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SCREENING STUDY OF VARIOUS CATALYSTS SYSTEMS FOR A HYDROCRACKING/HYDROTREATING OF VACUUM RESIDUE OIL: MEREY

EVALUACIÓN DE SISTEMAS CATALÍTICOS PARA HIDROCRAQUEO/HIDROTRATAMIENTO DE RESIDUO DE VACÍO: MEREY

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Abstract

Ultra-dispersed catalysts are the alternative for heavy oil hydroprocessing because of their high activity, low deactivation rate and low catalysts metal concentration. However, metals used for ultra-dispersed catalysts are expensive, therefore it is necessary to consider different strategies to improve catalysts for heavy oil hydroprocessing. In this study, we have evaluated the catalytic performance of four catalytic emulsion formulations containing molybdenum and nickel and two solid dispersed formulations containing iron. Results showed that at tested conditions, the percentage of converted products for VR 500°C$^+$ and asphaltenes are comparable for emulsion formulations, showing no nickel synergistic effect. Also, VR 500°C$^+$ conversion for iron formulations are comparable with thermal cracking conversion for the same feedstock. Even so, iron formulations had a poorer performance than emulsion formulations, Fe-m showed a 7 wt% coke yield, a 57 wt% VR 500°C$^+$ conversion (higher than emulsion formulations) and 4 wt% liquid yield increase (87 wt%) in comparison with thermal cracking (83 wt%) meaning that this type catalyst could be used to upgrade heavy oil feedstocks at medium severity.

Keywords: ultra-dispersed, iron, hydrocracking, hydrotreating, hydroprocessing.

Resumen

Los catalizadores ultradispersos son una alternativa para el hidroprocesamiento de crudos pesados, debido a su alta actividad, baja tasa de desactivación y baja concentración de metales. Sin embargo, los metales usados para este tipo de catalizadores son costosos, por lo que es necesario mejorar los catalizadores para este tipo de procesos. En este estudio, se evalúa el desempeño catalítico de cuatro formulaciones emulsionadas conteniendo molibdeno y níquel y dos sólidos dispersos conteniendo hierro. Los resultados indican que a las condiciones probadas, los productos convertidos del RV 500ºC$^+$ y los asfaltenos son comparables para las formulaciones emulsionadas, indicando que no existe sinergía del níquel. Además, la conversión de RV 500ºC$^+$ para las formulaciones de hierro es comparable con la conversión de craqueo térmico para la misma alimentación. Aunque, las formulaciones de hierro muestran un peor desempeño catalítico que las formulaciones emulsionadas, Fe-m obtuvo un 7 %p de rendimiento a coque, 57 %p de conversión RV 500ºC$^+$ (superior a las formulaciones emulsionadas) y 4 %p de aumento del rendimiento a líquido (87 %p) en comparación con el craqueo térmico (83 %p), indicando que este tipo de catalizador puede ser utilizado para el mejoramiento de cargas pesadas a media severidad.

Palabras clave: ultradisperso, hierro, hidrocraqueo, hidrotratamiento, hidroprocesamiento.

1 Introduction

Currently, light crude reserves around the world have decreased and technologies aim to process heavy oil feedstocks and petroleum residues with catalysts have to be optimized. One of the ideal alternatives is the use of ultra-dispersed catalyst with a high dispersion (Noguera *et al*. 2012) due to an elevated activity toward main reactions of interest as a result of a high ratio area/volume (Panariti *et al*. 2000a-2000b, Marchionna *et al*. 1994), but as consequence of the metal cost (usually nickel and molybdenum) some less expensive alternatives for the medium severity processes should be considered.

As stated by Noguera *et al*. (2012) ultra-dispersed catalysts can be classified as: heterogeneous and homogeneous depending on their miscibility under reaction conditions. Homogeneous catalysts can be divided in soluble compounds in aqueous phase or

in organic phase. Heterogeneous solids are introduced to the process through dry dispersion of the catalytic solid or precursor, finely divided into the crude (Ren 2004, Thompson 2008). Main disadvantage of heterogeneous solids is that they have a lower activity and generate by-products of difficult handling, even so depending on the reaction severity and the use of the generated products, this could be a problem or not.

