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Review

Catalysis for heavy oils and bitumen upgrading

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ABSTRACT

More than half of the world oil reserves are heavy oil and bitumen, with vast deposits in Canada and Venezuela. They are more difficult to produce and refine than conventional oils. Even though the current commercial processes are based on thermal treatment of the heavy feeds, it is recognized that catalytic processes with hydrogen addition produce higher yields of liquid fractions with better quality. Most of the catalysts reported for upgrading of heavy oils and bitumen are similar to those commonly used in hydrotreating/hydroprocessing, i.e., Co(Ni)Mo(W) supported on alumina. However, it has been shown that catalyst's textural properties need to be tuned up according to the targeted reactions (HDM/HAD or HDS/HDN) to avoid poisoning. Due to the problems associated with the poisoning of supported catalysts the use of unsupported particles have been proposed as an alternative for treating heavy oils and bitumen. Catalysts containing Mo, W, Ni and Co, tested under high pressure of hydrogen produce better conversions, and lipophillic precursors seem to perform better than emulsion or dispersed powders. Catalytic aquathermolysis of heavy oils with water soluble and oil-soluble metallic compounds, as well as amphiphilic and ionic liquids, or dispersed particles of different metals, have been reported to produce important viscosity reductions. Also, downhole processing has been proposed to produce synthetic oils in the reservoir thus reducing energy demands and decreasing emissions. Different process configurations have been reported: *in situ* combustion coupled with a supported NiMo/Al_2O_3; injection of an amphiphillic metal compound in aquathermolysis conditions; and the injection of catalytic nanoparticles dispersed in a hydrocarbon carrier with dissolved hydrogen. All of them report important viscosity reductions and increase in API gravity. Finally, only a few reports on kinetics for upgrading of heavy oils and bitumen can be found. Models based on lumps according to the distillation cuts seem to produce consistent results for different oils, catalysts and reaction conditions.

KEYWORDS: heavy oils, bitumen, upgrading, *in situ* upgrading, catalytic upgrading

1. INTRODUCTION

The world's population is steadily growing with higher demands on the quality of life, in turn increasing the energy consumption. According to the International Energy Agency base scenario, world demand for primary energy should have risen 20% in 2010 and will continue to rise 66% by 2030 [1]. To cope with this ever-increasing world energy demand, the exploitation of all possible energy resources will be necessary. In this scenario, hydrocarbons will continue to play a very prominent role in meeting world energy requirements, and in particular heavy crude oils, given the magnitude of their resources, are expected to have a more significant role.

Between 30 and 47% of the world total oil reserves is in the form of conventional oil, with the rest (53-70%) being unconventional heavy oils and bitumen [2, 3], and the world wide trends indicate that the supply of conventional oil will

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continue to decline with the corresponding increase in the production of heavy crudes. However, due to the increase in the demand of light feeds, together with stricter regulation regarding the protection of the environment, refineries now face the need to process and convert heavier oils into lighter and more valuable products.

Heavy oil, extra-heavy oil and natural bitumen are the result of degradation of conventional oil, mainly by bacterial action [4]. Bitumen deposits are also called tar sand, oil sand or bituminous sand [4]. These oils are characterised by their high viscosity, high density (low API gravity), and high concentrations of nitrogen, oxygen, sulphur, and heavy metals.

Heavy and extra-heavy (H-XH) oils and bitumen are differentiated according to their viscosity and density or API gravity (See Table 1).

Even though H/XH oils and bitumen represent a huge amount of total oil resources, they are only a small share of the world oil production. Due to the huge deposits worldwide, however, they are getting a higher proportion of the market. In recent years refining processes are being technologically modified to be able to cope with heavier crude oils, i.e., refineries are processing feedstocks with lower API gravity, hydrogen-to-carbon (H/C) ratio, and a higher content of sulfur, nitrogen and metals.

In order to be transported and/or processed in refineries, H-XH crudes and bitumen first require upgrading. Upgrading can be defined as any thermal or chemical treatment of heavy oil or bitumen that increases its value by producing higher quality oil (synthetic crude oil, SCO). During the upgrading process the API gravity of the oil is increased, the viscosity is reduced and, in general, sulfur, nitrogen, metal and aromatic content are also decreased.

Table 1. Heavy oil, extra-heavy oil and bitumen [1, 4, 5].

Type of oil	Viscosity/cp	API gravity/°
Heavy	<10,000	10-20
Extra heavy	<10,000	<10
Bitumen	>10,000	<10

Viscosities are referenced to original reservoir temperature. API gravity = [(141.5/Specific gravity)-131.5]. Specific gravity is referenced to 15.6 °C (60 degrees °F) and atmospheric pressure.

Upgrading technologies developed in the 70’s and 80’s were aimed at the conversion of the bottom of the barrel to distillate oils, and were also explored for the upgrading of heavy hydrocarbons such as tar sand bitumen and Orinoco belt crude.

Two main processing routes for heavy oil and bitumen upgrading are normally employed: 1) Carbon rejection or thermal processes (e.g., de-asphalting, visbreaking, delayed-, fluid- and flexi-coking), which have been used commercially for decades, and 2) hydrogen addition processes.

The carbon rejection process is a thermal process, which consists of the formation of a solid carbonaceous product called coke by removing the hydrocarbons with the lowest hydrogen to carbon ratio (such as asphaltenes and Conradson carbon residue), and the production of cracked distillates. Part of the sulfur and nitrogen compounds and most of the organometallic compounds of nickel and vanadium are removed together with the coke.

Hydroprocessing is the best example of the hydrogen addition route and produces higher yields of liquid fractions than thermal processes, but requires a catalyst and the presence of high pressure of hydrogen. It is a thermal catalytic process that adds hydrogen to the feed, thus elevating the hydrogen to carbon ratio, and reduces the formation of coke. During hydroprocessing, hydrocracking of heavy fractions and removal of sulfur, nitrogen and metals is accomplished while also producing lighter oil products.

In the present contribution, the work published in the open literature concerning the catalytic upgrading of H/XH oils and bitumen is reviewed. The many reports on the use of upgrading catalysts using model molecules will not be considered since the focus of this review will be on papers dealing with the catalytic treatment of real feedstocks (heavy oils and bitumen). Also, a significant number of reports related to hydroprocessing and upgrading of heavy oils are in fact about processing atmospheric or vacuum residua, and will not be part of this publication.

For processes and technologies used in upgrading and hydroprocessing, the reviews by Kressmann *et al.* [6], Chrones and Germain [7], Rana *et al.* [8] and Liu *et al.* [9] are recommended.

The present report reviews both old and new ideas on catalysts and processes for H/XH oil and bitumen upgrading, such as:

- Supported catalysts, which were most commonly used in the early works about heavy oil upgrading.
- Unsupported catalysts, which are usually dispersed in the feedstock to be treated, and have been recently explored as an interesting alternative to supported catalysts.
- Catalytic aquathermolysis (treating the heavy oil in the presence of steam and catalysts at high temperature and pressure) has also been proposed as an alternative process for heavy oil upgrading that conduces to cracking and mild hydrogenation of the feed.
- *In situ* (or downhole, in reservoir) upgrading, which has been identified as a possible route to produce "synthetic" oil, with a few papers appearing on this subject. Research on *in situ* upgrading (ISU) is gaining interest since it could reduce the environmental footprint for heavy oil production and refining, as well as increase recovery factors.
- Kinetic studies regarding the hydroprocessing and upgrading of H/XH oils and bitumen.

2. Upgrading with supported catalysts

High concentrations of asphaltenes present in heavy oil are expected to have a detrimental effect on the activity and life of the catalysts. Since asphaltenes are large molecules with highly condensed heterocyclic and aromatic rings, and where most of the sulfur, nitrogen and metals are concentrated, their diffusion into catalyst pores will be difficult, and they will produce coke and metal sulfide deposition on the catalyst surface. This fact led to the initial developments on catalytic processes for heavy oils and bitumen upgrading to be derived from the processes specifically designed for the treating of the bottom of the barrel or vacuum and atmospheric residue. Those developments were driven by the belief that for effective heavy hydrocarbon upgrading, a commercial catalyst must have specific pore structures that will allow metals and carbon to be continuously deposited on the catalyst surface while keeping activities for demetallization and asphaltene conversion over a long period of time. Thus, Shimura *et al.* [10], reported the effect of the catalyst pore structure in vanadium removal and asphaltene conversion using Boscan crude oil (asphaltenes 11.9 wt.%, sulfur 5.52 wt.%, vanadium 1190 wppm, nickel 112 wppm and API 9.4°). A series of CoMo supported on alumina catalysts with median pore diameters of 128, 169, 264, 300, 360 and 610 Å (determined by mercury porosimetry) and surface areas of 175, 217, 183, 210, 113, and 83 $m^2 g^{-1}$, respectively, were used. The composition of the catalysts was not reported.

Using a continuous flow reactor (678 K, 1.0 h^{-1}, hydrogen to oil ratio 1000 standard (std). $cm^3 cm^{-3}$) it is reported that the deactivation of the catalysts show three distinct steps. An initial rapid deactivation curve, which is proposed to be due to the deposition of metal sulfides and carbon, was found. An intermediate step of almost no deactivation is followed by another accelerated decline in activity, attributed to constriction of the catalysts pore mouth due to further deposition of metal sulfides. An optimum media pore diameter was observed for maximum catalyst activity, which is around 200 Å, and seems to be slightly different for vanadium removal and asphaltene cracking reactions. A mathematical expression derived from a deactivation model that considers the loss in pore volume due to metal sulfides deposition with reaction time is proposed. This model predicts rather well the experimental values obtained for the deactivation as the metal sulfides are deposited in the catalysts.

Shimura *et al.* [10] main findings can be summarized as:

- To optimize the decomposition of asphaltenes in heavy oils an adequate pore size of a carrier, that allows sufficient diffusion of large asphaltenes molecules inside the pore structure of the catalyst, must be selected.
- For HDM and asphaltene removal reactions there is an optimum catalyst pore diameter.

