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A review of recent advances on process technologies for upgrading of heavy oils and residua

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Abstract

The term hydroconversion is used to signify processes by which molecules in petroleum feedstocks are split or saturated with hydrogen gas while tumbling boiling ranges and impurities content from petroleum fractions. Hydroprocessing is a broad term that includes hydrocracking, hydrotreating, and hydrorefining. To meet the gradual changes in petroleum stipulate, in particular a reduced demand for heavy fuel oil, advanced technologies for residue hydroprocessing are now extremely necessary. A refining process is needed for treating heavy petroleum fractions (atmospheric or vacuum oil residue) in the presence of catalysts and hydrogen at high pressure. In this article the different technologies for residua processing: thermal, catalytic fixed and ebullated types of hydroconversion are reviewed and discussed. A possibility of combining the advantages of these technologies together with suitable catalyst with enhanced and controlled cracking activity is also analyzed.

Keywords: Hydroprocessing; Residue; Heavy oil

1. Introduction

In the last century, catalysis became one of the most powerful tools in the petroleum sectors. Although it is often mentioned that the field of hydroprocessing catalysis is mature and there is not much compasses for researcher, the increasing demand of heavy oil has become hydroprocessing a challenging task for refiners as well as for researchers. During the last 50 years, hydrotreating (HDT) catalysis has been recognized as a multidisciplinary work about the support effect, catalyst characterization, and catalytic activity for deep hydrodesulfurization [1]. Now, when refiners are already using highly active catalyst like NEBULA™ (NEw BULk Activity, ExxonMobil) or STARS™ (Super Type II Active Reaction Sites, Akzo Noble Catalyst) for middle distillates (close to fulfill the EPA sulfur specifications) [2], the researcher's importance is increasing towards the heavy oil hydroprocessing. The HDT catalyst for heavy oil is entirely different than those for model molecules and middles distillate. Therefore, the importance of the catalyst is not only focused on its development but also tremendous work has to be done for catalyst formulation as well as process designing.

The demand for high value petroleum products such as middle distillate, gasoline and lube oil is increasing, while the demand for low value products such as fuel oil and residua based products is decreasing. Therefore, maximizing of liquid products yield from various processes and valorization residues is of immediate attention to refiners. At the same time, environmental concerns have increased, resulting in more rigorous specifications for petroleum products, including fuel oils. These trends have emphasized the importance of processes that convert the heavier oil fractions into lighter and more valuable clean products [3]. A number of technologies have been developed over the years for residual oil upgrading, which include process that are based on the carbon rejection and hydrogen addition routes

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Nomenclature

APD	average pore diameter
API	American Petroleum Institute
AR	atmospheric residue
CanMet	Canadian Research Center for Mineral and Energy Technology
CCR	conradson carbon residue
CASH	Chevron activated slurry hydroprocessing
DAO	deasphalted oil
EDX	energy dispersive X-ray analysis
EPA	Environmental Protection Agency
ESR	electron spinning resonance
EST	Eni slurry technology
FWUSA	Foster Wheeler-USA
FCC	fluid catalytic cracking
FCCU	fluid catalytic cracking unit
H/C	hydrogen/carbon
HCR	hydrocracking
HDAs	hydrodeasphaltenization
HDH	hydrocracking distillation hydrotreating
HDM	hydrodemetallization
HDN	hydrodenitrogenation
HDS	hydrodesulfurization
HDT	hydrotreating
HRI	Hydrocarbon Research, Inc.
HTI	Hydrocarbon Technology Inc.
HYCAR	hydrovisbreaking process
HYCON	Shell's trade mark for a hydroconversion process
HYD	hydrogenation
Hyvahl-F	IFP's trade mark for a fixed bed reactor hydrotreating process
Hyvahl-M	IFP's trade mark for a moving bed reactor hydrotreating process
Hyvahl-S	IFP's trade mark for a swing reactor hydrotreating process
IFP	Institut Français du Pétrole
IGCC	integrated gasification combined cycle
MHC	mild hydrocracking
MICROCAT	EMRE's trade mark for a residue hydroconversion process
MRH	Mild Residue Hydrocracking
NEBULA™	NEw BULk Activity, ExxonMobil
OCR	on-stream catalyst replacement
PV	pore volume
PdVSA/Intevep	Petroleos de Venezuela S.A.
RDS	residuum desulfurization
RFCC	residue fluid catalytic cracking
SDA	solvent deasphalting
STARS™	Super Type II Active Reaction Sites, Akzo Noble catalyst
STEM	scanning transition electron microscopy
SSA	specific surface area
SEM	scanning electron micrograph
UFR	up-flow reactor
TEM	transition electron microscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

[4,5]. In general, a fixed bed reactor is employed for HDT process. A series of catalyst (MoCo/MoNi) with different functionalities is usually loaded sequentially in the reactor(s), which will depend on the activity, selectivity and stability [6]. There are two types of process, the single-stage process and the two or multiple stage process. The single-stage process may contain two reactors but without separation. On the other hand, in the two-stage processes, the undesirable products (H_2S, NH_3, etc.) of the first stage are eliminated before the second stage. The most common reactor design for residue hydroprocessing is the down-flow and fixed bed reactor. The limitation in fixed bed reactor is the catalyst bed poisoning with time. Catalyst life depends on the rate of deactivation by coke and metal deposits and sintering of the active phases [7]. Information regarding the activity, selectivity, and deactivation of the individual catalyst is, therefore, highly desirable for optimizing reactor loading in the multiple catalyst systems. These parameters have to be optimum for hydroprocessing operation, which can be achieved by properly matching the type of reactor and catalyst, along with properties of heavy feeds.

The residue conversion adds a new dimension to refinery operations that requires the use of units to prevent high yields of coke and more beneficial yields of distillate products. Typically, heavy oil conversion involves two general routes: (i) carbon rejection, high coke formation, that is low atomic H/C ratio compound, and (ii) hydrogen addition, by means of a hydrocracking (HCR)/hydrogenolysis mechanism by which the yield of coke is reduced in favor of liquid products. Thus, process optimization is the key measurement for heavy oil in any petroleum refinery. Moreover, production of heavy crude is a changing scenario towards extra-heavy crude oil with higher sulfur, nitrogen and metal contents; simultaneously the demand for gasoline ends (<150 °C) is growing. Therefore, refiners are in dilemma to keep oil prices more or less steady in spite of treating the crudes with more expensive methods of processing. Apart from the desired refined products, the crude oil price depends on its specifications principally API gravity as is shown in Fig. 1. In this figure, the reported values are referred to year 2002 [8] and a comparison is made with values of year 2006.

The intention of this contribution is to review the basic aspects dealing with actual trends towards process technologies for upgrading of heavy crude oil and residua. Thus, a specific process or a sequence of them can be selected or

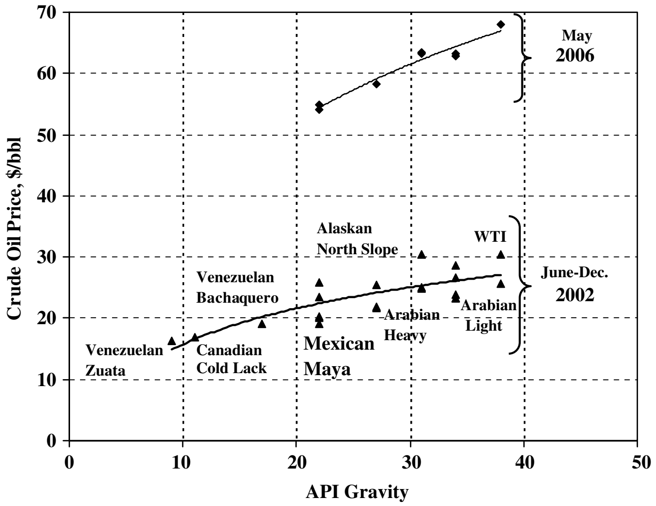

Fig. 1. Relationship between crude oil price and API gravity.

approved for each precise liquid yield, since refining world wide is towards increasing heavy oil and residua processing. The major objective is to cover the following elements of enormous interest in today's refineries:

1. to stress the recent advances in residue oil processing based on the literature;
2. to address the limitations when using heavy and extra-heavy oil for catalytic hydroprocessing.

