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STUDY OF THE ORGANIC GEOCHEMICAL PARAMETERS OF THE PIMIENTA FORMATION AND ITS IMPLICATION AS A GAS AND OIL GENERATING ROCK.

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SUMMARY

In order to determine the quality of the Pimienta Formation in the state of Veracruz as a hydrocarbon-generating rock and its role as an unconventional reservoir (shale gas/oil), the average values of TOC, Tmax, S2/S3 and IP of fourteen wells located in the northwestern portion of the state of Veracruz were analyzed. in the range of 1590 m to 3272 m depth. Due to the TOC content (1.14 to 2.79%), in some wells present in the study area, the Pimienta Formation can be classified as a hydrocarbon generator, with a fair to excellent quality. The Tmax data (423°C to 457°C) place the source rock in an early to late phase of thermal maturity. The producing potential (PP) of the area is weak to medium and the calculation of the type of hydrocarbon generated (S2/S3) indicates the presence of oil and gas in the formation, and the existence of oil may occur at depths from 2100 m in the studied area, if the hydrogen index (IH) vs. oxygen index (IO) are observed. Its evolution indicates that the predominant kerogen is a mixture formed mainly of types III and II, which can be interpreted as the precursors of gas and oil.

KEY WORDS: *Pimienta, kerogen, shale gas, Total Organic Carbon, hydrocarbons.*

RESUMEN

Con el fin de determinar la calidad de la Formación Pimienta en el estado de Veracruz como roca generadora de hidrocarburos y su rol como un yacimiento de tipo no convencional (shale gas/ oil), se analizaron los valores promedios de COT, Tmax, S2/S3 e IP de catorce pozos ubicados en la porción noroeste del estado de Veracruz, en el intervalo de 1590 m a 3272 m de profundidad. Por el contenido de COT (1.14 a 2.79%), en algunos pozos presentes en el área de estudio, la Formación Pimienta se puede catalogar como generadora de hidrocarburos, con una calidad regular a excelente. Los datos de Tmax (423°C a 457°C), ubican la roca generadora en una fase de madurez térmica temprana a tardía. El potencial productor (PP) de la zona se encuentra entre débil a medio y el cálculo de tipo de hidrocarburo generado (S2/S3) indica la presencia de aceite y gas en la formación, pudiendo ocurrir la existencia de aceite a profundidades a partir de los 2100 m en el área estudiada, si se observan el índice de hidrógeno (IH) vs. índice de oxígeno (IO), su evolución nos indica que el kerógeno predominante es una mezcla formada principalmente del tipo III y II los cuales se pueden interpretar como los precursores del gas y aceite.

PALABRAS CLAVES: *Pimienta, kerógeno, shale gas, Carbono Orgánico Total, Hidrocarburos.*

INTRODUCTION

The Energy Information Agency (EIA) ranks Mexico among the top ten countries with technically recoverable reserves in type reservoirs *shale gas y shale oil*, ranking sixth in gas reserves with 545 tcf and eighth in oil reserves with 13 mmmb (DOE/EIA-0383, 2016)[3]. The National Hydrocarbons Commission (CNH) locates these resources in 6 zones throughout the northeastern portion of the country; Figure 1 (CNH 2016)[2]: 1.- Chihuahua. 2.- Sabine women. 3.- Donkey – Picachos. 4.- Burgos. 5.- Tampico – Misantla and 6.- Veracruz (**Figure** 1).

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Figure 1. Shale provinces in Mexico (modified from CNH 2016).

Meneses S. J. (2015) in his doctoral work supported by the regional context provided by Humphrey (1958) cites that during the Cenomanian-Late Turonian, a global transgression produced a transgressive cycle, which allowed communication between the Gulf of Mexico and the western inland sea.
Terrigenous and calcareous sediments were deposited in eastern and northeastern Mexico in shallow, intermediate, and deep facies.

