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A batch reactor study of the effect of deasphalting on hydrotreating of heavy oil

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ABSTRACT

The effect of deasphalting of heavy oil with different degrees of asphaltenes precipitation on catalytic hydrotreating is reported in this work. Deasphalted oils were obtained in a pressurized vessel using n-heptane and n-pentane as solvents. Various samples with different amounts of asphaltenes were prepared by varying precipitation conditions. Hydrotreating of deasphalted oils was conducted with a commercial NiMo catalyst in a batch reactor at the following reaction conditions: hydrogen pressure of 100 kg/cm^2, temperature of 400 °C, stirring rate of 750 rpm and reaction time of 4 h. The heavy oil, the deasphalted oils and the hydrotreated products were characterized by sulfur, metals (Ni, V), asphaltene contents, and API gravity. Metals and carbon contents as well as textural properties and X-ray diffraction were also determined on fresh, spent and regenerated catalysts.

1. Introduction

Studies of asphaltenes precipitation and characterization have been traditionally carried out with the main objective of understanding the asphaltene deposition problem: flocculation, aggregation and precipitation mechanisms from crude oils, and the influence of metallic particles present [1]. However, the declining production of light crude oils together with the continuous growing up in the production of heavy and extra heavy crude oils, have caused an increase in the asphaltenes content of the produced oils which are sent to petroleum refineries [2].

Ongoing advances in established technologies, together with recent commercial applications of residue fluid catalytic cracking (RFCC), hydroprocessing, solvent deasphalting and gasification of pitch and coke, have markedly enhanced options for processing and economically using residues [3]. In addition, processing of heavy oils to obtain more gasoline and other liquid fuels is nowadays a necessity; hence the knowledge of the constituents of these higher boiling point feedstocks is of great importance. It has been recognized that the problems associated to processing of heavy feedstocks can be equated to the chemical character and the amount of complex and higher boiling components in the feedstock. Refining heavy oils is not just a matter of applying know-how derived from refining conventional light crude oils but requires knowledge of the chemical structure and chemical behavior of these more complex feedstocks [4]. Asphaltenes, being the most intrincate molecules present in petroleum, are also the most refractory and difficult to process portion of the crude oil. The main problems associated with hydroprocessing of heavy oils having high amount of asphaltenes are: precipitation on the catalyst surface and blocking of the catalyst pore mouth, they act as coke precursors which ends up as catalyst deactivation, and limit the maximum level of conversion due to sediment formation [5].

Common fixed-bed catalytic hydroprocesses, which use atmospheric residue, vacuum residue, or heavy crude oils as feed, are multiple reactor units with graded catalyst systems to achieve desired levels of impurity removals and conversion. The catalytic system is frequently integrated by a hydrodemetallization (HDM) catalyst for metal removal, a balanced hydrodemetallization/hydrodesulfurization (HDM/HDS) catalyst and a hydrodesulfurization (HDS) catalyst, at the front, middle and last sections respectively [4,6,7]. The first catalyst is designed to have optimized textural properties, shape, active metal loading, etc. in order to achieve high metal retention capacity to protect the following catalysts against premature deactivation and allow the process for long-term operations [8]. Since most of the amount of metals present in heavy crudes, mainly V and Ni, are concentrated in asphaltenes, removing this high-molecular weight material will consequently reduce the metal content in the feed to hydroprocessing. Therefore, deasphalting a heavy feed before its hydrotreating seems to be very convenient from operational and economical points of view.

Solvent deasphalting (SDA) is a molecular weight-based separation process member of the family of carbon rejection

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technologies, which has been used for more than fifty years to separate heavy fractions of crude oil beyond the range of economical commercial distillation. SDA process produces a low-contaminant deasphalted oil (DAO) rich in paraffinic-type molecules, and a pitch product rich in aromatic compounds and asphaltenes containing of course the majority of the feed impurities. The application of SDA process has been reported for production of lube oil feedstocks from vacuum residue using propane as solvent, for preparation of feedstocks for catalytic cracking, hydrocracking and hydrodesulfurization units, as well as for the production of specialty asphalts [9–11].

The increasing production of heavy crude oils has forced petroleum refiners to deal with heavier feedstocks, which possess high amounts of asphaltenes. When sending these heavy feeds to hydroprocessing units the catalysts will be exposed to severe deactivation, in such cases deasphalting these heavy materials would be more appropriate to prepare suitable hydroprocessing feeds. Hydrotreating is a better choice for processing vacuum residua with relatively low content of heavy metals. The combination of solvent deasphalting with asphalt gasification would be a feasible upgrading way to convert heavy feedstock with high metal content [12–14]. The aim of this study is then to analyze the effect of different degrees of deasphalting of heavy oils on catalytic hydroprocessing behavior.

2. Experimental

2.1. Materials

A vacuum residue (538 °C+ VR) obtained from Maya heavy crude oil was employed for hydrotreating experiments and for preparing different deasphalted oils. The main properties of Maya crude and its VR are given in Table 1. The catalyst used in all hydrotreating experiments was a commercial sample with the following main properties: 0.58% Ni, 2.2% Mo, 197 m^2/g specific surface area, 0.85 cc/g pore volume and 173 Å mean pore diameter. n-Heptane, n-pentane and nitrogen were used for asphaltenes precipitation while hydrogen was utilized for hydrotreating tests.