In this work, a study relating to the effect of six catalytic formulations on hydroconversion activity, for the vacuum residue (VR) 500°C$^+$ Merey, is presented, taking into account, changes in the catalytic precursors (Mo, MoNi or Fe) and the type of catalyst (emulsion w/o, solid dispersed in the VR or nano particles dispersed in a hydrocarbon phase), to evaluate catalytic formulations performance.

2 Experimental

This section shows a feedstock and products characterization; and, also, a description of the experimental procedure.

2.1 Feedstock

The vacuum residue 500°C$^+$ Merey, was used as feedstock for the deep conversion process. This residue was characterized in accordance with standard procedures and properties are listed in Table 1.

2.2 Catalysts

Four of the six catalytic systems evaluated in this study, consist of ultra-dispersed catalyst from w/o emulsions, two of Mo/Ni named AT-48/Ni and ET/Ni and two of Mo named AT-48 and ET, differentiated by the Mo pre-sulfide treatment. For these formulations, the active specie was generated in situ through thermal decomposition of the emulsified system in a high-pressure reduction environment as explained by Noguera *et al*. (2012). Properties of the high vacuum gasoil (HVGO) used for emulsions preparation are showed in Table 2. Atomic ratio Ni/(Ni + Mo) for both emulsions is equal to 0.32.

Table 1. Properties of feedstock VR Merey

Parameter	Merey
Gravity API at 60°F	4.05
Asphaltenes (n-C7 Insolubles) (wt %)	19.9
Asphaltenes (IP-143) (wt %)	20.6
Toluene Insolubles (wt %)	0.178
Microcarbon (wt %)	23.3
Kinematic viscosity at 135 °C (cSt)	3412
Residue 500°C+ (wt %)	92

Table 2. Properties of HVGO Merey

Parameter	Merey
Gravity API at 60°F	16.2
Asphaltenes (n-C7 Insolubles) (wt %)	0.0595
Toluene Insolubles (wt %)	0.0263
Microcarbon (wt %)	0.33
Residue 500°C+ (wt %)	5

The other two formulations contain iron, the first one as mineral hematite named Fe-m with a mean particle size of 5.28 μm with a surface area of 30 m^2/g and a mean pore size of 182.5 Å, and the second one as dispersed nanoparticles catalyst named Fe-nano. For Fe-m there was any pre-treatment or preparation before using it in the reaction. In the other hand, the preparation of the Fe-nano was similar to the procedure explained by Vera *et al*. (2015) adding a presulfiding agent, which generates iron pre-sulfide nanoparticles dispersed in HVGO.

2.3 Experimental scheme

The catalysts performance was tested using a laboratory plant with one 500 ml Parr reactor, where the hydrogen flows continuously and the feedstock remains in the reactor during the entire reaction time. This system has a reactor heating mantle, a gas preheating system, a two-phase separator with a heat exchanger (to cold down and separate light liquid products), and a gas purge system with a sour water vessel. The process flow diagram of this unit is shown in Fig. 1.

