# USE OF A DISPERSED IRON CATALYST FOR UPGRADING EXTRA-HEAVY CRUDE OIL USING METHANE AS SOURCE OF HYDROGEN.

Cesar Ovalles, Eduardo Filgueiras, Alfredo Morales, PDVSA-INTEVEP, Apdo. 76343,
Caracas 1070A, Venezuela.
Carlos E. Scott, Centro de Catálisis, Petróleo y Petroquímica. Facultad de Ciencias,
Universidad Central de Venezuela, Apdo. 47102, Caracas 1040A, Venezuela.
Fernando Gonzalez-Gimenez, B. Pierre Embaid, Depto. de Fisica, Ciencias, UCV, Apdo.
47586, Caracas 1041A, Venezuela.

Key Words: Extra-heavy Crude Oil, Upgrading, dispersed iron catalyst

## INTRODUCTION

The use of natural gas (methane) as hydrogen source for the upgrading of extra-heavy crude oil [1-6] and coal [7-15] has been the subject of numerous studies during the last few years. In this particular, the reaction of Hamaca crude oil (°API = 8.3) under thermal conditions (380°C, 11.0 MPa of $CH_4$ for 4 hours residence time) and in the presence of water as additive, led to a decrease of two orders of magnitude in the viscosity of the upgraded product (from 500 to 1.99 Pa s at 30°C), conversion of the >540°C fraction of 60%, and 11.3% of reduction of sulfur with respect to the original crude [1-3]. By $^1$H- and $^2$D-NMR analysis, the most probable pathway is a free-radical mechanism, which involves incorporation of methane via production of methyl radicals [3].

Using an alumina supported molybdenum-nickel catalyst and at similar conversion of the >540°C fraction, a relatively higher percentage of desulfurization (28%) and lower percentage of asphaltenes (9.3%) was obtained than those found in thermal reaction (11% and 11.8%, respectively) [1, 4]. These results indicate that methane can be catalytically activated and used for upgrading of extra-heavy crude oil. Furthermore, using a dispersed molybdenum catalyst, derived from $MoO_2(acac)_2$ (where acac = acetyl-acetonate) and by carbon isotope ratio mass spectrometry analysis, labeled methane ($^{13}CH_4$) was found to incorporate into the crude oil (estimated value 0.01% w/w) giving conclusive evidence on the involvement of $CH_4$ in the extra-heavy crude oil upgrading process [5-6].

In this work, we studied the use of an iron dispersed catalyst, derived from $Fe_3(CO)_{12}$ for extra-heavy crude oil upgrading using methane as source of hydrogen. The iron catalyst was isolated from the coke produced from the upgrading reaction and was analyzed by XPS, EDAX, and Mössbauer Spectroscopy. Also, the characterization of the products by $^1$H-RMN were carried out in order to understand the methane activation processes that are occurring during the crude oil upgrading reactions.

## EXPERIMENTAL

The crude oil employed in this work came from the Hamaca oil field in the Orinoco Belt and its analysis is as follows: API Gravity at 15.6°C = 8.7, Water (% w/w) = <1, H/C wt. Ratio = 0.115, Sulphur (% w/w) = 3.40, Nickel (ppm) = 91.9, Vanadium (ppm) = 412, Asphaltenes (% w/w) = 12.5, % of Residue (500$^{+}$°C) = 57%, Viscosity at 30°C (Pa s) = 500. The upgrading reactions were carried out batchwise in a stainless-steel 300 ml Parr reactor with 250 ppm of Fe at a temperature of 410-420°C, a pressure of 11 MPa of $CH_4$ and a residence time of one hour as described elsewhere [5-6].