2.2. Preparation of DAO

VR was loaded in a pressurized system (Parr reactor model 4522 and controller model 4841) equipped with stirring system, temperature and pressure controls, and vent. To obtain different degrees of deasphalting, precipitation conditions were varied in the following ranges: solvent-to-oil (S/O) ratio between 2 and 10 mL/g, 750–1000 rpm stirring rate, 15–30 min stirring time, atmospheric-25 kg/cm^2 of nitrogen pressure and temperature from ambient to 100 °C. Typically, 200 g of VR were put into the reactor and 1400 mL of n-heptane were added for the case of a solvent-to-oil ratio of 7 mL/g. The reactor was pressurized with nitrogen and stirring began when the temperature was adjusted to the desired value. Stirring was kept for the desired time, stopped and then the reactor content was settled for 60 min, and withdrawn by means of a valve located at the bottom of the reactor. The remaining sample adhered to reactor walls was removed with n-heptane washing and collected in a beaker. The reactor content was filtered by using a vacuum system and a Whatman 3 filter paper with 6 μm pore size to retain asphaltenes. The deasphalted oil was finally weighed and characterized. A schematic representation of this experimental methodology is shown in Fig. 1.

2.3. Hydrotreating experiments

Hydrotreating tests were carried out in a batch reactor (1 L, Parr reactor model 4573 and controller model 4842). The following constant hydrotreating conditions were utilized: 100 kg/cm^2 hydrogen pressure, 400 °C reaction temperature, 750 rpm stirring rate, and 4 h reaction time. Temperature, pressure and stirring are controlled automatically using a digital controller. In each experiment, 5 g of catalyst and 200 g of sample were loaded to the reactor. Prior to the activity tests the catalyst was sulfided *ex situ* in a fixed-bed glass reactor at the following conditions: atmospheric pressure, 400 °C temperature, 40 mL/min H_2, and 3 h. Hydrogen is passed through a container having carbon disulfide, and then the H_2/CS_2 mixture is passed through the glass reactor. The sulfided catalyst was transferred into the batch reactor in nitrogen atmosphere so that contact with air was avoided. After closing the reactor, it was purged several times with hydrogen to assure there was no air left inside the reactor. Heating was then started from room temperature to 400 °C. The reaction began until all conditions were established and stirring rate was initiated. After reaction, the reactor was depressurized and hydrotreated products were filtered to separate the catalyst from liquids. Fig. 1 shows the schematic representation of this procedure.

2.4. Characterization of oils and catalyst

Oil samples were characterized by sulfur content by X-ray fluorescence (HORIBA model SLFA-2100/2800), Ni and V contents by atomic absorption (Thermoelectron model Solaar AA), specific gravity by means of picnometers and then transformed to API gravity (ASTM D-70). Asphaltene is defined as that material insoluble in n-heptane (ASTM D-3279).

Metals content on catalysts was analyzed by atomic absorption (Thermoelectron model Solaar AA), carbon content with a Leco SC-444 instrument using ASTM C-1408 method with direct combustion-infrared detection, and textural properties (specific surface

Table 1
Properties of Maya crude oil, Maya VR (538 °C+) and DAO's.

	Maya	VR	DAO-7	DAO-4	DAO-0
Yield of DAO, wt%	–	–	69.6	64.5	40.2
API gravity	22.0	1.46	10.01	17.87	11.27
Total S, wt%	3.60	5.32	4.62	4.46	4.29
nC_7 insol., wt%	9.51	27.86	7.10	4.18	0.45
Ni, wppm	53	140	59	44	30
V, wppm	260	698	314	206	60
Total Ni+V, wppm	313	838	373	250	90
Hydrotreated products					
API gravity	–	10.78	17.76	20.86	22.96
Total S, wt%	–	3.06	2.61	2.20	1.79
nC_7 insol., wt%	–	16.24	6.18	5.88	1.67
Ni, wppm	–	144	84	36	36
V, wppm	–	534	125	117	30
Total Ni+V, ppm	–	678	209	153	66