2.3.1 Test procedure

Test procedures for evaluating the catalyst performance, using all formulations (ET/Ni, AT-48/Ni, ET, AT-48, Fe-m and Fe-nano), were the same. Details of the procedure are as follows (see Fig. 1): 250 g of VR and the catalyst were placed in a 500 ml Parr reactor, the reactor was closed and pressurized to 1200
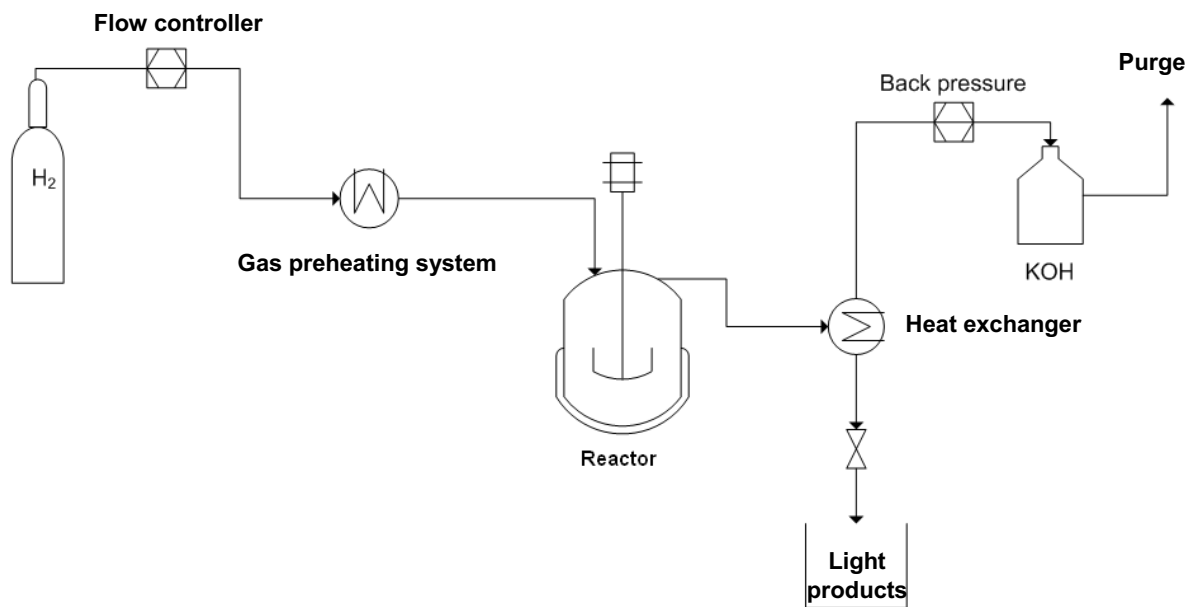
Figure 1. Flow diagram

psig H_2. For Fe-m catalyst certain quantity of HVGO was added to maintain RV/HVGO relation in all tests. After leak test was checked, hydrogen flow was fixed in 1.1 l/min. Afterward, preheating gas system temperature was increased until reaching 500ºC, and subsequently reactor heating mantle temperature was increased to reach the desired reaction temperature (410ºC). Reactor stirring started up at 100ºC (600 rpm) and was maintained during the whole reaction. The mixture remains at the operation conditions for 72 min, after which reactor was cooled dawn to room temperature by applying a cold air around the heating mantle to stop reaction. Products were collected from the reactor: heavy products named VR not converted or liquid heavy products (LHP) and coke (CK), and from the two-phase separator: liquid light products (LLP). All the formulations were in the same metal concentration respect to feedstock.

As part of this study a comparison reaction (CR) was carried out containing only VR and HVGO in the same ratio (VR/HVGO) for the formulations tests in order to verify catalyst effect in the hydroprocessing.

2.3.2 Characterization

Heavy products were first filtrated using an Advantec thimble filter grade 84 and after resultant solids where washed using toluene to obtain VR not converted and coke as separated products. Light and heavy products were analyzed, to compare catalysts performance. Samples were taken following the same procedure each time. Liquid light products were taken after the reactor was cold down, carefully, in glass jars that were seal after sampling to avoid lighters leak from the jar. Coke was dried in a laboratory furnace at 115ºC to evaporate all toluene present in the sample.

