# Organic richness and source rock potential of the La Peña Formation in the Sabinas and Piedras Negras basins, NE of Mexico

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## ABSTRACT

This paper investigates the petroleum generation potential of the Lower Cretaceous organic-rich rocks of the La Peña Formation in the Sabinas and Piedras Negras Basin (SB-PNB) of northeastern Mexico. In order to provide insights into the source rock potential of this unit, a total of 25 cutting samples collected from 15 wells at different stratigraphic intervals along the study area were analysed using Rock-Eval Pyrolysis technique. The analytical results revealed that all the analysed samples can be described as hydrogen-poor organic matter with HI <200 mg HC/g TOC. The organic richness indicates a poor to excellent Total Organic Carbon content suggesting that existed different conditions during the deposition and burial of this unit, causing variable organic matter production and preservation. Also, the results revealed a variation in the kerogen types that may be attributed to the relative stratigraphic positions of the selected samples in the wells.

With respect to the organic matter thermal maturity, given by the geographical distribution of the Tmax values, the mature and overmature zone (435–508 °C) correspond to the Sabinas basin (SB).

Overall, these results show a variability in the organic richness, thermal maturity and petroleum potential of the La Peña Formation, differentiating the values of the TOC content, petroleum potential and HI content for the samples from the Sabinas Basin and Piedras Negras Basin, respectively.

Keywords: Sabinas-Piedras Negras Basin; petroleum generation potential; Rock-Eval Pyrolysis; organic richness; thermal maturity; Mexico.

#### RESUMEN

El presente trabajo investiga el potencial de generación petrolero de la Formación La Peña del Cretácico Inferior en las cuencas de Sabinas y Piedras Negras del noreste de México. Con el propósito de proveer datos actualizados acerca del potencial como roca generadora de dicha formación, un total de 25 muestras de recortes de perforación correspondientes a 15 pozos a diferentes intervalos estratigráficos dentro del área de estudio, fueron analizadas usando la técnica de Pirólisis Rock-Eval. Los resultados de este estudio revelan que la totalidad de las muestras analizadas presentan materia orgánica con bajo contenido en hidrógeno, con un IH<200 mg HC/g COT. La riqueza orgánica indica valores en el contenido de Carbono Orgánico Total que van desde pobre hasta excelente, sugiriendo que existieron diferentes condiciones durante la depositación y enterramiento de la Formación La Peña, causando variabilidad en la producción y preservación de la materia orgánica. Además, los resultados revelan una variación en los tipos de kerógeno, lo cual puede ser atribuido a los diferentes niveles estratigráficos de las muestras seleccionadas en los pozos dentro del área de estudio.

En lo que respecta a la maduración de la materia orgánica, dada por la distribución geográfica de los valores de Tmax (°C) se indica que la parte central del área de estudio (cuenca de Sabinas) representa la zona madura y sobremadura (435–508 °C).

En general, los resultados muestran variabilidad en la riqueza orgánica, la madurez térmica y el potencial petrolero de la Formación La Peña, diferenciando los valores en el contenido de COT, el potencial petrolero y el contenido de HI para las muestras provenientes de la cuenca de Sabinas y la cuenca de Piedras Negras, respectivamente.

Palabras clave: cuenca de Sabinas-Piedras Negras; potencial de generación petrolero; Pirólisis Rock-Eval; riqueza orgánica; madurez térmica; México.

# INTRODUCTION

Jurassic and Cretaceous argillaceous-carbonate successions in Mexico are precursors of petroleum source rocks of interest for exploration of unconventional oil and gas resources, with equivalent productive shale *plays* in the United States. Despite this, their exploration and production in Mexico are still in an incipient stage (Stevens and Moodhe, 2015).

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In the current scenario of energy demand, the unconventional resources located in the Sabinas and Piedras Negras basins (SB-PNB) could play a significant role. According to geological and geochemical studies, four geologic units have been identified as the primary source rocks: La Casita (Kimmeridgian-Tithonian), La Peña (Aptian), Eagle Ford (Cenomanian-Turonian) and Olmos (Maastrichtian) formations. These are siliciclastic-carbonated units, predominantly rich in organic matter type III and II with a thermal maturation above 1 and 3 % Ro (Eguiluz de Antuñano, 2001; Menetrier, 2005; Camacho-Ortegón, 2009). For these reasons, the SB-PNB area has a potential as an unconventional petroleum reservoir (see Santamaria-Orozco, 1991; Eguiluz de Antuñano, 2001).