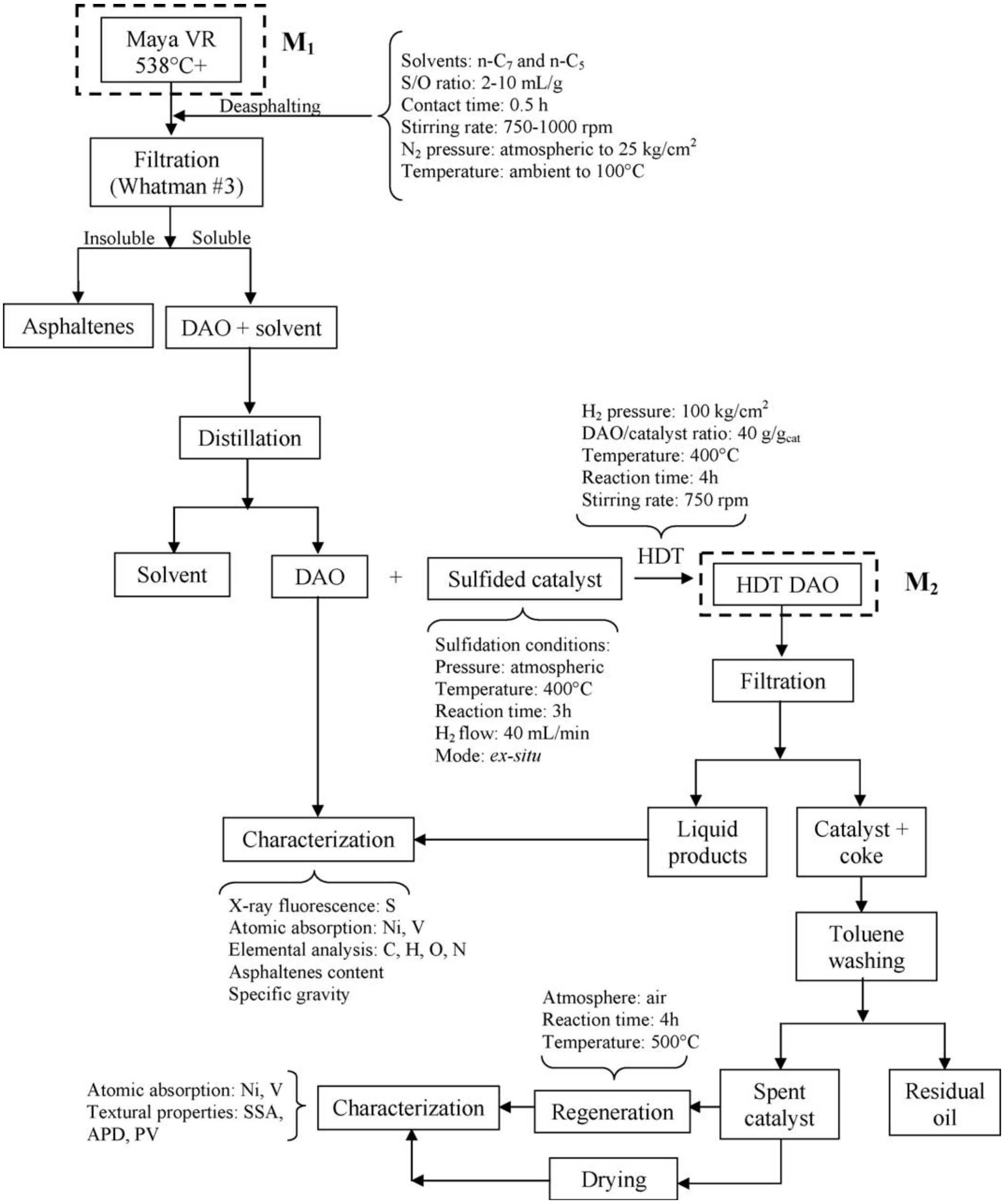

Fig. 1. Experimental methodology.

area, pore volume and pore size distribution) by nitrogen adsorption at 77 K (Quantachrome Nova 4000). Spent catalyst was washed with toluene under reflux to remove adsorbed residual oil whereas solids obtained (spent catalyst + coke) were dried at 100 °C before characterization to analyze textural properties. Dried catalyst was regenerated by oxidation under air atmosphere at 500 °C during 4 h and the amount of coke was determined as the weight difference among solids after and before calcination. Both the spent and regenerated catalysts were analyzed by X-ray diffraction in a diffractometer model Siemens D-500 with Cu Kα radiation (λ = 1.5418 Å) operating at 40 kV and 30 mA in the 5–70° scan range of 2θ, with a scan rate of 0.02°/s.

3. Results and discussion

3.1. Preparation of DAO

The effect of conditions on asphaltenes precipitation has been studied in previous works in a pressurized system [15]. It is well

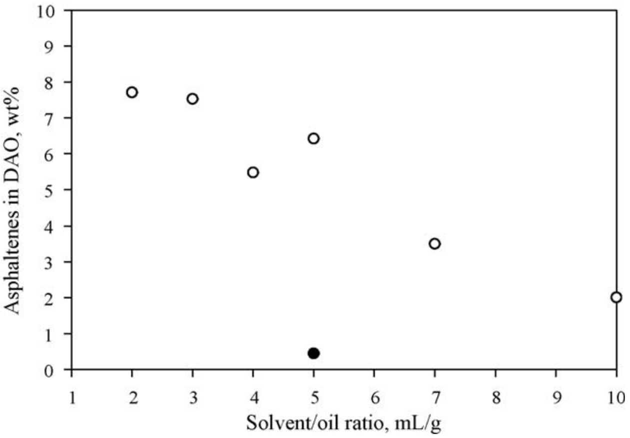

Fig. 2. Effect of solvent-to-oil ratio and solvent on asphaltenes content in DAO. (○) n-Heptane and (●) n-pentane.

