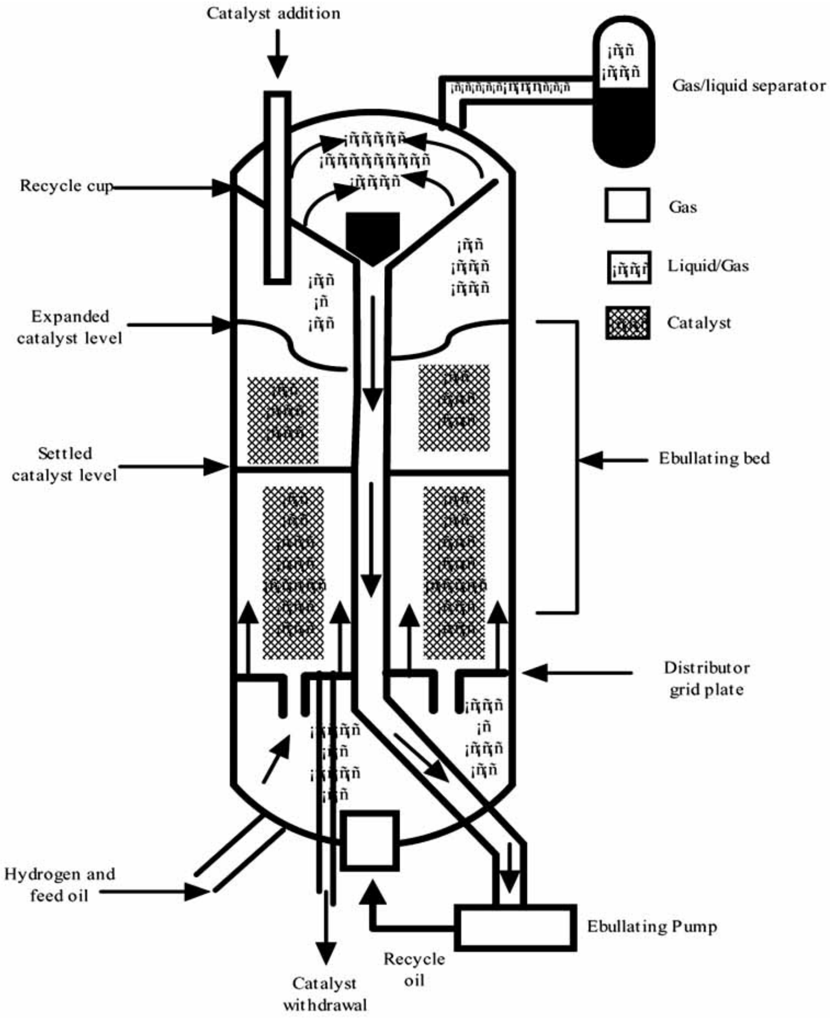

Fig. (5). Schematic of the H-Oil reactor [28].

H-OilDC process are as follows: Temperature 415-427°C, pressure 17-18 MPa, LHSV 0.1-0.8 h^{-1}. The products of H-OilDC can be directly used as oil product blending component, and if further hydroprocessing is needed, the bottoms can be fed to FCC, RFCC or Hydrocracking units [28].

Recently, the latest development of the H-OilDC process focuses on new novel catalysts, regeneration process of catalysts and multistage reactor system. New generation catalysts were developed by Hydrocarbon Research Corp. in the 1990s and have been used in commercial plants. Onstream replacement of catalyst has been realized to reduce the cost and the regeneration technology of deactivated catalysts has made a great progress [29].

Conversion of single stage reactor system can achieve 60-65%, while two-stage reactor system can obtain even higher conversion. With high HDM and asphaltene cracking activity, the H-OilDC process can handle heavier residues with Conradson carbon residue of 40wt% and metals contents of 800 ppm. Conversion of the process can be kept up to 80% and low sulfur fuel oils can be produced [30].

