

EXTRAHEAVY CRUDE OIL UPGRADING IN THE PRESENCE OF NATURAL GAS AS HYDROGEN SOURCE. CONTINUOUS FLOW EXPERIMENTS AND ECONOMIC EVALUATION
 Cesar Ovalles, Ely Saul Arias, Antonia Hamana, Carmen B. Badell and Gustavo Gonzalez, Department of Petroleum Chemistry, INTEVEP, S. A., Apdo. 76343, Caracas 1070A, Venezuela

Key Words: Upgrading, Extraheavy Crude Oil, Methane, Economic Evaluations

INTRODUCTION

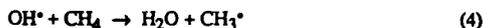
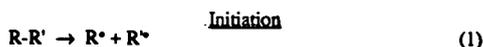
The presence of vast reserves of natural gas available in different parts of the world has motivated continuous research efforts in new routes for the utilization of this raw material [1-8]. Specifically, the direct use of methane as a source of hydrogen for coal and crude oil upgrading has received the attention of several research groups during the last few years [5-8].

Sundaran and coworkers [5] employed natural gas (methane) as hydrogen source for coal liquefaction and found a 73% conversion of a Illinois #6 coal at 425°C and 1000 psi using tetralin as a donor solvent. When employing nitrogen instead of methane, lower conversion was found (67%) indicating that, most probably, methane was involved in the liquefaction process.

Egiebor and Gray reported [6] 60-70% conversion to liquid products for the liquefaction of Highvale coal using methane atmosphere in the presence or not of a catalyst (Fe₂O₃) with tetralin as a donor solvent at 450°C and a pressure of 270-350 psi. The characterization of the hydrocarbon products by ¹H-NMR showed similar spectra for the hydrogen and methane reactions, and by GC and GC-MS analysis of the donor solvent, methyl and dimethyl substituted products were detected.

Ovalles and coworkers studied [7-8] the upgrading of Orinoco-Belt extraheavy crude oil (Hamaca, API 8.6°) using methane as a source of hydrogen under thermal conditions, in the presence of water as additive. The reaction of Hamaca crude oil (water content 4.4%) with methane at 380°C and 1600 psi for 4 h, led to a decrease in two orders of magnitude in the viscosity of the upgraded product (from 500,000 to 1990 cP at 30°C), a percentage of conversion of the 540°C⁺ fraction of 60% and 11.3% of HDS, with respect to the original crude. Compared to the CH₄-containing experiment, a reaction carried out under nitrogen as an inert gas (control experiment) led to a product with higher viscosity (2600 cP), lower conversion of the heavy fraction (54%) and lower HDS (8.3%). These results indicated [7] that methane was involved in the upgrading reactions and, most probably, was behaving as a source of hydrogen for the thermal processes.

According to the ¹H- and ²D-NMR data [7], the most probable pathway is a radical chain mechanism which involves incorporation of methane to the hydrocarbon molecules via the production of methyl radicals. The proposed mechanism is as follows:



Termination



Where R and R' are hydrocarbons.

Reactions carried out using a dehydrated crude oil (less than 1% of H₂O) under methane and nitrogen atmospheres gave approximately similar results (2400 cP, 45% of conversion and 8% of HDS), indicating that the presence of water is necessary in order to achieve methane incorporation into the upgraded products. The beneficial effects of water in the CH₄-containing upgrading reactions of bitumens can be rationalized by the reaction of OH[•] with methane (eq. 4) with the concomitant production of methyl radicals to continue the chain process [7].

In this paper the upgrading of extraheavy crude oil (Hamaca, API 8.6°) was demonstrated in a continuous flow system using natural gas as a source of hydrogen in the presence of water as additive. The effects of the natural gas pressure (1600, 800 and 200 psi), residence time (30 and 45 min) and percentage of water (10 and 20% w/w) were studied using a 0.11 barrels/day hydrovisbreaking unit modified to use natural gas. From now on, we refer to this process as Methanetreatment for comparative reasons.

Due to the vast reserves of Orinoco Belt extraheavy crude oil and the difficulties in its transportation we evaluate the feasibility of using Methanetreatment for this purpose due to availability of natural gas and low cost energy in the vicinities of the production wells. For these reasons, a conceptual engineering design and an economic evaluation were conducted for a 100 MBPD module. Finally, comparisons with conventional technologies were carried out.