known in the literature that the lower the precipitation time and solvent-to-oil ratio, the lower the asphaltenes precipitation; and when temperature is increased and pressure is decreased asphaltenes content tends to diminish. The opposite behavior, of course, is observed for asphaltenes content in DAO. That is, when S/O ratio, time and pressure are decreased or temperature is increased, DAO asphaltenes content tends to increase. To examine the effect of precipitation conditions on the particular feed (VR from Maya crude oil) of the present work, experiments varying some parameters were done. Fig. 2 illustrates the effect of solvent-to-oil ratio on asphaltenes content in DAO. In the range of 2–10 mL/g solvent-to-oil ratio asphaltenes content in DAO varied from about 2 to 8 wt%. Earlier studies have also reported the use of S/O ratio of 10:1 [16]. Neither higher than 10 nor lower than 2 solvent-to-oil ratios were tested since either very low quantity of DAO was obtained and a number of precipitations would be required or when filtering the sample different problems were experienced. By varying other precipitation conditions within the aforementioned ranges it was not possible to obtain neither higher nor lower amounts of asphaltenes in DAO. Instead, the solvent was changed to n-pentane and concentration of asphaltenes in DAO was reduced to a value very close to zero. As summary, we were forced to use different solvents because when using n-heptane only, it was not possible to obtain DAO free of asphaltenes. The use of n-pentane allowed us to meet the requirements for a feedstock with almost no amount of asphaltenes.

The option of blending DAO either with virgin VR or with asphaltenes was also considered to prepare DAO with different asphaltenes content. However, since asphaltenes properties may vary during precipitation and its effect on hydrotreating can also be different, this alternative was discarded. On the other hand, dilution of VR with light petroleum fractions, e.g. straight-run gas oil has been already studied in our group and reported elsewhere [17].

Based on these results, the following feeds were prepared at the indicated conditions, whose main properties are presented in Table 1.

- DAO-0, with 0.45 wt% asphaltenes, precipitated with n-pentane at 5 mL/g S/O ratio, 1000 rpm stirring rate, 30 min stirring time, 25 kg/cm^2 pressure and 100 °C temperature.
- DAO-4, with 4.18 wt% asphaltenes, precipitated with n-heptane at 7 mL/g S/O ratio, 1000 rpm stirring rate, 30 min stirring time, 25 kg/cm^2 pressure and 100 °C temperature.
- DAO-7, with 7.1 wt% asphaltenes, precipitated with n-heptane at 3 mL/g S/O ratio, 1000 rpm stirring rate, 30 min stirring time, 25 kg/cm^2 pressure and 100 °C temperature.

API gravity was substantially increased when different portions of asphaltenes were separated from the VR feed. The DAO-0, with the lowest amount of asphaltene, did not follow the expected trend when reducing asphaltene content, which might be due to the use of n-pentane instead of n-heptane as in the cases of DAO-4 and DAO-7.

API gravity of DAO-0 is higher compared with DAO-4 and DAO-7 due to the presence of microwaxes that cannot be properly dissolved by n-pentane since it takes longer time to dissolve them. In addition, when using n-pentane as solvent, a fewer yield of DAO is obtained as observed in Table 1; however, the sulfur concentration is still higher in DAO. In this way, microwaxes, sulfur compounds along with metals could be responsible for the increase of API of DAO-0 because its concentrations are more notorious in a smaller amount of recovered DAO-0 (40.2 wt%) compared with DAO-4 (64.5 wt%) and DAO-7 (69.6 wt%). In addition, asphaltenes precipitated with n-pentane are lighter than those obtained with n-heptane as reported in previous work in which aggregate molecular weights by Vapor Pressure Osmometry of asphaltenes precipitated from Maya crude had values of 3680 and 5190 g/mol when using n-pentane and n-heptane, respectively [18].

Sulfur content in DAO's was slightly reduced compared with the original VR, and not much effect is observed when changing the concentration of asphaltenes. On the contrary, metals (Ni and V) notoriously vary at different asphaltenes content in DAO. This behavior in both S and metals indicates that the amount of asphaltenic sulfur is lower than that of the asphaltenic metals, since most of the sulfur concentrated in DAO and most of the metal was found to be asphaltenic in nature (i.e. it was concentrated in asphaltenes). For the case of Maya crude, it has been reported in the literature that about 30% of the sulfur and 60% of the metals are asphaltenic [18], which is in line with our findings.

The increase in API gravity of DAO's compared with that of VR feed, corroborates that apart from reduced impurities content deasphalted oil became rich in paraffinic-type molecules. The change in API gravity roughly indicates that DAO's are less aromatic at low amount of asphaltenes. The low aromaticity of DAO will favor hydrocracking of heavy molecules into smaller ones.

3.2. Hydrotreating of DAO

Hydrotreating experiments were carried out in a batch reactor. Since the catalyst is subject to deactivation by coke and metals, and initial concentration of asphaltenes (and those of the other impurities) is changing during time, samples at different times were not obtained such as when experiments are performed in continuous flow reactors, in which initial concentrations are always the same. Experiments may be conducted by loading and unloading fresh catalyst and performing the reaction at different times for each test [19] however, it would take much time to do so. Instead, only one sample was taken at the end of reaction at 4 h.