2. Residue feed properties and its composition

The major problem with heavy oil fractions is the complexity of feedstock and analysis of its components. Efforts have been committed in order to analyze crude oil, using different methods which have given improved impending to the understanding of heavy oil composition [4,6]. Apart from the several other complex structures, asphaltene remains as one of the common uncertain molecules in heavy oil. Asphaltene is thought to be the most complex, high molecular weight, polar and highly aromatic in nature molecule present in petroleum. Nevertheless, microstructure of asphaltene residue has been studied [9,10], and it has been reported that in general, it is a large aromatic sheet, having high molecular weight, which is piled up on each other to form an unit cell and large associated asphaltene molecule. Additionally, few metalloporphyrins are also associated with asphaltene molecule via a π-electronic interaction as shown in Fig. 2.

Heavy crude oil and residue have many similarities in composition such as low H/C ratio (1.2–1.4), high metals and sulfur contents as shown in Table 1. Hence, one of the most important parameter is to convert residue into lighter products by increasing the H/C ratio [7]. Thus, in spite of some similarities between residue and heavy oil, residue feedstock differs in several ways such as its higher concentration of asphaltene, sulfur, nitrogen and metal compounds. However, the composition of such residua will depend on the origin of heavy or extra-heavy crudes (bitumen). Further extensive information on the properties of residue can be obtained in the literature [3,4,7,11].

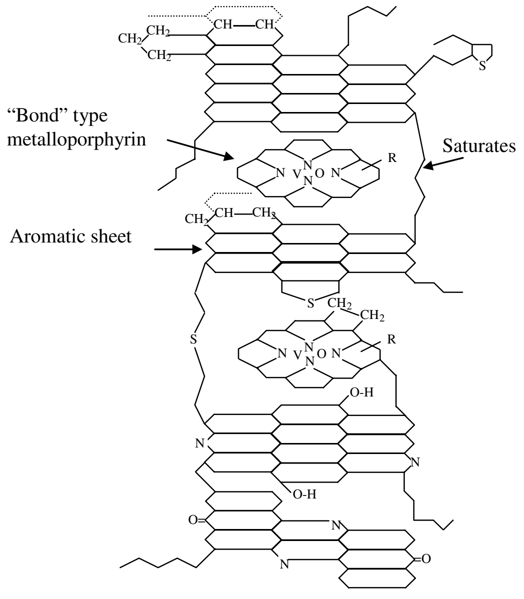

Fig. 2. Hypothetical asphaltene molecule and its interaction with metalloporphyrins [adapted from 10].

Table 1
Different residue composition and physical properties [8]

Crude oil	Gravity (°API)	Ni + V (ppmw)	S (wt.%)	C-residue (wt.%)	Residue yield (vol.% of crude)	
					AR, 343 °C+	VR, 565 °C+
Alaska, north slope	14.9	71	1.8	9.2	51.5	21.4
Arabian, safaniya	13.0	125	4.3	12.8	53.8	23.2
Canada, Athabasca	5.8	374	5.4	15.3	85.3	51.4
Canada, Cold Lake	6.8	333	5.0	15.1	83.7	44.8
California, Hondo	7.5	489	5.8	12.0	67.2	44.3
Iranian	–	197	2.6	9.9	46.7	–
Kuwait, Export	15.0	75	4.1	11.0	45.9	21.8
Mexico, Maya	7.9	620	4.7	15.3	56.4	31.2
North Sea, Ekofisk	20.9	6	0.4	4.3	25.2	13.2
Venezuela, Bachaquero	9.4	509	3.0	14.1	70.2	38.0

3. Residue upgrading background

The need to convert bottom of the barrel into cleaner and more valuable liquid products is continuously increasing. Residue represents a significant portion (up to 85% vol.) of a barrel of crude and its disposal treatment is not yet up to the mark. Thus, residue must be converted into more valuable products. On the other hand, to fulfill the fuel oil demand, processing of bottom residue of distillation column is an important process. The process economy of residue conversion is strongly affected by the amount of low value by-products and the amount of hydrogen in-put requirements. However, economy is not a constraint on the way of upgrading residue for refiners, but constantly a better amalgamation of economy and a product flexible slate, which will be an attractive route for hydroconversion of residue. There are two types of residue, depending on the source: atmospheric residue (AR, >343 °C) from atmospheric distillation tower and vacuum residue (VR, >565 °C) from vacuum tower obtained at 25–100 mmHg. The processing of these residues using various technologies can be classified in two main routes as shown in Table 2.

3.1. Non-catalytic residue processes

3.1.1. Solvent deasphalting

The residue contains high concentration of asphaltene, which can be solvent deasphalted by a separation process [12–14]. Solvent deasphalting (SDA) is a unique separation process in which residue is separated by molecular weight (density) instead of by boiling point. Solvent deasphalting process produces low contaminant deasphalted oil (DAO) that is rich in paraffin type of molecules. Solvent deasphalting has the advantage of being a relatively low cost process that has flexibility to meet a wide range of DAO qualities.

During SDA process, the feed is mixed with a light paraffinic solvent (propane, butane, pentane, or *n*-heptane), where the oil is solubilized in the solvent. The insoluble pitch will precipitate out of the mixed feedstock as asphaltene. The separation of the DAO phase and the pitch phase occurs in the extractor. The extractor is designed to efficiently separate the two phases and minimize contaminant entrainment in the DAO phase. At a constant solvent composition and pressure, a lower extractor temperature increases the DAO yield and decreases the quality. While an increase in solvent the DAO yield remains constant and improves the degree of separation of individual components and results in the recovery of a better quality DAO. The solvent recovered under low-pressure from the pitch and DAO strippers is condensed and combined with the solvent recovered under high pressure from the DAO separator, which is then recycled back to initial stage. DAO is normally used as FCC and hydrocracking feedstocks due to its low metal (Ni + V) contents.

Table 2
Classification of residue hydroconversion

Non-catalytic processes	Catalytic processes
Solvent deasphalting	Residue fluid catalytic cracking (RFCC)
Thermal	Hydroprocessing
Gasification	Fixed bed hydrotreating
Delayed coking	Fixed bed hydrocracking
Fluid coking	Slurry hydrocracking
Flexicoking	Ebullated bed hydrotreating
Visbreaking	Ebullated bed hydrocracking

3.1.2. Thermal processes (carbon rejection process)

Thermal conversion is an important process for residue conversion [15]. In general thermal cracking of residue is carried out relatively at moderated pressures and it is often called coking process. Coking process transfers hydrogen from the heavy molecules to the lighter molecules, resulting in the production of coke or carbon. The residue is hydrogen donors at high temperature and this process further decreases H/C ratio to values between 0.5–1, which significantly increase the coke formation. Individual description of these processes will give an idea about the merits and demerits in subsequent sections.

3.1.2.1. Gasification. This process involves complete cracking of residue into gaseous products, due to its un-controlled selective coal conversion, gasification has received comparatively less attention than other processes. The gasification of residue is carried out at high temperature (>1000 °C) producing syngas, carbon black and ash as major products [16,17]. Integrated gasification combined cycle (IGCC) is an alternative process for heavy residue conversion and an immerging technology for efficient power generation or electricity sector with minimum effect on the environment (low SO_x and NO_x) [18,19].

3.1.2.2. Delayed coking. Delayed coking has been selected by many refiners as their preferred choice for bottom of the barrel upgrading, because of the process inherent flexibility to handle any type of residua [20–22]. The process provides essentially complete rejection of metals and carbon while providing partial conversion to liquid products (naphtha and diesel).

The product selectivity of the process is based on the operating conditions mainly pressure and temperature. This process is more expensive than SDA, although still less expensive than other thermal processes [21]. The foremost disadvantage of this process is high coke formation and low yield of liquid products. Although these disadvantages, delayed coking is the most frequently preferred process for refiners to residue processing.

3.1.2.3. Fluid coking and flexicoking. Fluid coking and flexicoking are fluid bed processes developed from fluid catalytic cracking (FCC) technology. Fluid as well as flexicoking technologies are comparatively front runner technologies in residue processing [23]. In these processes, circulating coke carries heat from the burner back to the reactor, where the coke serves as reaction sites for the cracking of the residua into lighter products. Fluid coking can have liquid yield credits over delayed coking [23]. The shorter residence time can yield higher quantities of liquids and less coke, but the products have lower quality. Flexicoking is an extended form of fluid coking and uses a coke gasifier to convert excess coke to syngas, but the temperature (1000 °C) used is insufficient to burn all the coke. Fluid coking is a vaguely better process than delayed coking because of the advantage of a slightly improved liquid yield, also because delayed coking has higher utilities cost and fuel consumption. A detail account of these technologies was summarized by McKetta [24], whereas the mechanism of coke formation were described by Wiehe [25] and Speight [26].

