

Heavy Oil Resources and Upgrading in Venezuela

by M. Josefina Pérez-Zurita

The total crude reserves of Venezuela amount to 221 billion barrels, of which 76 billion are proven reserves. Of the proven reserves, 69% are heavy and extra-heavy crudes, which predominate in Venezuela, with condensates, light and medium crudes making up the rest. If the Orinoco Oil Belt reserves are added, Venezuela has the largest store of liquid combustibles on the planet: 300 billion barrels. These enormous energetic potential has lead researchers from academia and industry alike, to do research in the area.

Petroleum, commonly called crude oil or oil, is a complex mixture of hydrocarbons and organic compounds. Its physical properties and chemical composition vary strongly depending on its origin. Although the majority of crude oil is black, it can be amber, red or brown and shows a greenish fluorescence when light is reflected on it. Hydrocarbons constitute approximately between 50 and 90% of petroleum, while the rest is composed by organic compounds which have O, N, S and organometallic molecules.

In general, hydrocarbons derived from petroleum can be grouped in several families depending on their boiling point and number of carbon atoms: naftas (42-175 °C, C₃-C₁₀), kerosene (175-240 °C, C₁₀-C₁₃) and diesel (240-340 °C, C₁₃-C₂₀) among others. They also can be classified in four big groups according to their general chemical composition:

- 1) saturates (alkanes and cicloalkanes from methane to n-hexacontane-C₆₀H₁₂₂);
- 2) aromatics (mono-, di- and polinuclear hydrocarbons with or without alkyl branches);
- 3) resins (aggregates composed by sulfoxides, amines, tio-phenes and pyridine);
- 4) asphaltenes (extense aggregates of poliaromatics, naphthenic acids, phenols, metalloporphyrines among others).

Depending on the proportion of each group of hydrocarbon, crude oil is classified in condensed, light, medium, heavy and extra heavy. The Table shows this classification.

M.J. Pérez-Zurita, Universidad Central de Venezuela - Facultad de Ciencias - Escuela de Química - Centro de Catálisis Petróleo y Petroquímica - Apartado Postal 47102 - Caracas (Venezuela). marperez@reacciun.ve

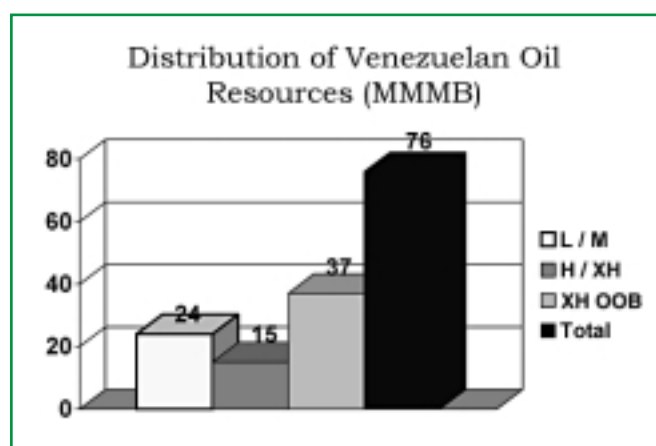


Figure 1 - Distribution of the Venezuelan resources of crude

The heavy and extra heavy crude oils flow with great difficulty mainly due to its high content of resins and asphaltenes. These fractions have high molecular weight and high concentration of heteroatoms [1]. In the world there are big deposits of heavy and extra heavy crude oil, concentrated mainly in seven big deposits existing in Canada, Russia and Venezuela. United States, Madagascar, Italy, Albany, Trinidad and Rumania also have smaller deposits of heavy and extra heavy crude oil [2].

Exploitation of this resources have serious problems mainly because the difficulty in transportation and treatment, which is a consequence of its high viscosity (between 100.000 and 500.000 cp at room temperature), low content of destilable products (% of residues at 500 °C around 60% w/w) and content of heavy metals (400-600 ppm V and 50-100 ppm Ni).

Upgrading of heavy and extra-heavy oil technologies

The main objective of upgrading heavy oil is to increase the H/C ratio with the aim of converting it into useful products or at least, facilitate its transportation to the refinery.

The interest in conversion of heavy oils and residuals (due to the enormous world resources) have lead to the development of different procedures which are well described in the Heavy Oil Processing Handbook published by the Research Association for Residual Oil Processing (Rarop) [3].