Ancheyta *et al.* [11] studied the hydrodemetallization of Maya crude oil (asphaltenes 12.4 wt.%, sulfur 3.44 wt.%, nitrogen 3700 wppm, vanadium 299 wppm, nickel 55 wppm and API 20.9°) in a continuous flow reactor working at 6.86 MPa of hydrogen, hydrogen/oil ratio of

890.5 std. cm^3 cm^{-3}, temperatures of 653-673-693-713 K and LHSV of 1.0-2.0 h^{-1}. Three different $NiMo/Al_2O_3$ catalysts with different Ni and Mo contents and ratios (one catalyst contained Ti) as well as different shapes, sizes, surface areas, total pore volumes and pore size distributions, were used. It is reported that HDM activity ratio between the three catalysts is dependent on the reaction temperature and LHSV, thus, at low temperature the catalyst with medium surface area (175 m^2 g^{-1}) and mean pore diameter (MPD, 127 Å) shows the highest HDM and asphaltene (HAD) conversion. However, this is also the catalyst that contains Ti in its composition, and this effect on the activity is not discussed in the paper. Contrarily, the catalyst with the highest surface area and the lowest mean pore diameter (278 m^2 g^{-1} and 86 Å respectively) showed the lowest HDA at low temperature and higher LHSV. At the most severe conditions (713 K and LHSV of 0.5 h^{-1}) HDM activities are very similar for all the tested catalysts, while the catalysts with larger MPD present the best HDA activity.

Regarding hydrodesulfurization (HDS) activities, it is reported that the catalyst with medium surface area and MPD shows the best conversion at lower temperatures, while all catalysts present similar conversions at higher temperatures. The hydrodenitrogenation (HDN) activity, on the other hand, is always far better with the catalyst with higher surface area and lower MPD. The high HDN activity for this catalyst is assumed to be due to the presence of acid sites in this catalyst; however, no experimental characterization that supports the presence of acid sites in this catalyst is given.

Based on previous findings the authors [11] propose:

- For any given feed there is an optimum pore size that produces the best HDM activity.
- For HDS and HDN activities, the optimum pore size is smaller than that required for HDM and asphaltene removal.
- Catalysts having high percentage of pore volume in the 100-250 Å region are more appropriate to get a high HDM activity.
- Coke formation tendency is proportional to the surface area.

In an early work on heavy oil hydrotreating (HDT) Takeuchi *et al.* [12] proposed a catalytic process called Asphaltenic Bottom Cracking (ABC). The process is based on a catalyst that was reported to exhibit high demetallization and asphaltene conversion activities. The ABC catalysts (developed by Chiyoda Chemical Engineering & Construction Co.) had proprietary chemical composition and pore structure (no more details given in the publication). In the process, unreacted asphaltenes are separated by solvent extraction and recycled to the reactor. It is claimed that by using the ABC catalysts and this process configuration it is possible to convert the asphaltenic residue completely to deasphalted oil.

Boscan crude oil and Athabasca bitumen (see Table 2 for oil properties) were treated at 678 K and 13.7 MPa of hydrogen, using the ABC catalysts in a once-through reaction configuration, i.e., no recycling of unreacted asphaltenes. Asphaltene conversion of 70% and 78%, as well as desulfurization of 90% and 80% were obtained for Boscan crude oil and Athabasca bitumen, respectively. Likewise, vanadium and nickel removal were 91% and 75%, for Boscan, and 80% and 79% for Athabasca, respectively.

In a subsequent paper [13] the asphaltene fraction (obtained by n-heptane precipitation) for Boscan crude oil and Athabasca bitumen, before and after reaction using the ABC catalysts, was characterized by metal and sulfur content, molecular weight determination, Electron Spin Resonance (ESR), and X Ray Diffraction (XRD). Reactions were carried at 8.83-17.65 MPa, 633-703 K, LHSV of 0.2-1.5 h^{-1} and a hydrogen to feed ratio of std. cm^3 cm^{-3} = 600-1000.

A reaction mechanism for the destruction-decomposition of the asphaltenes, which is based on the generally accepted model for the

Table 2. Typical analysis of Athabasca bitumen and Boscan heavy oil [12].

Oil	Boscan	Athabasca
API/°	10.3	9.2
Asphaltenes/wt.%	11.5	9.0
Sulfur/wt.%	5.18	4.40
Vanadium/wt. ppm	1130	177
Nickel/wt. ppm	106	77

macrostructure of the asphaltene “molecule”, i.e., asphaltenes composed of individual sheets which associate to form unit cells and larger associated micelles, is proposed. In the model, the first step in the asphaltene decomposition is the destruction of the asphaltene micelles, which is accompanied by the removal of metals (if present in the asphaltenic fraction). The second step is the depolymerisation of the molecules as a result of the breakage of carbon heteroatoms bonds (called weak links). Important differences were found in the asphaltene conversion as well as molecular weight distribution in the produced asphaltenes for the reactions with Boscan crude oil and Athabasca bitumen. These differences were ascribed to different contributions of the two reactions (micelles destruction and depolymerisation) for the two types of feeds used.

The effect of the metal loading on $CoMo/Al_2O_3$ catalysts (200 $m^2\ g^{-1}$) on the hydroprocessing of Athabasca bitumen (API 8.7º, sulfur 4.48 wt.%, nitrogen 0.45 wt.% and >798 K fraction of 51.5 wt.%) was studied by Kriz [14]. The catalysts were prepared using the same methodology but with different metallic content (molybdenum or cobalt and molybdenum) and different molybdenum precursors (sodium molybdate, or ammonium heptamolybdate, AHM). Reactions were carried out in a bench scale fixed-bed continuous upflow reactor at 13.9 MPa, 1 h^{-1} and a hydrogen to oil ratio of 890 std. $cm^3\ cm^{-3}$. It was found that the catalysts’ performance improved markedly up to a total metal loading (molybdenum or molybdenum plus cobalt) of 3 wt.%, and that after 5 wt.% total metal the increment in sulfur removal and API gravity was less pronounced. As expected, cobalt promoted catalysts showed more activity than the unpromoted ones, as also were those in which AHM was used as a precursor.

More recently, Ancheyta *et al.* [15] also studied the changes in the structure of the asphaltene fraction when a Maya crude oil was hydrotreated at 653-713 K, hydrogen to oils ratio of 890.5 std. $cm^3\ cm^{-3}$, 6.86 MPa and a LHSV of 0.5 h^{-1}, using a supported $NiMo/Al_2O_3$ catalyst (175 $m^2\ g^{-1}$, pore volume of 0.56 $cm^3\ g^{-1}$ and mean pore diameter of 127 Å). The asphaltenes were precipitated with n-heptane and were characterized, before and after reaction, by sulfur, nickel and vanadium analyses, and ^1H and ^{13}C NMR and molecular weight (by vapour phase osmometry) determinations.

It was found that, for the whole Maya crude oil, the conversion of asphaltenes, as well as the removal of sulfur and metals increased as the severity is increased (temperature 653 to 713 K). However, the removal of nitrogen goes up rapidly after increasing the temperature from 653 to 673 K, but from there on it reaches a plateau. When comparing the asphaltenes precipitated from the reaction products at different temperatures with the asphaltenes in the original oil, it was found that the quantity of sulfur, nitrogen, vanadium and nickel in the asphaltene derived from the products is similar or higher than that on the untreated Maya asphaltenes, and this behaviour was attributed to different localization of the heteroatoms in the asphaltene structure, suggesting that the easier to remove are located at the external part of the asphaltene molecules.

Ancheyta *et al.* [16] also explored the hydrotreating of a heavy Maya crude oil (21º API, sulfur 3.52 wt.%, nitrogen 3006 wppm, C7-asphaltenes 11.3 wt.% and metals 318.9 wppm) with a $NiMo/Al_2O_3–TiO_2$ catalyst in a fixed bed continuous flow reactor working at different pressures of hydrogen (5.3, 7.4 and 9.8 MPa), temperatures (653, 673 and 693 K), hydrogen/oil ratios (890.5, 1335.8 and 1781.0 std. $cm^3\ cm^{-3}$) and LHSVs (05, 1.0 and 1.5 h^{-1}). Synthetic crudes were obtained from Maya crude oils with improved properties (see Table 3).

In summary it was found [16] that there was an important increase in API gravity, as well as a decrease in the amount of sulfur, nitrogen,

Table 3. Product properties after HDT of Maya crude oil at 9.8 Mpa of hydrogen, LHSV of 0.5 h^{-1} and a hydrogen/oil ratio of 1781.0 $cm^3\ cm^{-3}$.

Reaction Temperature/K	653	673	693
API gravity	27.79	29.76	34.50
HDS/%	75.4	88.07	92.33
HDN/%	56.09	73.05	79.64
HDAs/%	24.76	57.31	73.05
HDM (Ni + V)/%	50.05	71.78	87.49

asphaltenes, Ramsbottom carbon and metals in the reaction products (synthetic crude oil) as the temperature, pressure, and hydrogen to oil ratio was increased or space-velocity decreased.

In another work [17] the Maya crude oil was treated in a process configuration consisting of two stages (or reactors). In the first reactor, a catalyst was used with specifications such that it is more selective for HDM reactions, while the second reactor used a catalyst that was more oriented towards HDS reactions. The HDM catalyst was a $NiMo/Al_2O_3$ one (175 $m^2 g^{-1}$, pore volume 0.56 $cm^3 g^{-1}$, mean pore diameter 127 Å, 10.7 wt.% Mo and 2.9 wt.% Ni), and the HDS catalyst a $CoMo/Al_2O_3$ one (218 $m^2 g^{-1}$, pore volume 0.51 cm^3 g^{-1}, mean pore diameter 91 Å, 12.9 wt.% Mo and 2.5 wt.% Ni). For the HDM catalyst about 70% of the pores had a diameter in the range of 100-205 Å and the HDS catalyst had ~60% of the pores in the region of 50-100 Å.

It is reported that in the HDM stage (6.9 MPa, 673-693 K, 890.5 std. cm^3 of hydrogen per cm^3 of oil and 1.0 LHSV) the API gravity of the oil is increased to 25.2 API (from 20.9) and metal content (Ni + V) decreased from 354 to 299 wppm (35.3% HDM). HDS and HDN were 48.5 and 29.3%, respectively. For the HDS stage (6.9 MPa, 633-673 K, 890.5 std. cm^3 of hydrogen per cm^3 of oil and 0.5-2.0 LHSV) API gravity was further increased to 29.9 and metals, sulfur and nitrogen content were further decreased. When compared to a single stage process [11] the two stage process gives a better quality SCO at less drastic conditions (LHSV of 1.0 Vs 0.5 h^{-1}).

As expected, the catalyst in the HDM stage suffers more textural changes than the one in the HDS stage. This is attributed to the amount and properties of the asphaltenes that enter each reactor, i.e., fresh asphaltenes in the first stage and partially converted asphaltenes in the second stage.