3.1.2.4. Visbreaking. Visbreaking is a mature process that may be applied to both AR, VR and even solvent deasphalter pitch, which means a mild thermal decomposition or improvement in viscosity. A common operation is to visbreak residue along with a thermal cracker to minimize fuel oil while producing additional light distillates. Visbreaking is a process in which residue stream is heated in a furnace (450–500 °C) and then cracked during a low specific residence time, to avoid coking reactions within a soaking zone under certain pressure and moderate temperature conditions. The cracked product leaves the soaking zone after the desired conversion is reached, and then quenched with gas oil to stop the reaction and prevent coking. Although an increased conversion during visbreaking will turn to more sediment deposition [27]. In general, visbreaking is used to increase refinery net distillate yield.

The main operating conditions for thermal processes are compiled in Table 3. These processes are characterized by having low investment and operating costs than hydroprocessing as shown in Fig. 3, but the yield of light products tends to be lower, which is not likely by refiners. Moreover, liquid products obtained from thermal processes contain S, N and metals (V, Ni, etc.) that indeed need further purification by HDT process like HDS, HDN and HDM respectively. Thus, thermal process or coking based technologies suffer from the disadvantage of producing a large amount of low value by-products and require extensive further processing of its liquid products. Therefore, the importance of thermal processes remains lower than catalytic processes, but due to their lower investment these processes continue to be the most common for residue upgrading [8].

Table 3
Thermal processing technologies[a]

Residue technology	Licenser	Operating conditions	
		Temperature (°C)	Pressure (MPa)
Delayed coking	ABB LUMMUS FOSTER Wheeler/UOP ConocoPhillips	480–515	0.61
Visbreaking	ABB Lummus Global	450–510	0.34–2.0
Fluid coking	ExxonMobil	480–565	0.07
Flexicoking	Conoco-phillips Halliburton KBR	830–1000	
Gasification	Chevron Texaco	>1000	–

[a] Several literature based data.

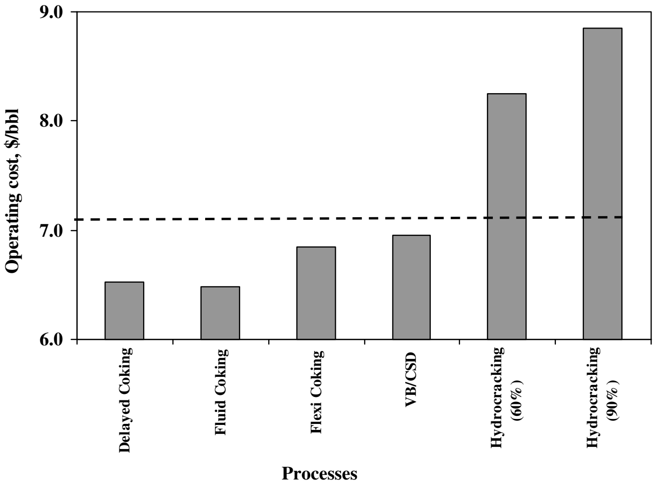

Fig. 3. Operating cost for some processes.

3.2. Catalytic residue processes

3.2.1. Residue fluid catalytic cracking

FCC is a well established approach for converting a significant portion of the heavier fractions of the crude barrel into a high-octane gasoline blending component. RFCC is an extension of conventional FCC technology that was developed during the early 1980, which offers better selectivity to high gasoline and lower gas yield than hydroprocessing and thermal processes. Because RFCC requires better feed quality, which makes this process less likely than hydroprocessing. In order to control heat balance and to recover part of the heat for steam production, RFCC process design includes two-stage regeneration, mix temperature control and catalyst cooler. The catalyst properties also play an important role to resist metal content and carbon deposition. In this respect catalyst pore structure limits the diffusion of residue on the catalytic sites. The catalyst used for RFCC is of acidic matrix such as crystalline aluminosilicate zeolite (USY or rare earth exchanged HY) in an inorganic matrix, which fulfills the required physico-chemical properties [28,29]. The major limitation of RFCC process is the need of good quality feedstocks (high H/C ratio and low metal content), which avoid perverse high coke yield, high catalyst consumption and unit operability. Therefore, this process can only treat atmospheric residue, which predominantly contains relatively low amounts of metals, sulfur and carbon. However, such kind of feeds are limited in refineries, moreover, the crude from which they are derived are high in price.

3.2.2. Hydroprocessing of residue

Hydroprocessing consumes a substantial amount of hydrogen and is relatively high in investment and operating costs compared with thermal processes with the expense of high product selectivity of light products [30]. In addition, hydroprocessing offers better selectivity of liquid yield (85% and higher) than any other process discussed above. The residue HDT improves the quality of liquid products, whereas residue HCR is the most rigorous form of residue hydroprocessing [31,32]. Various HDT processes developed over the years now provide the necessary toolbox, at the disposal of industry, to its objectives, with continuously improvement and of considerable diversity, for instance HDS, HDN, HDM and HCR. Therefore, not only the better product selectivity is one characteristic of hydroprocessing but also we can obtain cleaner fuel specifications. However, the race to high activity per volume unit for a long run is still matter of catalyst formulation and some process parameters optimization. The diversity stems from the hydroprocessing is not only the catalyst development, but also process technology, which can be selectively chosen on the basis of desired product yield. To maintain profitability, it is essential that these improvements should be made without compromising product yield. Moreover, these processes have enough scope to modify the process parameters and so the product selectivity and shifted the commercial importance of the technology [33]. The loading of catalyst into the reactors of a fixed bed residue HDT is generally composed of different types of catalysts, which are designed for the specific objectives e.g. HDS, HDM, HDN, mild hydrocracking (MHC) and CCR removal. Thus, basically residue hydroprocessing is a combination of catalyst development as well as process operation and its conditions.

3.2.2.1. Catalyst properties and composition. The catalysts used for residue hydroprocessing are sulfides of Co, Ni, W and Mo supported catalysts, which have a variety of pore structure and active metal dispersion (active sites). The most important property for residue hydroconversion catalyst is pore diameter because feedstock contains large molecules of asphaltene, metal chelated, etc. Broadly the bottom fraction or residuum of distillates crude is typically processed in trickle-bed reactors at temperatures of 350–450 °C and pressures of 5–15 MPa. Under these conditions, much of the metals such as Ni, V and Fe, which are present as porphyrin or chelating compounds, are deposited as metal sulfides (Ni_3S_2, V_3S_2 and V_3S_4, having 2–30 nm crystal size) over the catalyst. These deposited transition metal sulfides poison the catalyst by decreasing catalytic sites, hinder the transport of reacting molecule or eventually plugging the pores. The deposited metal sulfides can be confirmed by XRD as shown in Fig. 4, for spent catalyst used in Maya crude hydrotreating [34]. The deposited metal sulfides have been characterized by Smith and Wei [35,36] (TEM, EDX, STEM and XPS) for the HDM of model molecules on deactivated catalyst and by Takeuchi et al. [37] (XRD, ESR and SEM) on the catalysts used in HDM of heavy oil. The V_2S_3 phase was observed in acicular or rod shaped crystallites about 100 nm in length. Toulhoat et al. [38] reported that nickel is always associated with vanadium [$Ni(V_3S_4)$] and its crystallite grew perpendicular to the support surface. Apart from these metals, Ca, Mg and Fe sulfides are also possible to deposit on the exterior surface of the catalyst [39]. The major problem in residue oil is to eliminate asphaltene with respect to conversion as well as characterization due to its complex nature [40,41]. Additionally, the chemistry of asphaltene is not totally understood and its molecules are precursor to the most problematic organic deposits in residue e.g. sediment formation. During the reaction these huge molecules are allowed to diffuse into the catalyst pore and their metal-atoms (V and Ni) are removed from the ring structures. These results will lead to instability and finally to dry sludge, which is the dead point for any kind of catalyst stability. Therefore, the preferred catalyst design will result in the large quantity of metal deposition with time-on-stream, which will represent the catalyst life or stability.