4.2. LC-Fining Process

The first LC-Fining process unit was set up in 1984 with a processing capacity of 3 Mt/a. LC-Fining is well suited to extra-heavy residue, bitumen and vacuum residue feedstocks. Fig. (**6**) [31] is a schematic of the LC-Fining reactor. The extruded catalyst $CoMo/Al_2O_3$ with the diameter of 0.8 mm was used in the process. This technology possesses excellent HDS, HDM and hydrocracking (HCR) performance.

In the process, the residue feed and H_2 are fed into the bottom of the reactor and flow upward to contact with the catalysts in the bed. Catalysts in the reactor can be added and withdrawn during the running period, the heat of reaction is absorbed by the fresh feed and the entire process is kept isothermal. The LC-Fining process can achieve conversion for HDS of 80%, HDM of 88%, and CCR reduction of 62%. The different conversion can be attained by adjusting residence time in the reactor. Generally speaking, the effluent from the ebullated bed reactor needs further processing before entering the next process unit.

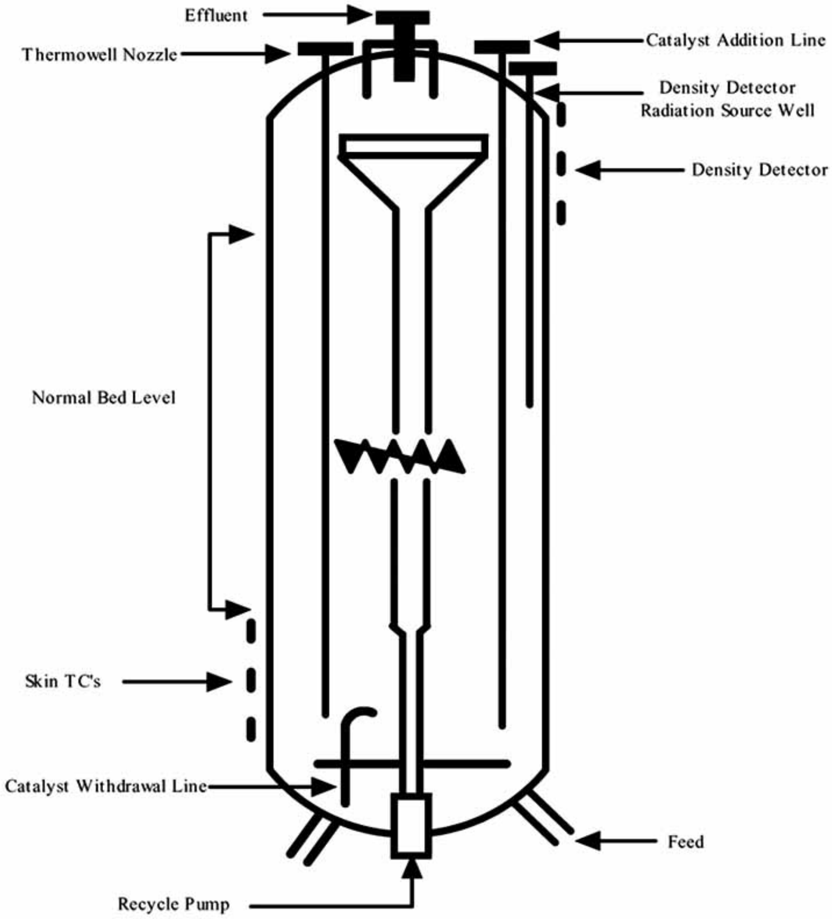

Fig. (6). Schematic representation of the LC-Fining reactor [31].

5. SLURRY BED PROCESS

5.1. Characteristics of Slurry Bed Process

Briefly, the slurry bed process is a hydrocracking process in the presence of catalysts and hydrogen at high pressure and temperature. The reaction involves mainly thermal cracking and the main goal is to convert residue into high-value lighter distillates. The presence of catalyst and hydrogen restrains coke formation and leads to more stable products [32]. The slurry bed process shows its special superiority in treating heavy oils containing large amount of metals, carbon residue and asphaltene. Another feature of the process is its flexibility with respect to product selectivity and yield. On the whole, the slurry bed process as a residue processing technology has several advantages such as a more simple process flow scheme, flexible operation and process reliability, high space velocity and conversion rates, no bed plugging problems and a wider adaptability to different sources of raw materials. The main disadvantage is that the operability is more difficult than for the other processes.