EXPERIMENTAL

The extraheavy crude oil employed in this work came from the Hamaca oil field in the Orinoco Belt and its analysis can be found in Table 1. The percentages of volatile material were determined by the method reported by Ceballo and coworkers [9] using a Hewlett-Packard gas-chromatograph, model 5880. The percentage of conversion of the residue >500°C was defined as:

$$\frac{(\% \text{ of residue } 500^{\circ}\text{C}^+ \text{ in crude oil}) - (\% \text{ of residue } 500^{\circ}\text{C}^+ \text{ in upgraded product})}{(\% \text{ of residue } 500^{\circ}\text{C}^+ \text{ in crude oil})} \times 100$$

The viscosities of the crude oils were measured in a Brookfield apparatus, model RVTDV-II. The water concentrations were determined by the Karl Fisher method according with the ASTM standard test D-1744-83. The composition of the natural gas can be found in Table 1. The Conradson carbon contents were measured by the ASTM standard test D-189.

The upgrading reactions were carried out in a 0.11 barrels/day hydrovisbreaking unit modified to use natural gas. The plant consists of three sections: preheating, reaction and separation zone. In the preheating section, the hydrocarbons, water and natural gas were mixed and heated near the reaction temperature (320°C) at the reaction pressure (1600, 800 or 200 psi). The reaction zone included a coil and a soaker reactors connected in series with a volume of 0.285 and 4.7 liters, respectively. Both reactors were kept at the same temperature (390 and 410°C) during each experiment.

The products of the upgrading reactions were distilled by separating the gases from the liquid using a flash unit at 150°C. The unreacted natural gas was recompressed and recycled with a ratio of 20 to 1 with respect to the purge gas. The liquids were stripped with nitrogen at 150°C and top products were condensed. From the last stream, water and light hydrocarbons were separated and the later compounds were mixed with the bottoms of the stripped unit to obtain the reconstituted crude oil. Mass balances were taken every 10-12 hours without formation of coke in the soaker reactor.

The conceptual engineering designs for Visbreaking, Methanetreatment and Hydrovisbreaking processes as well as for more conventional methods for heavy oil transportation such as Heating and Dilution, were carried out. Technical bases for all alternatives were the same (Crude properties, flowrate, pipelenght, etc.). Investment costs (order of magnitude, 25% contingency and grass root) were estimated using INTEVEP's own database and recent vendor quotations. Operating costs were estimated from INTEVEP's recent experiences in similar projects and from feedback from our operating affiliates.

RESULTS AND DISCUSSION

Upgrading Reactions

The reaction of extraheavy crude oil (API = 8.6°) with 1600 psi of natural gas at 410°C with a concentration of water of 10% w/w and a residence time of 30 min (Table 2, exp. 1), led to an increase in the API gravity from 8.6° to 12° in the upgraded product, a decrease in two orders of magnitude in the viscosity (from 500,000 to 1700 cP at 30°C) and a conversion of the 540°C⁺ residue of 35%, with respect to the original crude. During a 10-days run, mass balances were taken every 12 hours without formation of coke in the soaker reactor after the experiment.

Similar value of viscosity (1990 cP) was obtained [7] using a 300 ml-batch reactor under 1600 psi of methane at 380°C for 4 h. Higher percentage of conversion (60%) was found for

the later run than that in continuous flow experiment and can be attributed to the longer residence time.

An increase in the residence time to 45 min (Table 1, exp. 2) did not further elevate the API gravity of the upgraded reconstituted crude oil. However, the viscosity of the product decreased (1100 cP) and the percentage of conversion of the residue increased (49%) due to the longer residence time. On the other hand, the amount of Conradson carbon in the reconstituted crude oil increased from 16.5 to 18% as the residence time was raised from 30 to 45 min. These results indicate that coke was produced during the crude oil upgrading and is consistent with other thermally upgrading processes as for example Visbreaking and Hydrovisbreaking [10-11].

An experiment (Table 1, exp. 3) carried out with 20 % w/w water concentration led to an upgraded product with slightly better properties (1590 cP, 36% conversion of the 540°C⁺ residue and 16.2% of Conradson carbon) in comparison with those obtained with 10% water content (exp. 1). The effect of water as additive for visbreaking type of reaction is very well known in the literature [12]. Its beneficial properties are attributed to the reduction of coke formation and to its hydrogen donor capabilities [7, 12].