In this work we focus on the Aptian La Peña Formation to conduct a source rock geochemical assessment using Rock- Eval pyrolysis data, which nowadays is considered a very common technique to obtain the information needed to evaluate the petroleum potential of sediments (Espitalié *et al.*, 1985), by assessing the type of organic matter (which is related to depositional setting), its thermal maturity and influence in the petroleum generation, as well as the remaining potential to petroleum generation in its present state (Akande, 2012; Hart and Steen, 2015).

Most studies have focused on the Eagle Ford Formation (Ortega-Lucach, *et al.*, 2018; González-Betancourt *et al.* 2020; Enciso-Cárdenas *et al.*, 2021), which in Texas produced significant amounts of gas and was one of the most prolific unconventional *plays* in the U.S. In contrast, little research has been done on the other units. This work contributes with new geochemical data for the La Peña Formation in the SB-PNB, which has been employed to investigate and characterize the petroleum generation potential of this geological unit, as unconventional resource prospect.

#### **GEOLOGICAL SETTING**

The Sabinas basin is one of Mexico's largest onshore marine shale basins, extending over 37000 km<sup>2</sup>, which originated as a consequence of the Gulf of Mexico opening and the subsequent separation of Pangea (Goldhammer *et al.*, 1991, 1993, Goldhammer, 1999; Goldhammer and Johnson, 2001; Pindell and Dewey 1982, Pindell, 1985, 1993; Salvador, 1987, 1991a, 1991b, 1991c). The basin was subsequently closed and inverted between Late Cretaceous and Eocene (González-Sánchez *et al.*, 2007, 2009), being delimited by structural highs such as the Coahuila Block, the Burro-Peyotes Peninsula, the Tamaulipas Archipelago, the islands of La Mula and Monclova and two major structures: the San Marcos and La Babia faults (Longoria 1984; McKee *et al.*, 1984; Padilla y Sánchez, 1986; Salvador,1991a, 1991b, 1991c; Chávez-Cabello *et al.*, 2005; Figure 1).

The sedimentary successions constituted by siliciclastic, carbonate, and evaporitic rocks were deposited on marine environment with terrigenous input and the source rocks are represented by La Casita, La Peña and Eagle Ford formations (González-Partida *et al.*, 2016; Figure 2).

Approximately 6000 m of marine, evaporitic, and fluviatile sedimentary rocks accumulated from the Middle Jurassic to the Paleogene, between ~170 and 40 Ma, in three principal stages: 1) a rapidly subsiding rift-fill stage (Middle–Late Jurassic), with siliciclastic sedimentary rocks and evaporites, mostly in response to changes in accommodation space related to the extensional process and the progressive incursion of marine waters; 2) a stage of platform-dominated facies with carbonate, evaporite, and coastal siliciclastic deposits (Early Cretaceous); and 3) a regressive stage with terrigenous sedimentation in a foreland setting (Late Cretaceous–Paleogene) (*e.g.*, Padilla y Sánchez, 1986; Goldhammer, 1999; Eguiluz de Antuñano, 2001; Pindell *et al.*, 2020).



Figure 1. Location of the Sabinas-Piedras Negras basin (SB-PNB) area, (Northeastern Mexico) with simplified structural context. Modified from Camacho-Ortegón *et al.*, 2022.