In the process, the residue, finely dispersed catalyst or additive and hydrogen are mixed before being routed to the reactor. The reactants are well-mixed and kept in suspension and flow upward in the reactor. The product and catalyst are separated at the top of the reactor (high pressure high temperature separator). The coke formed during the reaction will deposit on the surface of catalyst and discharge from the reactor, thus there is no bed plugging problem. Solids particles are recovered with the unconverted organic fraction at the bottom of the separation section by distillation or by solvent deasphalting. To obtain better performances, some important parts including hydrogen distributor and internal loop reactor are used in the process.

As discussed previously, the slurry bed process has the flexibility to produce, after severe hydrotreatment and/or hydrocracking to remove the heteroatoms and the olefinic and aromatic structure created in the process, gasoline, jet fuel, diesel fuel or vacuum gas oil to meet seasonal swings in product demand. Product yields depend on the extent of the conversion and to obtain high-quality products further processing is needed. Typical operating conditions in the reactor are temperatures of 420-460°C, a pressure of 10-20MPa, LHSV 0.5-2.0 h^{-1} and single pass conversion of 70-85%.

The slurry bed process was first used in Germany as early as 1929 for hydrogenation of coal to produce oil. Later, the process was used to handle crude oil when the oil supplies were limited. Recently, this process was adapted to convert vacuum residue feeds. There are many versions of slurry bed processes developed such as VCC, SRC Uniflex^{TM}, SOC, $(HCAT/HC)_3$, HDH/HDHPLUS, EST and so on.

5.1.1. Veba Oel's Combi-Cracking (VCC) Process

The Veba oel's Combi Cracking process is based on the Bergius hydrogenation technology in Germany. Veba built a demonstration unit at the Bottrop refinery in 1983, and in 1988 the unit was modified to treat vacuum residue. In the process, the residue is slurried with finely powdered additive such as Bayer red mud or lignite with H_2. The addition amount of catalysts is as high as 5wt%. The liquid phase reactor is used in an upflow mode and the operating conditions are: Temperature 440-485°C, pressure 15-30MPa. The once-through conversion rate of residue was kept above 95% [33, 34].

5.1.2. PetroCanada's SRC Uniflex^{TM} Process

The SRC Uniflex^{TM} is the new trade name for the catalyst technology and it was previously known as CANMET process. It was developed to handle heavy oil and tar sand bitumen. A low-cost additive (iron sulfate monohydrate)was used to inhibit coke formation and allowed the unit to operate in more severe reaction conditions. Catalysts used in the process were about 2-3wt% and the spent additive remained in the unconverted vacuum residue. The conversion as high as 90% was reached [35-38].

5.1.3. Intevep's HDH/HDHPLUS Process

The HDH technology was developed by the Venezuelan INTEVEP Company for converting heavy oils. This process uses a kind of inexpensive indigenous ore as a catalytic additive. The additive has dual function: promote hydrogenation and inhibit coke formation and the addition is 2-5wt%. In the process, the operating conditions are mild, 7-14MPa, 420-480°C. A number of heavy oils have been processed in the pilot plant and 90% conversion could be obtained. However, a complicated separation system is needed to recover the spent catalysts. INTEVEP claims that 99% of the additive solids can be separated from the unconverted residue. Recently, INTEVEP, IFP and AXENS company have developed an improved process named “HDHPLUS” [39-42]. This technology is suitable for treating refractory feedstock with high-level of contaminants through the elimination of all metal contents in the load. When compared to the prevailing conversion process in the market today, HDHPLUS process produces a higher yield of products and a reduced load of byproducts and pollutants. This HDHPLUS process with the Puerto La Cruz project in Venezuela is scheduled to be started in early 2012.