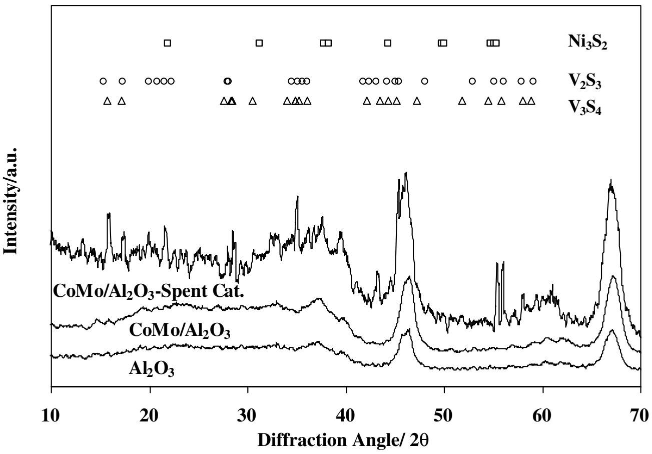

Fig. 4. Spent catalyst XRD and deposited metal sulfides (Maya crude, temperature of 380 °C, pressure of 5.4 MPa and LHSV of 1 h^{-1}, 60 h TOS; average pore diameter of catalyst of 17.3 nm) [34].

3.2.2.2. Catalyst deactivation. From the catalyst point of view this is the principal objective of the studies on design and preparation of catalysts for hydroprocessing of heavy feeds. This is carried out simultaneously with testing catalysts to identify optimal operating parameters for a heavy feed of interest. In general when the ratio of the intrinsic HDM activity to the asphalthene diffusion into and through the catalyst pore structure is too high, the metals will be removed from their organic environment towards the pore mouth, thus, restricting diffusion of reactant species into the pores. Since pore diameter plays an important role to control the heavy fraction HDT catalyst activity, therefore, the deposition of metal will depend on the pore diameter of catalyst as shown in Fig. 5. This figure also indicates the deposition of metal around the pore mouth, which increases with decreasing the pore diameter.

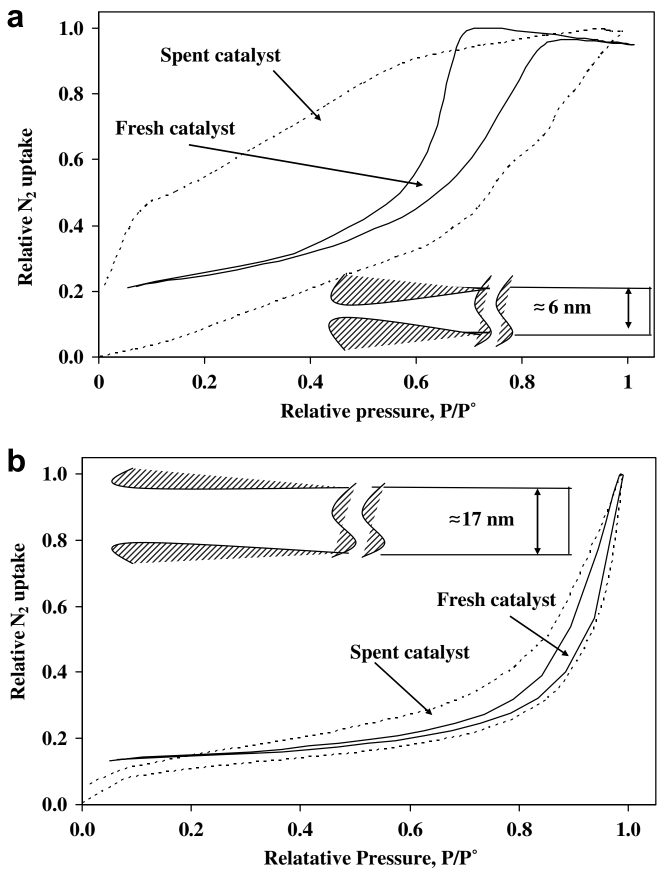

Fig. 5. Fresh and spent catalysts adsorption–desorption isotherms. (a) CoMo/γ-Al_2O_3 (6 nm average pore diameter) and (b) CoMo/γ-Al_2O_3 (17 nm average pore diameter) [43].

However, the location of reactor also will be a deciding factor with respect to pore diameter of the catalyst. In multi- and two-stage reactors the tail end catalysts have smaller average pore diameters, sharp pore distribution, high surface area, and high HDT activities. As these catalysts are more susceptible to pore mouth plugging, they have to be "protected" by the guard-bed catalyst, which should have large pore diameter, low surface area and high metal retention capacity. The effect of surface area and pore diameter and/or pore volume on catalyst deactivation and their applicability are different e.g. high surface area is expected to have high dispersion of active sites (high activity) while pore diameter controls the diffusion of complex molecule into the pores or the catalytic sites. Therefore, there is an optimum balance of surface area and pore diameter of the catalyst [42,43] as shown in Fig. 6, which balances the activity, diffusion properties and dispersion of active metals. Catalyst stability is improved as the macro-pores remain accessible to large molecules even after significant Ni and V deposition. The characteristic bi-modal pore structure provides high activity or metals retention capacity and stability [44]. In this regard several studies were carried by using different models as well as theoretical experiments to predict the deactivation through pore mouth [45–49].

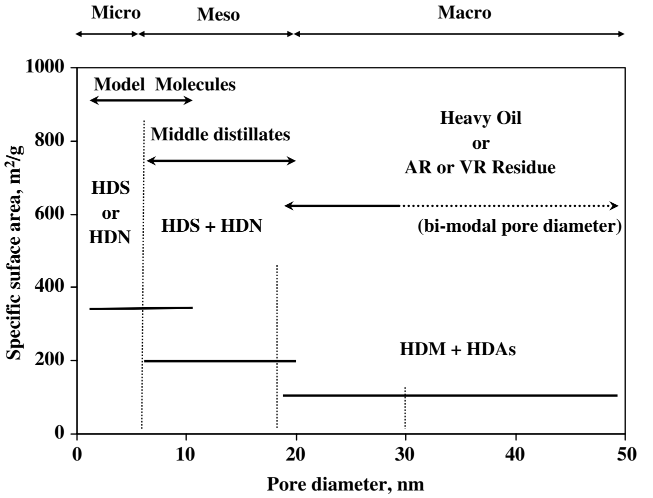

Fig. 6. Effect of pore diameter and specific surface area on hydrotreating catalyst activities [42].

3.2.2.3. Shape and size of catalyst particles. In spite of the significant advances of macro-porous or bi-modal pore catalyst development, diffusion problems encountered during hydroprocessing of residue cannot be entirely eliminated. The size of catalyst particles is another parameter deserving attention, especially for hydroprocessing technology in ebullating bed. For fixed bed reactor, the optimization of the catalyst size and shape requires a number of considerations, for instance extrudates and pellets allow the maximum quantity of catalyst to be packed in a given reactor volume. Spheres may offer improved abrasion resistance and lower pressure drop (ΔP). To consider the ΔP, rings are currently the most common shape favored, moreover, they have greater geometric surface area and improved diffusion of the reactants to the catalytic surface. Attrition is the second limitation, which is created during the reactor loading and causes high ΔP by plugging the filter and loss of costly active ingredients (active sites). Usually traditional hydroprocessing catalyst shape is a different lobed catalyst [42,50]. The tri-lobe and penta-lobe extrudate shapes also provide lower pressure drop compared with the traditional cylindrical extrudates [51]. Thus, a selection of proper size and shape of the catalyst can overcome the ΔP problem and in some extend the stability of the catalyst. Some shapes of particles, which may be suitable for hydroprocessing of heavy feeds were recently studied by reactor modeling [50]. The dense and sock loading, size and shape of particles are crucial physical characteristics of a fixed bed catalyst performance. The optimal matching of the particles shape with different types of catalytic reactors is reported in literature [51,52].

3.3. Residue hydroprocessing and its process technologies

Hydroprocessing is the combination of HDT and HCR processes in which residue feedstock is treated at low temperature but at high hydrogen pressure with or without catalyst. Most of the hydroconversion processes require catalyst, except few of them such as hydrovisbreaking. In general a working hydroprocessing catalyst is made of transition metal sulfides dispersed on high surface area support. Typical composition of the catalyst is 3–15 wt.% Group VIB metal oxide and 2–8 wt.% Group VIII metal oxide [11]. The catalyst has to be sulfided before its use. Detailed characterizations of sulfided catalysts can be found in the literature [1,53]. The catalyst loaded to fixed bed reactors is generally composed of a number of different types of catalyst, which are designed for specific process objectives as well as position of catalyst in multi reactor systems. Apart from the catalyst composition and multi reactor positions, various companies develop their own methodology to catalyst location as well as one-stage, two-stage or even multi reactor processes based on their available feedstock and required product selectivity [54,55]. Thus, considering one and other options there are a wide variety of process parameters, which are part of residue hydroconversion process. The upgrading process technologies selection is based on the combination of catalyst life, product yield and economy [56]. Usually, hydroprocessing technologies are of high investment due to the consumption of hydrogen, but the liquid product selectivity enhances by several fold than thermal processes. Hydrogen plays an important role in inhibiting coke formation over the catalyst by hydrogenation of coke precursor and removing hetero-atoms. Considering the different technologies, various kinds of processes are reported in Table 4 together with type of process and their licenser. In general the hydroprocessing technologies include fixed bed/moving bed/ebullated reactors and their combinations of two or multiple options.