The upgrading of Maya crude oil using CoMo and NiMo catalysts supported on alumina, prepared by different methods in order to get different surface areas and pore size distributions, has also been reported [18]. Reactions were carried out in a micro-reactor working in up-flow mode, with two different feedstocks; the HDS feed consisted of a previously demetallized or hydrotreated Maya oil diluted (50/50 w/w) with diesel. The demetallized feed was obtained by hydrotreating the Maya oil diluted 50/50 w/w with diesel (HDM reaction). The catalysts for the HDM and HDS operations were chosen to have appropriate pore volume, average pore diameter and surface area for the type of reaction that was targeted (HDM or HDS). Two commercial catalysts, one for HDM and another for HDS, containing 3.7 and 5.6 wt.% of Ti, respectively, were also tested. Both treatments were carried out at 653 K, LHSV of 1 h^{-1}, hydrogen/hydrocarbon ratio of 356 std. cm^3 cm^{-3}, and pressure 5.4 MPa.

For the HDM reaction, the best performing catalysts for metal (Ni + V) removal was a CoMo supported on Al_2O_3 with the larger average pore diameter (173 Å), while the best performance for hydrodesulfurization was obtained with catalysts with higher surface areas. It appears that when treating the crude oil, the characteristics of the catalysts have to be tuned up depending on the reaction (HDM or HDS) that is preferred.

For the HDS reaction (using the pre-hydrotreated feed) the catalyst that produced higher metal and sulfur removal, as well as stable activity, was the one with higher surface area ($CoMo/Al_2O_3$). It was found that for feeds with lower metal content, a catalyst with larger surface area would produce better HDS and HDM. Results presented in this work [18] reaffirms the importance of pore size distribution and average pore diameter in controlling the HDM and HDS activity of the catalysts when treating a heavy oil (Maya in this case). Thus, demetallization and deasphaltation are mostly dependant on pore sizes, while desulfurization activity is higher when surface area (and may be the active metal dispersion) is also higher.

In another work [19] the results obtained in the fixed bed up flow microreactor were compared with those in a down flow bench-scale reactor. The feeds used in the microreactor (Maya oil or partially hydrotreated Maya oil) were always diluted 50% feed and 50% diesel. Two types of supported catalysts were used: one was a $CoMo/Al_2O_3$ (5.93 wt.% Mo and 2.10 wt.% Co) and the other a $NiMo/TiO_2$-Al_2O_3 (6.56 wt.% Mo, 4.12 wt.% Ni and 5 wt.% TiO_2).

Reaction conditions used in the micro-flow reactor were: temperature 653 K, LHSV of 1 h^{-1}, hydrogen/hydrocarbon ration of 356 std. cm^3 cm^{-3} and pressure 5.4 MPa; and for the bench scale reactor: temperature 673 K, LHSV of 1 h^{-1}, hydrogen/hydrocarbon ration of 891 std. cm^3 cm^{-3} and pressure 7.0 MPa.

Deactivation trends observed in the micro-flow and bench scale reactors were similar, despite the difference in the composition of the feedstocks used in each (50% diesel diluted Maya oils in the micro-reactor and “pure” Maya oil in the bench scale reactor). However, while the conversion of sulfur compounds was fairly similar in the experiments carried out in the micro and bench scale reactors, that was not the case for the removal of metals. For bench scale reactor experiments the HDM activities were substantially lower than in the micro-reactor, for both untreated Maya oil and pre-hydrotreated oil (31.2% Vs. 50.0% and 15.7% Vs. 35.4% respectively). This difference could be linked to the fact that the amount of metal deposited in the spent catalysts after the process is 36-40% more in the bench scale reactor as compared to the micro-reactor, which may be attributed to the difference in the feeds and the higher severity used in the bench scale reactor.

The hydrocracking of Athabasca bitumen (4.2, 83.1, 10.2 and 14.4 wt.% of sulfur, carbon, hydrogen, and Conradson Carbon Residue (CCR), respectively; as well as 4430, 196 and 74 wppm of nitrogen, vanadium and nickel respectively) has been reported by Sanford [20], using a commercial CoMo or NiMo supported on γ-Al_2O_3 catalysts (no specifications reported). The reactions were carried out in batch (623-713 K, 3-27 MPa of hydrogen and 60-240 minutes of reaction time), or in a continuous up-flow reactor (pilot plant) with a feed rate of 50-100 L per day (WHSV 0.5-1.0 h^{-1}, 653 K for hydrotreating conditions, and 703-723 K for hydrocracking runs). In most of the cases the catalyst was not pre-sulfided and was assumed to get sulfided with the feed during the heat-up period, since differences in the conversion of sulfur, nitrogen and CCR were minimal in similar experiments using a fresh (oxidic) catalyst or a presulfided one. It was also found that the deactivation of the catalysts for the removal of sulfur, nitrogen, vanadium, nickel and CCR was very fast (the drop in activity for nitrogen conversion was more drastic). Also, the conversion after 28 days of use at 703 K in the pilot reactor was similar to a thermal reaction (no catalyst used), with the exception of sulfur removal, which remained about double of what was obtained in the thermal run, suggesting that the catalysts had lost their ability to increase reaction rates for all but HDS reactions. A mechanism for the hydrotreating/hydrocracking of the large molecules contained in heavy oils is proposed where different thermal and catalytic routes are considered. It is suggested that the supported catalyst has two separate roles: at low temperature (hydrotreating or non-cracking conditions) aromatic saturation and heteroatoms removal, due to catalytic hydrogenation and hydrogenolysis, are the main catalytic pathways; at hydrocracking conditions (temperatures higher than 703 K) coke builds-up on the catalysts leading to poisoning of the hydrotreating sites, however, there are still sites for hydrogen activation and the mechanism changes to one where activated hydrogen reacts with carbon radicals formed during the cracking of hydrocarbons. Eventually, these hydrogenation sites are also lost over a period of several weeks.

Likewise, Richardson *et al.* [21] studied the effect of coke deposition on a NiMo/Al_2O_3 catalysts (12.5% MoO_3, 3.5% NiO, 317 m^2 g^{-1}) during Athabasca bitumen hydroprocessing. Coke deposition as a function of hydrogen pressure, time on stream and liquid composition was measured. Main observations reported are:

- A constant value for coke deposition on the catalysts (~11.7 wt.%) is approached as oil to catalyst ratio is increased.
- Coke deposition smoothly decreases as total hydrogen pressure is increased (from 17.9% at 6.9 MPa to 11.3% at 15.2 MPa).
- Coke deposition remains constant (~13%) when feedstocks with different residue concentration (8 to 32 wt.%) are treated.

Taking into account these observations, a model for coke deposition is proposed. The model assumes that coke is accumulated until a monolayer coverage of the surface is reached, and that there is a zone around the metal sulfide crystallites where no carbon is deposited due to the hydrogenating activity of the active sites. In fact, this is consistent with previous reports indicating that, for similar catalysts, the hydrogenating activity remains even after an important amount of coke deposition [20]. The model predicts that, except under more severe conditions, the hydrogenation sites on the metal crystallites will remain exposed.

Also, experiments carried out only using the maltene fractions of the bitumen indicated that coke deposition on the catalyst was one-third of that observed when the whole bitumen is hydroprocessed. This suggests that coke precursors are mainly present in the asphaltene fraction.

The concept of co-processing bitumen and coal has been reported by Medina *et al.* [22]. The hydroprocessing of a Kentucky bitumen (sulfur 4.53 wt.%, asphaltenes 19.7 wt.%, >797 K fraction equal to 54.8 wt.%) either alone or mixed with coal (35:65, coal:oil) in a 1/8 tons per day continuous flow pilot plant, using a sulfide CoMo/Al_2O_3 catalyst at 12.1 MPa hydrogen pressure, 700 K, was studied. It was found that the synthetic crude oil produced by either processing or co-processing is fairly similar. Conversion for the >797 K fraction is 56.9% and 54.5% for processing and co-processing respectively. HDS and HDN are also similar. The main difference is found in the sulfur and nitrogen content in the residue fraction, which are higher in the co-processing derived residue fraction than in the residue fraction derived from bitumen processing.

Additionally, the effect of adding CO to the hydrogen stream during the hydrocracking of Athabasca bitumen has been reported [23]. A bench scale fixed bed continuous up-flow reactor was used working at 6.9-13.9 MPa, 673-573 K, LHSV 1 h^{-1} and 445 std. cm^3 of gas (hydrogen or CO 50% in hydrogen). Water was also added to the feed in some experiments, in order to promote water gas shift reactions. Different catalysts (CoMo/Al_2O_3, CoMo-K/Al_2O_3, Mo/Al_2O_3 and $FeSO_4$/SiO_2) were tested. Best results were obtained with the CoMo/Al_2O_3 catalyst operating under pure hydrogen at high pressure.

Catalysts different than the more conventional Co(Ni)Mo(W)/Al_2O_3 have also been tested in the HDT of heavy oils. For example, Rana *et al.* [24] tested a US-Y zeolite based CoMo catalyst in the HDT of Maya oil. The zeolite (US-Y, 25 wt.%) was mixed with two types of commercial alumina and cylindrical extrudates (1/12” in diameter) were formed. The support thus prepared, with an average pore diameter of 68 Å and surface area of 182.7 m^2 g^{-1}, was sequentially impregnated with Mo and Co (7.4 and 2.0 wt % respectively). Maya crude oil was then hydrotreated with the catalyst (presulfided) at 653-693 K, LHSV of 1 h^{-1}, Hydrogen/hydrocarbon ratio of 356 std. cm^3 cm^{-3} and pressure 7.0 MPa.

Characterization of the US-Y zeolite used for the preparation of the catalysts showed it to be mainly mesoporous (88% of meso and 9% of macro pores). The zeolite was evenly distributed as micro-structures into the alumina matrix. The fresh CoMo catalysts had a surface area of 182.7 m^2 g^{-1} and pore volume equal to 0.31 cm^3 g^{-1}. The CoMo impregnated catalysts showed a bi-modal distribution of pores, with most of them in the range of meso (50 Å) and macro (120 Å), which is, according to previously shown work, beneficial for having a balance between HDM and HDS activities for heavy oil hydroprocessing. It was found that at reaction temperatures of 653 and 673 K the order of activity was HDS > HDN > HDM > HDAs, however, at 693 K the HDM reaction became more important than HDS. HDM and HDA reactions followed a similar trend as temperature was increased, while HDN and HDS followed a different one. It is suggested that HDM and HDAs reactions are controlled by the temperature and the HDS and HDN reactions depend more on the number of catalytic active sites available. It is also proposed that at temperatures higher than 673 K, thermal hydrocracking dominates as the reaction pathway while at lower temperatures the reaction is subjected to a hydrogenation route, which partly agrees with the mechanisms proposed by Sanford [20] and Richardson *et al.* [21]. Characterisation of the catalysts after reaction showed that, as expected, the textural properties were significantly altered (in particular the pore structure) by deposition of carbon and metals, and that the main poisoning mechanism is pore mouth blocking by deposited species.