The percentages of volatile material were determined by the method reported by Ceballo and coworkers using a Hewlet-Packard gas-chromatograph, model 5880 [16]. The percentage of conversion of the residue >500°C was defined elsewhere [3,5-6]. X-ray Photoelectron Spectroscopic (XPS) experiments were carried out in using a Leybold-Heraeus Surface Analysis System which was operated with an aluminium anode (1486.6 eV). Pass energy was set at a constant value of 50 eV and the data acquisition and manipulation were performed using a 486 IBM compatible computer. The instrument sensitivity factors used for scaling the photoelectron peak areas were calculated using the method reported by Leon and Carrazza [17]. The Mössbauer spectroscopy was carried out at room temperature, with a constant acceleration spectrometer, in the triangular symmetric mode for the velocity. The source was a $^{57}$Co in palladium.

## RESULTS AND DISCUSSION

The reaction of Hamaca extra-heavy crude oil (Table 1) at 11 MPa of methane and 410°C for 1 h (Table 1, control run) led to a reduction of two order of magnitude in the viscosity (from 500 to 2 Pa s), 10% of reduction in sulfur content and 41% conversion of the >500°C fraction in the upgraded product with respect to the original crude. Analogous reaction carried out in the presence of $Fe_3(CO)_{12}$ as dispersed catalyst (Table 1, run 1) yielded a product with further reduction in the viscosity (1.3 Pa s), higher reduction in sulfur content (14%) and similar value of conversion of the heavy fraction (40%). Additionally in the presence of the catalyst, a slightly reduction of coke formation (from 7.7 to 6.9%) was observed in comparison with the control experiment. These results indicate that the presence of the iron catalyst is necessary in order to enhance the upgrading of extra-heavy crude oil in the presence of methane

A reaction carried out in an inert argon atmosphere (Table 1, run 2) yielded a product with higher viscosity (2.7 Pa s), less reduction of sulfur content (8%) and lower conversion of the >500°C fraction (36%) with respect to the methane containing experiment (Table 1, run 1). These results indicate that methane is involved, as a source of hydrogen, in the upgrading reaction and that it can be activated by the metal catalyst.

An experiment (Table 2, run 3) conducted under hydrogen atmosphere afforded an upgraded product with slightly better properties (1.2 Pa s, 22% HDS, 40% conversion of >500°C fraction and 5% coke) than those obtained under methane (run 1) and argon (run 2) atmospheres. Thus, the order of reactivity is $H_2 > CH_4 > N_2$ as found by Ovalles *et al.* [3] and Sundaran [7] for thermally activated processes. Also, similar order of reactivity was reported by Egiebor and Gray in their iron catalyzed coal liquefaction experiments [9] and Ovalles *et al.* for $Mo\text{-}Ni/Al_2O_3$ catalyzed extra-heavy crude oil upgrading [4, 6].

From the methane upgrading reaction using $Fe_3(CO)_{12}$ as dispersed catalyst, the coke formed was characterized by EDAX, XPS and electron microscopy. X-ray diffraction and XPS analyses (after 1 h etching with $Ar^+$ ions) showed the presence of iron and sulfur.

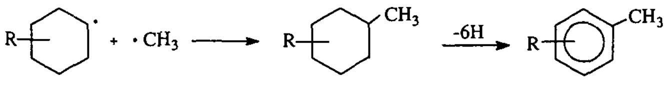
Furthermore, the binding energy for the Fe 2p3/2 was found (Table 2) at 707.4 eV and can be assigned to $Fe^{+2}$ according to the data reported in the literature [18]. Additionally, a sulfur species detected in the S2p region at 161.3 eV, which can be assigned to $S^{-2}$ [19].

The ratio of the atomic percentages of $Fe^{+2}$ (0.54) and $S^{-2}$ (1.31) is 0.53, which is lower than that (1.1-1.4) reported by Reucroft and coworkers [19].To determine which type of Fe compound was present, a Mössbauer study was undertaken. The recorded spectrum is shown in Fig. 1A with the continuous line representing the result of a computer adjustment, which included, apart IS (Isomer Shift), FWHM and QS (quadrupole splitting), a hyperfine field distribution whose histogram is also shown in Fig.1B. Due to the small concentration of iron, the spectrum has a rather poor statistics, however the histogram obtained indicates the unambiguous presence of an Fe and V mixed sulfide, when compared with the spectra obtained in the systematic study of those sulfides [20-22]. According to the previous results, the composition of the present mixed sulfide should be near: $(Fe_{0.6}V_{0.4})_z$ S, where z is in the range of 0.8-0.9 .