5.1.4. Asahi's Super Oil Cracking (SOC) Process

The SOC process was developed by Asahi Chemical Industries, Nippon Mining Company and Chiyoda Co.. The main features of SOC technology are as follows: Only a small amount of dispersed catalyst is needed, catalyst exhibits excellent activity and anti-coking performance, tubular reactor is used, high reaction temperature (475-480°C) and pressure (20-22MPa), short residence time, conversion levels of 90% are obtained. Furthermore, one important point worth mentioning is the catalyst, it consist of two components: a transition metal compound (Mo) and ultra fine particle (carbon black). Mo plays a significant role in hydrogenating and the carbon black inhibits coke formation. When the conversion of residue reaches 90%, the coking yield is only 1wt% [43-45].

5.1.5. EniTechnologie's EST Process

EST technology was developed by EniTechnologie to process heavy oils, vacuum residue and tar sand bitumen with high content of metal and carbon residue. Fig (**7**) is a schematic of the process. During the hydroprocessing, asphaltenes in the feed are becoming less soluble and will be

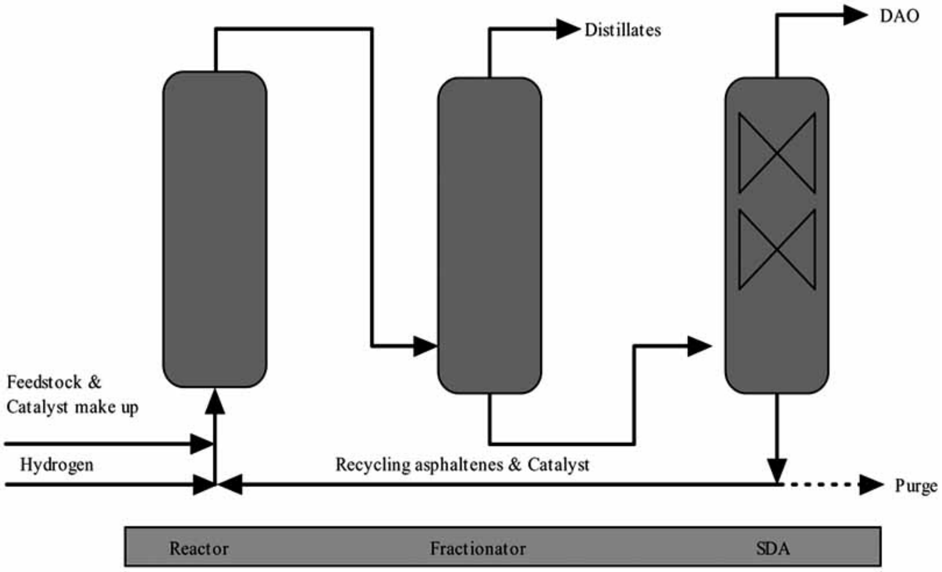

Fig. (7). Eni EST Slurry Technology process scheme [48].

incompatible with oil and precipitate to cause coke deposition when the conversion is over a certain level. EST technology provides an effective way to overcome this problem. In the process, before the mixtures become unstable, the asphaltenes are separated and then blended with fresh feedstock. In this way, the partially converted asphaltenes, dissolved in a more aromatic stream, can regain stability. Moreover, this solution allows the dispersed catalyst to be recovered and recycled. Catalyst is added as oil-soluble molybdenum compounds (microcrystalline molybdenite) which react with sulfur to form finely dispersed MoS_2 online. This type of catalyst can be well mixed with the feedstock and has high hydrogenation activity. Catalyst concentration in the reactor is up to thousands of ppm, this is related to the technological process design. In the process, catalyst and feed are contacted with H_2 at about 16 MPa and 400-425°C. The reactor effluent is fractionated and the vacuum residue is sent to solvent deasphalting. The bottoms which contain the catalyst are recycled [46-48].

A number of heavy oils from different sources have been processed in the pilot units. Table **4** shows the results of processing several different residues. As can be seen from that, in all cases the process assures a high conversion (> 99%) and a complete metal removal (> 99%HDM), an excellent CCR reduction (> 95%HDCCR), a fairly good desulphurization and a reasonable denitrogenation. The EST slurry process is moving towards the commercial proof at a coastal refinery in Italy.