| RA       | PERI<br>OD          | EPOCH     | STAGE                  | FORMATION    |          | LITHOLOGY       | SR | PE | TRO<br>SeR | LEU<br>OR | M SY | YSTI<br>S | EM | СМ     | EVENT              |
|----------|---------------------|-----------|------------------------|--------------|----------|-----------------|----|----|------------|-----------|------|-----------|----|--------|--------------------|
|          | Quaternary          |           | ernary                 |              |          | Lm-Ar B         |    |    |            |           |      |           |    |        | .Ľ                 |
| Cenozoic | Pliocene<br>Miocene |           | cene                   | Sabi         | inas     | Cg-Ar-Lm        |    |    |            |           |      |           |    |        | Bas                |
|          |                     |           |                        |              |          |                 |    |    |            |           |      |           |    | and    |                    |
|          | e                   | Oligocene |                        |              |          |                 |    |    |            |           |      |           |    |        | orel               |
|          | oger                | Eocene    |                        |              |          |                 |    |    |            |           |      |           |    |        | ш.                 |
|          | Pale                | Paleocene |                        |              |          |                 |    |    |            |           |      |           |    |        | Mexican<br>Orogeny |
|          | Cretaceous          |           | Maastrichtian          | Escor        | ndido    | Ar-Lu           |    |    |            |           |      |           |    |        |                    |
|          |                     | Upper     |                        | Olm          | nos      | Ar-Lu           |    |    |            |           |      |           |    |        |                    |
|          |                     |           | Campanian              | San M        | liguel   | Arcz            |    |    |            |           |      |           |    |        |                    |
|          |                     |           |                        | Upson        |          | Lu-Lm           |    |    |            |           |      |           |    |        |                    |
|          |                     |           | Santonian<br>Conjacian | Austin       |          |                 |    |    |            |           |      |           |    |        |                    |
|          |                     |           | Turonian               | Eagle Ford   |          | Lu-Cz           |    |    |            |           |      |           |    |        |                    |
|          |                     |           | Cenomanian             | Buda         |          | Cz              |    |    |            |           |      |           |    |        | e                  |
|          |                     |           |                        | Del Río      |          | Lu              |    |    |            |           |      |           |    |        | denc               |
|          |                     | Lower     | Albian                 | Georgetown   |          | Cz              |    |    |            |           |      |           |    | indbsi |                    |
|          |                     |           |                        | Kiamichi     |          | Lu-Cz           |    |    |            |           | S pu |           |    |        |                    |
|          |                     |           |                        | Aurora       |          | Cz              |    |    |            |           |      |           |    |        | lg al              |
| <u>.</u> |                     |           |                        | La Peña      |          | Mg-Cz           |    |    |            |           |      |           |    |        | oolir              |
| Mesozoi  |                     |           | Aptian                 | Cupido       |          | Cz              |    |    |            |           |      |           |    | 0      |                    |
|          |                     |           | Barremian              | . La Vi      | rgen     | Do Y            |    |    |            |           |      |           |    |        |                    |
|          |                     |           | Under the second       | La M         | 1ula     | Lu-LuAr         |    |    |            |           |      |           |    |        |                    |
|          |                     |           | Hauterivian            | Padilla      |          | Cz              |    |    |            |           |      |           |    |        |                    |
|          |                     |           | Valanginian            | Barril       | Viejo    | Cz-Mg           |    |    |            |           |      |           |    |        |                    |
|          |                     |           | Berriasian             | Menchaca     | Taraises | CzLuAr-Do Cz-Mg |    |    |            |           |      |           |    |        |                    |
|          | Jurassic            | Upper     | Tithonian              | La Casita    |          | Lu-Ar-Cz        |    |    |            |           |      |           |    |        |                    |
|          |                     |           | Kimmeridgian           | Olvido       |          | X-Cz            |    |    |            |           |      |           |    |        |                    |
|          |                     | Oxiordian |                        | La Gloria    |          | Ar-Cz-ArLu      |    |    |            |           |      |           |    |        |                    |
|          |                     | Middle    | Callovian              | Minas Viejas |          | Y-Ar            |    |    |            |           |      |           |    |        | Aperture           |
|          |                     | Lower     |                        | Huiza        | achal    | Lu-Cg           |    |    |            |           |      |           |    |        |                    |
|          | Triassic            |           |                        | Baser        | ment     | lg-Mt           |    |    |            |           |      |           |    |        | Stability          |

Figure 2. A regional stratigraphic column of the SB-PNB. SR (Source Rock), RR (Reservoir Rock), SeR (Seal Rock), OR (Overburden Rock), T (Traps), S (Synchrony), P (Preservation), CM (Critical Moment). Modified from de la Rosa-Rodríguez, 2018.