The effect of the pressure of natural gas on the viscosity of the upgraded reconstituted crude oils can be seen in Fig. 1. The reactions were carried out at 390°C with 30 min residence time and the results are the average of 10 h mass balances for up to 30 h. In general, it can be seen that the viscosity of the upgraded product in the temperature range 30-60°C decreased as the natural gas pressure increased. These results indicate the involvement of natural gas during the crude oil upgrading reaction. Possible explanations can be attributed to the need of high pressure in order to carry out the methane activation reactions as shown in eq. 3 and 4.

From these results, it can be concluded that the process of upgrading extraheavy crude oil using natural gas as a source of hydrogen looks as a technically feasible option for the industrialization of these abundant raw materials.

Economic Evaluations

In order to assess the Methanetreatment process as an upgrading technology to be used with transportation purposes, an economic evaluation was conducted. Comparisons with similar processes as Visbreaking and Hydrovisbreaking were made as well as with conventional technologies as Heating and Dilution. The basis for the economic evaluations were as follows:

- 100,000 barrels per day plant located at the Orinoco Oil Belt equipped with a 300 Km oil pipe line from the Orinoco reservoir to the Caribbean Sea.
- The operation costs (for the first trimester 1993 Venezuelan based) included: labor, maintenance, insurance and utilities.
- An evaluation period of 17 years and an interest rate of 10% were considered. Investments and operating cost were estimated on 1993 basis
- A credit was added to the technologies with crude oil upgrading (Visbreaking, Methanetreatment and Hydrovisbreaking).
- Cash flows for the evaluation period were obtained considering the investments and annual balances between operating costs and credits for crude oil upgrading when applicable. Net present value analysis was performed in order to compare the different alternatives.

The results of the study are shown in Table 3. It can be seen that the conventional transport technologies (Heating and Dilution) present the lowest investments (145 and 143 MMUS\$, respectively) and operation costs (11 and 10 MMUS\$) that those calculated for Visbreaking, Methanetreatment and Hydrovisbreaking upgrading processes. Therefore, the present net cost for the first two technologies (216 and 212 MMUS\$) are lower than those found for the later three (246, 255 and 330 MMUS\$).

On the other hand, the visbreaking technology offers the lowest investment, operation cost and present net cost among the crude oil upgrading processes. However, the present net cost for the Methanetreatment is relatively close (255 MMUS\$) to that calculated for the visbreaking (246 MMUS\$), due to the higher credits (higher conversions and lower viscosities of the products) of the former in comparison with the later.

In conclusion, conventional transport technologies of Heating and Dilution have economical advantages over Visbreaking, Methanetreatment and Hydrovisbreaking upgrading processes used for transportation purposes. Between the later three technologies, visbreaking is only slightly more economically attractive than the methanetreatment process.

REFERENCES

- 1) Pitchai, R. and Klier, K. *Catal. Rev.-Sci. Eng.*, **28**, 13 (1986) and references therein.
- 2) Lee, J. S. and Oyama, S. T. *Catal. Rev.-Sci. Eng.*, **30**, 249 (1988) and references therein.
- 3) Amenomiya, Y., Birss, V., Goledzinowski, M., Galuszka, J. and Sanger, A. *Catal. Rev.-Sci. Eng.*, **32**, 163 (1990) and references therein.
- 4) Preprints of the Symposium on Methane and Alkane Conversion Chemistry, Division of Petroleum Chemistry, 207th National Meeting, American Chemical Society, San Diego, CA, March 13-18, 1994.
- 5) a) Sundaram, M. U.S. Patent 4.687.570. (1987). b) Sundaram, M and Steinberg, M. *ACS Fuel Chem. Preprints*, **28**, 77 (1986).
- 6) Egiebor, N. O. and Gray, M. R. *Fuel*, **69**, 1276 (1990).
- 7) Ovalles, C., Hamana, A., Rojas, I, Bolivar, R., Proceedings of 1993 Eastern Oil Shale Symposium and submitted to *Fuel* (1994).
- 8) Ovalles, C., Hamana, A., Rojas, I, Bolivar, R., US Patent 5,269,909. (1993)
- 9) Ceballo, C. D., Bellet, A., Aranguren, S. and Herrera, M. *Rev. Tec. INTEVEP*, **7**, 81 (1987).
- 10) Del Bianco, A., Panariti, Prandini, B., Beltrame, P. L., Carniti, P., *Fuel*, **72**, 81 (1993).
- 11) Peries, J. P., des Courieres, TH., Espeillac, M., Proceedings of International Symposium on Heavy Oil and Residue Upgrading and Utilization, Fushum, Liaoning, China, May 5-8, 1992.
- 12) Boone, M. G., Ferguson, D. F. *Oil Gas J.*, 1954, March 22nd, 166.