5.1.6. Headwaters' (HCAT/HC)$_3$ Process

The (HCAT/HC)$_3$ process was initially developed by Alberta Research Council and designed to upgrade indigenous heavy crude oils or bitumens. Now the process is called HCAT and licensed by Headwaters. In this process the catalyst is homogeneously dispersed as a colloid with particles similar in size to that of asphaltene molecules, and high conversion of the asphaltenes can be achieved. Catalysts used in the process are oil-soluble, such as iron pentacarbonyl or molybdenum 2-ethyl hexanoate with excellent anti-coking performance. Conversion ranged from 60-98% when the Cold Lake bitumen was treated in the pilot unit [49-55]. The (HCAT/HC)$_3$ process has also been proposed as low conversion process to upgrade heavy crude to a product which can be shipped by pipeline without a diluent. Headwaters has signed an agreement with a major European refinery to demonstrate the HCAT catalyst under

Table 4. EST Process-Comparative Performances of Different Feedstock [48]

Feedstock Properties	Ural	Arabian Heavy	Zuata	Maya	Athabasca
Specific gravity (g/cm^3)	1.0043	1.0312	1.0559	1.0643	1.0147
API gravity	9.4	5.7	2.5	1.5	7.95
500°C+ content (wt%)	91	96	95	99	60
H/C	1.494	1.366	1.349	1.333	1.420
S(wt%)	2.60	5.28	4.24	5.24	4.58
N(wt%)	0.69	0.45	0.97	0.81	0.48
Ni and V(ppm)	74/242	52/170	154/697	132/866	70/186
n-C_7 asphaltenes(wt%)	10.5	19.5	19.7	30.3	12.4
CCR(wt%)	18.9	22.9	22.1	29.3	13.6
Product yields(wt%)					
Gas (HC+H_2S)	11.5	10.9	15.0	9.9	12.9
Naphtha (C_5-170°C)	5.8	4.9	5.9	3.9	4.1
Atmo. Gasoil (170-350°C)	32.5	30.6	35.6	26.9	39.1
Vacuum Gasoil (350-500°C)	29.8	29.2	29.8	34.9	32.1
DAO (500°C+)	20.4	24.4	13.7	24.4	11.8
Upgrading performance					
% HDS	86	82	82	84	83
% HDM	>99	>99	>99	>99	>99
% HDN	54	41	51	52	47
% CCR reduction	97	97	98	96	95
% Conversion	>99	>99	>99	>99	>99

commercial operating conditions. The HCAT catalyst technology has also been deployed in two separate runs at a commercial heavy oil hydrocracking unit located in a major North American refinery.

There have been some other processes developed such as Exxon Mobil's Microcat [56], UOP's Aurabon [57,58], Idemitsu Kosan's MRH [59-61], Chevron's CASH [62-65], and also some other combined processes [66-68]. At present, many processes are in the industrial demonstration stage and there is still much room to be improved.

In the processes mentioned above, the metal active component is maily Fe and Mo, with the form of inexpensive natural ore or metal salt. In the process using natural ore as catalyst, the percentage of the natural ore catalysts added is higher than that of catalysts with Mo in order to obtain catalytic activity and to inhibit coking, such as the early processes VCC, HDH and CANMET, the amount of catalysts is about 2-5wt%. This will cause the problem about how to treat the unconverted bottom oil and catalyst recycle. The catalyst leaving the reactor can be recovered by separation with the conventional methods such as decanting, centrifugation or filtration. However, the catalyst recovered has a low activity with respect to the fresh catalyst and the suitable regeneration step is necessary. So far, there is no effective solution to this problem. In the processes using inexpensive ore as catalysts, except for increasing the percentage of catalyst content, increasing the pressure is another way to inhibit coke formation. The pressure of reaction in these processes is relatively high, and is about 15-25 MPa. As far as the conversion level is concerned, the VCC, SOC, SRC Uniflex^{TM} processes are high, about 85-90%, this is related to the temperature in the reaction. Generally, the higher the temperature is, the higher conversion will be obtained. Although the temperature of the EST technology is low, the process adopts the catalyst recycling scheme and the concentration of MoS_2 is very high so that the conversion level is also high and the coke formation can be inhibited.