In general, the processes for converting residuals and heavy oils can be classified in two categories [4, 5]:

- carbon rejection processes: the majority of these processes are thermic. The crude generated have a higher H/C ratio than that of the feed. Among these processes are the vis-

Table - Classification of crude oil depending on their properties

Crude oil	Density (m ² /g)	°API Gravity
Condensed	<0.83	>39
Light	0.87-0.83	31.1-39
Medium	0.92-0.87	22.3-31.1
Heavy	1.0-0.92	10.0-22.3
Extra heavy	>1.0	≤10.0

coreduction, coquification and pyrolysis processes;

- hydrogen addition processes: these processes involved the reaction of the heavy crude with an external source of hydrogen resulting in an increase of the H/C ratio. Among this processes are the hydroconversion and hydrotreatment processes which are conducted in the presence of a catalyst and made use of the carbon contained in the crude. In spite of the high pressures of hydrogen required, the quality and yield of the final product is superior to that obtained by removing the carbon.

Another classification of the technologies for upgrading heavy oils and residuals are through the following subdivisions: i) thermic processes (viscoreduction, coquification and pyrolysis), ii) physic processes (deasphalting with solvents) and iii) catalytic processes. The catalytic processes can be carried out with or without hydrogen addition. Among the processes without hydrogen addition are the well known Fluid Catalytic Cracking (FCC) and the Heavy Oil Treatment (HOT).

Venezuela crude oil resources

Venezuela, a country traditionally associated with oil, began the development of its vast resources in the early 20th century. Its Eastern and Maracaibo basins rank prominently among the 10 largest oil basins in the world, which together account for 60% of the planet's total hydrocarbon reserves. This enormous resource base ensures that the country will continue to be an important player in world supplies of oil and gas throughout the 21st century. The total crude reserves amount to 221 billion barrels, of which 76 billion are proven reserves [6]. Of the proven reserves, 69% are heavy and extra-heavy crudes, which predominate in Venezuela, with condensates, light and medium crudes - for which there is more demand on world markets - making up the rest. Figure 1 shows the distribution of the Venezuelan resources of crude. The country also has 147 trillion cubic feet of natural gas reserves (approximately 30% of the American Continent reserves). Venezuela has prospects of discovering an additional 23 billion barrels of condensates, light and medium crudes and 94 trillion cubic feet of gas. Its daily petroleum production capacity is 3.8 million barrels and the daily refining capacity 3.3 millions barrels spread

amongst 6 refineries in Venezuela, participation in 1 Caribbean refinery, 8 in the United States and 9 in Europe. The oil industry in Venezuela is run by Petr leos de Venezuela S.A. (PdvsA). It is an energy company owned by the Venezuelan State with operating and commercial activities within and outside Venezuela and infrastructure including 20,000 active wells located in 2,400 active fields, 300 active petroleum camps and more than 6,000 kilometers of pipelines. Its operations include hydrocarbon exploration, drilling, refining, transport and distribution, and other business such chemicals, petrochemicals and coal, in which promote maximum participation of private enterprise. PdvsA is one of the world's leading refiners with a crude processing system in Venezuela, the Caribbean, the United States and Europe [7]. For administrative purposes PdvsA has divided the country into three main operating areas: West region, East Region and South region, in each of which it carries out crude production, handling, transport and delivery. Figure 2 shows the location of these regions. In addition, the country have one of the major accumulations of crude oil existing in the world the Orinoco Oil Belt.

West region

This operating area catapulted Venezuela onto the world energy map early in the 20th century, first with a commercial discovery in 1914 through the Zumaque No. 1 well located in Mene Grande, on the eastern shore of Lake Maracaibo, and then as a result of the Los Barrosos-2 well blowout in 1922 on the outskirts of Cabimas, further north in the same area. The initial discoveries were on land but their proximity to the lake led to exploration activities in shallow waters in the Twenties and Thirties and eventually in deeper waters, further away from the shore. This pioneering activity, together with similar efforts in the Caspian Sea and Gulf of Mexico, was undoubtedly the foundation of advanced offshore operations that gradually developed worldwide. Crude and condensate pro-