It should be noticed that it is beyond the scope of this article analysis related gas products, and for that matter results taking into account gases are not shown in the following sections. Light products were characterized using simulated distillation (ASTM D-2887). The characterization of the heavy product was carried out using two laboratory tests: asphaltenes IP-143, and simulated distillation (ASTM D-7169). Heavy product analyses allowed calculating VR $500°C^+$, $500°C^+$ and asphaltenes conversion percentage. The percentage conversion of VR $500°C^+$ is given by:

$$\%X_{VR500C+} = \frac{VR_{Inlet} - VR_{LHP}}{VR_{Inlet}} \times 100 \qquad (1)$$

The percentage conversion of $500°C^+$ is given by:

$$\%X_{500C} = \frac{VR_{Inlet} - VR_{LHP-Coke}}{VR_{Inlet}} \times 100 \qquad (2)$$
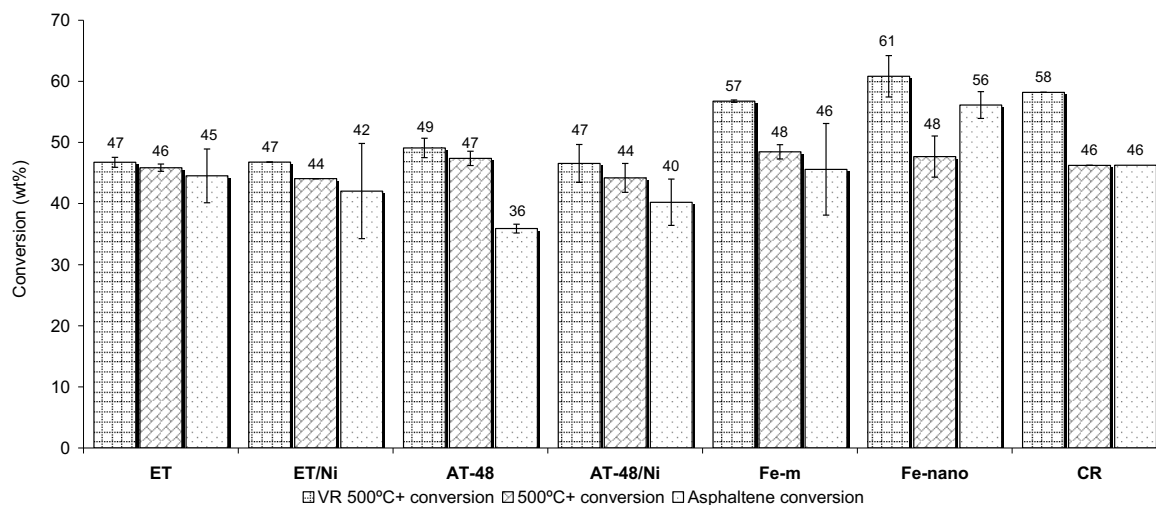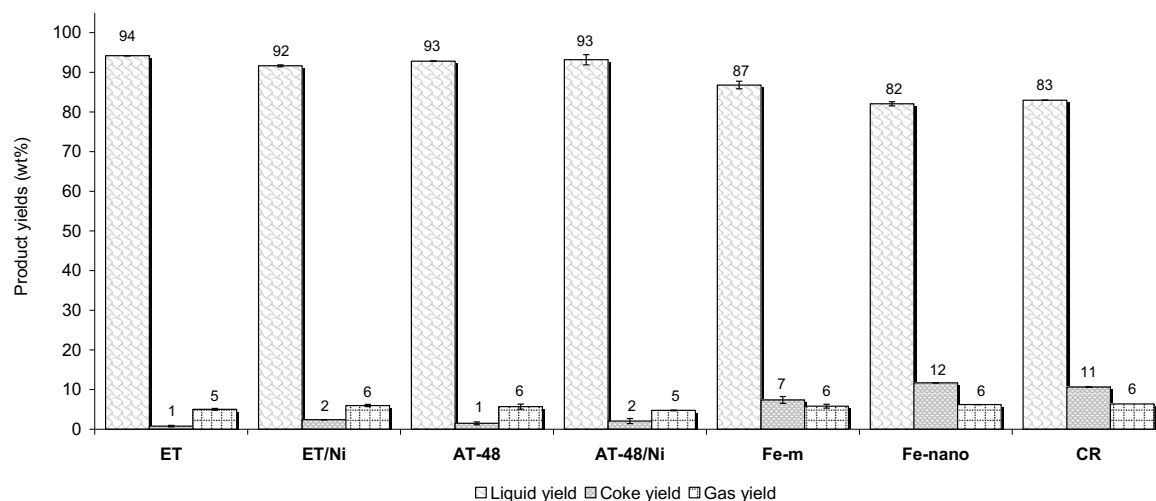
Figure 2. Conversions