Hydrovisbreaking Process (HYCAR): This is one kind of non-catalytic processes, which is based on visbreaking and involves treatment with hydrogen at mild conditions. This process is completed in three reactors: (i) visbreaking; (ii) demetallization; and (iii) hydrocracking. The first reactor uses mild thermal process in presence of hydrogen, the second reactor is to remove contaminants particularly metals, prior to HCR. The later reactor may employ inexpensive catalyst (CoMo catalyst) to remove metals and for cracking of complex molecule respectively.

Another extension of visbreaking process is *Aquaconversion (Hydrovisbreaking)*, which is a catalytic process using catalyst in slurry mode. This process was developed in 1996, UOP and Foster Wheeler-USA entered into a coalition with the research and technology support center of Venezuela's (PdVSA Intevep) Petroleum Organization. The alliance was to promote the commercialization and the ongoing development of Intevep's noble Aquaconversion process [57]. A shocker visbreaker is modified by the introduction of catalytic additives in feedstock and water steam. The presence of the oil soluble catalyst and water prevents the coke formation and deposition of sediment that often occurs during visbreaking [58,59]. In this process catalyst may be used as a support or mixed directly with the feedstock. The metals (metal salts) used for hydrovisbreaking are alkali metals such as potassium or sodium. The role of the catalyst is to enhance the dissociation of H_2O to release hydrogen (H^+) ions, which is subsequently consumed in hydroprocessing.

3.3.1. Fixed bed residue catalytic processes

Hydroprocessing of residue in fixed bed reactor is well established and reported in the literature [60–63]. The general characteristic of hydroprocessing technologies is also accompanied by simultaneous or sequential hydrogenation of hydrocarbon in presence of sulfided catalyst by reacting with hydrogen [64]. There is a wide variety of sulfided catalysts used for hydroprocessing but their application and effort in hydroprocessing reactions are not the aim of this

Table 4
Residue hydroconversion processes[a]

Reactor type	Process	Licenser
Fixed bed	Continuous catalyst replacement (OCR)	Chevron Lumus Global (CLG)
	UFR, Up-flow reactor	Shell (Bunker flow) Axen (Swing reactor)
	Hycon, Bunker type reactor	Shell
	Hyvahl, swing reactor concept	IFP (Axen)
Ebullated bed	H-Oil	Axen (HRI/IFP)
	T-Star	Chevron
	LC-Fining	ABB Lummus Amoco oil (BP)
Slurry system	Microcat – RC	ExxonMobil
	Veba combi-cracking	Veba Oel
	Hydrocracking distillation hydrotreating (HDH)	Intevep
	Cash, Chevron activated slurry hydroprocessing	Chevron
	EST, Eni slurry technology	Eni Technologies Snamprogetti
	CanMet	Energy Research Laboratories, Canada

HRI (Hydrocarbon Research Institute).

[a] Several literature based data.

review, nevertheless few major catalyst properties, which affect the process technology conditions as well as the conversion, are covered in short. The main problem with fixed bed catalyst is poisoning of catalyst over the time, which can be protected by a guard-bed reactor, in order to minimize the metal and coke deposition on the down stream reactors. Several processes combination using two or three processing steps can be implemented in the refining. Apart from the guard-bed reactor, the down streaming reactor contains typically an HDM catalyst or large pore catalyst [32,65,66]. It appears from the literature that an efficient residue hydrotreatment requires development of new catalysts including support and active metal, either by up-dating of former ones or developing new formulations. In this respect the catalyst development for residue hydroprocessing depend largely on support preparation [66–69], which plays an important role to generate porosity. Kressmann et al. [61] reported a microcrystalline form "chesnut-bur" like pores and non-acidic material. This catalyst has a large pore volume and an appropriate pore distribution, which allows the diffusion of asphaltenes into the catalyst pellet and their adsorption on the active sites. In this range of porosity, the catalyst has better metal retention capacity and asphaltenes elimination than HDS. The catalyst has high dispersion of metal and large pore diameter, which prevents plugging of the pore network and a high metal retention up to 100% based on the fresh catalyst [61].

Various improvements have been reported in the last decade such as run length, conversion, product quality and catalyst stability. Some of these improvements have been focused on mechanical design such as the use of bunker, swing reactors, guard-bed reactors, feed distribution, coke and metal deactivation resistant catalyst, including pore and particle grading and on-stream catalyst replacement.

3.3.1.1. Fixed bed residuum or vacuum residuum desulfurization (RDS/VRDS). In this process, AR or VR feedstock contacts with catalyst and hydrogen at 350–430 °C and 13–18 MPa consuming about 700–1300 scf H_2/bbl of feed [70]. The conversion increases with temperature, but due to the high coke deposition, the process is not feasible to use at high temperature. The RDS and VRDS do not convert directly to transportation fuel, but this process is able to produce acceptable feedstock for residue fluid catalytic cracking (RFCC). The basic process flow and catalyst for RDS and VRDS are the same.

RFCC is the extension of FCC technology and uses zeolite based catalyst in fluidized bed at temperature of 480–540 °C. The detail of this process is given in Section 3.2.1. Thus, a combination of RDS/VRDS and RFCC has gained wide acceptance due to the selective conversion of residue and smaller amount of by-products. The limitation for RFCC process is metal deposition, since Ni and V deposition increases olefin yields through dehydrogenation resulting in more coke formation, while gradual deposition of impurities in a catalyst eventually plugs the pores and deactivates catalytic sites [71]. Thus, nickel and vanadium adversely affect the behavior of cracking catalysts along with reducing product yield and quality. Additionally, after steam-stripping, the deactivated RFCC catalyst needs regeneration, which requires air or diluted oxygen in the regenerator to reduce carbon content. At the same time, vanadium, which is primarily deposited in the +4 oxidation state, is converted to the +5 state. During subsequent exposures to steam-stripping the vanadate becomes very mobile, presumably as vanadic acid, which is proficient to displace alumina from the zeolite structure [72,73]. This phenomenon is less severe in the hydrotreating and hydrocracking processes because in these cases catalyst regeneration takes place less frequently.

3.3.1.2. Hyvahl process. This process is used to hydrotreat AR and VR feedstocks to convert into naphtha and middle distillate respectively. Hyvahl process is mainly designed for feedstock containing high concentration of asphaltene, maltenes and metals that strongly limit catalyst performance. The reactor can be used in classical fixed bed (Hyvahl F) and moving bed (Hyvahl M). Recently IFP modified this process using "by-pass" guard reactor of a swing mode system under the brand name Hyvahl-S process. The major feature of this process is the fixed bed using swing mode reactor concept at high temperature, high hydrogen pressure and low contact time [74]. When the catalyst is deactivated in the first swing reactor or pressure drop is too high, the reactor switches off fast and the second reactor remains on stream, avoiding any product loss [75]. The switching of guard reactor and adjusting of conditions are fast and controlled by conditioning package.

3.3.1.3. Residue hydrocracking. The growing demand for middle distillates has increased the need for HCR in terms of process flexibility as well as configuration and product composition [76]. The catalysts used for HCR should have dual functionality, i.e. cracking and hydrogenation (HYD) functions. The process scheme of a typical HCR fixed bed system contains two reactors. The first reactor (1st stage HCR) contains HDT catalyst of high activity for the removal of hetero-atoms or metals, while second reactor (2nd stage HCR) contains the actual HCR catalyst. In general (HCR, IFP process) the first stage reactor contains NiMo catalyst, which removes S, N, metals and hydrogenated aromatics while the second reactor possesses acidic support (zeolite, mixed oxides) based catalyst that promotes hydrogenation as well as hydrocracking reaction.