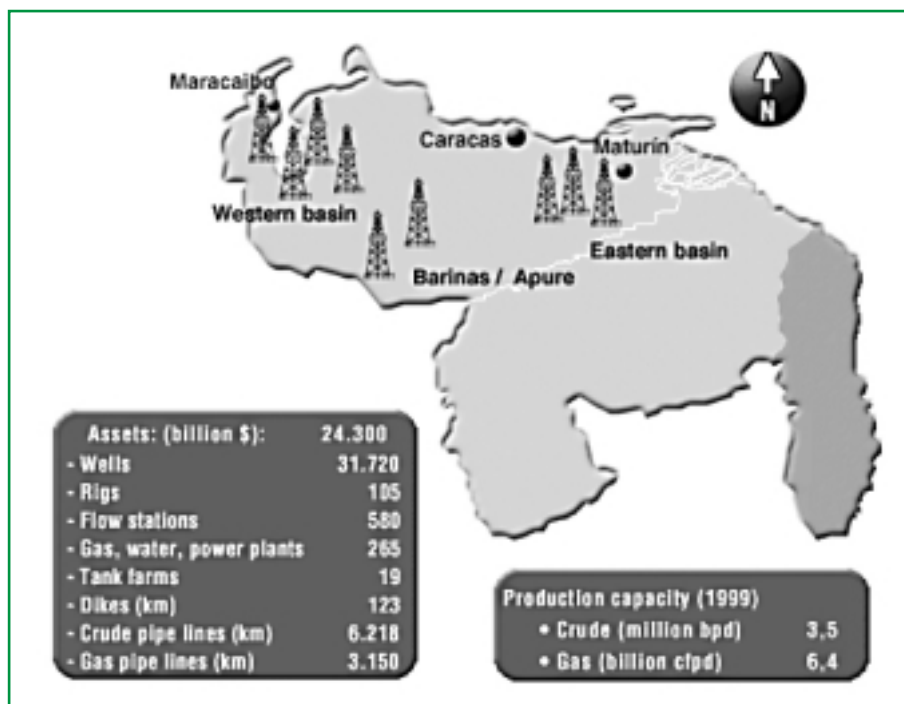


Figure 2 - Location of the main oil regions in Venezuela

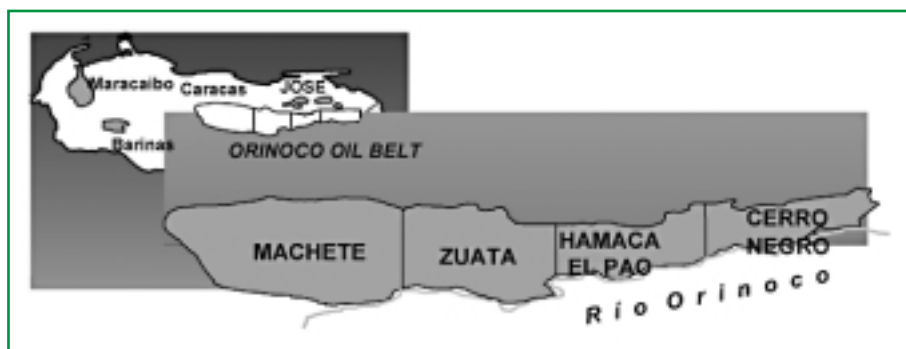


Figure 3 - Main regions inside the Orinoco Oil Belt

duction capacity is 1.7 million bpd and that of gas 2 billion cubic feet per day. As part of the 2000 program of activities, Pdvsa will drill 302 wells and workover 301. Its business plan envisages a crude and condensate production capacity of 1,925,000 bpd in this area by the year 2009.

East region

The history of this operating area goes back to the early 20th century with the extraction of bitumen in the states of Sucre (the Guanoco pitch lake) and Delta Amacuro. In the Twenties and Thirties exploration led to the discovery of fields and production in widely scattered areas in the jungle, swamps and plains: Quiriquire, Orocuai, Oficina, Jusepín, Leona, Pederuales, Temblador and Anaco. Despite this success, the emphasis was on development in western Venezuela because of the enormous potential of that area, a situation that remained unchanged until the discovery of the giant El Furrial field in Monagas state in 1986, which led to renewed interest in the eastern basin. Production capacity of crude and condensates is 1.7 million bpd and that of gas, 4.8 billion cubic feet per day. The 2000 operating plan stipulates the drilling of 25 wells and 281 workovers. Production capacity of crude and condensates is slated to increase to 3.06 million bpd by the year 2009, in accordance with Pdvsa's business plan.

South region

This operating area comprises the Barinas and Apure basins. Following the first important discoveries in Barinas in 1948 and 1953, commercial development was consolidated in the region in the Sixties. Production in the Apure basin is a more recent development, a result of the discovery in 1984 of the Guafita and La Victoria fields close to the Colombian border. There are no operating contracts in this area. Crude and condensate production capacity is 150,000 bpd, with very little gas present. The 2000 operations program stipulates the drilling of 12 wells and 35 workovers. Pdvsa's business plan envisages a production capacity of 260,000 bpd of crude and condensates by year-end 2009.