Co-Mo supported on wide pore carbon extrudates has been tested for the hydrocracking of Athabasca bitumen [25]. Reactions were performed in a fixed bed continuous up-flow reactor working at 673-723 K, hydrogen pressures of 6.9-20.7 MPa, LHSVs 0.5-1.5 h^{-1} and hydrogen to oil ratio equal to 890.5 std. cm^3 cm^{-3}. Two CoMo catalysts (3.0 wt.% of CoO and 15 wt.% of MoO_3), one supported on Al_2O_3 and the other supported on a wide pore carbon extrudate, were used. Alumina supported catalysts showed better conversion of sulfur and asphaltenes, however, the comparison was somehow difficult since the mass of catalysts used were different due to differences in bulk densities of the alumina and the carbon (the reactor was loaded with the same volume of catalyst) and in surface area for both supports (210.0 Vs. 116.0 m^2 g^{-1}, for the alumina and the carbon supported respectively).

In an early report, Gonzalez-Jimenez *et al*. [26] studied the HDM activity of natural clay (54 wt.% SiO_2, 17 wt.% Al_2O_3 and 17 wt.% Fe_2O_3) acid treated, calcined (823 K) and impregnated with Ni. The HDM of PAO XI heavy oil from the Orinoco belt region in Venezuela was used for the catalytic test.

Mössbauer spectroscopy was used to characterize the catalyst at different stages in the preparation, as well as after reaction. It is proposed that the formation of pyrrhotites (FeS_{1-x}) is important for the evolution of the HDM and HDS activity of the solids.

Scott *et al.* [27] reported the upgrading of Athabasca bitumen using supercritical fluids, hydrogen and activated carbon as catalyst. In all reactions, Athabasca bitumen (sulfur 5.0 wt.%, vanadium 223 wppm, nickel 82 wppm, iron 848 wppm and >797 K residue 55.1 wt. %) was mixed with 50 wt.% of the fluid (*n*-dodecane for most of the runs), pressurized and heated to supercritical conditions in the reaction. *n*-decane, *n*-hexadecane, tetralin, decalin and Varsol (52.6% naphthenes and 41.4% parafins) were also used as solvents. Activated carbons, obtained from different raw materials and/or after different pre-treatments (like oxidation, solvent wash, acid wash or re-used after solvent and acid wash and coke burn off) were used as catalysts. A CoMo commercial hydrotreating catalyst was also tested for comparison purposes.

A tubular up-flow co-current (hydrogen and liquids) reactor, packed with the catalyst, was used. Reaction conditions were:

- Temperature; 658-733 K.
- Pressure: 10-15 MPa.
- LHSV: 0.25-1.0 h^{-1}.
- Solvent/bitumen wt. ratio: 2:1-1:2.
- Time on stream 6-24 h.
- Gas/liquid ratio: 651.8 std. cm^3 cm^{-3}.

Preliminary experiments demonstrated that hydrogen, the supercritical fluid and the catalysts are needed to upgrade the bitumen, and the lack of any of these components in the reaction media produced none or very little conversion or rapid catalyst deactivation and low quality products. High residuum conversion (82-95%) was obtained with all the solvents utilized for reactions carried out at 13.7 MPa and temperatures between 695-723 K, with decaline (94.6%), decane (92.1%) and tetralin (91.8%) being the best ones. The commercial $CoMo/Al_2O_3$ catalyst gave high liquid and low coke yields but very low residue conversion when compared to activated carbons. The use of activated carbons from different origins or, after a variety of pre-treatments, produced only slight changes in product quality. It was also found that the products obtained at a pressure of 10 MPa presented better quality than those obtained at 7.0 or 15.0 MPa and that impregnating the activated carbon with 6 wt.% of iron or nickel did not increase the residue conversion, however, for the iron impregnated one, the removal of sulfur and nitrogen was improved by 15.6 and 16.5%, respectively.

3. Upgrading with unsupported catalysts

3.1. Dispersed catalysts

As observed in the previous section, the use of supported catalysts for the upgrading of heavy crude oils is limited by the catalysts' life which is shortened due to metal sulfides and coke deposition in the pore mouth of the support, therefore reducing the effective use of the active phases that are in major proportions inside the pore structure. Even though the use of supports with high proportion of macropores increase the catalysts life, this is still not sufficiently long and the supported catalysts have a short life span, which is dependent on the characteristics of the feed used.

The use of unsupported catalysts which could be used dispersed on a heavy feedstock (also called ultra-dispersed catalysts, UDC) is considered to be a promising way to improve hydrodesulfurization/ hydrotreating (HDS/HDT) process efficiency [28]. Since there is no support, the poisoning by pore plugging is avoided. When using a UDC instead of the reacting molecules going to the site where the active phase is located (mostly inside the pores for supported catalysts), the active site goes where it is needed, that is, where the reacting molecules (hydrogen and hydrocarbons) are. In order to increase the efficiency of the catalytic particles during the processing of heavy oils, they have to be as small as possible. That is why, when used as UDC, the particles should be submicrometric in size (preferably in the nano range, i.e., <100 nm).

The use of very small bulk particles presents several advantages:

- They show high surface areas (the smaller the particles the higher the external surface area).
- Deactivation problems are greatly reduced (no pores to be blocked).
- Diffusional problems are avoided or greatly reduced.
- High density of particles per unit volume of feed to be treated.
- Lower inter-particle distances that increase the probability of the active phase interacting with the reactants.
- Less settling tendency [29-31].

There are however, some issues associated with the use of the UDC, mainly the difficulty in recovering and recycling the particles, if the catalyst is not used in a once through mode.

A review on the hydroconversion of heavy petroleum fraction with dispersed catalysts has been presented by Del Bianco *et al.* [32]. Different ways of preparing and introducing the UDC in the processes have been proposed:

(i) Dispersion of fine powder in the hydrocarbon media.
(ii) Water in oil emulsion where oil soluble salts of the precursors are dissolved in the aqueous phase. The emulsion is decomposed during the processing of the heavy feedstock, which produces the metallic precursors that are then converted to the active species during the hydroprocessing.
(iii) Solubilisation of lipophilic metal compounds in the feed. During the processing of the feedstock these oil soluble compounds are converted into the catalytically active species.

Kennepohl and Sandford reported [33] the hydrocracking of Athabasca bitumen (4.2, 83.1, 10.2 and 14.4 wt.% of sulfur, carbon, hydrogen, and CCR, respectively; as well as 4430, 196 and 74 wppm of nitrogen, vanadium and nickel respectively) using dispersed and supported catalysts (either separated or mixed). For obtaining the dispersed catalysts liquid molybdenum di(2-ethylhexyl) phosphorodithioate, $Mo_2S_2O_2[PS_2(OR)_2]_2$, where R = 2-ethylhexyl, or a molybdenum containing oil commercially called MOLYVAN-L in aromatic petroleum oil (80:20) were used. Reactions were carried out in a 1.0 L batch reactor (673 K, 6.89 MPa of hydrogen, 600 rpm for 4 h) charged with Athabasca bitumen (400 g) and Molyvan-L (0-20 g). Another set of identical experiments were done but also adding 100 g of a $CoMo/\gamma Al_2O_3$ catalyst. Two runs were performed using molybdenum naphthenate as a dispersed catalyst precursor.

It was found that the supported catalyst shows higher residuum, sulfur, CCR and nitrogen conversion than dispersed molybdenum, even for experiments where 6,000 wppm of molybdenum were added, however, for metal removal (nickel and vanadium) adding 6,000 wppm of molybdenum as dispersed catalyst produced a metal removal conversion which was around 18 % higher than that of the supported CoMo catalyst. It is also reported that mixing the dispersed catalyst with the supported catalyst has a detrimental effect on conversions. It is suggested that when used in conjunction, some of the dispersed catalytic particles are deposited and tied to the supported catalysts, decreasing the number of particles dispersed in the oil, and hence the reaction proceeds as if lower concentrations of dispersed molybdenum were present, as well as blocking catalytic sites in the supported catalyst. The amount of solids suspended in the liquids (coke) after the reactions were found to decrease for experiments with low concentrations of dispersed molybdenum (up to 800 ppm), and then to increase steadily for higher molybdenum concentrations, independent of the dispersed catalyst molybdenum precursor used (Molyvan-L or Mo naphthenate). It is suggested that at high concentrations, MoS_2 microcrystal that are formed during the reaction can act as seeds for the precipitation of solids. It was also found that the amount of coke deposited in the supported catalyst was greatly reduced when both a supported and a dispersed catalyst were used together (about 10 wt.% for 6,000 wppm of molybdenum added), indicating that the dispersed molybdenum catalyzed reactions lead to stabilization of the coke precursor molecules possibly through hydrogen transfer.

Utilizing the approach described in (ii), Galarraga and Pereira-Almao [34] studied the hydrocracking of Athabasca bitumen (sulfur 4.25 wt.%, residue fraction 48 wt.%, microcarbon residue 12.0 wt.%, H/C atomic ratio 1.52 and API gravity 9.5°) at low severity conditions, with Ni-Mo-W (1000 wppm) dispersed catalysts. First a water in oil (w/o) emulsion was obtained by adding the aqueous solution of the different metals (nickel, molybdenum and tungsten) to a homogenized mixture of bitumen and surfactant (HLB = 8, 1 wt.%) in a 5/100 ratio by weight. Two types of emulsions were used as feed for the upgrading experiments. The first type (called fresh emulsion) was charged in the reactor almost immediately after preparation. The amount of water determined in these emulsions was around 4.4-4.3 wt.%. In the second type (called dry emulsions) the freshly prepared emulsions were left to stand for 8 hours at 313 K with stirring (200 rpm). The amount of water was reduced to less than 0.5 wt.% in these preparations. Then the reactor (100 cm^3 batch) was charged with the emulsion and the hydrocracking of the bitumen was performed (593-653 K, 2.5 MPa of hydrogen, 5-69 hours, 500 rpm). The reactions using dry emulsion produced an increase in the residuum and sulfur conversions (when compared with experiments using fresh emulsions) from 45 to 56% and 17.5 to 37.5%, respectively. Also, the amount of coke is reduced from 1.3 to 0.2%, as well as the microcarbon residue (MCR) from 14.6 to 11.1%, when dry emulsions were used. It is suggested that the water present in the fresh emulsion is released during the reaction as steam, consequently reducing the hydrogen partial pressure in the reactor, having a detrimental effect on the conversions. Increasing the reaction temperatures (623-653 K) leads to a rapid increase in residue conversion and, at all temperatures tested, as the reaction time increases, the conversion levels and reaches a pseudo state of equilibrium. In summary, it was found that using relatively low temperature and hydrogen pressure but long reaction times makes it possible to upgrade Athabasca bitumen, converting 56% of the residuum fractions with a significant reduction of the amount of coke produced (in relation to a thermal non-catalytic upgrading), and significantly decreasing the viscosity, sulfur and MCR in the final synthetic bitumen.