Since much of the sulfur and part of the metals were found to be non-asphaltenic in nature, their removals are expected to be high as shown in Fig. 3, in which different amounts of asphaltenes in DAO are plotted against sulfur and metals conversions after hydrotreating. S and metals conversions were calculated as $(M_1-M_2)/M_1$, where M_1 is grams of the impurity in VR and M_2 the grams of the impurity in hydrotreated DAO. The localization of M_1 and M_2 can be observed in Fig. 1. The yield of DAO during deasphalting of VR is necessary to do this calculation, so that conversions reported in Fig. 3 are on VR basis, and not on HDT reactor feed. This manner to compare conversions is more suitable since reactor feeds have different concentrations of S and metals. For DAO-0 sulfur conversion is high (~86%) along with metals conversion (~97%).

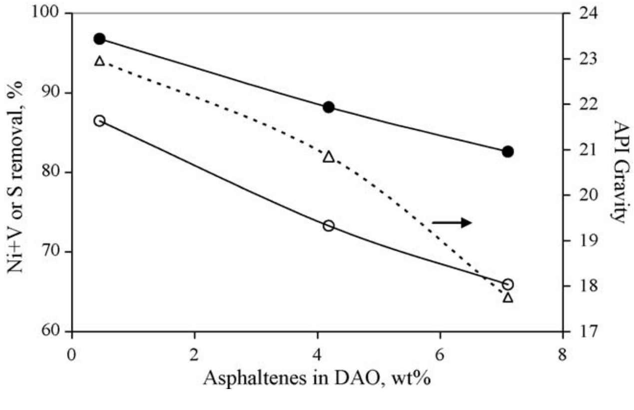

Fig. 3. Effect of asphaltenes in DAO on impurities removal and API gravity of hydrotreated products. (○) Sulfur, (●) Ni + V and (△) API gravity.

This is because during deasphalting, not only asphaltenes precipitate but also sulfur and metals attached to them do. Remaining contaminants are present in DAO but its nature is less refractory since they form part of maltenes and readily react during HDT having high conversions as can be seen in Fig. 3. It is also observed that metals conversion is also high. For DAO-4, sulfur and metals conversion were 73 and 88%, respectively and for DAO-7 66 (sulfur) and 83% (Ni+V). In this last case, the feedstock still contains a significant amount of asphaltenes and sulfur likely associated to them by which its reactivity during HDT would tend to diminish giving lower conversions compared with DAO-0.

The increase of API gravity (see Table 1) indicates that hydrocracking was more selective when using DAO as feed. This, as mentioned previously, is due to the less aromatic nature of DAO. The most refractory asphaltenic fraction remained in hydrotreated products, which were not hydrocracked in great extent for the case of DAO's.

3.3. Characterization of spent catalysts

Spent catalysts were recovered after reaction, washed with hot toluene by Soxhlet process and then characterized. As expected, metals and carbon were deposited onto the catalyst causing reductions in specific surface area (SSA) and total pore volume (TPV). Table 2 summarizes the characterization results of fresh and spent catalysts. For the non-deasphalted feed SSA and TPV reduced about 32 and 52%, while maximum reductions with DAO feed were 27.4 and 47.1% respectively in the whole range of asphaltenes content. It is observed that in all cases coke (reported as carbon content) is deposited on catalyst surface even when using DAO-0 which is almost free of asphaltenes. This is because resins also play an important role contributing up to 10 wt% in coke production [20]. In this case, naphthenes and alkyl chains can form free radicals which further condense to give coke as final product.

Deposited carbon and metals are higher as the asphaltenes content in feeds is increased. Carbon deposition is more or less the same for DAO's and non-deasphalted feeds, and also very similar to other previous experiments conducted in the same reaction system at similar conditions, but with Maya heavy crude as feed [19]. This behavior is quite common in hydrotreating processes, since being carbon deposition the first catalyst deactivation mechanisms it reaches a steady-state value, while metals continue to be deposited onto the catalyst for a long period [21,22].

Pore size distributions of fresh and spent catalysts are presented in Fig. 4. It is clearly seen that blockage of pores of spent catalysts obtained from hydrotreating of different feeds is higher as the amount of asphaltenes in feeds is also higher. Being asphaltenes the major cause of catalyst deactivation by coke and taking into account that catalyst samples were recovered at 4 h, most of the catalyst pore blockage may be attributed to coke formation. To confirm this assumption and distinguish the deactivation by carbon or metals, spent catalysts were regenerated (at 500 °C, 4 h, with air) and the deposited carbon was burnt off. Textural properties were determined in regenerated catalysts and are presented in Table 2. Recovery of both SSA and TPV is notorious, and the values are very close to those of the fresh catalyst. Regarding to SSA, 86% was recovered after calcination and about 90% of the TPV was reestablished (coke deactivated pores) while the rest 10% (metal deactivated pores) remained unaffected [23]. For all spent catalysts, textural properties were not recovered at 100% due to irreversible catalyst deactivation by metals deposition.