5.2. Catalysts for Slurry Bed Process

According to their physical properties, catalysts used in the slurry-bed process can be divided into three categories: Heterogeneous solid powder catalysts, oil-soluble dispersed catalysts and water-soluble dispersed catalysts. The way these catalysts are used (type of precursors, concentrations, etc.) are extremely important both from an ecnomical and environmental point of view.

5.2.1. Solid Powder Catalysts

Generally, the active metals of the solid catalysts are mainly Fe, Ni and V, and these fine particles catalysts are usually dispersed in heavy feed before processing. The processes using solids catalyst such as VCC, Canmet and HDH ususlly adopt once-through option, but in this case, the upgrading of the products is generally unsatisfactory.

The solid powder catalysts were used in the early developed slurry bed technologies such as VCC, Canmet and HDH processes. The main components include $FeSO_4$ additives, natural ore, pulverized coal or the like. These inexpensive additives have low catalytic activity and a few percents are needed to keep activity at a certain level. Therefore, the major problem with these processes is how to dispose the unconverted residue which contains a large amount of spent additive.

Breaden *et al.* provided a catalyst comprising a metal phthalocyanine and a particulate iron component used in the process. The iron component might be selected from the group consisting of iron oxides, iron sulfides, and mixtures thereof. When 7wt% of Fe_2O_3 and 400 ppm of cobalt was added, the coking yield was only 0.4% [69].

Khulbe *et al.* disclosed a method to use some finely divided fly ash as scorch retarder in the residue hydroprocessing process and greatly reduce coke precursors and thereby prevent the formation of carbonaceous deposits in the reaction zone [70].

Fouda *et al.* suggested that some coal, such as lignite, bituminous, sub-bituminous might be coated with up to about 10 wt.% of metal salts such as iron, cobalt, molybdenum salts as additives. The coal particles used should be quite small less than 60 meshes [71].

Lott *et al.* suggested an additive comprising Si and Al or Ti and Al oxides and 70% of the particles range from 4 to 20μm. These additives used with conventional Mo, Ni supported on carriers and could promote the production of middle distillate [72].

Jain *et al.* provided a process for the conversion of heavy oil in the presence of iron-petroleum coke catalyst. The iron-petroleum coke catalyst was prepared by grinding petroleum coke particles (8-16 mesh) and particles of an iron compound in oil to form additive slurry. The iron-petroleum coke catalyst was present in the feed slurry in an amount of up to 5% by weight, based on the oil [73].

5.2.2. Oil-soluble Dispersed Catalysts

The catalysts can also be introduced as an oil-soluble precursor which refer to the organometallic compounds that can disperse homogeneously in the residue and thus facilitate the sufficient contact between residue and H_2 to promote the reaction. Generally, the components of oil-soluble catalysts are mainly molybdenum, cobalt, iron and nickel as naphthenates or multi-carbonyl compounds. In this case, the active form of the catalyst (generally the metal sulfide) is formed *in situ* by thermal decomposition of the compound used, during the reaction or after suitable pretreament. More details can be seen in Table **5** [74-83].

5.2.3. Water-soluble Dispersed Catalysts

Oil-soluble catalysts have good dispersion and high catalytic activity, but compared with water-soluble catalysts, the cost is higher. To reduce the cost, many research institutes have developed water-soluble catalysts. In the water-soluble case, the pretreatments such as dispersion and emulsion and dehydration are also necessary before processing. If the catalyst are used with higher concentration (thousands of ppm), it is necessary to recycle the catalyst.

Phospho-molybdic acid and ammonium molybdate are two of the typical representatives. In the process, firstly, water-soluble catalysts are dissolved in solution and then mixed with parts of the residue feed to form an emulsion.