Dispersed exfoliated MoS_2 was used by Tye and Smith [35] as a catalyst for Cold Lake bitumen upgrading. Tests were conducted in a batch reactor (673-703 K, 3.5 MPa initial hydrogen pressure, 1 h of reaction time) charged with the bitumen (sulfur 4.09 wt.%, >798 K fraction equal to 55.7 wt.%, asphaltene content 17.9 wt.%, and 141 ppm of nickel and vanadium) and a water suspension (2%) of the exfoliated MoS_2 in such proportions that the Mo concentrations were 360, 600 and 900 ppm. MoS_2, derived from the decomposition of Molybdenum naphthenate, as well as commercial crystalline MoS_2, were also tested for comparison purposes. It was found that exfoliated and naphthenate derived MoS_2 had very similar coke yields, and sulfur and residuum conversion, however, the exfoliated material presented a significantly higher activity for nitrogen, metals and MCR reductions compared to the naphthenate derived sulfide. It is suggested that this increased activity is the consequence of an enhanced hydrogenation activity of the exfoliated sulfide which could be a result of the increased proportion of rim-edges in the exfoliated MoS_2. For experiments at three different molybdenum concentrations (360, 600 and 900 ppm) using exfoliated MoS_2, it is reported that coke production was minimal at 600 ppm molybdenum. Higher coke formation at higher molybdenum concentration was explained assuming that two parallel phenomena takes place during the bitumen upgrading: a) higher hydrogenation of the bitumen at higher catalyst concentration that causes instability and precipitation of asphaltene molecules, and thus promoting coke formation, and b) catalyst microcrystal at higher concentrations can be nucleation points and promote coke precipitation. It was also found that sulfur, nitrogen, metal, MCR and asphaltene conversion were higher and coke yield was lower when 600 ppm of molybdenum was used. Also, suspending the catalyst in an organic solvent (decahydronaphthalene, DHN) instead of water produced better quality products.

The use of methane as a hydrogen source for the upgrading of heavy and extra heavy oils with dispersed catalyst has also been tested. Thus, Ovalles *et al.* [36] studied the upgrading of Hamaca extra heavy crude oil (API 8.7°,sulfur 3.40 wt.%, >773 K fraction equal to 57 wt.%, asphaltene content 12.5 wt.%, and 424.5 ppm of nickel and vanadium) from the Orinoco belt in Venezuela. Upgrading reactions were performed in a batch reactor (300 cm^3, 4.8 MPa methane or argon, or 5.5 MPa hydrogen to produce a final pressure of ≈11 MPa, 683 K, 1 h) charged with the heavy oil containing 250 ppm of Mo dissolved as $Mo(acac)_2$ (molybdenum acetylacetonate). X ray photoelectron spectroscopy analysis of the coke isolated from the upgrading experiments where the catalyst was added showed a Mo signal similar to that of MoS_2, which indicates that the organometallic molybdenum precursor is converted to a sulfide during the reaction. Control experiments were also performed using CH_4 without any catalysts, or catalyst and argon, or catalyst and hydrogen. Treating the oil in methane (no catalyst) produced an increase in API gravity (from 8.7° to 14.6º) and reduction in sulfur content and of the residuum fraction (10% and 41% respectively). A similar reaction in the presence of the dispersed catalyst led to a slight increase in API gravity (16º), sulfur (15.6%) and residuum (55%) conversions.

When the reaction was carried out in argon with dispersed catalysts, reaction products were not as good as the ones obtained when methane is used. Also, increasing the methane working pressure leads to an increase in the conversion of sulfur and residuum, and a decrease in the amount of coke formed. These results evidence a beneficial role of methane in the catalytic upgrading process. A mechanism for the upgrading of the oil using methane is proposed, involving the activation of the methane molecule by MoS_2 thus producing $CH_x^{\bullet}$ and $H_{4-x}^{\bullet}$; the former is added to the hydrocarbons of the oil forming methylated products, while the latter are responsible for sulfur removal and hydrogenation of the asphaltenes.

Dispersed iron has also been used as catalysts for XH oil upgrading using methane as hydrogen source [37]. Upgrading of Hamaca extra heavy oil was studied in a batch reactor (300 cm^3, 683-693 K, 1 h, and 11 MPa of either methane, nitrogen or hydrogen) using 250 ppm of iron added as iron carbonyl $[Fe_3(CO)_{12}]$. A control reaction (no catalyst) at 683 K in methane produced a reduction of two orders of magnitude in the viscosity (from 500 to 2 Pa s), 10% of sulfur removal and 41% conversion of the residuum fraction with respect to the original crude. Similar reactions performed in the presence of dispersed iron carbonyl yielded a product with further reduction in the viscosity (1.3 Pa s) and sulfur content (14% more) and similar value of conversion of the heavy fraction (40%), which indicates that the iron catalyst was responsible for the further upgrading of the Hamaca extra-heavy crude oil in the presence of methane. A reaction carried out in an inert nitrogen atmosphere led to a product with higher viscosity (2.7 Pa s), less reduction of sulfur content (8%) and lower conversion of the residuum fraction (36%) with respect to the methane containing experiment, which may indicate that methane can be activated by the catalysts and probably intervenes in the upgrading reaction, providing the hydrogen needed for the saturation of free radicals formed. When the reaction is performed under hydrogen, the product shows slightly better properties than those obtained under methane. If the results reported for the upgrading of the Hamaca oil using iron as catalyst [37] are compared to those where molybdenum is used [36] one can observe that both catalysts produce about the same sulfur removal in methane (15.6 and 14.2 with molybdenum and iron, respectively) or hydrogen (22.3 with molybdenum and 22.0 with iron) but the molybdenum catalyst yields higher residuum conversions (55 Vs 41.0 in methane and 65 against 39.7 in hydrogen). The same trend is observed for the reaction carried out in an inert atmosphere, indicating that molybdenum is a better catalyst than iron for heavy oil upgrading. The coke produced during the upgrading reaction was characterized by TEM, EDAX, XPS and Mössbauer spectroscopy which showed the presence of iron and vanadium in sulfides structures, possibly as mixed iron-vanadium sulfide species.

3.2. Super-acid catalyst

Strausz *et al.* [38] reported the use of $HF{\cdot}BF_3$ in the hydrocracking of Athabasca and Cold Lake bitumen, as well as the asphaltenes precipitated from the oil. Reactions were performed batch wise in a 250 cm^3 reactor, which was fed with the oil and methylcyclohexane (MCH, solvent to oil ratio 0-15) and anhydrous HF. Then, gaseous BF_3 (3.45 MPa) and hydrogen (3.45 MPa) were added, heated to reaction temperature (463-483 K) and maintained at that temperature for the reaction time (2-24 h). It was found, for reactions done in the presence of MCH, that the amount of product recovered is in several cases higher than 100%, and that the relative amounts of maltene in the hydrocracked bitumen increases for higher amounts of MCH, indicating that the solvent intervenes in the reaction. However, when low amount of MCH are added the weight loss, due to the formation of volatiles and gaseous products, is very high (up to 50-52%). These results suggest that the superacid $HF{\cdot}BF_3$ could be a highly effective catalyst for the hydrocracking of bitumen at low temperature and reaction times (as low as 1 h).The addition of MCH, though, in high proportion is necessary to increase liquid yields.

3.3. Catalytic aquathermolysis

The term aquathermolysis, i.e. the reaction of organic compounds with superheated water [39], has been most commonly used to describe the thermal cracking of oils in the presence of water or steam. As the introduction of superheated steam into the wells is one of the processes most widely used for heavy oil production, the reaction of transformation of the organic molecules in H/XH oil and bitumen in superheated water is of significant interest. Due to their high viscosity, H/HX oils cannot be pipelined without a further treatment which makes the reduction in viscosity by steam assisted cracking an important area of research, as pipelinable oil could be produced that way.

The subject of catalytic aquathermolysis (CAQT) of H/XH oils has been recently reviewed by Maity *et al.* [40], and it will be only briefly presented in this work.

The work of Wu *et al.* [41] shows similar findings as those reported by Maity *et al.* [40], that is, using an amphiphilic nickel catalyst in the aquathermolysis of a heavy oil batchwise (473 K, 3 MPa initial nitrogen pressure for 24 h, 30% wt. of water and 0.5 wt.% of catalysts) an important viscosity reduction (96%) is obtained, however, the final viscosity (2300 cp) is not low enough for the oil to be pipelinable (as it will be shown later).

In summary, the reported work in catalytic aquthermolysis of heavy oil has shown [40]:

- Minerals generally present in reservoir sands, as well as water soluble metallic salts, oil-soluble and amphiphilic metallic compunds, ionic liquids and dispersed particles of different metals (Ni, Fe, Cu, Zn, Ru, V, Mo and Al) have been used as catalysts in the AQT of heavy oils.
- Almost all of the catalysts tested gave important viscosity reduction, however the order of effectiveness seems to be mineral < water-soluble salts < oil-soluble metallic compunds < dispersed nanoparticles.
- During catalytic AQT the content of saturates and aromatics increases while that of resins and asphaltenes diminishes.

4. Catalytic *in situ* upgrading

In a recent report by the Society of Petroleum Engineers Research and Development Committee, the *in situ* molecular manipulation (*in situ* upgrading) was identified as one of the major R&D challenges in the petroleum industry [42].