Pimienta Fm
Heim (1926) gave the name Pimienta Formation to a section of dense black limestone in thin strata with flint layers, which is exposed in the city of Pimienta in the state of San Luis Potosí.

The Pimienta Formation is widely distributed in the Tampico-Misantla Basin; It covers the Taman, San Andres, and Chipoco Formations, and underlies the Lower Tamaulipas Formation.

In the study area, the Pimienta Formation is composed of a sequence of fine to medium strata of dark gray black and brown, slightly pyritized limestone (mainly mudstone) with black shale, bituminous shale, and bentonite. Flint nodules are most conspicuous in the upper portion of this formation (Aguilera, 1972).

By means of ammonites, the formation was assigned an age from early Titonian to late Tithonian. This formation was deposited in a shallow, probably neritic, low-energy basin environment, with continental sources providing some fine detrital material (Cantu Chapa 1971).

Petróleos Mexicanos (PEMEX) through PEMEX Exploration Production (PEP) has drilled a series of exploratory wells, resulting in 7 non-commercial gas and condensate producing wells: Amatlán-2, Caballo-1, Chote-1, Donita-1, Furbero-102, Juan Rosas-1 and Sultepec-1 (CNH 2016)[2].

The studied area was delimited based on information collected from 14 exploratory wells:
Amixtlan-2, Arenas-1, Axoxotla-1A, Caballo-1, Charro-1, Chote-1, Donita-1, Entabladero-1, Grillo-1, Furbero-102, Juan Rosas-1, Puxtla-1, Sabaneta-2A and Sultepec-1 (**Figure** 2)

The objective of this work is to determine the current degree of thermal maturity of the organic matter present in the Fm. Pimienta in each of the 14 wells, its implication in the generation of oil-gas, and its consideration for the future realization of a type project in this region.

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Figure 2. Exploratory wells analyzed in the state of Veracruz.

METHODOLOGY

To define whether Fm. Pimienta can be classified as a hydrocarbon-generating rock, the Rock-Eval analysis analyzed the total organic carbon content present (TOC% wt), the maximum Rock-Eval temperature (Tmax °C), the type of hydrocarbons (S2/S3) and the Production Index (PI = S1/(S1+S2)).

Table 1 is based on the mean values of TOC, Tmax, S2/S3 and PI.

To determine the feasibility of carrying out a project of a typical reservoir *Shale* in this region, in addition to the amount of TOC and Tmax, the calculated reflectance value of vitrinite (Vrc %) as well as the Írate of transformation of kerogen to gas and oil (Tr%). It was decided to perform the % calculation VRc not having access to the data in the region, and then the equations proposed by Jarvie *et al*, 2005 , for the calculations of the above parameters.

	TOC Average	Tmax Average	S2/S3 Average	PI Average
Amixtlan-2	2.76	457	23.11	3.94
Arenas-1	1.74	427	10.26	3.14
Axoxotla-1A	0.51	431	0.53	0.09
Caballo-1	1.69	443	7.03	3.15
Charro-1	1.3	432	7.16	13.03
Chote-1	2.22	435	30.04	25.15
Donita-1	2.03	435	9.88	23.48
Entabladereo-1	1.46	443	12.87	6.44
Grillo-1	2.77	441	17.73	41.56
Furbero-102	0.54	440	7.62	0.77
Juan Rosas-1	1.49	434	18.75	13.60
Puxtla-1	1.86	431	33.29	26.91
Sabaneta-2A	0.34	440	5.35	0.34
Sultepec-1	1.91	437	17.70	7.92

Table 1. Geochemical characteristics of the wells in the study area.

Regarding the calculated reflectance value of vitrinite, it is known that this is not the most recommended since there is greater certainty when using VRo values measured in macerals of the samples, so the entry of the kerogen into the window of the oil and gas and its evaluation in the shale gas prospect of the four wells must be taken with caution .