Possibly marine sedimentation started in the Middle Jurassic with the deposition of the Minas Viejas Formation (Amezcua et al., 2020), continued in the Late Jurassic with La Gloria and La Casita formations, followed by cycles of transgression and regression in the Early Cretaceous, that controlled the accumulation of terrigenous, carbonates and evaporites, from the Berriasian to early Aptian (Menchaca, Barril Viejo, Padilla, La Mula, Carbonera, La Virgen and Cupido formations); these units were covered by shales and argillaceous limestone of the La Peña Formation during the Aptian (Charleston, 1973; Goldhammer, 1999; Eguiluz de Antuñano, 2011). The basin subsidence caused the accumulation of carbonates and terrigenous of relatively deep marine environment, during Albian and early Cenomanian (Upper Tamaulipas, Cuesta del Cura, Kiamichi, Georgetown, Del Río and Buda formations). During the Late Cretaceous and Paleogene, the basin was covered by foreland-type detrital sedimentation, which was tectonically deformed and uplifted (Eguiluz de Antuñano and Chávez-Cabello, 2022).

The deformation of the Sabinas basin occurred during various stages of progressive transition from thin to thick-skinned structural styles, between the Late Cretaceous and the middle Eocene as a result of a combination of Sevier and Laramide orogenic pulses (Eguiluz de Antuñano *et al.*, 2000; Eguiluz de Antuñano, 2001; Gray and Lawton, 2011; Ramírez-Peña and Chávez-Cabello, 2017; Fitz-Díaz *et al.*, 2018; Williams *et al.*, 2020; Perelló, 2021). The final inversion of the basin took place in the middle Eocene, with folding, thrusting, and highangle reverse faulting during the regional, relatively low-temperature shortening of the Laramide orogeny (Eguiluz de Antuñano, 2001; Chávez-Cabello, 2005; Chávez-Cabello *et al.*, 2005, 2007, 2009; Molina-Garza *et al.*, 2008; Fitz-Díaz *et al.*, 2011; Fitz-Díaz and van der Pluijm, 2013; Perelló, 2021; Figure 3). Recent literature refers to this major deformation event as the Mexican orogeny (Juárez-Arriaga *et al.*, 2019; Davison *et al.*, 2020; Gray *et al.*, 2020).

# Primary source rocks of the Sabinas and Piedras Negras Basins (SB-PNB)

The primary source rocks of the SB-PNB will be described briefly to cover the main aspects of each formation, based on the relevant literature.



Figure 3. East-West sections representing the geologic evolution of the north of Mexico. NAP: North American Plate, PPP: Paleo Pacific Plate, FP: Farallon Plate, SB: Sabinas Basin, CP: Coahuila Platform, CMB: Central Mexico Basin. Modified from Fitz-Díaz *et al.*, 2018.

La Casita Formation is a Tithonian unit that possesses the largest natural gas reserves and is considered the principal petroleum source rock in the study area. It consists of organic-rich shales deposited in a deep-water marine environment. (Santamaría-Orozco *et al.*, 1991; Eguiluz de Antuñano 2001). The main prospective target of this geological unit is a 300 m-thick shale interval in the central part of the basin, with an average 70 m of net pay thickness of organic-rich interval with 2.0 % average TOC gas prone (2.5 % Ro). This formation is economically significant since it is the principal dry gas potential source for various *plays* in the Sabinas basin (De La O-Burrola *et al.*, 2014).

In the case of the La Peña Formation, it consists of two units, the lower part is constituted by thin-to-medium beds of grey limestone with flint nodules and scarce clay material interbedded. The upper part presents abundant limestone strata, gradually thinning out into a flagstone aspect, with calcareous limonite transition and slightly reddish tones due to weathering (De La O-Burrola, 2013).

This formation is considered of economic interest for the SB-PNB since it is one of the source rocks for the petroleum system of this region and could be an unconventional source, primarily with gas production (De La O-Burrola, 2013).

The Eagle Ford Formation consists of thin black shales interbedded with sandy limestones and carbonate-cemented sandstones (Eguiluz de Antuñano, 2001). This geologic unit is approximately 300 m thick and has a wide distribution across the northwestern, northeastern and central portions of the SB-PNB. The Eagle Ford Formation has been previously interpreted as part of a transgression system deposited in a shallow marine environment. This is an anisotropic and heterogeneous rock succession due to facies changing and stratification, with TOC values between 0.5 to 8% and predominant Type II organic matter. Based on these attributes, it is considered a source rock in the shale gas unconventional system of the study area (González-Betancourt *et al.*, 2020, Enciso-Cárdenas *et al.*, 2021).