Figure 3. Product yields

3   Results and discussion

In this section, conversions, liquid product and coke yields, are presented, for all reactions and their duplicates. 3.1. Conversions and products yields VR $500°C^+$, $500°C^+$ and asphaltenes conversions values are presented in Fig. 2. It could be concluded that VR $500°C^+$ conversion values remained constant for formulations ET and ET/Ni with a mean equal to 46.8 ± 0.5 wt %, and the same behavior is seen for AT-48 and AT-48/Ni (47.8 ± 2.5 wt %), showing no particular effect over conversion values when nickel it added to these formulations, at the Ni/(Ni + Mo) atomic ratio

here studied equal to 0.32.

It should be noticed a low value conversion was reached because operating conditions were fixed at a severity that allows a differentiation between catalytic and thermal effect as stated by Ortiz-Moreno *et al.* (2014). The results showed that, under conditions tested in here, iron catalysts had higher VR $500°C^+$ conversions with values of 56.8 ± 0.2 wt % for Fe-m and 60.8 ± 3.4 wt % for Fe-nano, similar values to the CR.

For $500°C^+$ conversions, which are based only in liquid products, values had a slight decrease in comparison with VR $500°C^+$ conversions for ET, ET/Ni, AT-48 and AT-48/Ni due to a lower coke production.
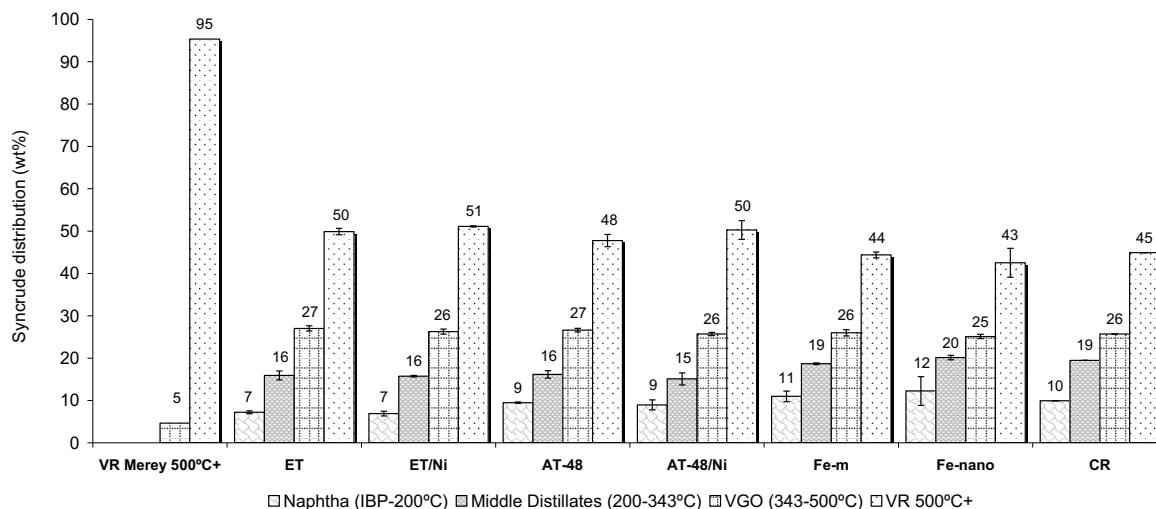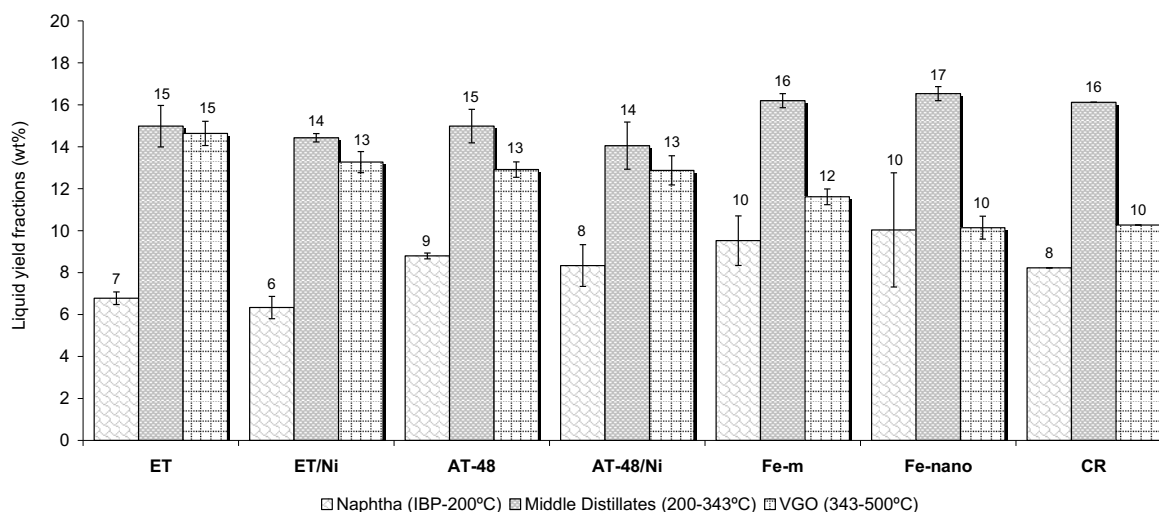
Figure 4. Syncrude distribution