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- Refectance Value of Vitrinite (VRo):
  Cal. % VRc (from T max) = 0.0180 x Tmax – 7.16 [%] (Equation 1)
- TOC original
  Calculated original TOC = current TOC / 0.64 [wt. %]. (Equation 2)
- The original generation potential can be calculated using the average value of carbon contained in hydrocarbons (83%) and increasing the generating potential S2.
  Transformed TOC = Original TOC – Present TOC [wt. %] (Equation 3)
  Original S2 = original TOC / 0.083 + S2 present [mg hc's $^{/}$g rock] (Equation 4)
- Original Hydrogen Index (IH) value:
  IH original = S2 original / COT original x 100 [$^{mg\ hc's}/_{g\ COT}$] (Ecuación 5)
- Kerogen transformation ratio (Tr).
  Tr (Transformation Index) = (Original IH – Present IH) / Original IH [%] (Equation 6)

The TOC content (% by weight) is essential to determine the presence of a hydrocarbon-generating rock, so it is necessary to know its spatial distribution. In this research, the computer programs *SURFER* were used, since both perform interpolation and extrapolation by means of geostatistics (*kriging)*. The TOC distribution map that was obtained is shown in **Figure** 3.

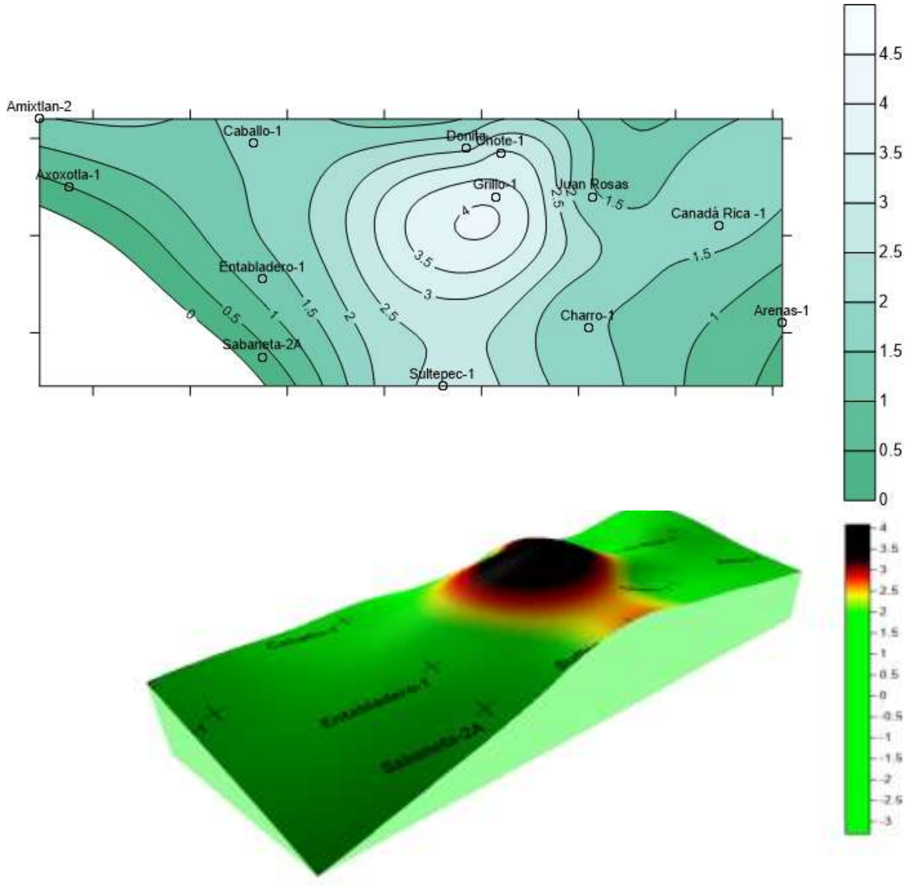

Figure 3. Spatial distribution of the TOC (%) of the 14 exploratory wells analyzed.