Finally, the Olmos Formation is also relevant as a source rock that generates Coal Bed Methane (CBM) due to the presence of 1 to 12 coal seams, with variable thickness ranging from 0.20 to 2 m (De La O-Burrola, 2013; González-Partida *et al.*, 2022). Previous studies of the organic matter in the SB-PNB highlight the Olmos Formation as a *play* with gas production potential. This unit has an appropriate thermal maturity (0.6 to 1.5 % Ro), with thermogenic gas generation at depths between 4 and 6 km (Eguiluz de Antuñano and Amezcua-Torres, 2003; Piedad-Sánchez *et al.*, 2005a, 2005b y 2005c, and González-Partida *et al.*, 2017, 2020).

Some of the main features for these four source rocks comprising the SB-PNB (vitrinite reflectance, TOC content, HI values, Tmax thermal maturity and thickness) are shown in Table 1.

#### La Peña Formation

The Lower Cretaceous La Peña Formation is a condensed limestone-shale geological succession. The name La Peña was originally

Table 1. Geochemical features for the four main source rocks of the SB-PNB area. Source: Eguiluz de Antuñano, 2001; Piedad-Sánchez, 2004; PEMEX, 2012; De La O-Burrola, 2013; De La O-Burrola *et al.*, 2014; Ortega-Lucach, *et al.*, 2018; this article.

| Formation  | %Ro        | TOC<br>(%wt) | HI<br>(mg HC/g TOC) | Tmax<br>(°C) | Thickness<br>(m) |  |
|------------|------------|--------------|---------------------|--------------|------------------|--|
| La Casita  | 2.5        | 0.5 - 2      | 50                  | 50 - 700     | 50 - 700         |  |
| La Peña    | 1.5        | 0.07 - 4.88  | 15 - 175            | 312-508      | 30 - 200         |  |
| Eagle Ford | 0.5 - 1.88 | 0.08 - 6.61  | 24 - 129            | 442 - 471    | 90 - 125         |  |
| Olmos      | 0.6 - 1.53 | 0.98 - 47.58 | 25 - 680            | 456 - 489    | 0.5 - 3          |  |

applied by Imlay (1936) to the unit of limestones and shales that lies between the Parritas Formation below and the Aurora Limestone above, located on the western part of the Sierra de Parras in Coahuila State. At these locations the facies of this unit developed different characteristics that allowed Imlay to divide it into two members: the lower La Peña composed by around 430 m-thick limestones ranging between 9 to 18 m-thick, and the upper member composed by a 15 to 24 m-thick argillaceous beds. Humphrey (1949), redefined Imlay's La Peña Formation, delimiting it to "the lithologically distinct unit of marls, shaly limestones, and shales which carries a late Aptian fauna and which is extensive throughout northern Mexico", therefore, the Humphrey's redefinition of La Peña Formation is analogous to Imlay's original upper member of the La Peña (Barragán, 2000). The facies of this unit in the study area exhibit stratigraphical and geochemical variations attractive for the oil industry.

Upper Aptian sea level rises are represented by the argillaceous strata of the La Peña Formation, with up to 200 m variable thickness (Santamaría-Orozco, *et al.*, 1991; Eguiluz de Antuñano, 2001), irregularly deposited, which were affected by the rugged topography's marine substrate that regulated the sedimentation rate (Cantú-Chapa, 1989, Camacho-Ortegón *et al.*, 2017).

During the beginning of deposition of the La Peña Formation in the late early Aptian, the increase input of terrigenous materials and significant decrease in the abundance of benthic fauna took place. The accumulation of this unit continued throughout the end of the Aptian and records changes in conditions of sedimentation and productivity in the water column. (Barragán, 2000).

Upper Aptian ammonites in this unit allowed the establishment of stratigraphic correlations at great distances. The succession of these fossils and their relationship with the fossil-bearing strata, allowed to infer the occurrence of hiatuses that affects their thickness, which varies from 15 to 170 m over very short distances (Cantu-Chapa, 1989).

## **EXPERIMENTAL METHOD**

We analysed 25 cutting samples of the La Peña Formation selected from 15 wells within the SB-PNB: 10 from the Piedras Negras basin and 15 from the Sabinas basin (Figure 4). The depth of the samples was selected based on the stratigraphic interval corresponding to the La Peña Formation and considered representative of the whole formation, according to the PEMEX well reports in the study area. It is worth mentioning that only two wells in the Sabinas basin have more than three samples, comprising the entire thickness of the La Peña Formation at those locations.