The formation of the Fe-V mixed sulfide is certainly achieved *in situ*, by decomposition of the iron carbonyl ($Fe_3(CO)_{12}$) and subsequently the reaction of sulfur and vanadium coming from the feedstock [23]. A very similar mechanism, which demonstrated the appearance of those mixed-sulfides as the active phases, has been put in evidence in HDM reactions [24-25] undertaken with clay catalysts (the precursor is $Fe_2O_3$) acting on a Pao-X1 heavy crude from the Orinoco belt.

In order to gain mechanistic information, H-NMR analyses were carried out to the upgraded crude oil and the results are shown in Table 3. For $Fe_3(CO)_{12}$ soluble catalyst, an increase (17.2%) in the amount of $\alpha$-hydrogen bonded to aromatic rings was observed in comparison with those observed for the control run (14.7%) and for the crude oil (15.5%). Similar catalytic runs carried out under argon and hydrogen atmospheres and $Fe_3(CO)_{12}$ led to lower amount of $\alpha$-hydrogen bonded to aromatic rings (16 and 15 % for Ar- and $H_2$-containing experiments, respectively) than that found in the $CH_4$-containing experiment (17%).

Furthermore, an intense aromatization occurred for all the upgrading reactions as shown by the increase in the percentages of aromatic protons from 5.1% in the original crude to approximately 10% for runs 1-3. These results can be rationalized by incorporation of the methyl groups (or, in general, $CH_x$ species where x = 1, 2, or 3) to the crude oil molecules, as shown in eq. 1 [6].



(1)

Where R = hydrocarbon (aliphatic or aromatic)

Naphtenic radicals shown in eq. 1 can be generated by either thermal or catalytic breaking of C-H bond under the reaction temperature (410°C). Egiebor and Gray found methyl and dimethyl products by GC analysis of the donor solvent (tetralin), which was attributed to direct alkylation by reaction with methane in their iron catalyzed coal liquefaction experiments [9]. Also, similar results were obtained previously for extra-heavy crude oil upgrading under thermal [3] and catalytic conditions [6]. The incorporation of $CH_x$ species, coming from methane, into the crude oil molecules was confirmed by isotopic carbon distribution measurements ($^{13}C/^{12}C$) using $^{13}CH_4$ as a source of hydrogen [6].