A catalytic *in situ* upgrading process has to consider the following aspects in order to be applicable:

- Placement of the catalyst in the reservoir.
- Injection of co-reactants (hydrogen, carbon monoxide, etc.).
- Assuring good contact between the catalyst, co-reactants and oil in the heated zone of the reservoir.
- Reaching sufficiently high temperatures and pressures to produce reasonable upgrading. However, the low temperatures and pressures attainable in the reservoir can be compensated by the long residence time in the mobile oil (see next section).

Also, due to the limitations of temperature and pressure that can be reached in the reservoir, *in situ* upgrading developments do not target high residuum conversion, and recently more interest has been paid to get an important reduction in viscosity and moderate increase in API gravity than very high conversions. As heavy oils and bitumen have very large viscosities (see Table 1) they require additional treatments to be transported on conventional pipelines. These treatments most commonly consist either in heating or diluting with solvents to decrease the oil viscosity. Nowadays, blending the heavy oils with a less viscous hydrocarbon, such as light crude oils, naphtha, kerosene and condensate, is common practice, but a fraction as high as 30% in volume of diluents is necessary. Dilution with such a large amount of diluents poses problems such as the need to increase pipeline capacity and the high costs of the diluents. Even though recycling of diluents can be a solution, a large investment to install an additional pipeline is required, which in many cases is not economical.

An alternative method to reduce the viscosity of the oil is to upgrade it in the reservoir prior to reaching the surface, thus producing a synthetic crude oil that is pipelinable (without the need of diluents addition) and that can be readily accepted in refineries adapted for heavy oils. The viscosity specification for oil transportation varies by region and the recommended value for Europe and North America is 25 cSt at 323 K (50 °C) [43], and for Canadian crudes is 350 cp at 284 K (11 °C) according to Dehkissia *et al.* [43] or 350 cSt at operating temperature according to Rahimi and Gentzis [44].

It has been reported that *in situ* (or downhole) processing yields higher rate of return than above ground processing [45]; likewise when comparing *in situ* upgrading (using nano-catalysts) with production by Steam Assisted Gravity Drainage (SAGD) followed by surface upgrading [46]. This may be expected since in thermal recovery processes energy is applied to produce the oil, by viscosity reduction, but once on surface, the oil partially recovers its viscosity and energy needs to be added again in the upgraders to produce a permanent viscosity reduction (as well as improvement of other characteristics). Doing only one thermal treatment, for both recovery and upgrading in the reservoir, may lead to a substantial reduction in energy consumption that will also be beneficial from the point of view of emissions.

The criteria chosen in this review for a work to be considered as related to catalytic *in situ* upgrading are: the use of catalysts, sand (or reservoir minerals), and temperatures below 623 K and pressures under 10 MPa. However, for shallow reservoir like those found in the province of Alberta in Canada, the maximum workable pressure is around 3.5 MPa.

Most of the work reported in the review on aquathermolysis [40] were done at conditions suitable for *in situ* upgrading [41, 47-52] as well as the work by Galarraga *et al.* [34], Strausz *et al.* [38], Sánchez *et al.* [53] and Loria *et al.* [54]. They do, however, lack the presence of sand or minerals from oil formation and would not be considered in this section.

Weissman and Kessler [45] studied the upgrading of 5 heavy oils from different origins (although most of the results were obtained using a Middle Eastern heavy oil) in batch and in continuous flow mode. Batch experiments were conducted using specific amounts of oil, brine solution, quartz sand and catalyst, under different atmospheres (hydrogen, nitrogen or syngas, i.e., a 50/50 mixture of CO and hydrogen), at 10.3 MPa, 523-598 K and reaction times 0.5-7 days. Sulfur, nitrogen, asphaltenes and vacuum residuum conversion, as well as specific gravity changes, were determined for the reaction products. Different supported (Co-Mo and Ni-Mo) catalysts with varying amounts of metals, as well as oil soluble (iron and cobalt naphthenates) and water soluble (Ammonium tetrathiomolybdate, cobalt nitrate and ammonium heptamolybdate) catalytic precursors were used. It was reported that catalytic experiments showed higher conversion than the ones carried out without catalysts. Also, runs done under hydrogen pressure resulted in higher conversions than the ones done under nitrogen or synthesis gas. In spite of having different metals and metallic contents, all supported catalysts behaved similarly.

Continuous flow experiments were performed in an up-flow hydroprocessing reactor working at

10.3 MPa, 180 std. cm^3 of hydrogen per cm^3 of oil, LHSV from 0.6 to 2.0 h^{-1} and temperatures in the range of 523 to 598 K. It is reported that the quantity of sulfur removed was strongly dependent on the oil tested, which suggests that *in situ* upgrading at the conditions studied is feasible depending on the reactivity of the original crude oil.

The combination of *In situ* Combustion (ISC) and a supported hydrotreating catalyst has been proposed as a possible way of producing *in situ* upgrading of a Middle Eastern (density 0.964 g cm^3 at 298 K, viscosity 490 cP at 313 K and 6.33 wt.% of sulfur) heavy oil [55, 56] or an Argentinian one (density 0.9669 g cm^3 at 298 K, viscosity 10460 cP at 313 K, 2.08 wt.% of sulfur, 0.32 wt.% of nitrogen and 16.36 wt.% of asphaltenes) [57].

Experiments were run in a combustion tube apparatus using simulated cores (silica and brine mixed with oil) having the appropriate oil and water saturations. For the catalytic runs, the zone closest to the production end of the core was packed with 50/50 v/v mixture of sand and catalyst (NiMo supported on alumina in 1/16 inch extrudates without pre-sulfiding) and externally heated to 598 K. Combustions were conducted such that combustion gases and fluids were passed over the heated catalyst before exiting the combustion tube and the initial pressure was 10.3 MPa (Helium).

For the experiments using the Middle Eastern oil [55, 56], less oil was produced in the catalytic runs compared to the thermal ones, however, density, viscosity, asphaltene, metal and sulfur content were significantly reduced. The increased coke deposition in the catalyst sand pack zones, along with the increase in production of light hydrocarbons in the catalytic runs may indicate that the upgrading is produced by a cracking-coking mechanism. Also, the decrease in the amount of oil produced in the catalytic experiments could be due, in part, to coke formation.

Tests done using the Argentinian oil [57] produced similar results, i.e.:

- Oil recoveries were lower for catalytic run (73.6% Vs. 84.8% for thermal).
- Increase in API gravity (24° Vs. 15°).
- Decrease in viscosity (10 Vs. 10,460 mPa·s).
- Important sulfur (64.3%) and nitrogen (71.9%) removal.
- Significant asphaltene conversion (≈69%).
- Important coke deposition in the catalysts zone as well as surface area reduction for the catalyst (≈64% surface area reduction).

The use of zeolites for the upgrading of oil sands has also been experimented. In the work of Kuznicki *et al.* [58], a natural sedimentary chabazite was treated with alkaline silicate mixtures, which is claimed to convert the contaminant clinoptilolite and erionnite present in the raw chabazite, in order to produce a high purity material. The material was then ammonium exchanged and heated in nitrogen, to produce the acid form of the zeolite. A commercial Y zeolite was also tested as catalyst. Thermal and catalytic reactions were conducted in a batch reactor that was loaded with oilsand with or without 10% of catalyst, and the reactions were carried out under nitrogen, at 673 K for 1 h. After each reaction, the products were recovered by extraction with toluene and subsequent evaporation of the solvent at 343 K under vacuum. When compared to a thermal experiment (no catalyst added), the products obtained for the reactions in the presence of zeolites (in particular the modified chabazite) showed important reductions of the >798 K fraction of the oil (form 40.8% to 29.4%), the viscosity at 298 K (16,000 to 3,920 cP), sulfur (4.1 to 2.7%), nitrogen (0.46 to 0.17%) and V + Ni (287 to 220 ppm). These results show that upgrading oil sands by thermal treatment in the presence of a natural modified chabazite is feasible, however, it would be important to get the yield and stability of liquid products and the amount of coke formed or deposited on the catalysts, to have a better understanding of the process for a possible commercial deployment.

Junaid *et al.* [59, 60], also reported the upgrading of oil sands using different natural and commercial zeolites as cracking catalysts. Thus, using a micro-batch reactor [59] the reactivity of Athabasca oilsands mixed with different zeolites (commercial Y, natural chabazite and clinoptilolite; the last two were ammonium exchanged and converted to the acid form) in a 10:1 ratio, and heated under nitrogen to 685 K for 1 h, was explored.

After the reactions the oilsand treated samples were extracted either with toluene, hexane or pentane, and the solvent evaporated. The percentage of liquid products extracted with toluene varied between 97.0 and 78.3 (the amount recovered is 85.3% for the reaction with no catalyst). The solid that produced the highest amount extracted was Ca-chabazite and the ones with lower liquid yield extracted the two clinoptilolites used (78.3 and 79.3%). Also, the use of the clinoptilolites leads to higher residue conversion and increased distillate fractions in the products extracted with hexane or pentane. It is possible that the low extraction yield for the clinoptilolites is associated with higher coke formation and hence also leading to a better quality products.

Working with a bigger batch reactor [60] using Athabasca oil sand, natural zeolite (clinoptilolite and chabazite, 5 wt.%) and water (3 wt.%), upgrading reactions were carried out, at 573-623 K under helium for 1 h. In order to assess the deactivation of the zeolite, the experiments were performed using bitumen and 10 wt.% clinoptilolite at 573 K for 24 h, and then, after extracting the reaction products, the process was repeated with the recovered solid. It was found that the viscosity decreased to 51,600 cP (from 144,900) in the first reaction cycle (64% reduction), and only to 100,000 cP (31% reduction) when the process was repeated but using the recovered zeolite. Evidently, the catalyst is poisoned possibly by coke deposition, however, some activity was retained after the two 24 hour reactions. It was also found that the zeolite with higher acid site density produce higher residue conversion than the one with lower acid site density (both have similar acid strength). Also, with both catalysts the viscosity of the liquid products was significantly reduced, as well as the sulfur and metal content, when compared to the ones obtained by an analogous thermally cracked sample.

The reaction between water, heavy oil, minerals and/or catalysts has been reported [61]. Laboratory tests (batch reactor, 513 K, 10 wt.% of mineral and water, for 24 h) were carried out using heavy oils samples from Shuguang and Huanxiling factories in China. It was found that asphaltenes and resins content decrease and saturates and aromatics increase in the reaction products when minerals and steam coexists during the reaction. When VO^{2+}, Ni^{2+} and Fe^{3+} (1:1:5 molar ratio) are also added the product quality improves, for example, the viscosity is reduced from 85,200 and 116,800 to 12,100 and 18,900 cP, for each one of the oils tested. This represents an important viscosity reduction (around 85%), however, it is not low enough for transportation without the use of diluents. The catalytic effect of the mineral is suggested to be due to reaction between steam and clay minerals that produces hydroxyl groups with strong acidity, as well as by adsorption of the transition metals (when added) on the clay, thus producing a supported catalyst. Similar results were reported [62] using a heavy oil from Liaohe oil field, and different temperatures (433-553 K) and reaction times (12-48 hours) with 30 wt.% of water.