The Rock-Eval pyrolysis analysis were performed using a Rock-Eval 6 TURBO\*, instrument developed by the Institut Français du Pétrole (IFP) for assessing petroleum source rocks' quality and maturity level (Espitalié *et al.*, 1977; Katz, 1983), at the laboratory of Centro de Investigación en Geociencias Aplicadas, at the Universidad Autónoma de Coahuila (CIGA-UAdeC). To carry out the analysis, approximately 70 mg of powdered sample material was first heated at 300 °C under a helium atmosphere and then gradually pyrolyzed up to 850 °C. Released hydrocarbons were measured by a FID detector, while  $CO_2$  and CO were measured by an IR detector. The measurements were calibrated using the standard IFP 160000.

## RESULTS

The Rock-Eval S1 peak indicates the amount of detectable free hydrocarbons before thermal pyrolysis present within a sample (Karg



Figure 4. Location of the 15 wells in the SB-PNB, where rock samples were used for the Rock-Eval analysis of the La Peña Formation. Sabinas basin wells: pink color, Piedras Negras basin wells: blue color.

and Littke, 2020). The S1 peak values from the studied samples fluctuate from 0.02 to 22.23 mg HC/g rock (avg. 6.48 mg HC/g rock). The present petroleum generation potential, given by the S2 peak varies from 0.06 to 4.79 mg HC/g rock (avg. 1.96 mg HC/g rock). The Production Index (PI), a maturity proxy defined as the ratio of hydrocarbons liberated under the S1 peak to the total amount of hydrocarbons released under S1 and S2 peaks, ranges between 0.22 to 0.84 (avg. 0.55). The main Rock-Eval pyrolysis results are shown in Table 2.

The Total Organic Carbon (TOC) content of a rock represents all the biogenically derived carbon, which consists of two components: hydrocarbons (oil, gas) and solid organic matter known as kerogen (Hart and Steen, 2015). The La Peña Formation TOC content varies from 0.07 to 2.39 % (avg. 0.64 %) and from 0.77 to 4.88 % (avg. 2.96 %) in the Piedras Negras and Sabinas basins, respectively.

The Hydrogen Index (HI) has values ranging from 15 to 175 mg HC/g TOC (avg. 64.80 mg HC/g TOC) for the Piedras Negras basin and from 37 to 137 mg HC/g TOC (avg. 103.13 mg HC/g TOC) for the Sabinas basin. All the analysed samples can be described as hydrogen-poor organic matter with HI <200 mg HC/g TOC.

The Tmax values range between 325 to 466 °C (avg. 411.40 °C)

and between 312 to 508 °C (avg. 415.13 °C) for the Piedras Negras and Sabinas basins, respectively. Overall, nine samples are located close to the oil generation zone and just two presented a thermal maturity enough to the generation of wet and dry gas, the rest showed Tmax values for an immature source rock. The distribution of this thermal maturity parameter indicates that the mature and overmature samples (435 to 508 °C) are in the center of the study area (Sabinas basin; Figure 5).

# DISCUSSION

#### Content and origin of preserved organic matter

The studied samples of the La Peña Formation have organic richness appropriate for hydrocarbons generation, with poor to excellent source rock potential; according to the classification of Peters and Cassa (1994). The dispersion of the data points in the TOC *vs.* S2 diagram (Figure 6) and the observed distribution of the TOC content of the La Peña Formation probably reflects different organic-rich levels through this unit, as those described by Barragan (2000). Changes in the

| Table 2. Rock-Eval pyrolysis data for the 25 rock samples of the La Peña Formation. PNB: Piedras Negras Basin, SB: Sabinas Basin. S3 peak: amount of generated |
|--|
| CO2 during thermal pyrolysis The Hydrogen Index (HI) (mg HC/g TOC) and the OI (mg CO2/g TOC) were calculated to distinguish the type of kerogen, derived       |
| from the S2 and S3 peaks, respectively, by normalization to the TOC content (Karg and Littke, 2020).   |