RESULTS & ANALYSIS

Spatial distribution of TOC content

As can be seen in **Figure 3**, the average TOC content is more evenly distributed in the central and western area of the study area, with average values of 1% to 2% in the Arenas-1, Axoxotla-1A, Caballo-1, Charro-1, Entabladero-1, Furbero-102, Juan Rosas-1, Puxtla-1, Sabaneta-2A and Sultepec wells; while in the Amixtlan-2 wells, Chote-1, Donita-1 and Grillo-1 had more than

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2% of TOC. Therefore, it is considered that this area has an organic content indicative of a good quality generating rock.

TOC content (wt%) present

From **Figure** 4, it was interpreted that, in general, the TOC content (% weight) in each of the wells presented a higher concentration as the depth increases, in such a way that for the Sultepec-1 well it is considered as regulated to good from 2143 m and as excellent at 2199 m depth. with values from 1.0 to more than 2 COT (wt%).

In the Donita -1 well, it is medium to good at 2780 m to 2.7990 m depth, and excellent at 2788 m depth.

While in Juan Rosas-1 the concentration of TOC is more homogeneous at depths of 3,153 m to 3,192 m with content of 0.9 to 1.82 TOC (% weight).

On the other hand, the Caballo-1 well presented a better concentration of TOC between 2,279 m and 2,430 m with values of 1.57 (wt%) to 1.69 (wt%).

Based on the above information, it is confirmed that, although the Pepper presents variation in thickness and deepening in this area, it has an average thickness of 84 m that can be classified as a hydrocarbon generator, with a quality of fair to excellent.

The TOC content is related to the paleoenvironment and paleogeography represented by the Pimienta Formation, which is shallow to deep marine, together with the differential uplift and folding of that area of the country, which explains these differences in organic richness. The TOC is apparently related to the nature of the shales and their petrophysical characteristics analyzed, and it can be considered that the formation studied is a shale that behaves from this information as an unconventional petroleum system.