Laboratory and field tests on the aquathermolysis of different heavy oils using an amphiphilic catalyst have also been reported [63]. The catalyst was prepared by adding Fe_2O_3 or metallic iron to a hot aromatic sulfonic acid. Laboratory experiments were performed batchwise under nitrogen at ~6-7 MPa. Important viscosity reductions were reported, for example, for one of the oils treated at 473 K, water to oil ratio 1:3, and 0.16 wt.% of catalyst, the reduction was 90.7% (note: absolute viscosity values are not given), and a 14.7% conversion of heavy to lighter fractions is reported.

Field tests were performed in a huff and puff mode. Steam and nitrogen (if reservoir pressure was not high enough) were injected and the wells closed for a period of 3 days, after which the wells were reopened and then, after 14 days of production, the yield and viscosity of the produced oil was determined. Water was added by injecting high temperature and pressure steam, to which NaOH was added to adjust the pH to basic (pH value is not reported) and the catalyst was injected along with the steam. For two different wells it is reported that the production increased by 153 and 72%, while the viscosity was reduced 80 and 82% (to 23,500 and 9,511 cP, respectively).

The use of nanocatalysts for bitumen *in situ* upgrading has been proposed by Pereira-Almao [46]. The *in situ* upgrading method proposed is based on replacing steam (in a Steam Assisted Gravity Drainage, SAGD process) with a bitumen fraction that would be used as catalyst (suspended as nanoparticles), heat, and dissolved hydrogen carrier.

Reported results were obtained at low pressure (5.0 MPa) like those found in shallow reservoirs typically present in the Canadian province of Alberta. Temperatures in the range of 593-653 K, and residence time in the range of 0.5 to 100 days, were typically used. It is reported that estimated residence times for the mobilized bitumen using a SAGD recovery method are in excess of 100 hours (4.2 days) and that those residence times can compensate for the low temperatures and pressures that are required for an *in situ* upgrading process. Kinetic determinations seem to show that this is indeed the case [53, 54]. It was also found that a reaction carried out with 1200 wppm of a trimetallic catalyst formulation (no other details given) in a batch reactor at 613 K, 2.6 MPa of hydrogen partial pressure and 16 hours of reaction, upgraded a bitumen from 8º API to 17º API, and that another catalyst formulation working at 633 K yielded an oil with 16º API and 220 cP (measured at 298 K). Another aspect of the proposed process that was studied is the flow of the nanoparticles in a porous sand pack (0.5-5 Darcy of permeability). It was reported [64] that the quantity of particles retained by the sand depends on the type of sand; thus pure sand retained 20% of the particles flown through, while a higher amount is deposited in Athabasca sand, both without an appreciable impairment of the porosity.

5. Kinetics

Only a few reports that deal with kinetic determinations for the hydrocracking or hydroprocessing of H/XH oils and bitumen are found in the literature, and initial studies were directed to getting the kinetic parameters, specifically reaction orders, for demetallization. Thus, Shimura *et al*. [10], working with Boscan crude oil (see section 2) found that surface reactions are first-order for vanadium removal and second-order for asphaltene cracking.

Gray *et al*. [65] studied the kinetics of hydrodesulfurization, for different types of sulfur (thiophenic and sulfide), in Athabasca bitumen. A commercial NiMo/Al_2O_3 catalyst (12.5 and 3.5 wt.% of MoO_3, and NiO, respectively) was used. Reactions were carried out in a continuous stirred reactor at 703 K and 13.7 MPa, with residence times of 0.47-1.88 h^{-1}. The concentration of total and sulfide sulfur in the naphtha, middle distillate, gas oil and residue fractions, as a function of residence time, was determined for thermal and catalytic hydroconversion of the bitumen. The reaction scheme shown in Figure 1 was proposed, and assuming first order kinetics for each reaction, the kinetic constant for the residue's sulfur removal was determined. The best fit for the experimental data was obtained with k_1, k_2 and k_3 1.2, 1.1, and 1.2 h^{-1}, respectively. It is proposed that the presence of the series of reactions as shown in the Figure 1 can account for the sometimes-unusual apparent kinetics reported for the total sulfur removal from heavy hydrocarbon fractions.

The kinetics of hydrocracking of the bitumen, with and without catalyst, was also studied over a wide range of residue conversions (30 to 95%) [66]. Reactions were carried out in a multipass mode of operation, that is, product from one experiment was used as a feed for the next, and so on, until very high conversions were obtained. For residue conversions below 65% (two passes)

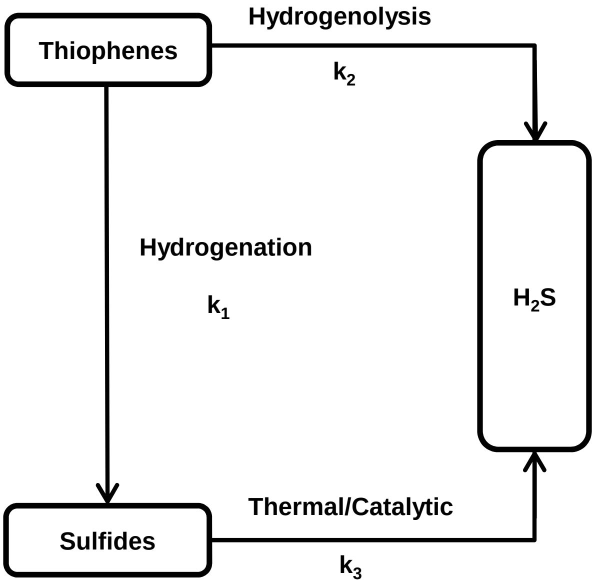

Figure 1. Reaction network for the HDS of residue fraction of Athabasca bitumen [65].

thermal and catalytic experiments produced similar conversion, which is assigned to the dominance of thermal cracking reaction at this conversion level. Also, the conversions for multipass operations were higher than the ones obtained for single pass operations at equal total residence time, which is suggested to be due to changes in the reactivity of the residue when working in multipass mode. However, one aspect that can also explain the higher conversion produced in multipass operation has to do with the fact that a fresh catalyst was used for each new pass. Thus, the catalysts used for a certain time in single pass mode should have suffered the effects of poisoning by coke and metal deposition more severely when compared with the experiments in multipass operations at the same residence time. In fact, the carbon content of the spent catalysts is reported to be between 11 and 15%, for the first three passes, and around 7 for the fourth pass. That entire amount of coke is expected to be accumulated in one load of catalysts for a single pass experiment. The rate constants k_1, k_2 and k_3 obtained in the previous work [65] also produce a good agreement with the experimental data for sulfur conversion in multipass mode operation. It was also found that the rate constant for residue conversion decreased as conversion increased, which was correlated with an increase in the aromatic carbon in the more converted residue fraction.

Also, Ancheyta *et al.* [11] studied the HDM of Maya crude oil (see section 2 for oil characteristics), using three different NiMo/Al_2O_3 catalysts with different Ni and Mo contents and ratios (one catalyst contained Ti) as well as different shapes, sizes, surface areas, total pore volumes and pore size distributions. The best fit for the experimental data was obtained assuming second order reaction for HDS, HDM and HDAs. Activation energy values obtained for HDS, HDM and HDAs using the three catalysts are presented in Table 4.

It is observed (Table 4) that the highest values of apparent activation energies were obtained for asphaltenes removal for all the three catalysts, which is indicative of higher temperature dependence for this reaction, however, for catalyst M-1 the activation energies reported are of the same order for the three reactions. Also, activation energy values were quite different (in particular for HDM and HDAs) for the three catalysts, which suggest that other non-kinetic phenomena (like intra-particle mass transfer) may have influenced the measurements.

Köseoglu and Phillips [67] studied the hydrocracking of Athabasca bitumen in a batch reactor at 7.2 MPa of hydrogen (initial) pressure, temperatures between 620-693 K and reaction times of 0-5.25 hours. A CoMo/Al_2O_3 catalyst with 90 Å of MPD was used (no further details given). The experimental data

Table 4. Catalyst composition and activation energy for the hydrotreating of Maya oil.

Catalyst	M-1	M-2	M-3
Surface area/m^2 g^{-1}	175	120	278
Pore volume/cm^3 g^{-1}	0.56	0.62	0.60
MPD*/Å	127	180	86
Shape	Tetralobe	Sphere	Cylindrical
Diameter/cm	0.254	0.254	0.079
Molybdenum/wt.%	10.66	11.1	8.84
Nickel/wt.%	2.88	1.8	2.37
Titanium/wt.%	3.73	--	--
Ea** HDM/KJ mol^{-1}	75.3	98.3	161.1
Ea** HDAs/KJ mol^{-1}	77.0	112.1	201.3
Ea** HDS/KJ mol^{-1}	72.8	100.4	88.7

*Mean pore diameter; **Apparent activation energy.

regarding product yield was fitted to three different reaction models assuming first order reactions, as shown in Table 5. Best fit was obtained for model III, but model II also provided an acceptable prediction of the experimental data.

A kinetic model for the hydrocracking, at moderate temperature and pressure, of Maya heavy oil and Athabasca bitumen (see characteristics in Table 6) have been presented by Sánchez *et al.* [53] and, Loria *et al.* [54] and Galarraga *et al.* [68], respectively. Sánchez *et al.* [53] used a pilot plant reactor working in downflow mode with a $NiMo/Al_2O_3$ commercial catalyst (175 m^2 g^{-1}, 0.56 cm^3 g^{-1} of pore volume and mean pore diameter of 127 Å) at the conditions shown in Table 7. Loria *et al.* [54] worked in a pilot plant reactor also working upflow (reaction conditions shown in Table 7) and the catalyst was introduced with the bitumen in the form of an emulsion, having nickel, molybdenum and tungsten (1200 wppm total metal), prepared according to a previous work [34] (this preparation is claimed to produce particles of 100-200 nm). On the other hand, Galarraga *et al.* [68] worked with a laboratory (100 cm^3) batch reactor (conditions shown in Table 7) using ultradispersed-type catalyst obtained from a water in oil (w/o) emulsion and containing 1000 wppm of nickel, molybdenum and tungsten.

