

Relationship between organic porosity and thermal maturity from cretaceous source rocks in the middle Magdalena Valley Basin, Colombia

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Objectives an Novelty

In accordance with the interest of Colombia in the evaluation of its USHR (Unconventional Shale Reservoir), this work has been focused on the study of the Cretaceous sedimentary rocks, from the Middle Magdalena Valley (MMV) basin in central Colombia, to know if they can be considered as USHR. For this, the following 4 objectives were established and accomplished: (1) To evaluate the type, amount and quality of the organic matter in the Cretaceous series, its sedimentary paleoenvironments and its degree of thermal maturity; (2) To determine the potential hydrocarbon levels, and to identify the sedimentary intervals as Unconventional Generating Rock Reservoirs in these Cretaceous series; (3) To understand the porosity system in the organic matter and its evolution with increasing thermal maturity; and (4) To determine if the reflectance of solid bitumen can be used as a paleothermometer for Colombian rocks void of vitrinite or with high thermal maturity. To accomplish these objectives an organic geochemistry, organic petrography, palynofacies and textural research was carried out. TOC-Leco and Rock Eval pyrolysis data were analyzed for 4235 samples, organic petrography analyses to 104 samples and palynofacies analyses to 469 samples; these samples are distributed in 6 wells of the MMV Basin. In addition, a set of samples were artificially matured by hydrolysis to reproduce the evolution of organic matter and to analyze the development of its porosity.

Results

The evaluation of the Cretaceous sedimentary sequences in the central part of the MMV basin shows two different intervals of interest as USHR. The original organic matter in the Early Cretaceous is, in general, a type II of Kerogen derived from pseudo-amorphous organic matter, but with some contributions of kerogen type III towards the bottom and to the east of the study area. The presence of solid bitumen (a secondary organic product derived from the hydrocarbon generation) is significant. The proposed sedimentary paleoenvironment for this series is a carbonate platform, with fluctuations in the mid-shelf to proximal marine environment. The Late Cretaceous sequence is very rich in organic matter of type II kerogen, except in the case of the Middle Turonian(?) interval (with a mix of kerogen type II and III). The sedimentary paleoenvironment of this sequence is fluctuations in a distal marine

platform and a proximal suboxic-anoxic basin. The sedimentary environment for the Middle Turonian(?) is shallow, an environment from medium to proximal marine platform.

The organic matter in the Early Cretaceous is highly thermally evolved, but this thermal evolution is variable both, along the sedimentary series (with increasing burial depth) and laterally in the basin. This thermal maturity ranges from: rocks at the peak of liquid hydrocarbon generation to those in the phase of volatile oil window (north of the study area); rocks in the volatile oil window to rocks in the wet gas window (northwest of the study area); rocks in the wet gas window to rocks in the phase of dry gas window (southeast of the study area). Due to the organic richness of this series and the appropriate thermal maturity it was identified an interval of 30.5 m (north of the study area) with potential for oil production and, a second interval (southeast of the study area) with gas, associated to a sequence of approximately 129 meters.

The thermal maturity of the Late Cretaceous is at / or near the hydrocarbon generation peak and shows intervals of interest for hydrocarbons (oil) generated by the rock itself of more than 30 meters thickness in the Cenomanian - Coniacian. The Coniacian - Campanian sequence is in an early thermal maturity stage with some intervals of interest as producible reservoirs for oil along the entire sequence, probably as result of a mixture of migrated and non-migrated hydrocarbons.

The textural study shows a porosity development in rocks artificially evolved by hydrolysis processes under increasing temperature from the beginning of the oil window to the gas generation window (Figure 1). Mercury porosimetry shows that the raw sample free of hydrocarbons displays a higher pore volume than the raw sample with hydrocarbon in pores. N₂ adsorption isotherms shows that the total pore volume increased in the raw sample free of hydrocarbons (VTOT: 0,004 cm³/g in raw sample vs 0,009 cm³/g in raw sample free HCs). The ultramicropore volume, also increased in the raw sample free of hydrocarbons (W0: 0,002 cm³/g in raw sample vs 0,007 cm³/g in raw sample free HCs). All this indicates an important contribution of porosity (macro-meso-micro-pores and ultra-micro-pores) to the pore volume of these rocks and the important role of free hydrocarbons occluded in the rock porosity. Mercury porosimetry also shows a macro-mesopore volume increase with the thermal evolution of the organic matter (Pore Vol.,

5.5-12000 nm: from 0.046 to 0.072 cm³/g). Nitrogen adsorption shows an increase in total pore volume and a specific surface area (SBET) with increasing thermal maturity (VTOT from 0,016 to 0,024 cm³/g and SBET from 3,1 to 9,6 m²/g, Figure 2-a. Finally, there is also a small increase in the ultra-micropore volume with increasing thermal maturity (W₀ from 0.004 to 0.006 cm³/g), Figure 2-b. During the hydrolysis process, there is a porous space that is filled by hydrocarbons generated by primary and/or secondary cracking of the organic matter. This is confirmed by the most evolved sample (365°C/72 h) which, after 110 washes with DCM still presents a high S₁ value (1.56 mgHC/gR). All this indicates a significant porosity increase in these rocks, in which hydrocarbons can be stored, however, since the pores are so small, the extraction capacity of these hydrocarbons (producibility) is limited.