Orinoco Oil Belt (OOB)

The Orinoco Oil Belt is a wide basin considered as one of the major accumulations of crude oil existing in the world. 71% of all the heavy and extra-heavy Venezuelan crude oil is located in the Orinoco Oil Belt, which make of these region one of the world biggest basins. Exploring activities reveal the existence of additional 1,985 billions barrels on site from which 272 billions are heavy and extra-heavy and can be produced with existing technologies. If the Orinoco Oil Belt reserves are

added to the total Venezuelan proven reserves mentioned before, Venezuela has the largest store of liquid combustibles on the planet: 300 billion barrels. Its extension goes from Orinoco river 54,000 km² north and start at Calabozo in Guarico State.

Figure 3 shows the main regions inside the Orinoco Oil Belt.

The belt contains a great amount of crude oil types which varies in properties and characteristics. The petroleum sands extend to different deepness, from 1,600 to 13,000 meters and are

non consolidated porous and permeable sands from the Ternary. The crude oils from the belt, in spite of their low API gravity which oscillate among 3 and 13°, displace easily due to the relatively high basin temperatures (50-60 °C). The majority of the crude oil from the belt are biodegraded. The water coming from the Orinoco river pass through the petroleum sand transporting bacteria able to biodegrade the crudes. It has been reported that the micro-organism use hydrocarbons according to the following sequence [8]:

Aromatics < Naphtenes < *i*-alkanes < *n*-alkanes

According to this sequence, the lighter part of the crude oil disappears by biological mechanisms producing a lowering of API gravity and H/C ratio, as a consequence, the enrichment on the heavy components (resins and asphaltenes) is produced.

Pdvsa's 2000-2009 Business Plan called for an aggressive exploration effort aimed at reducing the tendency - in response to market demand - to make greater use of reserves of condensates, light and medium crudes, which constitute the lesser portion of the country's oil reserves, in contrast with a slower rate of depletion of the more abundant reserves of heavy and extra-heavy crudes. In addition, extraction and production of these crude oils are linked with economical and environmental factors. To counteract this situation, which was having a negative impact on the country's resource base, Pdvsa initiated the oil opening in 1999. The objective of the opening was the production and upgrading of heavy crude from the OOB. Four strategic associations with international companies and duration of 35 years [9, 10] were signed:

- 1) Petrozuata: 49.9% Pdvsa, 50.1% Conoco;
- 2) Sincor: 38% Pdvsa, 47% Total and 15% Statoil;
- 3) Cerro Negro: 41.7% Pdvsa, 41.7% Exxon-Mobil and 16.6% Veba Oil;
- 4) Ameriven: 30% Pdvsa, 40% Phillips and 30% Texaco.

All four projects will convert the virgin crude oils (heavy and extra-heavy) with 9 °API (average) in synthetic crudes with qualities which will go from 16 °API to 32 °API [6, 9, 11, 12]. In February 2002 Sincor inaugurated its Production Main Station in San Diego de Cabrutica (at the OOB) and in March 2002 inaugurated their "Upgraded Mejorador Complex" in Jose.

Sincor produces 180,000 bpd of extra heavy crude (8.5 °API) in the Main Station in the OOB. After mixing and diluting to 17 °API the crude is transported by pipeline to the "Upgraded Mejorador Complex" in Jose where it is converted into 180.000 bpd of upgraded crude ready for marketing over-

seas. This product (also known as Zuata sweet) is considered the highest quality light crude from the belt (32 °API), with less than 0.1% sulfur and no metals.

Research and development efforts in Venezuela

The enormous energetic potential of Venezuela has lead researchers from academia and industry alike, to do research in the area.

Within the academia, various groups in universities (Universidad Central de Venezuela, Universidad de los Andes, Universidad de Carabobo and Universidad del Zulia) and research centers (IVIC) are devoted to different kind of studies mainly oriented towards two alternatives, one dealing with improvements on existing catalysts [13-16], and the other towards the development and applications of new materials [17, 18].