Table 1. Analysis of the Hamaca Crude Oil and Composition of the Natural Gas Used for the Upgrading Reactions

Hamaca Crude		Natural Gas	% Molar
API Gravity at 60°F	8.6	Methane	75.4
Asphaltenes (% w/w)	12.5	Carbon dioxide	11.2
Nitrogen (ppm)	7500	Ethane	8.8
Sulfur (%w/w)	3.71	Propane	3.65
Nickel (ppm)	102	Butanes	0.77
Vanadium (ppm)	450	Pentanes ⁺	0.12
% of residue 500°C ⁺	57%	Nitrogen	0.02
Viscosity at 30°C (cP)	500,000	Hydrogen	0.04

Table 2. Effects of the Residence Time and the Percentage of Water on the Properties of the Upgraded Reconstituted Crude Oils.^a

Exp.	Residence time (min) ^b	% H ₂ O (w/w) ^c	^a API	Viscosity at 30°C (cP) ^d	% Conv. Residue ^e (± 1%)	Conradson carbon (% w/w)
Crude	-	-	8.6	500,000	-	13.4
1	30	10	12.0	1700	35	16.5
2	45	10	12.0	1100	49	18.0
3	30	20	11.8	1590	36	16.2

^aThe reactions were carried out in 0.11 barrel/day continuous flow plant at 410°C, 1600 psi of natural gas of final pressure. The results are the average of 12 h mass balances for up to 36 h.

^b Residence time in minutes for the coil and soaker reactors. ^c Percent of water by weight in the feedstock. ^d Values ± 100 cP. ^e Percentage of conversion 500°C⁺ is defined in the experimental section. Percentage of volatile material in the crude oil 54% w/w.

Table 3. Investments and Net Present Value (in million of US\$) for the Technologies Used in the Transportation of Extraheavy Crude Oil^a

Costs	Visbreaking ^b	Methanetreatment ^b	Hydrovisbreaking	Heating	Diluent
Total on-sites	180	244	348	-	-
Total off-sites	127	172	247	-	-
Oil pipe line system	88	86	87	145	143
Total Investment (in 3 years)	395	502	582	145 ^c	143 ^c
Annual Operation Costs	(21)	(23)	(40)	(11)	(10)
Annual Upgrading Credits	46	64	97	-	-
Net Present Value	(246)	(255)	(330)	(216)	(212)

^aFor the basis of the study see text. Calculus based on 1993 US\$ over a 17 years life of the plant.

^bA topping step was added previous to the upgrading reactor.

^cTotal Investment in a two years period.

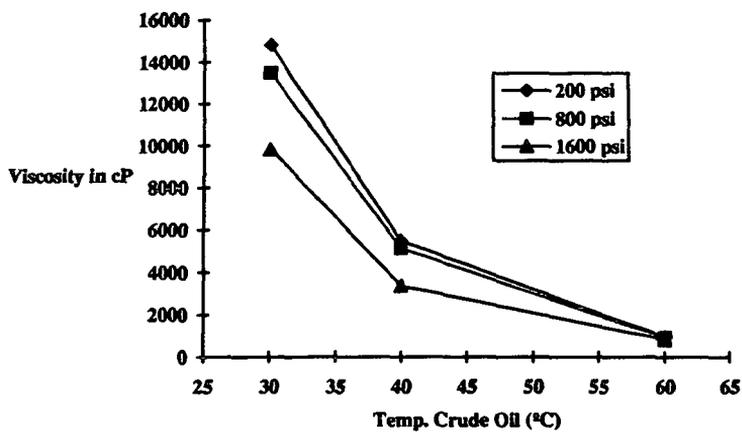


Fig. 1. Effects of the Pressure of Natural Gas on the Viscosity of the Upgraded Reconstituted Crude Oils.