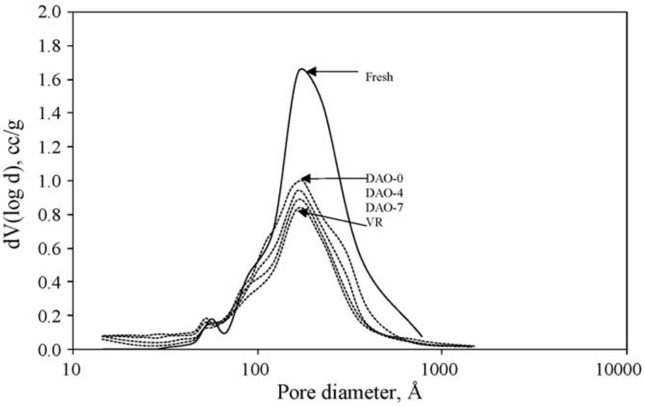

Fig. 4. Pore size distribution of fresh and spent catalysts after hydrotreating of DAO's with different asphaltenes content.

An example of pore size distributions for fresh, spent and regenerated catalysts after hydrotreating of VR is shown in Fig. 5. VR feed was selected for this comparison to highlight the dissimilarity among catalysts with different deactivation pattern. The differences in fresh (non-deactivated), regenerated (metal deactivated) and spent (metal + coke deactivated) catalysts is clearly demonstrated. During regeneration, pores are released of coke and metals remained into the pores. Since pore size distribution of regenerated catalyst is quite similar to that of fresh catalyst, it is then confirmed that the predominant deactivation mechanism is coke formation for the feed, catalyst, reaction conditions and experimental setup used in this work.

Spent and regenerated catalysts were also analyzed by X-ray diffraction and no drastic changes were observed as compared with fresh catalyst, which means that concentrations of vanadium and nickel sulfides were low and its dispersion on catalyst surface

Table 2
Characterization of fresh, spent and regenerated catalysts.

	Fresh	Spent catalysts			
	Catalyst	VR	DAO-7	DAO-4	DAO-0
SSA, m^2/g	197	134	148	143	151
TPV, cc/g	0.85	0.41	0.45	0.45	0.54
MPD, Å	173	124	124	127	147
C, wt%	–	19.6	17.0	15.0	13.0
Metals content, wt% (g metal/100 g fresh catalyst)					
Ni	0.58	0.575	0.567	0.420	0.460
V	–	0.551	0.354	0.353	0.239
Ni[a]	–	(0.251)	(0.194)	(0.046)	(0.017)
V	–	(0.796)	(0.483)	(0.448)	(0.292)
		Regenerated catalysts			
SSA, m^2/g	197	175	172	170	170
TPV, cc/g	0.85	0.76	0.75	0.77	0.77

[a] Initial amount of Ni in fresh catalyst has been discounted.

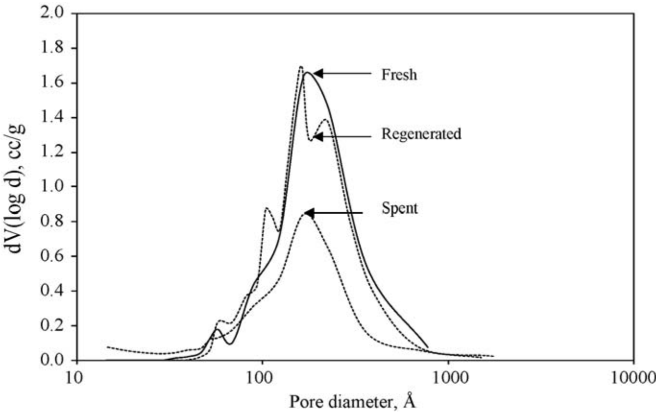

Fig. 5. Pore size distribution of fresh, spent and regenerated catalysts during hydrotreating of VR.

did not allowed us to detect them with this technique. Fig. 6 shows the diffractograms corresponding to spent (Fig. 6A) and regenerated (Fig. 6B) catalysts. It is observed that in the case of spent catalysts, the diffractogram for VR feedstock shows a prominent peak around 26° in the 2θ axis which corresponds to crystalline graphite [24]. The height of this peak indicates that graphite is highly stacked covering the catalyst surface being asphaltenes majorly responsible for coke deposition. After regeneration (Fig. 6B), carbon deposits have been burned off recovering the catalyst surface at long extent as reported in Table 2. Other authors have stated that rapid coke deposition as high as 10 wt% is observed on the catalyst surface during the first 3 h of run diminishing around 40% the specific surface area of the catalyst [25] which is in agreement with our results. In other reports, coke deposition has reached up to 20–30 wt% during the initial deactivation stage [26]. It is also observed that the recovered SSA after regeneration is in the range of 100–500 Å that corresponds to mesoporous region.