The use of hydrogen donors solvents for underground crude oil upgrading [19] and ultrasound application for heavy oil upgrading [20] has also been investigated in academia-industry joint programs. The research strategy of Pdvsa is the incorporation and use of technology aimed at increasing its resource base, reducing its operating costs and providing support to the creation of clean products: ecologically acceptable energy products. Through its subsidiary Intevep, holds 1,046 patents spread through 24 countries and associated with a wide variety of processes, products, catalysts, and production equipment. These patents represent important contributions to the continuing development and ecological responsibility of the worldwide energy industry. Among the main technologies developed by Pdvsa-Intevep for heavy oil treatment is the HDH process, developed in 1986 [22]. HDH is a process for hydro-conversion of heavy oil using a natural catalyst and a slurry reactor. This process was further improved in the Nineties by replacing the natural catalyst by a petroleum-coke based catalyst [21]. The Aquaconversion technology was developed in 1997 [23]. In this process, the feed is heated in the presence of steam and a catalysts. The main feature of the process is the catalytic system and the way it is incorporated in the process. The catalytic system (which is soluble in the crude) is a dual system composed of two non noble metals. One of the catalysts promote the formation of hydrogen free radicals from water and the second catalyst minimized the condensation reactions making easier the addition of hydrogen to the olefinic radicals and aromatics [24]. Finally, it should be mentioned the fuel Orimulsion. Orimulsion is the brand name given to a fossil fuel produced from 70% natural bitumen and 30% water, plus additives to stabilize the emulsion. It has been widely used commercially, proving its value as an economically attractive fuel alternative in electricity generation. Venezuela's vast natural bitumen reserves (42 billion metric tons) guarantee a reliable supply of Orimulsion until well into the XXII century.

Final remarks

The author would like to express that the present contribution aims to give an overall view of the resources of heavy oil and upgrading effort in Venezuela.

By any means was conceived as an exhaustive review on the state of the art of research and development on heavy oil upgrading in Venezuela.

References

- [1] a) J.G. Speight, *J. Pet. Sci. & Eng.*, 1999, **22**, 3; b) M.F. Mir-Babaev, *Chem. & Tech. of Fuels and Oils*, 1996, **32**(6), 325.
- [2] W.E. Rudzinski, T.M. Aminabhavi, *Energy & Fuels*, 2000, **14**(2), 464.
- [3] Research Association for Residual Oil Processing (RAROP), *Heavy Oil Processing Handbook*, 1991, Japon.
- [4] G. Ertl *et al.*, *Handbook of Heterogeneous Catalysis*, Vol. 4, VCH, Weinheim, 1997.
- [5] J. Speight, *The Chemistry and Technology of Petroleum*, 2nd Ed., Marcel Dekker, New York, 1991, 570.
- [6] R. Páez *et al.*, 16th World Petroleum Congress, Forum N° 6, Canada, 2000.
- [7] <http://www.pdvsa.com>
- [8] A. Agüero, Doctoral thesis, Universidad Central de Venezuela, 1997.
- [9] M. Pulido, 7th UNITAR, China, 1998.
- [10] M. Treviño, 7th UNITAR, China, 1998.
- [11] V. Paglioni, 7th UNITAR, China, 1998.
- [12] J.C. Soligny, 16th World Petroleum Congress, Forum N° 17, Canada, 2000.
- [13] J.A. Rodríguez *et al.*, *Stud. Surf. Sci. Catal.*, 2000, **130D**, 2795.
- [14] J.L. Brito, A.L. Barbosa, *J. Catal.*, 1997, **171**, 467.
- [15] C. Scott *et al.*, *App. Catal. A*, 2000, 197, 23.
- [16] C.E. Scott *et al.*, *Stud. Surf. Sci. Catal.*, 2000, **130C**, 2813.
- [17] C.E. Scott *et al.*, *Proc. Iberoamerican Congress of Catalysis*, 2000, **1**, 333.
- [18] C.E. Scott, J.G. Biomorgi, B.P. Embaid, F. Gonzalez-Jimenez, A. Scaffidi, M.J. Perez-Zurita, submitted for publication in *App. Catal.*
- [19] C. Scott *et al.*, *Am. Chem. Soc. Preprints*, 2000, **45**, 588.
- [20] C. Scott *et al.*, Technical report N° INT-03412,97, Intevep S.A.
- [21] R. Galiasso *et al.*, Special Edition of Vision Tecnologica, 1999, 63.
- [22] *US Pat.* 4.591.426, 1986.
- [23] *US Pat.* 5.688.741, 1997.
- [24] P. Pereira, R. Marzin, NPRA Annual Meeting, Paper AM-98-09, San Francisco, California, 1998.