| Well           | Basin | Depth<br>(m) | TOC<br>(%wt) | HI<br>(mg HC/g TOC) | OI<br>(mg CO <sub>2</sub> /g TOC) | Tmax<br>(°C) | <b>S1</b><br>(mg HC | <b>\$2</b><br>/g rock) | PI<br>(\$1/\$1+\$2) |
|----------------|-------|--------------|--------------|---------------------|-----------------------------------|--------------|---------------------|------------------------|---------------------|
| Coconal-1      | PNB   | 2267         | 1.05         | 36                  | 14                                | 335          | 0.15                | 0.38                   | 0.28                |
| Casa Roja-1    | PNB   | 1984         | 0.32         | 21                  | 6                                 | 418          | 0.05                | 0.07                   | 0.42                |
| Gabriel-1      | PNB   | 1991         | 0.32         | 55                  | 41                                | 423          | 0.08                | 0.17                   | 0.32                |
| Casa Roja-11   | PNB   | 1922         | 0.14         | 88                  | 22                                | 423          | 0.04                | 0.12                   | 0.25                |
| Vacas-1        | PNB   | 1747         | 0.12         | 175                 | 10                                | 432          | 0.11                | 0.21                   | 0.34                |
| Cien Cazas-1 A | PNB   | 2022         | 1.12         | 30                  | 8                                 | 466          | 0.13                | 0.33                   | 0.28                |
| Fuente-1       | PNB   | 2402         | 0.21         | 78                  | 0                                 | 433          | 0.1                 | 0.17                   | 0.37                |
| Piojo-1        | PNB   | 2138         | 0.62         | 73                  | 22                                | 430          | 0.13                | 0.46                   | 0.22                |
| Cien Cazas-1   | PNB   | 2055         | 0.07         | 77                  | 0                                 | 429          | 0.02                | 0.06                   | 0.25                |
| Centella-1     | PNB   | 2571         | 2.39         | 15                  | 6                                 | 325          | 0.13                | 0.37                   | 0.26                |
| Silencio-1     | SB    | 910          | 4.63         | 40                  | 6                                 | 508          | 0.58                | 1.84                   | 0.24                |
| Barroteran-1 A | SB    | 580 - 585    | 0.77         | 75                  | 0                                 | 350          | 1                   | 0.58                   | 0.63                |
| Florida-1      | SB    | 1375 - 1380  | 1.99         | 37                  | 5                                 | 312          | 1.52                | 0.74                   | 0.67                |
| Florida-1      | SB    | 1410 - 1415  | 1.15         | 54                  | 4                                 | 326          | 0.94                | 0.63                   | 0.60                |
| Pirineo-71     | SB    | 1315         | 2.1          | 137                 | 5                                 | 434          | 15.03               | 2.87                   | 0.84                |
| Pirineo-71     | SB    | 1320         | 2.55         | 133                 | 15                                | 433          | 11.64               | 3.39                   | 0.77                |
| Pirineo-71     | SB    | 1335         | 2.48         | 114                 | 12                                | 432          | 7.43                | 2.82                   | 0.72                |
| Pirineo-71     | SB    | 1350         | 3.45         | 131                 | 30                                | 432          | 15.29               | 4.5                    | 0.77                |
| Pirineo-71     | SB    | 1355         | 3.43         | 131                 | 12                                | 432          | 13.74               | 4.49                   | 0.75                |
| Pirineo-21     | SB    | 995          | 3.06         | 127                 | 19                                | 430          | 12.83               | 3.89                   | 0.77                |
| Pirineo-21     | SB    | 1000         | 4.88         | 98                  | 12                                | 426          | 18.17               | 4.79                   | 0.79                |
| Pirineo-21     | SB    | 1020         | 4.24         | 93                  | 20                                | 425          | 9.83                | 3.94                   | 0.71                |
| Pirineo-21     | SB    | 1035         | 3.04         | 122                 | 12                                | 430          | 11.28               | 3.7                    | 0.75                |
| Pirineo-21     | SB    | 1055         | 3.78         | 118                 | 18                                | 428          | 22.23               | 4.46                   | 0.83                |
| Pirineo-21     | SB    | 1060         | 2.89         | 137                 | 22                                | 429          | 19.63               | 3.95                   | 0.83                |

intensity of upwelling currents and/or the arrival of continental-derived nutrients linked to climate conditions could explain changes in organic richness, as these processes caused variations in productivity and seafloor redox conditions (Barragan, 2000; Núñez-Useche *et al.*, 2015).