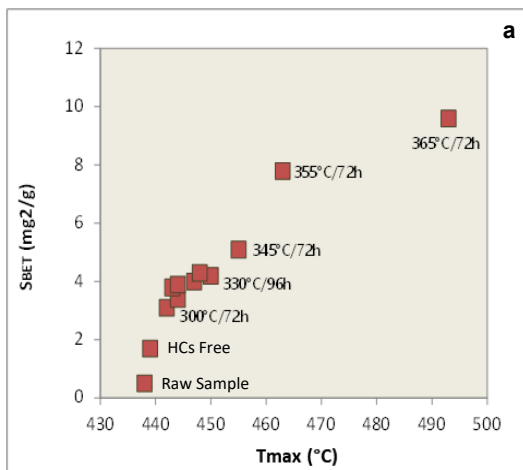


Figure 2. a) Evolution of the specific surface BET (S_{BET}) with thermal maturity (T_{max}); b) Evolution of the ultramicropore volume (W_0) with thermal maturity (T_{max}).

The study of solid bitumen as a potential paleothermometer has made it possible to propose an equation ($Roequibs = 0.8607Robs + 0.2358$) to obtain the degree of thermal maturity by transforming the reflectance of solid bitumen into the equivalent reflectance of vitrinite. This equation, developed using multiple samples from different basins, ages, and parameters, is applicable to Colombian rocks.

CONCLUSIONS

The Cretaceous sedimentary sequences in the central part of the MMV basin can be described as unconventional source rock reservoir, in which the Early Cretaceous sequence shows good potential as producible hydrocarbons for gas, while the Later Cretaceous, shows characteristics to produce liquid hydrocarbons. The study of the porosity system shows a gradual increase of pores (Hg porosimetry), particularly in the amount of macropores and mesopores (sizes: 5.5-12000 nm) with the increase in thermal maturity of organic matter. The nitrogen adsorption also shows a significant increase in the total volume of adsorbed gas representing an increase in micro-mesopores and small macropores, and in the specific surface area BET. The CO₂ adsorption isotherms display a substantial increase

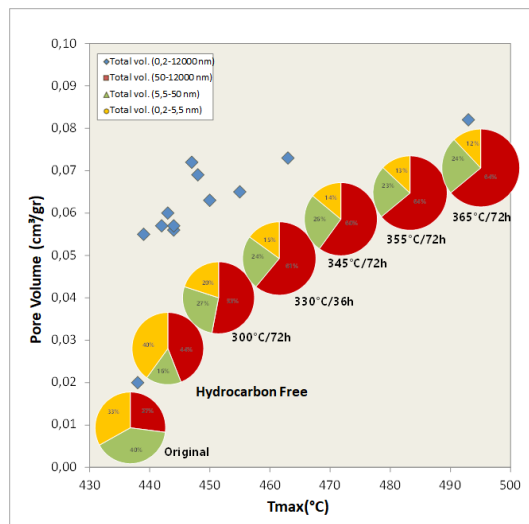
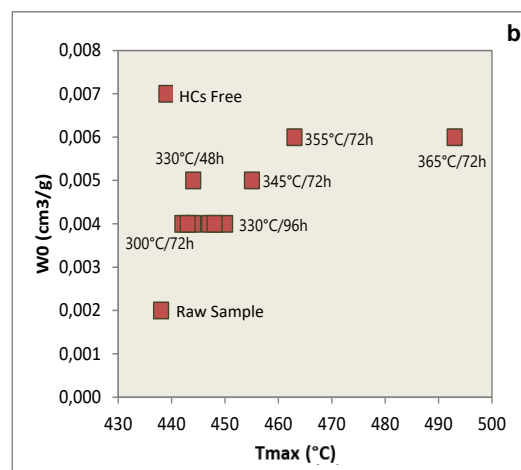


Figure 1. Evolution of different ranges of pores in the total pore volume with the thermal maturity given by the values of the maximum pyrolysis temperature (T_{max}).



in the volume of ultra-micropores. All this is due to the cracking of the primary organic matter to produce oil and, later to the cracking of solid bitumen in gas.

RELATED PUBLICATIONS

Juliao, T., Suárez-Ruiz, I., Márquez, R., Ruiz, B., 2015. The role of solid bitumen in the development of porosity in shale oil reservoir rocks of the Upper Cretaceous in Colombia. *International Journal of Coal Geology* 147-148, 126-144.

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Juliao, T.M., Márquez, R.E., Plata, A., Carvalho, M., 2017 (b). Estudio de Palinofacies de la formación La Luna en el sector norte y centro de la Cuenca Valle Medio del Magdalena. *Memorias del XVI Congreso Colombiano de Geología y III Simposio de Exploradores*. Santa Marta, Colombia. ISBN: 978-958-57950-3-7.

Suárez-Ruiz I, Juliao T, Suárez-García F, Marquez R, Ruiz B., 2016. Porosity development and the influence of pore size on the CH₄ adsorption capacity of a shale oil reservoir (Upper Cretaceous) from Colombia. Role of solid bitumen. *Int J Coal Geol*; 159: 1-17.