The proposed kinetic model used in these works [53, 54, 68] which includes 5 lumps: residue,

Table 5. Reaction model and kinetic parameter for the hydrocracking of Athabasca bitumen [67].

Model	I	II	III
Reaction network	Bitumen + H_2 → Gases (k_1)	Heavy ends + H_2 → Light oils (k_1) Light oils + H_2 → Gases (k_2)	Asphaltics + H_2 ↔ Maltenes (k_1/k_2) Maltenes + H_2 → Gases (k_3)
Ea_1/kJ mol^{-1}	112	83.5	161
Ea_2/kJ mol^{-1}	--	96.5	169
Ea_3/kJ mol^{-1}	--	--	111
A_1/h^{-1}	54.8 10^6	1.2 10^6	19 10^{12}
A_2/h^{-1}	--	4.9 10^6	5.8 10^{12}
A_3/h^{-1}	--	--	5.0 10^9

Table 6. Feed characteristics.

Feed	Maya heavy oil [53]	Athabasca bitumen [54, 68]
API	21.97	11-9.5
Viscosity at 40 ºC/cP.	---	7443-7890
Sulfur/wt%	3.51	4.8
Asphaltenes /wt%	12.4	11.67
V/wppm	292	---
Ni/wppm	53	---
Naphtha/wt% (boiling point range K)	12.1 (IBP-477)	3.4 (IBP-489)
Distillates/wt% (boiling point range K)	20.4 (477-616)	13.48 (489-616)
VGO/wt% (boiling point range K)	28.1 (616-811)	13.48 (616-823)
Resid/wt% (boiling point range K)	39.4 (>811)	50.66 (>823)

Table 7. Reaction conditions.

Reference	Sanchez *et al.* [53]	Loria *et al.* [54]	Galarraga *et al.* [68]
Temperature/K	653-693	593-653	593-653
LHSV/h^{-1}	0.33-1.5	0.020-0.11	
Hydrogen to oil ratio/std. cm^3 cm^{-3}	890.5	625	---
Pressure/MPa	6.86	2.76	3.45

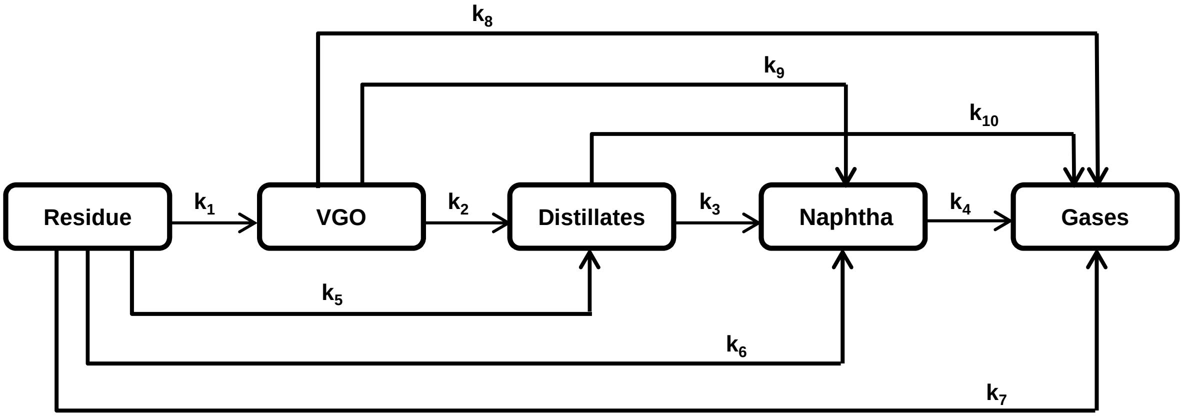

Figure 2. Kinetic model for catalytic hydrocracking of Maya heavy oil and Athabasca bitumen [53, 54, 58].

vacuum gas oil (VGO), distillates, naphtha, and gases, and 10 reactions (k_1, ..., k_{10}), is depicted in Figure 2, and the activation energies for each of these reactions are reported in Table 8.

Remarkably, in spite of important differences in charge used (Maya oil with 22 API gravity and 39% residue Vs. Athabasca bitumen with 11 API gravity and 51% residue), catalysts used (supported NiMo Vs. ultradispersed NiMoW), reaction pressure and temperature (see Table 7), and operation mode (batchwise and continuous flow), the three works coincide in that:

a) Naphtha hydrocracking is insignificant since the values obtained for k_4 are null.
b) The kinetic constant for the conversion of VGO into gases (k_8) is also reported as 0.
c) Likewise, the value obtained for k_9 (distillates to gases) is null.

These results suggest that gas production comes exclusively from the hydrocracking of the residue fraction. In addition, the fact that $k_4 = 0$ means that naphtha conversion is negligible, for the reaction conditions used. Also, the values of the activation energies, shown in Table 2, are within the same range, although in some cases there are significant differences, which is not surprising given the aforementioned differences in reaction conditions.

From the values reported in all the three works, the residence time needed to achieve 50% residue conversion at different temperatures (working at the conditions used in each one) can be estimated at 1.2 h at 693 K [53], 42 h at 623 K [54] and 49 h at 623 K [68], which indicates that reduction in temperature can be compensated with an increase in residence time to obtain similar residue conversions. This is important from the view point of *in situ* upgrading where the maximum temperature and pressure attainable in the reservoir are lower than those normally used in surface hydrocracking process, but residence time downhole could be several days.

Interestingly, Loria *et al.* [54] shows that there is an exponential decrement in the viscosity with respect to residue conversion (for conversions higher than 9%) and that viscosity measurements can be used to determine the extent of bitumen upgrading.

Table 8. Activation energy for the hydrocracking of Maya heavy oil and Athabasca bitumen for the model shown in Figure 2.

Reference	Sanchez *et al.* [53]	Loria *et al.* [54]	Galarraga *et al.* [68]
Reaction	Activation energy/KJ mol^{-1}		
1	203.0	136	172.1
2	165.3	145	157.0
3	224.8	146	242.0
4	---	---	---
5	185.0	167	276.7
6	159.1	192	271.7
7	114.3	261	303.1
8	---	---	---
9	155.3	190	342.9
10	---	---	---

6. CONCLUDING REMARKS

There is no doubt that the interest on research and development in the productions and upgrading of heavy oils and bitumen is growing due to the presence of their vast resources worldwide and the ever decreasing amount of light oil reserves.

Catalytic processes for the upgrading of heavy oils and bitumen produce better liquid yields of higher quality products with no solid wastes, than thermal processes do, however there are challenges associated with the catalytic upgrading of these materials.

Thus, the main results of the work reported in the open literature can be summarized as follows:

Most of the supported catalysts used in the work reported in the open literature for heavy oils and bitumen upgrading are similar in composition to those commonly used in hydrotreating/ hydroprocessing, i.e., molybdenum or tungsten promoted by cobalt or nickel supported on alumina. However, catalyst textural properties for processing heavy oils need to be tuned up according to the targeted reactions (HDM/HAD or HDS/HDN) and to avoid, as much as possible, poisoning by metal and coke deposition. Then, the reactions of demetallization and deasphaltation are more dependent on the median pore diameter and pore volume of the catalysts (in order to have very high metal and coke storage capacity), while catalysts with higher surface area (which may be related to a higher dispersion of the active phases) show higher activities for HDS and HDN. Thus the optimum media pore diameter for a Co(Ni)Mo/Al_2O_3 catalyst, when the reactions of HDM/HDA are to be favoured, should be in the range of 100-250 Å, but if the HDS and HDN are the desired reactions, catalysts with higher surface areas (200-280 m^2 g^{-1}) and average pore diameters in the range of 80-150 Å should be used.

Another interesting observation is that when coke is deposited on the catalysts, the hydrogenolysis sites are the ones that are initially poisoned; however, the hydrogenation sites remain active even after an important amount of coke is covering the catalyst. It has been proposed that MoS_2 crystallites remain uncovered by coke due to the hydrogenating activity of the active sites, maintaining their activity for hydrogenation even after extensive coking of the catalyst.

Other types of supports (like clays, SiO_2, zeolites and active carbon), metals (for example Fe and V) and gaseous atmospheres (syngas, supercritical fluids) have been experimented but till now it seems that the best combination is Co(Ni)Mo supported on alumina under pressure of hydrogen.

Also, due to the problems associated with the poisoning of supported catalysts caused by coke and metal deposition during upgrading, the use of unsupported catalysts have been proposed as an alternative for treating heavy feeds like heavy oils and bitumen. Unsupported catalysts are usually dispersed in the reaction media, and three different ways of dispersing the catalysts have been reported: Dispersion of fine powders, preparation of water in oil emulsions (the metal precursors are dissolved in the aqueous media) which is decomposed during the upgrading process, and solubilization of a lipophillic metal compound in the oil to be treated.

The reports presented on the subject essentially deal with catalysts containing molybdenum, tungsten, nickel and cobalt (although iron has also been tried), tested under high partial pressure of hydrogen (the use of methane has also been reported), because they produce better conversions. Also, lipophillic compound seems to perform better than emulsion or dispersed powders.

Another area that has been extensively researched lately is Catalytic aquathermolysis (CAQT). Different types of catalytic precursors have been reported for CAQT, thus: water soluble, oil-soluble and amphiphilic metallic compounds, as well as ionic liquids and dispersed particles, of different metals (Ni, Fe, Cu, Zn, Ru, V, Mo and Al) have been used as catalysts in the CAQT of heavy oils. Important viscosity reductions, as well as better final product characteristics, are reported.

Finally, *in situ* (or downhole) processing has been proposed as a way of producing synthetic oils from heavy oils and bitumen in the reservoir, therefore reducing energy demands for field hydroprocessing and decreasing emissions.

Different process configurations have been reported: *in situ* combustion coupled with a supported $NiMo/Al_2O_3$ catalyst packed in the producing end of the combustion tube; injection of an amphiphillic metal compound (as an aqueous solution) in CAQT like conditions; and using nanoparticles dispersed in a hydrocarbon carrier with dissolved hydrogen. All of them result in an important viscosity reduction (although in CAQT the viscosity is not low enough for transportation) and an increase in API gravity. Also, stability of the oil, which is important for storing and transportation, is usually not reported. Stability could be a concern for processes that are mainly thermal since it is recognized that thermal processes increase the content of olefin (the primary cause of instability) in the products.

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