Figure 5. Liquid yield fractions

This difference, conversely, had a major impact for iron catalysts which have a decrease of around 9-13 wt%

Asphaltenes conversions presented were calculated using IP-143 method. As can be seen for formulations ET, ET/Ni, AT-48, AT-48/Ni and Fe-m, conversions cannot be distinguished one from other, having a mean value equal to 41.7 ± 5.5 wt %, showing again no particular effect of adding nickel at this operation conditions, and almost no difference with the CR value. In the other hand, Fe-nano had the higher asphaltene conversion equal to 56.1 ± 2.2 wt %, which can be related to a condensation of these compounds to form coke, as can be seen in the next section.

The broad deviation for asphaltene conversion values for each formulation can be a consequence of the difficulties associated with the extraction of asphaltene by precipitation in this type of sample as explained by Lababidi *et al.* (2014), who considered that asphaltene content obtained by this method is an indicative that not reflects the absolute asphaltene content in the samples.

Finally, product yields are shown in Fig. 3, liquid yields showed no difference for molybdenum formulations with or without nickel with a mean equal to 93.0 ± 1.1 wt %. For catalysts Fe-m and Fe-nano, there was a reduction in liquid yield of around 6 wt% for Fe-m and 11 wt% for Fe-nano. When comparing ET, ET/Ni, AT-48, AT-48/Ni and Fe-m versus CR it

can be seen an increase in liquid yield, on the contrary Fe-nano reported a poor behavior since it had no difference with CR. Gas yield for all conditions test with or without catalyst had almost no variation with a mean value of 5.7 ± 0.6 wt %.