Fig. 7 shows the adsorption–desorption isotherms for fresh and spent catalysts with each feedstock. The hysteresis loop of fresh catalyst corresponds to type II isotherm because it is mainly composed by mesopores. The hysteresis loop tends to increase as the catalyst is deactivated by coke and deposited metals as observed when processing different feedstocks; however, the deactivation pattern is very similar for all catalysts. An approach to determine degree of catalyst deactivation is by calculating the hysteresis area, that is the difference in the area under the curve between desorption and adsorption isotherms:

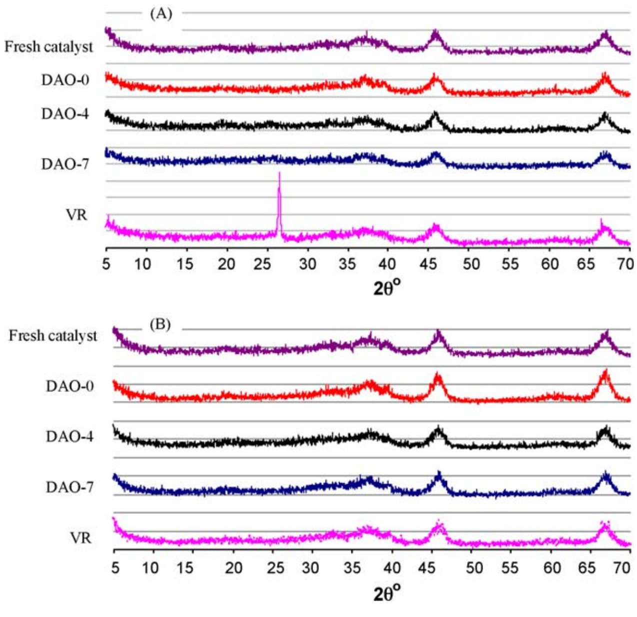

Fig. 6. X-ray diffractograms for different catalysts. (A) Spent catalysts and (B) regenerated catalysts.

$$\text{Hysteresis area (HA)} = \text{Area}_{\text{desorption}} - \text{Area}_{\text{adsorption}} \quad (1)$$

Before calculating the areas, data must be normalized to one. When regenerating spent catalysts the hysteresis loop tends to be similar to that of the fresh catalyst since the pores are released by coke elimination. However, it was not possible to recover neither the total SSA nor the original pore volume after calcination due to deposition of metals.

The HA value is higher for the catalysts when processing VR feedstock. Fig. 8 shows the relationship between the asphaltenes content in the feedstock defined as n-heptane insolubles and the corresponding HA value. A linear dependence is obtained, e.g. the lower the amount of asphaltenes in the feedstock, the lower the hysteresis area. Another way to examine the catalyst deactivation based on results of adsorption–desorption isotherms is by dividing the areas of adsorption and desorption of fresh and spent catalysts as follows:

$$\text{Ratio of areas} = \frac{\text{HA}_{\text{spent catalyst}}}{\text{HA}_{\text{fresh catalyst}}} \quad (2)$$

Fig. 8 shows the ratio of areas calculated with Eq. (2) in function of the asphaltenes content in the feed and a linear relationship was also obtained. This way to analyze the results can be considered as a semi-quantitative approach to determine the extent of catalyst deactivation. For instance the ratio of areas for DAO-0 is 1.006, which is very close to one, indicating that catalyst deactivation with this feed is very low as compared with DAO-7, which has a ratio of areas of 1.123. Non-deasphalted feed (VR 538 °C+) exhibited a ratio of areas of 1.253, this number is indicative of very high deactivation rate compared with deasphalted feeds. In other words, if HA for fresh catalyst is taken into account as a reference, it was possible to obtain different percentages of catalyst deactivation when processing different feedstocks as follows: 25.3% for RV, 12.3% for DAO-7, 7.2% for DAO-4 and 0.6% for DAO-0. The low catalyst deactivation rate for DAO-0 was a consequence of removal of asphaltenes during SDA process.

3.4. Perspectives and future work

The results presented in this exploratory study for upgrading of heavy oils by combination of solvent deasphalting and hydrotreating processes are promissory and more work in this research area must be continued. Samples with a wider range of asphaltenes content need to be prepared in order to optimize the degree of deasphalting, based on the behavior of deasphalted oil during hydrotreating. The effects of reaction conditions (reaction temperature and pressure, contact time) on impurities removal and hydrocracking need also to be evaluated. Longer experiments are indispensable to differentiate catalyst deactivation by metals and coke. More characterization studies on spent catalysts need to be carried out in order to envisage the most probable deactivation mechanism. In this regard, the nature of deposited coke can be studied by Temperature Programmed Oxidation (TPO), Nuclear Magnetic Resonance for solids (NMR) and Scanning Electron Microscopy (SEM) among other characterization techniques. Kinetics can be determined from these experimental data and the effect of deasphalting on hydrotreating catalyst activity and selectivity can be elucidated based on theoretical approaches. Other options, such as blending low-asphaltene DAO with virgin