In contrast to HDT, the support plays an active role in the conversion of the feed in HCR catalyst [77]. Many papers have been published on the detailed mechanism of rearrangement of cracking and the involved intermediate [78,79]. The performance of HCR catalyst is gauged by the ratio or balance between the hydrogenation metal (sulfide) site and the acid sites of support [80–82]. When the number of hydrogenating sites are low in comparison with the number of acid sites, secondary cracking processes can take place, resulting in light products. Additionally the hydrogenation function also prevents the oligomerization and coking over the acid sites. A deficient hydrogenation function will lead to rushed catalyst deactivation. On the other hand, when a very strong hydrogenation function is used, cracking is suppressed in favor of isomerization. In the so-called "ideal HCR" catalyst requires balanced between metal/acid functions [83]. There are several other hydrocracking processes used by refiners on the basis of their product selectivity such as: mild hydrocracking, isocracking, unicracking HDS, IFP hydrocracking process, MRH process etc.

Based on fixed bed reactor, we suggest that the problem can be partially solved by the selection of appropriate HDM and HDT catalysts, which contribute to increase the performance of new processes for residues refining. Until now, most of residue hydroprocessing reactors are fixed bed reactors. To have a look on their limitations, these processes must be shut down to remove (regenerate) the spent catalyst when catalyst activity declines below an acceptable level due to accumulation of coke, metals, and other contaminants [40]. In the fixed bed reactors, generally deactivation occurs in three steps: a rapid initial deactivation, slow gradual deactivation at the middle of the run and very rapid at the end of the run [84–88]. In this respect, fixed bed reactors may not likely use effectively for further processing of heavy oil and its residue.

3.3.2. Moving/ebullated bed residue catalytic process

There are a few types of hydroprocessing reactors with moving, or ebullating catalyst beds. In ebullated bed hydroprocessing, the catalyst within the reactor is not fixed. In such a process, the hydrocarbon feed stream enters at the bottom and flows upward through the catalyst; the catalyst is kept in suspension by the pressure of the fluid feed. Ebullating bed reactors are capable of converting the most problematic feeds, such as AR, VR and all other heavy oil feedstocks, which have high content of asphaltenes, metals and sulfur [89]. Ebullating bed reactors can perform both HDT as well as HCR functions thus; these reactors are referred as dual purpose. Ebullating bed catalysts are made of pellets or grains that are less than 1 mm in size to facilitate suspension by the liquid phase in the reactor [3,64,90]. In general, scaling up and design of these reactors requires data of feedstock composition, catalyst used and methods for complex units involved, in addition to the catalysis and chemical kinetics aspects, hydrodynamic phenomena but also mass and heat transfer problems at the catalyst pellet and bed scales [91–93]. From the catalyst point of view, moving bed catalysts are chemically quite similar to the fixed bed catalyst, except that catalyst particle and their mechanical strength and shape should meet the more demanding situation.

3.3.2.1. HYCON moving bed hydroprocessing. The HYCON process is typically operated in fixed bed mode but with increasing the metal content in feedstock, one or more moving bed "bunker" reactors are added as the leading reactors for HDM. In this process catalyst and residue operates in co-current flow, the fresh catalyst enters at the top of the reactor, while deactivated catalyst is removed from the bottom. Shell moving bed bunker technology was successfully demonstrated in Pernis HYCON unit in 1989 [94–96]. The catalyst is replaced at a rate to insure a total plant run time of at least a year, which depends on the metal contaminants in the feed.

For catalyst technology used in HYCON moving bed, different bunker catalysts have been developed. A type regenerable catalyst with high metal uptake capacity is suited to process very high metal content feedstocks. The Pernis unit (HYCON) has been started up with this catalyst, but regeneration (Shell-designed) of the spent HYCON catalyst has never been economic. Another type of catalyst with a high metal uptake capacity at high temperature operation and regenerable can be ideally suited for economic processing of very high metal (>500 ppm) feeds [39].

3.3.2.2. Ebullating bed residue hydroprocessing technology. In the ebullating bed process, hydrocarbon feed and H_2 are fed up-flow through a catalyst bed, expanding and backmixing the bed, minimizing bed plugging so the lower ΔP. The ebullated bed technology utilizes a three-phase system that is gas, liquid, and solid (catalyst). In this process, oil and catalyst is separated at the top of the reactor and catalyst is re-circulated to the bottom of the bed to mix with the new feed. On the other hand, fresh catalyst is added on the top of the reactor and spent catalyst is withdrawn from the bottom of the reactor. There are two most important ebullated bed processes, which are similar in concept but different in mechanical details that are given individually in subsequent sections.

3.3.2.2.1. H-Oil process. The schematic ebullating bed reactor of the H-Oil process is shown in Fig. 7 [97]. This process was first commercialized in 1960s by HRI (Axen). The H-Oil ebullated bed process can operate over a wide range of conversion levels and is particularly adapted to heavy vacuum residua with high metals and conradson carbon [94,98,99]. Another major advantage of H-Oil is to maintain constant product properties during the cycle length. Since H-Oil reactor has the unique characteristic of stirred reactor type operation with a fluidized catalyst, it has the ability to handle exothermic reactions, solid containing feedstock and a flexible operation while changing feedstocks or operating objectives such as the use of single-stage or two-stage processes.

The T-Star is an extension of H-Oil process and is another ebullated bed process. T-Star units can maintain global conversions in the range of 20–60% and specifically HDS in the 93–99% range. The unit can act as either an FCCU pretreater or VGO hydrocracker. H-Oil catalyst can be used in the T-Star process. A T-Star reactor can also be placed in-line with an H-Oil reactor to improve the quality of H-Oil distillate products such as virgin distillates,

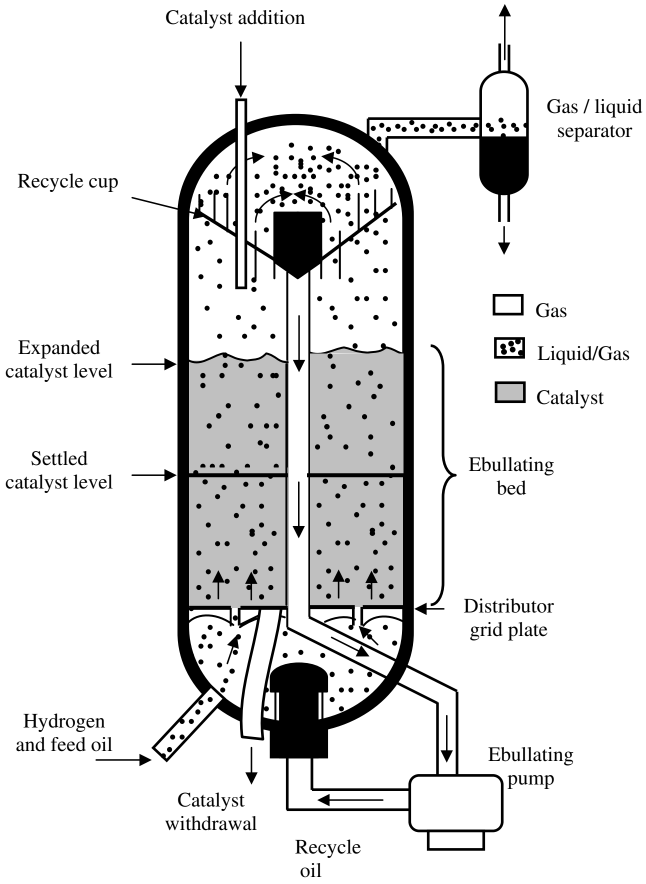

Fig. 7. Schematic representation of the H-Oil reactor, IFP [97].

FCCU light or heavy cycle gas oil, and coker gas oils. In mild hydrocracking mode, the T-Star process can reach conversions up to the 60 vol.%. An advantage of operating the T-Star unit in mild hydrocracking mode is that the T-Star catalyst is not sensitive to sulfur and nitrogen levels in the feed and will provide constant conversion, product yields, and product quality [100]. This consistency in output is due to the reactor catalyst being replaced while the unit remains on-line. A commercial scale demonstration of the T-Star process in conjunction with the startup of H-Oil units was done as a joint venture between Husky Oil, Canada and IFP [64].

3.3.2.2.2. LC-Fining. The LC-Fining ebullated bed process is a hydrogenation process which can be operated for HDS, HDM, and HCR of atmospheric and vacuum residues. LC-Fining is well suited for extra-heavy residue, bitumen and vacuum residue HDT feedstocks and has demonstrated long cycle lengths [101]. The general advantages of LC-Fining are: low investment, more light-ends recovery and lower operating costs. This process yields a full range of high quality distillates; heavy residue can be used as fuel oil, synthetic crude, or feedstock for a resid FCC, coker, visbreaker or solvent deasphalter. The LC-Fining process can achieve conversion for HDS of 60–90%, HDM of 50–98%, and CCR reduction of 35–80%.