Table 5. Oil-Soluble Dispersed Catalysts for Slurry Bed Process

Licenser	Catalyst Components	Feed	Amount of Catalyst	Result	Reference
Exxon Research and Engineering Co.	Molybdenum alicyclic or naphthenate	Heavy oil with CCR＞5%	50-200ppm Solid, noncolloidal catalyst	50% reduction of CCR	[74,75]
	Fe_2O_3 and molybdenum naphthenate	Cold Lake crude oil	50-200ppm Prepared in situ Can be recycled	50% reduction of CCR Coke yield ＜1%	[76]
	Iron molybdenum	Cold Lake crude oil	0.5-2.0wt% Solid particles with low surface area and pore volume	Conversion＞50%	[77]
	CrO_3 tert-butyl alcohol	Heavy oil with CCR 5-50%	0.1-2.0 wt% Solid chromium-containing catalyst	Conversion of 80-85%	[78]
Alberta Oil Sands Technology& Research Authority	iron pentacarbonyl or molybdenum 2-ethyl hexanoate	Athabasca bitumen +50% diluent	0.1-0.5 wt% Well-dispersed colloidal particles	Conversion of 90% coke yield of 0.3%	[79]
	Mo,Ni acetylacetonates or 2-ethyl hexanoate	Athabasca bitumen	50-300ppm Mixture of asphaltene and metal-doped coke Can be recycled	Coke yield is low	[80]
Chevron Inc.	Molybdenum or tungsten salts of fatty acids (C_7-C_{12})	Arabian crude	300-l000 ppm	80%	[81]
Universal Oil Products Co.	Non-stochiometric vanadium sulfide	Wyoming sour crude oil	Well-dispersed colloidal particles	High Ni,V removal activity	[82]
Institut Francais du Petrole	Molybdenum or cobalt naphthenate	Aramco VR Kuwait AR	20-100 ppm	Asphaltene conversion 70-90%	[83]

Dehydration and sulfurisation are subsequent steps, and finally the catalysts react with the residue feed in the reactor. Table **6** [84-94] shows some typical catalysts.

All the processes, whether the catalyst is soild powder, water-soluble or oil-soluble, if the high active metals are used, such as molybdenum, and the catalyst concentration is higher (thousands of ppm metal), the quality of the product obtained is higher, but it is necessary to consider the recycling of the catalyst, otherwise, the cost of catalyst will be too high. As far as the recycle of catalyst is concerned, the Chevron Inc.'s water-soluble and EniTechnologie's oil-soluble catalyst technologies have distinguishing features. Chevron Inc. have developed a new residue full hydro-conversion slurry reactor system, the water-soluble catalyst (containing MoO_3), unconverted oil and converted oil circulate in a continuous mixture throught an entire reactor. The mixer is partially separated to remove the converted oil while permitting the unconverted oil and the catalyst to continue on into the next sequential reactor and part of the unconverted oil is converted to lower boiling point hydrocarbons, and the further hydroprocessing may occur in additional reactors. The highly concentrated catalyst in unconverted oil can be recycled directly to the first reactor [95-98]. EniTechnologie provides a process for the conversion of heavy oil which comprises the following steps: Sending the feed to a deasphalting unit (SDA), obtaining two streams, one consisting of deasphalted oil (DAO), the other containing asphaltenes, mixing the stream consisting of DAO with a catalyst precursor to a hydrotreatment reactor containing hydrogen and H_2S, and then the stream containing the product and catalyst in dispersed phase to the distillation steps, whereby the most volatile fractions are separated, recycling of a portion of the distillation residue coming from the flash unit, containing catalyst in dispersed phase to the hydrotreatment section [99, 100] .