For coke not significant differences were obtained in these percentages for formulations ET, ET/Ni, AT-48, AT-48/Ni with a mean equal to 1.7 ± 0.7 wt %. These coke yields had an increase of approximately 5 wt% when using Fe-m formulation and 10 wt% with Fe-nano, which is similar to CR coke yield. These results showed that using iron as mineral suppressed coke formation around 4 wt% in comparison with a thermal cracking using the same RV/HVGO ratio, and formulation containing molybdenum significantly suppressed coke formation around 9 wt%, similar results were found by Al-Marshed *et al.* (2015) when using MoS_2, NiO and Fe_2O_3 ultra-dispersed particles for in situ catalytic upgrading of a heavy oil sample partially upgraded. These results shown the effectiveness of using mineral iron as an alternative choice for heavy oil upgrading thinking in cost and availability when comparing with molybdenum catalysts.

3.1 Syncrude distribution

Syncrude distribution is presented in Fig. 4. For all cases there where significant differences between VR Merey $500ºC^+$ and the liquid products (LHP + LLP), with a decrease of around 48 wt% for VR $500ºC^+$ fraction, and an increase in all liquid fractions 500ºC-.

When comparing VR $500ºC^+$ fraction for ET, ET/Ni, AT, AT-48/Ni versus CR it could be seen a higher value for reactions with catalyst include, this is due to a lower coke production, instead, for Fe-m and Fe-nano VR $500ºC^+$ fraction remains almost equal to the fraction for CR, meaning that Fe-m and Fe-nano had a poorer catalytic reaction control.

For naphtha and middle distillates, there is a higher value for Fe-m and Fe-nano, similar to CR, when comparing with molybdenum formulations, this is due to a higher hydrocracking reaction extension, as said before due to a poorer catalytic reaction control for iron formulations. VGO fraction remains almost constant for all cases.

3.2 Liquid yield fractions

Liquid yield fractions are presented in Fig. 5. It could be observed a difference between both ET formulations, respect to the rest, in naphtha yields with approximately 2 wt% decrease. AT-48 formulations not shown significant difference in naphtha production in comparison with CR. An increase in VGO yield could be observed for all formulations containing molybdenum. For iron formulations almost no difference in all fractions was seen in comparison with CR. Total liquid yield with molybdenum formulations had an increase of around 10 wt% in the other hand, no increase was observed when using Fe-nano and a slight increase was seen for Fe-m. Based on these results it could be concluded that AT-48 formulations have a better performance than the rest when comparing liquid yield and product quality.

3.3 Dunnett's test for VR 500ºC⁺ and asphaltene conversions, coke and liquid yields

In order to measure the real difference between CR and the catalytic performance, Dunnett's test was carried out. This test allows a comparison between a control case (CR) and a variety of study cases (catalytic tests). The explanation of this test is out the scope of this article but it can be found elsewhere (Dunnett 1955, 1964), although a brief description is given below. As result of the test it can be known if the variation in conversions and yields values are or not significantly different from the control case (CR). For the Dunnett's test a 90% confidence level was used. Results are shown in Table 3 for all cases.

In the first column there are the variables to compare with control case (VR $500ºC^+$ conversion, asphaltene conversion, coke yield and liquid yield), for each case (control and test) there is the mean value (X), the standard test deviation from the control case mean value (s) and the comparison value (q) given by the following equations:

$$S E = [MS E \cdot (1/n_c + 1/n_p)]^{0.5} \qquad (3)$$

$$q = (X_c - X_p)/S E \qquad (4)$$

The q value is compared with the critic value (q_c) which is obtained from Dunnett's test tables. When the absolute q value is greater than q_c, then is considered that the difference between control and test case is significant.