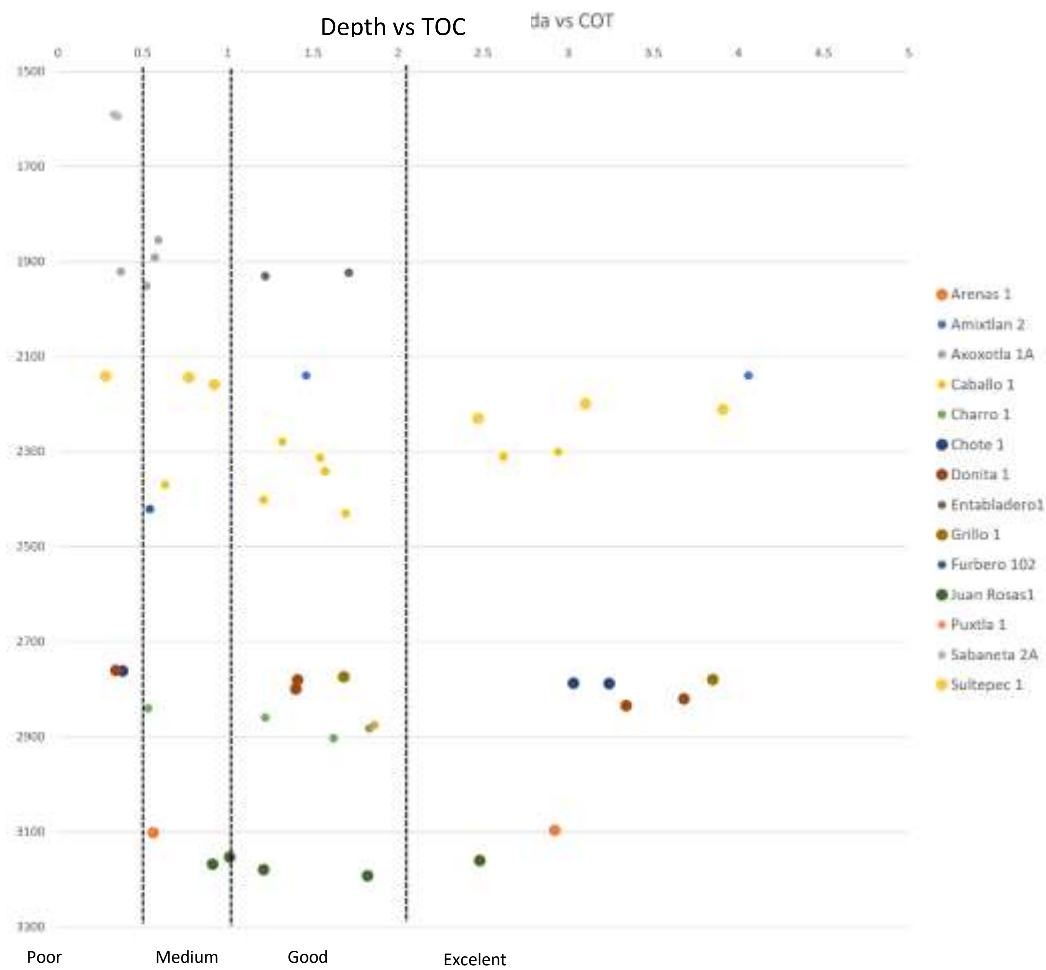

Figure 4. Classification of the quality of the rock as a hydrocarbon generator based on the TOC content (Total Organic Content).

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Temperature máxima [Tmax (°C)]

Figure 5 shows that, for the wells, the Tmax Rock-Eval reported in the geochemical studies began with values close to 423°C, which placed them in a stage of early immaturity. This temperature showed an increase when exceeding 435°C, but after 444°C there is a decrease in temperature values, this could be associated with a variation of organic composition in sedimentation due to a differentiated regional tectonic uplift of the area. In the Caballo-1 well, Tmax values were essentially grouped between the temperatures of 435°C to 443°C, reaching the medium maturity stage. On the other hand, the Sultepec-1 and Donita-1 wells presented a minimum temperature variation with values of 435°C to 436°C. While the Tmax values in the Juan Rosas-1, Chote-1, Arenas-1 and Donita-1 wells place them as immature.

The Tmax values of the wells analyzed, in general, indicated that the Fm. Pimienta reached the stage of thermal maturity necessary for the exploitation of oil and gas generation.

IH vs. IO

In Van Krevelen's pseudo diagram, the values of Hydrogen Index (IH) against Oxygen Index (IO) (**Figure** 6) showed that the predominant type of kerogen in the area is type II, although type II kerogen is also present in the Charro-1 and Donite-1 wells. On the other hand, the Axoxotla-1 well only has type IV kerogen.

When analyzing the Hydrogen Index, it was generally observed that, in the area, the kerogens present were precursors of gas and condensate.