## REFERENCES

1) Ovalles, C.; Hamana, A., Bolivar, R. and Morales, A., U. S. Patent 5,269,909 **1993**.
2) Ovalles, C.; Arias E. S., Hamana, A.; Badell, C. B. and Gonzalez, G., *ACS Fuel Chem. Preprints* **1994**, 39: 973.
3) Ovalles, C.; Hamana, A., Rojas, I. and Bolivar, R., *Fuel* **1995**, 74, 1162.
4) Ovalles, C.; Hamana, A., Bolivar, R. and Morales, A. Proceeding X Conference of UNITAR, Houston , Texas, Feb. 1995.
5) Morales, A., Salazar, A., Ovalles, C. and Filgueiras, E., Procedings 11th International Congress. Catalysis-40th Anniversary. Studies in Surface and Catalysis, J. W. Hightower, E. Iglesia and A. T. Bell (Eds.), **101**, 1215 (1996).
6) Ovalles, C., Filgueiras, E., Morales, A., Rojas, I., de Jesus, J. C. and Berrios, I., to be published in Energy & Fuels.
7) Sundaram, M. U.S. Patent 4,687,570 (1987). b) Sundaram, M. and Steinberg, M. *ACS Fuel Chem. Preprints*, **1986**, 28: 77.
8) Steinberg, M., *Int. J. Hydrogen Energy* **1986**, 11: 715.
9) Egiebor, N. O., Gray, M. R., *Fuel* **1990**, 69: 1276.
10) Qin, Z. and Maier, W. F. *Energy & Fuels* **1994**, 8, 1033.
11) Maier, W. F. and Franke, R. *Fuel* **1994**, 73, 5.
12) Steinberg, M. and Fallon, P. T. *Hydrocarbon Process* 1982, Nov, 92.
13) Calkins, W. H. and Bonifaz, C. *Fuel* **1984**, 63, 1716.
14) Braekman-Danheux, C.; Cypres, R.; Fontana, A. and van Hoegaerden, M. *Fuel* **1995**, 74, 17.
15) Yang, K., Batts, B. D., Wilson, M. A., Gorbaty, M. L., Maa, P. S., Long, M. A., He, S. X., Atalla, M. I., *Fuel* **1997**, 76, 1105.
16) Ceballo, C. D., Bellet, A., Aranguren, S., Herrera, M., *Rev. Tec. INTEVEP*, **1987**, 7, 81.
17) Leon, V., Carrazza, J., *Rev. Tec. INTEVEP* **1989**, 9, 81.
18) Kim, J. Y., Reucroft, P. J., Taghiei, M., Pradhan, V. R., Wender, I., *Energy & Fuels* **1994**, 8, 886.
19) a) Des Marais, D. J., Hayes, J.M., *Anal. Chem.*, **1976**, 48, 1651. b) Gillet, S., Rubini, P., Delpuech, J-J, Escalier, J-C, Valentin, P. *Fuel* **1981**, 60, 221.
20) Embaid, B. F., Gonzalez-Jimenez, F., Scott, C. E., *Hyperfine Interactions* **1994**, 83, 385.
21) Scott, C. E., Embaid, B. P., Luis, M, A., Gonzalez-Jimenez, F., Gengembre, L., Hubaut, R., Grimblot, J., *Bull.Soc.Chim.Belg.*, **1995**, 104, 331.
22) Scott, C.E., Embaid, B.P., Gonzalez-Jimenez, F., Hubaut, R., Grimblot, J., *J. Catalysis*, **1997**, 166, 333.
23) Derbyshire, F. *CHEMTECH* **1990**, 20, 439 and references therein. b) Weller, S. W. *Energy & Fuels* **1994**, 8, 415 and references therein.
24) Gonzalez-Jimenez, F., Constant, H., Iraldi, R., Jaimes, E., Rosa-Brussin, M.. *Hyperfine Interactions*, **1986**, 28, 927.
25) Gonzalez-Jimenez, F., Bazin, D., Dexpert, H., Villain, F., Constant, H. Rosa-Brussin, M., *Physica B*, **1989**, 158, 215.

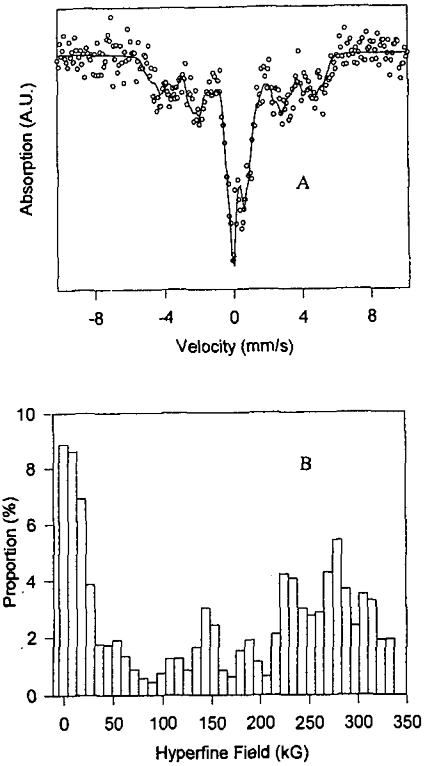


Fig. 1. A) Mössbauer spectrum with the continuous line representing the result of a computer adjustment including, IS (Isomer Shift), FWHM and QS (quadrupole splitting).