As can be seen in VR $500ºC^+$ conversion only molybdenum formulations have a significant difference from the CR. On the contrary, for asphaltene conversion neither formulation presented a significant difference in comparison with CR, this could be a consequence of the difficulty on the asphaltene extraction as was stated before,

Table 3. Dunnett's test with $\alpha = 0.10$

XVR500ºC+	*Control*	*ET*	*ET/Ni*	*AT-48*	*AT-48/Ni*	*Fe-m*	*Fe-nano*
X	58	47	47	49	47	57	61
s		0.8	0	1.6	3.1	0.2	3.4
q		4.6	4.6	3.7	4.7	0.6	-1.1
		Significant	Significant	Significant	Significant	No significant	No significant

SE = 2.47; k = 7; qc = 2.906

Xasphaltene	**Control**	**ET**	**ET/Ni**	**AT-48**	**AT-48/Ni**	**Fe-m**	**Fe-nano**
X	46	45	42	36	40	46	56
s		4.4	7.8	0.7	3.8	7.5	2.2
q		0.3	0.7	1.7	1	0.1	-1.6
		No significant	No significant	No significant	No significant	No significant	No significant

SE = 6.25; k = 7; qc = 2.906

Coke yield	**Control**	**ET**	**ET/Ni**	**AT-48**	**AT-48/Ni**	**Fe-m**	**Fe-nano**
X	11	1	2	1	2	7	12
s		0.2	0	0.4	0.6	0.9	0
q		17.1	14.3	15.8	14.8	5.7	-1.8
		Significant	Significant	Significant	Significant	Significant	No significant

SE = 0.58; k = 7; qc = 2.906

Liquid yield	**Control**	**ET**	**ET/Ni**	**AT-48**	**AT-48/Ni**	**Fe-m**	**Fe-nano**
X	83	94	92	93	93	87	82
s		0	0.2	0.1	1.3	1	0.5
q		-13.3	-10.3	-11.7	-12.1	-4.6	0.9
		Significant	Significant	Significant	Significant	Significant	No significant

SE = 0.85; k = 7; qc = 2.906

this can be seen clearly in the standard deviation for each catalyst.

For coke yield and liquid yield all formulations, except Fe-nano, showed a significant difference in comparison with CR, in all cases with a suppression of coke and with an increase of the liquid fraction. For these results Fe-nano did not offered any advantages from a thermal hydroprocessing in the conditions here studied.

The poor performance of Fe-nano could be because of the possible aggregation of the nano particles during the reaction as stated by Al-Marshed *et al*. (2015) for Fe_2O_3 ultrafine catalysts (≤ 50 nm).

Further investigations related to Fe-m catalyst are being carried out to study the observed effects and improving hydroconversion of VR and asphaltenic fractions.

Conclusions

Under the study conditions the advantages of the molybdenum ultra-dispersed catalyst formulations over iron catalysts have been clearly established. Showing that w/o emulsions had a superior performance than solid dispersed catalysts as expected.

The ultra-dispersed catalyst AT-48 using no nickel showed a similar or better catalytic performance than the other formulations (ET, ET/Ni and AT-48/Ni, Fe-m and Fe-nano), in the VR Merey hydroconversion at the Ni/Mo atomic ratio studied here. The AT-48 reached a $X_{VR500C+}$ of 49 wt %, a liquid product yield of 93 wt% (10 wt% more than thermal hydroprocessing), and a coke suppression of 10 wt%.

Under operation conditions of this study no synergistic effect between molybdenum and nickel could be seen, showing no significant difference between formulation Mo and Mo/Ni, which could lead to a reduction in the catalyst cost.

Although iron formulations had a poorer performance than molybdenum formulations, Fe-m could be used in an upgrading process with a low or medium severity to obtain a synthetic crude with a low coke yield and a with a superior liquid product distribution, having as advantage a lower catalyst

cost and less process units to prepare and handle formulations in the emulsion form.

The use of iron as a nano pre-sulphurated formulation, at conditions hereby studied, did not show any improvement in comparison with a thermal hydroprocessing.

Nomenclature

k	number of cases
MSE	mean square sample error
n_c	number of control replicates
n_p	number of test replicates
q	comparison value
q_c	critic value
s	standard deviation
SE	standard error
X	mean
$X_{asphaltene}$	asphaltene conversion
X_c	mean control sample
X_p	mean test sample
$X_{RV500C+}$	vacuum residue conversion

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