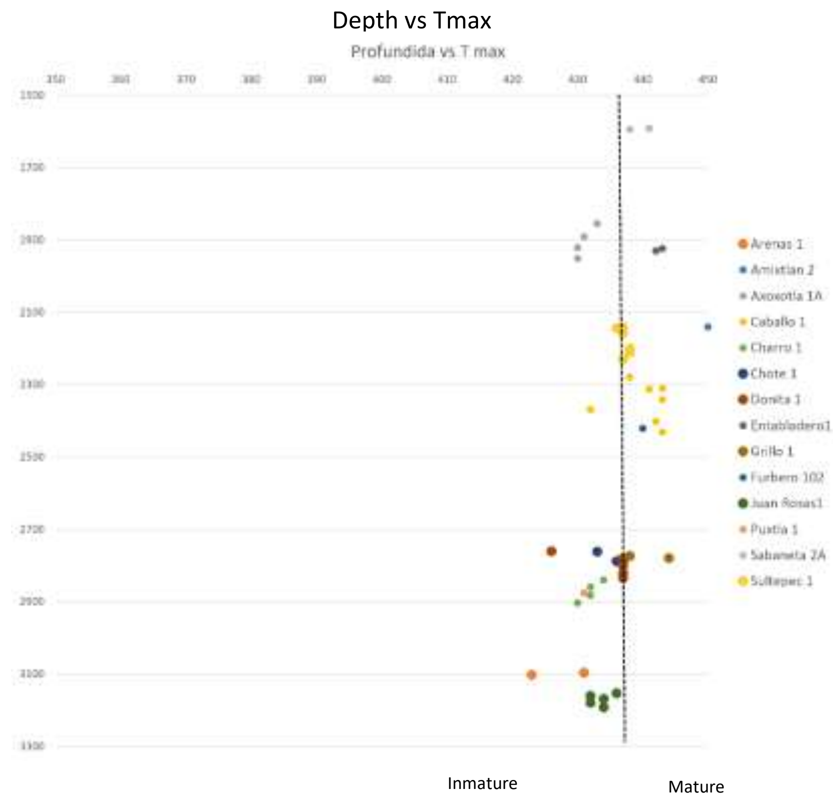

Figure 5. Variation of Tmax with respect to depth in the study area.

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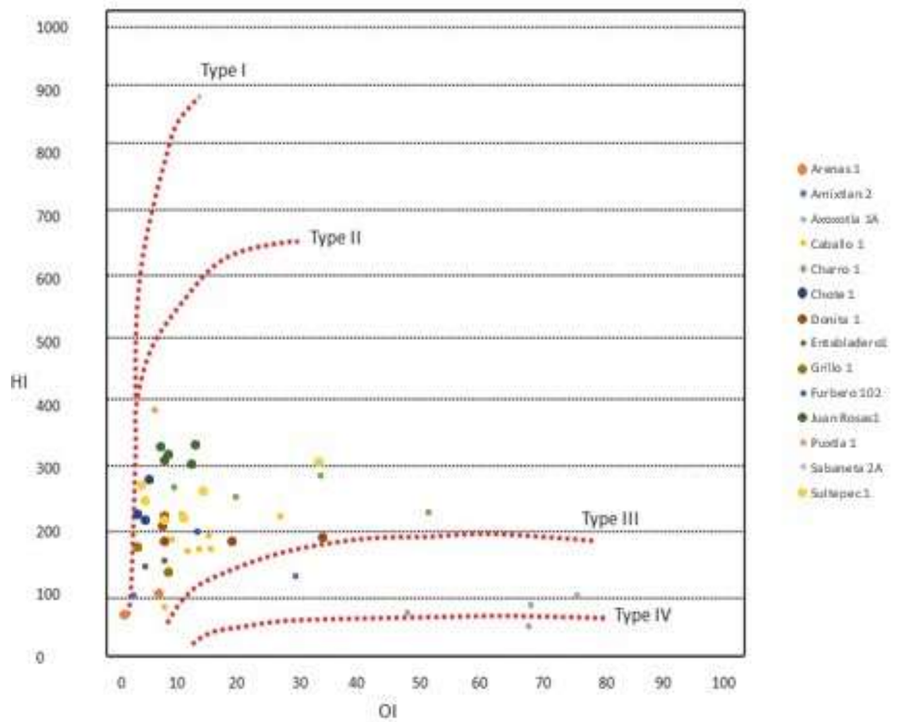

Figure 6. Van Krevelen pseudo diagram showing the type of kerogen and its predominant thermal evolution in the study area.

IP

Index of Production (PI) is determined by the ratio

S1 / (S1 + S2).

From these basic parameters, certain inferences can be made to define the type of organic matter, the level of thermal maturation, the generative potential of petroleum, and the migration of hydrocarbons within the source rock or in a non-generating area (oil sample) or contamination (Espitalie et al., 1977).