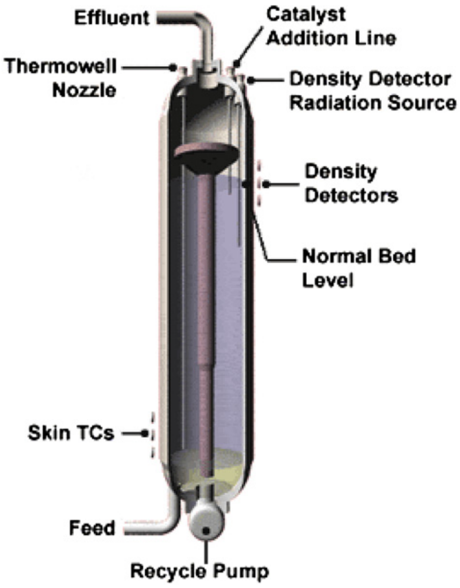

Fig. 8. LC-Fining reactor [101].

The process parameters and reactor design are marginally different than H-Oil process as shown in Fig. 8 [101]. Fresh liquid feed is mixed with hydrogen and both react within an expanded catalyst bed that is maintained in turbulence by up-flow liquid to achieve efficient isothermal operation. Product quality is constantly maintained at a high level by sporadic catalyst addition and withdrawal. Reactor products flow to the high-pressure separator, low-pressure separator, and then to product fractionation. Recycled hydrogen is separated and purified. Process features include on-stream catalyst addition and withdrawal, thereby eliminating the need to shut down for catalyst replacement. The expanded bed reactors operate at near isothermal conditions without the need for quenches within the reactor. The reaction section uses a commercially proven low-pressure hydrogen recovery system. Separating the reactor effluent and purifying the recycled hydrogen at low-pressure results in lower capital investment and allows design at lower gas rates.

Operating conditions of ebullated bed processes (H-Oil and LC-Fining) are summarized in Table 5. Ebullated bed processes can use extra-heavy feeds residues with elevated sulfur, nitrogen, and metals content (i.e. compared with other crude oil distillation cuts) and do not require pretreatment prior to the ebullated bed process. These processes have high liquid yield, however the conversion is not 100%. For any type of feedstock, high sulfur reduction is seen in all products with significant nitrogen reduction, but to a lesser degree than the sulfur.

3.4. Slurry residue hydroprocessing

Slurry hydrocracking has an unusual history; it was first used in Germany as early as 1929 for hydrogenation of coal and two units were successfully working during the World

Table 5
Some of the ebullated bed process and operating conditions [90][a]

Parameter		H-Oil	LC-Fining
Temperature (°C)		415–440	385–450
Pressure (MPa)		16.8–20.7	7.0–18.9
LHSV (h^{-1})		0.4–1.3	–
Catalyst replacement rate (kg/ton feed)		0.3–2.0	–
Single train throughput (bpsd)		up to 34,000	–
H_2 use pie^3/b		1410	1350
Conversion (%)		45–90	40–97
HDS		55–92	60–90
HDM		65–90	50–98
Products (% w/w)			
C_1–C_4	3.5	C_4=	2.35
C_4–204 °C	17.6	C_5–177 °C	12.6
204–371 °C	22.1	177–371 °C	30.6
371–565 °C	34.0	371–550 °C	21.5
C_4>	22.8	550 °C+	32.9

[a] Several literature based data.

War II, which were switched to VR feed and operated until 1964. Different commercial slurry units gain importance such as Veba combi-cracking, CanMet, Microcat, CASH process etc. Later Veba unit shut down while the Petro Canada CanMet unit operates when refinery conditions dictates [8]. But recently both units have operated again for very poor quality feedstocks. Eni slurry technology (EST) process is moving towards the commercial proof at one of the Agip's refinery in Italy. The important modifications have been claimed by ENI for slurry processes (EST); the modifications mainly concern the possibility of obtaining high conversions while maintaining the stability and processability of the residues. In general, in slurry hydroprocessing a selected catalyst is dispersed in the feed to inhibit coke formation, which has been studied extensively for full and partial upgrading applications [102–104].

The CanMet HCR process was intended to hydrocrack heavy oils, AR, VR and the technology was developed by Canadian Research Center for Mineral and Energy technology, which was through Petro Canada Montreal refinery. The process was developed with the aim of hydrocracking heavy pitch containing indigenous clay mineral using a coke inhibiting additive, which would not be poisoned by the high metal content in the feed. The inhibition additive was prepared with iron sulfate, which promotes hydrogenation and prevent coke formation. Coal and a disposable coal-based catalyst are slurried with a petroleum vacuum residue or bitumen, mixed with H_2 and fed to a single-stage up-flow reactor. Typical operating conditions are: reactor temperatures of 440–460 °C, pressures of 10–15 MPa with feedstock coal concentrations of 30–40 wt.% (mineral matter-free basis). The reactor product is separated and fractionated to recover distillate products and distillable residue. The extent to which coal is converted is highly dependent on coal characteristics, but may be as high as 98% on a dry ash-free basis. The conversion of high-boiling material in the bitumen or VR may be up to 70%, depending on reaction severity. The process also offers attractive options for reducing coke yield by slurring the feedstock with less than 10 ppm molybdenum naphthanate catalyst [105].

However, the effectiveness of the slurry hydroprocessing technology is highly dependent upon catalyst selection that is, a slurry catalyst with poor activity will result in coke formation and a biphasic, incompatible product. Initial guidelines used to screen the potential of a catalyst for the hydroconversion process include coke suppression and product compatibility; the latter defined as the asphaltenic fraction of the product oil remaining in solution [106]. Hydroconversion research using finely dispersed catalysts in the process feed has typically been approached via two methods. The first approach involves an in situ preparation of finely dispersed (slurry) catalysts from oil soluble/oil dispersible or water soluble precursors, and the second by impregnating small particle supports with catalytic metals. Slurry catalysts, typically molybdenum-based, prepared from oil soluble or water soluble precursors have been investigated extensively [107,108]. These catalysts characteristically possess high surface areas and micron scale particle sizes that consist of a metal sulfide within an asphaltenic matrix. These so-called micro-metallic-coke or micro-cat catalysts efficiently convert low value heavy feeds to a single-phase product with increased API gravity, lower viscosity and reduced contaminants.

Other metals have been screened as potential slurry catalysts and include transition metal-based catalysts derived from vanadium, tungsten, chromium, iron, etc. [108]. Recently, Headwaters Technology Innovation Group (HTIG) proposed an homogeneous catalyst based hydrocracking technology [$(HC)_3$™ Technology], which has been developed for upgrading of indigenous heavy crude or bitumen [109]. In this process the HCR catalyst is homogeneously dispersed as a colloid with particles similar in size to that of asphaltene molecule, which results in high conversion of asphaltene. The $(HC)_3$ process also has been proposed as a process for crude oil transportation shipped by pipeline without a diluent [8,110].

4. Selection of residue upgrading process (developing technologies)

The summary of the above discussed processes indicated that the carbon rejection processes include visbreaking, thermal cracking, coking, deasphalting, and catalytic cracking. The hydrogen addition processes include catalytic HDM, HDS, HDN, hydrogenation, and HCR fixed bed, moving bed, ebullating bed, or slurry phase reactors. On the basis of low value product a comparison of these processes is reported in Table 6. These results indicated that thermal process produce large amount of coke and undesirable products, while RDS/RFCC strongly favor the residue processing but due to unavailability of good

Table 6
Comparison of residue conversion processes [70]

Process	Coke yield (wt.%)	Products	
		Low value by-products	Direct products (%)
Delayed coking	32	Coke	0
Fluid/flexicoking	29	Coke or low Butane gas	0
RDS/delayed coking	17	Coke	0
H-Oil/LC-Fining	–	10–40% Un-converted bottom	0
RDS/RFCC	13	Steam	50–60
VRDS/RFCC	8	Steam	50–60

Coke yield on Arabian heavy VR basis.
Direct products are transportation fuel blendstocks without further processing.

quality feedstock this process is not likely by refiners. A general selection process for residue hydroconversion as a purification of metal, carbon, sulfur and API gravity of the feed is shown in Fig. 9. Recently the hydroprocessing application range has been reported to cover feeds with heavier amount of contaminants with lower API gravity, which is mainly due to the use of catalyst with improved stability as well as operating conditions and proper reactor selection to work under moderate conversion regime so that sediment formation is minimized. This process is still at demonstration scale [111]. The major problems in fixed bed residue processing are the coke and metal depositions on the catalyst. Coke deposit is almost impossible to avoid and occurs during the first hour on-stream while metal deposit is found during the whole on-stream time. Hence, to expand the applicability of fixed bed reactor based technologies the use of catalyst with high metal retention capacity together with guard-bed reactor is mandatory.