6. CURRENT & FUTURE DEVELOPMENTS

In the upcoming years, there will be a continuous trend that the crude oils are getting heavier with higher content of impurities such as nitrogen, sulfur and metals. Meanwhile, refineries have to make efforts to improve the residue processing technologies and convert the heavy feedstock into valuable and environment-friendly products with more and more stringent specifications. Nowadays, as one of the major

Table 6. Water-Soluble Dispersed Catalysts for Slurry Bed Process

Licenser	Catalyst Components	Feed	Amount of Catalyst	Result	Reference
Chevron Inc.	Mo, Ni oxide with aqueous ammonia	Athabasca VR 60% VGO 40%	4-10wt% MoO_3 with aqueous ammonia to form a mixture	Sulfur, nitrogen and metal removal＞98%	[84-86]
Exxon Research and Engineering Co.	Phosphomolybdic acid ammonium heptamolybdate molybdenum oxalate	Arabian VR or Cold Lake crude oil	0.2-5wt% Solid molybdenum and phosphorus-containing catalyst	Coke yield is low	[87-89]
	Ni and Mo multimetallic catalyst	Arab Light VR	Ratio of Ni and Mo varied from 0.1 to 10	High HDM activity	[90]
	Nickel carbonate ammonium dimolybdate ammonium metatungstate	Low sulfur diesel oil	Bulk multimetallic catalyst	High HDS, HDN activity	[91]
Universal Oil Products Co.	Molybdenum, vanadium and iron metal oxide or salt and heteropoly acid	Lloydminster VR	Solid, non-colloidal catalyst	Conversion 60-65% coke yield ＜1%	[92, 93]
PetroChina Company Limited	Nickel, iron, molybdenum and iron cobalt liquid catalyst	Karamay AR	Highly dispersed multimetallic catalyst	Conversion 80-90% coke yield ＜1%	[94]

methods to upgrade heavy oils, a variety of residue hydrocracking processes using fixed bed, moving bed or ebullated bed reactors are available. Furthermore, the economics of the slurry bed processing technology indicates an attractive rate of returns with the existing crude oils and product price structure.

Due to the complexity of the heavy oils, processing of those heavy oils poses numerous problems and the most important one is how to combine the processing technologies with catalysts at reasonable capital and operating costs. Generally speaking, only by comprehensively considering related factors such as the properties of feed, catalyst performance, requirement of products, chemical kinetics, operating conditions and running period, optimal results could be achieved. Therefore, further improvement of the hydroprocessing process and catalysts, which can tolerate a high content of impurities and metals, are two major challenges for the refineries.

As far as integrated processes are concerned, some state-of-the-art technologies have been developed, such as Chevron's OCR System, Shell's Hycon System and Axens/IFP's Hyvahl System. These online catalyst replacement systems integrated with the fixed bed process will enable the refineries to handle the heavier oils with higher impurities. Indeed, there is still much space for a variety of improvements in these aspects such as reactor design and operation optimization. The ebullated bed process can be operated under high space velocity or higher conversion level and good selectivity and high liquid yield and relatively low hydrogen consumption are obtainable. However, some challenges such as reactor efficiency decrease due to the backmixing and high investment and operating cost need to be decreased. Although there are still further steps before the slurry bed process can be commercialized, it would be more competitive after optimizing the design, decreasing the cost and adding high-activity catalysts to the process.

Another significant improvement of the discussed hydroprocessing technologies is catalyst design. The recent patents published indicate that a novel catalyst is one of reasonable design and integration of the active, supporting and promoting components. It also has been gradually recognized that there is an optimal combination of activity, surface area and pore diameter, giving the highest activity. Therefore, some attentions have to be paid to the size of the particles, pore volume and size distribution, pore diameter and the shape of the particles to maximize utilization of the catalyst. The transition metal sulfides such as Mo, Co, and Ni are still the industry favorites, because of their excellent hydrogenation, HDS, and HDN activities, as well as their availability and cost price. Nowadays, most commercial catalysts are still based on alumina or silica–alumina as a carrier material, and additionally, zeolites, activated carbon and mesoporous materials MCM-41 carriers have also been exploited. In the near future, the residue upgrading technological advancements are likely to be combination of various hydroprocessing technologies with other processes such as thermal processes and solvent deasphalting processes. And as yet underlined, catalyst grading will be more and more important to optimize purification and conversion levels versus catalyst life and product quality.

CONFLICT OF INTERESTS

No conflict of interest exits in the submission of this manuscript.

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