The Tmax **in Figure 5 and the Production Index S1/ (S1 + S2)** in Figure **7** provide us with information on the thermal maturity of the organic matter studied and its potential to produce oil-oil-gas-gas in the catagenesis stage. Figure 7 shows that the wells analyzed in the study area are potentially oil-generating wells since the IP values range from 0.1 to 0.4, while the Grillo-1 and Donita-1 wells are mainly potential gas producers (PI > 0.4), so it is interpreted that the presence of oil is limited to the wells located in the central portion of the studied area. with the appearance of gas at a depth greater than 2,700 m.

From the analysis of TOC, Tmax, IH/IO and IP, it can be seen that the area between the Sultepec-1, Caballo-1, Donita-1 and Juan Rosas-1 wells is the one with the highest probability of having generated hydrocarbons, so its Tr (%) is analyzed.

VRo(%), Tr(%)

The values calculated using the equations proposed by Jarvie et al. (2005)[4] for the wells with the highest possibility of generating hydrocarbons analysed are shown in Table 2.

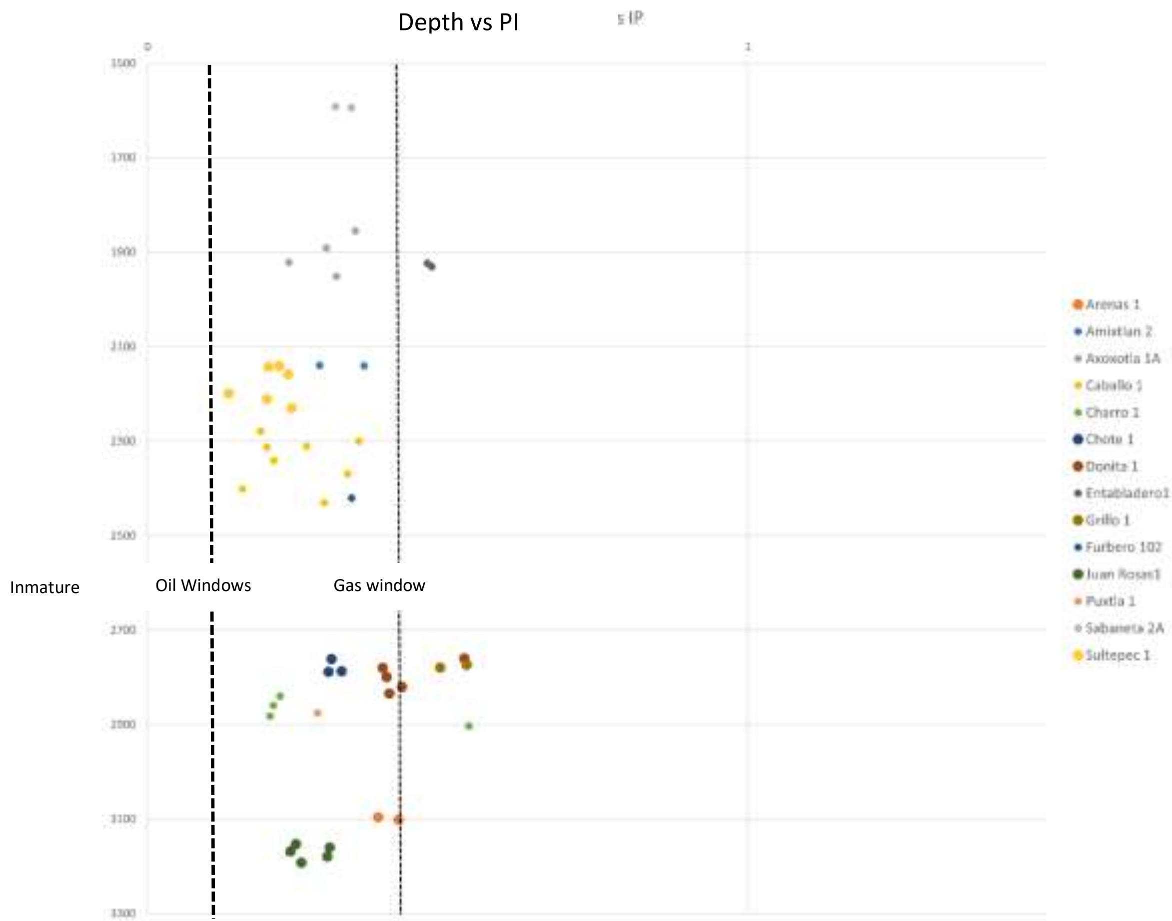

Figure 7 Variation of the Production Index (PI) with respect to the depth of the wells analyzed in the study area