Using one or other process, a low value material is converted to a high value fuel. However, for producing low sulfur fuels, the costs associated with the deep HDS suggest that individual application of these methods for production of liquid fuels should be re-examined and compared with the cost of fuel products produced by conventional methods. Other process alternatives, such as hybrid schemes of fixed bed or ebullated bed technologies with thermal processes, may deserve more analysis from technical and economic point of view.

It has been noted that high conversions were achieved when fine catalyst particles were slurried/dispersed in a residue feed. With respect to catalysts, this may be a "once-through" option. Thus, it may not be possible to recover catalyst for reuse. Low cost, throw-away materials possessing catalytic activity may be identified. In this case, the once-through option may be more attractive. The properties of AR and VR feedstocks, particularly content of metals and asphaltenes, should be clearly established above which hydroprocessing becomes less attractive than carbon rejection methods. Thus, coking of high metals and asphaltenes heavy feeds, such as residues derived from heavy crudes, may have more merit, particularly if it is integrated with an efficient utilization of petroleum coke. Thus, asphaltene is the target molecule, which deactivates catalyst either using fixed bed or moving bed processes. In this regard, the solvent deasphalted could be an important process. Therefore, separation of asphaltene before hydroprocessing could be an option to modify the process and one step advance towards the deeper and stricter environmental legislation as well as catalyst stability. A proposed process based on these considerations is shown in Fig. 10. The integrated process indicates that once the asphaltene separated from the residue, the deasphalted oil (DAO) is easier to process in hydroprocessing units. While the heavy asphalt or pitch can be processed through thermal process using gasification to complete conversion, which will produce synthesis gas (CH_4, H_2, CO) as a major products. Further depending on the need of fuel oil, the synthesis gas may be

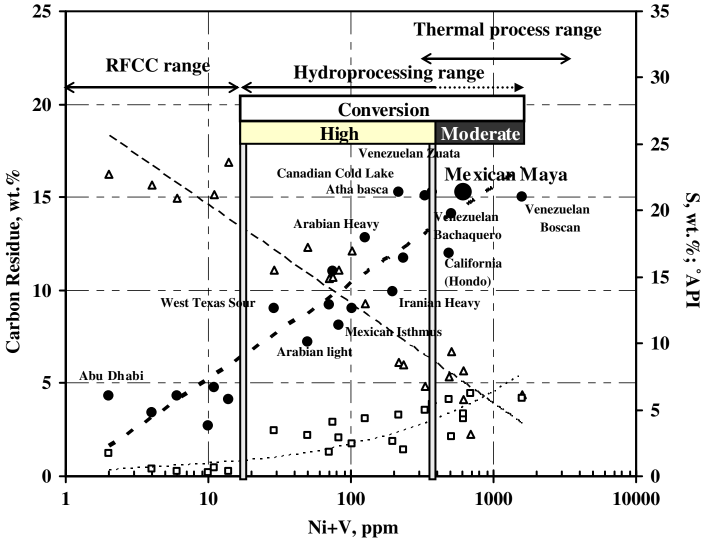

Fig. 9. Choices of process for residue hydroconversion as a function of 343 °C residue properties [(●) Carbon Residue; (□) Sulfur; (△) API gravity].

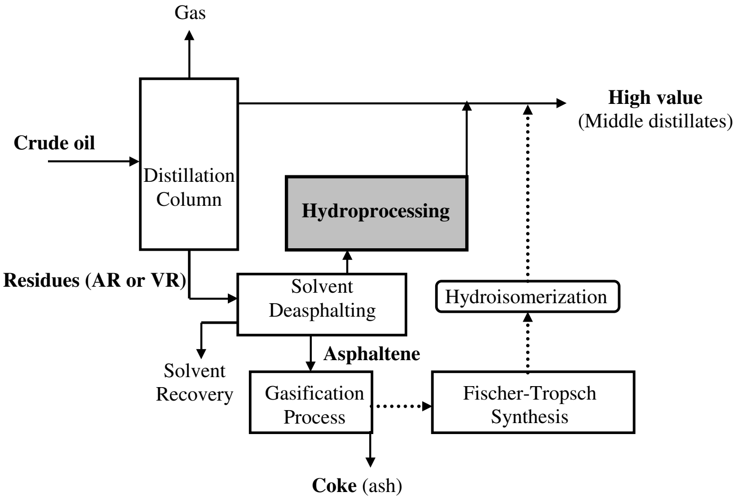

Fig. 10. Integrated solvent deasphalting (SDA), thermal and hydroprocessing processes.

converted into kerosene or gas oil pool by using Fischer Tropsch synthesis and Isomerization processes [112]. Apart from the suggested process there are several other process options which have potential capacity for residue hydroprocessing such as slurry process, H-Oil, LC-Fining, HYVAHL multibed unit and moderate hydrotreating [111]. Using these catalytic processes, in order to maximize both performance and cycle length, catalyst designed must be macro-porous, which avoid poisoning of active phases, pore plugging by metal sulfide and coke deposition with time-on-stream. In any case, using guard-bed reactor system is highly desired, since it retains multifaceted organometallic and obstinate particulate.

Unfortunately there is not a general rule that can give a solution to all refineries in one option, because there are many factors to take into consideration like: oil prices of products, market trends, local needs, physical and chemical properties of the available heavy oil and residua, as well as refinery configuration, which are closely involved and must be taken into account to define an specific upgrading scheme process. Therefore, each refinery will define its own scheme for heavy oil upgrading. In other words, there is not one single upgrading solution that fits for all refineries.

5. Future prospective

Recent advances in residue upgrading technology are focused on the production of high quality transportation fuels from low quality and low H/C ratio or high boiling fraction of crude oil. Significant literature compilations have been made to understand the role of various conventional processes during residue hydroconversion. Different processes have shown beneficial effect to slow down deactivation and thus prolonging catalyst life. In regard to catalyst activity, it can be modified by supports by using more acidic (zeolites) material than conventional catalyst (supported γ-Al_2O_3) which improves cracking activity, but they also may increase the rate of coke formation. This increase in acidic properties will enhance selectivity towards light distillates, which will impact positively on the process global profitability. It has been shown earlier that properties of supports are crucial for defining the desirable porosity and surface area of catalysts. However, the catalyst performance can be modified by chemical composition of supports, in this sense it is well established that mixed oxide support can be prepared with acid–base sites [66–69], which improve cracking functionality of the catalyst [113–115]. Therefore, with respect to catalyst development, additional research is needed to design a catalyst with desirable HCR activity (bi-function), and at the same time be resistant to deactivation. However as was already mentioned, with an increase in acidity of catalyst more coke production is expected but if acidity is controlled properly beneficial effects may be obtained on the cracking functionality. It is believed that during hydroprocessing of heavy feeds, catalyst life can be further prolonged by applying balanced (high pore volume and low surface area) textural properties of catalyst. On the other hand, for two-stage reactor process H_2S and NH_3 scrubber is advised due to the inhibition effect through competitive adsorption or poisoning of acidic sites respectively. Inhibition effect has been shown to be effective only for HDS, HDN and HCR, while HDM activity is likely to increase with partial pressure of H_2S [116]. These process medications and development mainly depend on the reduction of operating cost and commercial investment. Moreover, any change or improvements need to be under feasibility of refinery and methodology applicable to the industrial scale. In fixed bed units, catalyst deactivation during the run is compensated by a progressive increase in bed temperature up to a certain value dictated by metallurgical constraints or product qualities. The end-of-cycle is usually determined by a level of activity, which turn too low to meet product specifications, but it also can be due to a unit upset (high ΔP, compressor failure, hydrogen shortage), or to a scheduled unit shutdown. Deactivation is due to three main causes: carbon (or coke) lay down, metal poisoning and active phase sintering. The detrimental effects of coke are a reduction of support porosity, leading to diffusional limitations, and finally blocked access to active sites. Nevertheless, moving bed or ebullated bed processes alone or in combination with fixed bed reactor technology and/or also coupled with thermal processes employing suitable catalyst with metal retention capacity represent the most efficient way of handling petroleum bottoms and other heavy hydrocarbons for upgrading. The features of the resulting process configuration will be high liquid yields, high removal of contaminants, and reliable operation.

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