Table 1. Upgrading of Extra-Heavy Crude Oil using $Fe_3(CO)_{12}$ as Organometallic Precursor[a]

| Run | Gas used | HDS[b] (wt%) | % Conv. >500°C[c] | Viscosity (Pa s)[d] | Coke (wt%) | Gases (wt%) | Liquids (wt%) |
|---|---|---|---|---|---|---|---|
| Hamaca crude oil | - | (3.40% S) | - | (500) | - | - | - |
| Control[e] | $CH_4$ | 10.0 | 41 | 1.99 | 7.7 | 4.6 | 87.7 |
| 1 | $CH_4$ | 14 | 40.5 | 1.34 | 6.9 | 4.6 | 88.5 |
| 2 | Argon | 8 | 35.8 | 2.77 | 6.0 | 3.1 | 90.9 |
| 3 | $H_2$ | 22 | 39.7 | 1.20 | 5.0 | 4.5 | 90.5 |

[a]The reactions were carried out in a 300-ml batch reactor at 410°C, 250 ppm of Fe, 11 MPa of final pressure for a 1-h period. The results are the average of at least two different reactions. [b]Percentage of desulfurization with respect to the starting crude oil. [c]Percentage of conversion of the residue >500°C as defined in ref. 3, 5-6. [d]Viscosity measured at 30°C. [e]Control experiment, i. e. **no catalyst** was used.

**Table 2.** Results of the XPS analysis of the coke isolated from upgraded Hamaca crude oil using $Fe_3(CO)_{12}$ as catalyst precursor after 1 h etching with $Ar^+$ ions[a]

| Element | Binding energy (eV) | Atomic %[b] | Assignment[c] | Reference |
|---|---|---|---|---|
| Fe2p3/2 | 707.4 | 0.54 | $Fe^{+2}$ as in FeS | 18-19 |
| S 2p | 161.3 | 1.31 | $S^{-2}$ as in FeS | 20 |
| C 1s | 284.6 | 97.24 | Adventitous carbon | 18-20 |
| O 1s | 532.8 | 0.91 | Organic Oxygen | 18-20 |

[a] The reactions were carried out as described in Table 1. The coke was isolated by filtration after diluting the upgraded crude oil in toluene. [b] Atomic percentage on the surface. [c] Most probable assignment according to the published literature.

**Table 3.** Protons distributions for upgraded Hamaca crude oil measured by $^1$H-NMR using $Fe_3(CO)_{12}$ as catalyst precursor[a].

| Run | Gas used | $H_{arom}$[b] | $H_{aliph}$[c] | $H_\alpha$[d] | $H_\beta$[e] | $H_\gamma$[f] |
|---|---|---|---|---|---|---|
| Hamaca crude oil | - | 5.1 | 94.9 | 14.7 | 56.2 | 24.0 |
| Control[g] | $CH_4$ | 9.0 | 91.0 | 15.5 | 52.0 | 23.5 |
| 1 | $CH_4$ | 8.4 | 91.6 | 17.2 | 51.2 | 23.0 |
| 2 | *Argon* | 8.9 | 91.1 | 16.2 | 51.3 | 23.3 |
| 3 | $H_2$ | 8.7 | 91.3 | 15.2 | 51.5 | 24.6 |

[a] The reactions were carried out as described in Table 1. [b] $H_{arom}$ = Hydrogen bonded to aromatic carbons. [c] $H_{ali}$ = Hydrogen bonded to aliphatic carbons. [d] $H_\alpha$ = Hydrogen bonded to aliphatic carbons in α position to an aromatic ring. [e] $H_\beta$ = Hydrogen bonded to aliphatic carbons in β position to an aromatic ring. [f] Hγ = Hydrogen bonded to aliphatic carbons in γ or more position to an aromatic ring. [g] Control experiment, i. e. ***no catalyst*** was used.