Parameter	Sultepec-1	Horse-1	Donita-1	Juan Rosas-1
VRc (%)	0.71	0.8	0.67	0.64
Tmax (°C)	437	443	435	434
Tr (%)	59.27	70.07	66.72	51.41

Table 3. VRc, Tmax, and Tr values of the wells analyzed.

If the results in this table are compared with the values of the geochemical characteristics of the Barnett Basin in the USA (Table 4**)** that show the cut-off values proposed by Jarvie (2007**)** 5, it was observed that none of the four wells mentioned do not exceed the cut-off values of the Barnett Basin, which may indicate poor profitability since their potential is more akin to generating oil (Figure 10).

Tmax (°C)	Tr (%)	VRo (%)
455	80	1.0

Table 4. Cut-off values of Tmax, Tr and VRo, for a shale gas play (Jarvie 2005).

DISCUSSION

In the data analysis, the presence of Tmax early maturity values was observed in the wells Amixtlan-2, Axoxotal-1A, Charro-1, Entabladero-1, Grillo-1, Sabaneta-1, Entabladero-1, Amixtlan-1, Caballo-1, Furbero-102, Puxtla-1, Sabaneta 2A and Sultepec-1. The limitation of the number of wells and data analyzed does not allow us to know precisely the thermal history of each well and therefore the thermal evolution of the area, since there were no geothermal gradient and vitrinite reflectance (VRo) data. I consider these VRc values to be considered anomalous, however, according to the tectonic evolution of the area, regional uplift during the late Tertiary caused widespread erosion of Mesozoic rocks in most of northeastern Mexico, with the exception of the

Burgos Basin, which was subjected to rapid subsidence during the Tertiary. This could have influenced the increase in thermal maturity towards the southeast of the analyzed area.

The analysis of the parameters of TOC, Tmax, S1/S2 and IH, carried out on the 14 wells located in the study area, indicates that it presents characteristics of generator rock in most of the interval studied, presenting greater potential for oil, oil and associated gas.

Likewise, the two wells located in the center of the analyzed area (Chote-1, Sultepec-1 and Charro-1) are prone to generating oil, while the Grillo-1 and Entabladero-1 wells are mainly generators of associated gas.

CONCLUSIONS

1. Pepper, as indicated by its geochemical properties of COT, IH/IO, Tmax, S2/S3 and PP has a poor to excellent total organic carbon content, coming from type III and II kerogen, entered the hydrocarbon generation window in the early and late mature stages, producing gas, condensate and oil, although its production potential is weak to medium and it can be considered as a hydrocarbon-generating formation.
2. The Chote-1, Charro-1 and Sultepec-1 wells located in the Pimienta Fm. in the center of the study area, present better values of Tmax and VRo, generators of oil and associated gas, however, the Tr indicates that it cannot be considered as an appropriate area for the development of a shale oil type project. But it is advisable to consider more data to define its viability.
3. The spatial distribution of the COT content in the study area shows less variation in the N-W direction, so the other geochemical properties should be analyzed in this same direction.

Nomenclature

IH	Hydrogen Index [mgHC/g TOC]
IO	Oxygen Index [mgCO2/g TOC]
PP	Potential Producer
VRo	Vitrinite Reflectance [%]
S1	Free hydrocarbons [mg HC/g rock]
S2	Kerogen Yield [mg HC/g roca]
Tmax	Maximum Temperature (Pyrolysis) [°C]
COT	Total Organic Carbon [wt]
Tr	Transformation Index [%]
V	Heterogeneity index

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