The Tmax vs. HI diagram (Figure 7) exhibits scattered data points indicating the presence of different types of organic matter in the La Peña Formation (kerogen type IV, III and II-III mix). Only two samples are located in the wet/dry gas window, but with low HI content, indicating an inert organic matter. This variable behaviour of kerogen type could be associated with the high rates of continental runoff and nutrients supply occurred during the deposition of the La Peña Formation in the early Aptian (Núñez-Useche, *et al.*, 2014), in addition to paleoenvironmental condition changes during the Early Cretaceous, like transgressive stages associated with global sea level rises, with intercalated periods of different oxygenated conditions and local upwelling systems (Núñez-Useche and Barragán, 2012), resulting in differences in the organic matter composition.

#### Thermal maturity

The PI vs. Tmax diagram (Figure 8) exhibits variable degree of maturation, ranging from immature to overmature conditions. The samples from the Piedras Negras and the Sabinas basins have different PI values. Some samples from the Sabinas basin possess anomalous high PI values compared to their level of thermal maturity, which suggests that this samples are contaminated with drilling additives or migrated oil (Peters and Cassa, 1994). As with the previous diagram, altogether, these data exhibit a wide range of thermal maturity. According to Hart and Steen, (2015) such a variability may be related to the different thermal maturities areas that the wells come from

brought by the different stratigraphic levels where the samples were collected. Furthermore, the pattern of behaviour shown in the PI *vs.* Tmax diagram may be associated to the existing mix of different types of kerogens at different stratigraphic levels (Akande, 2012) of the La Peña Formation, affecting the performance of the petroleum production during the pyrolysis.

#### **Petroleum Potential**

The TOC-HI diagram shows a hydrocarbon generation potential ranging from little or no potential to rich gas prone (Figure 9). These data suggest that the organic matter was thermally altered, reflecting that the samples from the SB reached a greater thermal maturity, allowing them to develop greater gas generation potential, with respect to the samples of the PNB that shows a reduced potential. The decrease of the organic matter maturity towards the NW of the study area may be attributed to different burial degrees related to the combination of different tectonic events of the Mexican Orogeny, which contributed to the cooling of the geological successions, causing erosion and leading to modify the kerogen transformation (Camacho-Ortegón *et al.*, 2017).

# CONCLUSIONS

The analysis of the Rock-Eval pyrolysis parameters (TOC, Tmax, S1, S2, HI and PI) carried on selected samples from 15 wells in the SB-PNB indicated that: the organic richness of the La Peña Formation varies from poor to excellent, with a petroleum potential (S2 peak) and a TOC content clearly higher for the wells in the SB, compared to the obtained values for the PNB. Similarly, the greater values of



Figure 5. Iso-value map of the La Peña Formation showing the geographical distribution in the study area for Thermal maturity (Tmax).



Figure 6. Diagram of the La Peña Formation Total Organic Carbon (TOC) vs. Petroleum Generative Potential (S2 peak) according to the Rock-Eval pyrolysis results. SB: Sabinas Basin, PNB: Piedras Negras Basin.



Figure 7. Diagram of the La Peña Formation Hydrogen Index vs. Tmax (°C), showing type of Kerogen and thermal maturity for the analysed samples in the study area.



Figure 8. The La Peña Formation Production Index (PI) vs. Tmax (°C) diagram for the analysed samples in the study area.



Figure 9. The La Peña Formation TOC vs. HI cross plot showing the potential hydrocarbons according to the Rock-Eval pyrolysis data.

free hydrocarbon content (S1 peak) and Production Index (PI) are also observed for the samples of the SB, which indicate its higher hydrocarbon resource potential compared to the La Peña Formation in the PNB. Furthermore, the Rock-Eval data suggest a variability in the thermal maturation for both basins, emphasizing that most of the marginal mature and overmature samples correspond to the SB. On the other hand, the petroleum potential data indicates that the SB samples exhibits a greater gas generation potential, compared to the limited potential given by the HI and TOC content for the PNB samples.

The burial and deposition changing conditions for the La Peña Formation proposed (Barragan, 2000; Barragán, 2001; Núñez-Useche and Barragán, 2012; Núñez-Useche, *et al.*, 2014; Núñez-Useche *et al.*, 2015), could explain the apparent combination of different types of kerogens (III-II, III, IV). However, the results of this work demonstrate that the petroleum potential for the samples is only prone to the gas generation. Furthermore, other types of advanced geochemical and sedimentologic studies should be integrated with the Rock-Eval pyrolysis results in order to obtain a better and complete interpretation.

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