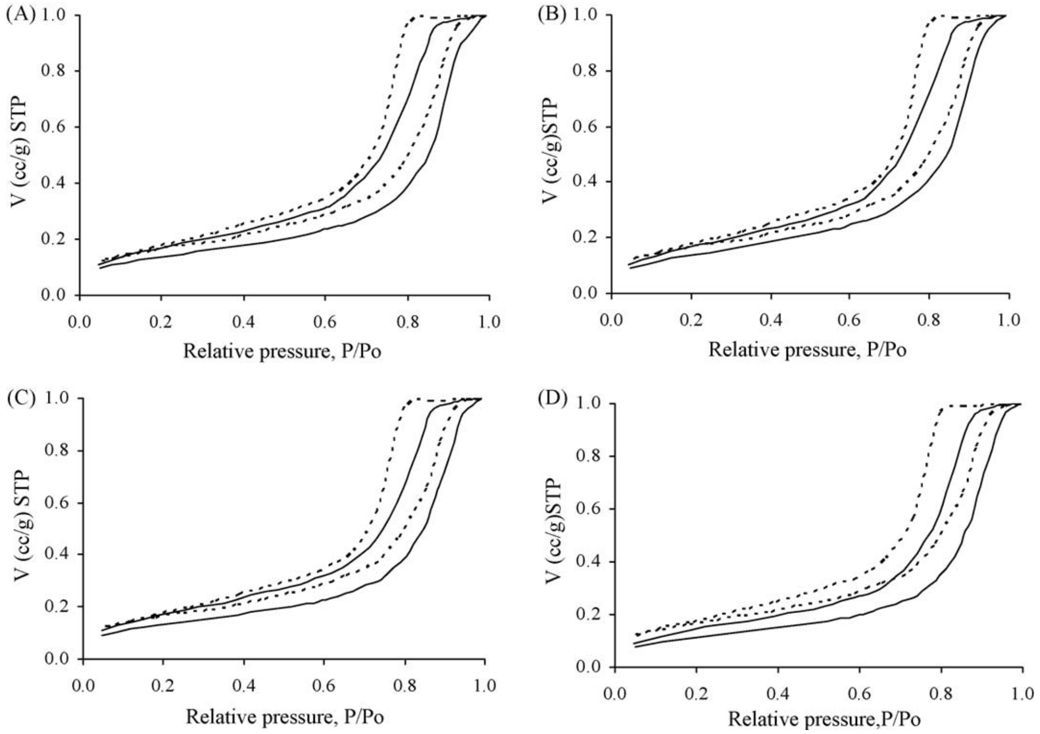

Fig. 7. Adsorption–desorption isotherms for fresh and spent catalysts under different feedstocks. (A) Vacuum residue, (B) DAO-7, (C) DAO-4, (D) DAO-0, (- - -) spent catalyst, (—) fresh catalyst.

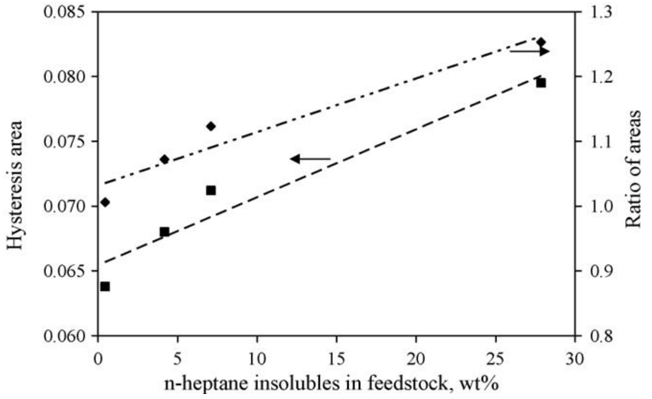

Fig. 8. n-Heptane insolubles in feedstock vs. hysteresis area of spent catalysts and ratio of areas.

feed, e.g. VR, need to be explored to prepare hydrotreating feeds with different amounts of asphaltenes. Deeper characterizations of both asphaltenes and DAO are necessary to establish the global performance of a combined SDA-HDT process scheme. Experiments conducted not only in batch mode but also in continuous mode of operation are mandatory to determine catalyst deactivation pattern, cycle life, impurities removal, product quality, etc. in order to evaluate the feasibility of the application of a hybrid process (SDA-HDT) for upgrading of heavy oils.

4. Conclusions

Various deasphalted oils with different asphaltenes contents obtained from vacuum residue of Maya crude by solvent precipitation were hydrotreated in a batch reactor at moderate reaction conditions (100 kg/cm^2 and 400 °C). The effect of asphaltenes in the feed on sulfur and metals removal as well as changes of API gravity was evidenced. Feeds with low amount of asphaltenes exhibited higher hydrocracking selectivity (measured as an increase in API gravity) and impurities (S and metals) removals than those with high amount of asphaltenes.

Characterization of fresh, spent and regenerated catalysts indicates that the main cause of deactivation at the conditions of the present work was coke deposition during the first hours of run. Spent catalysts were able to recover specific surface area at high extent by releasing the blocked pores after coke calcination. Catalyst deactivation measured as hysteresis area was linearly correlated with the n-heptane insolubles in the feedstock since lighter feeds form less coke on catalyst surface. A linear trend was also obtained when calculated the deactivation percentage based on hysteresis area indicating more catalyst deactivation when using feedstocks having higher asphaltenes content. The effect of asphaltenes on catalyst deactivation and product quality indicates that solvent deasphalting before hydrotreating is an attractive process alternative for conversion of heavy feedstocks. It was recognized that more experiments conducted at different reaction conditions in batch and continuous flow units are necessary to determine catalyst stability, and other process parameters. Further economical studies are also indispensable to evaluate the profitability of a combined process scheme (SDA-HDT) for upgrading of heavy and extra-heavy crude oils.

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