Pore Structure Characterization of Shale Reservoir Using Nitrogen Adsorption-Desorption

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Abstract

This research paper aimed to quantitatively characterize the pore structure of shale reservoirs. Six samples of Silurian shale from the Ahnet basin were selected for nitrogen adsorption-desorption analysis. Experimental findings showed that all the samples are mainly composed of mesopores with slit-like shaped pores, as well as the Barrett-Joyner-Halenda pore volume ranging from 0.014 to 0.046 cm³/100 g, where the lowest value has recorded in the AHTT-1 sample, whereas the highest one in AHTT-6, while the rest samples (AHTT-2, AHTT-3, AHTT-4, AHTT-5) have a similar average value of 0.03 cm³/100 g. Meanwhile, the surface area and pore size distribution were in the range of 3.8 to 11.1 m²/g and 1.7 to 40 nm, respectively. Nanoparticle size was in the range of 540 to 1589.2 nm, this parameter showed a strong negative correlation with both the surface area and pore volume. Findings can contribute significantly to the pore structure evaluation and characterization of the Silurian shale reservoir in the Ahnet basin.

Keywords: Pore structure; Silurian shale; Nitrogen adsorption-desorption; Surface area; Mesopores; Ahnet basin

1. Introduction

Shale gas which is generated and stored in the organic-rich shale source rocks is considered an unconventional natural gas type, this type of unconventional reservoir is characterized by the complicated pore network structure, where the petrophysical parameters differ significantly from conventional reservoirs. Algeria ranks fourth in the world after the United States, China, and Argentina in the classification of the largest technically recoverable shale gas resources with 707 trillion cubic feet (TCF) (EIA, 2013). Porosity is the key factor parameter in the assessment of shale gas resources. Contrary to conventional reservoirs, shale gas reservoirs required advanced methods to characterize the pore structure, this axis of research attract more attention from researchers in recent years. Due to the lack of interconnected pores in shale gas reservoirs, the effective porosity is much lower and reduces the permeability, for this reason, it is necessary to introduce new technologies and methods to enable us to characterize the non-conventional reservoirs. Previous studies have performed new technics and

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methods to characterize non-conventional reservoirs such as Carbon Dioxide (CO\textsubscript{2}) adsorption-desorption to compare the pore structure of Silurian Longmaxi formation shales with other lithofacies in southern Sichuan basin, China by (Wang et al., 2020), Mercury Injection porosimetry have used to evaluate shale gas reserve by Whitelaw et al. (2019), Point Count to quantify the porosity lacustrine shale-hydrocarbon system in the Late Triassic Yanchang Formation in the southeastern Ordos Basin, China, using ImageJ software by Loucks et al. (2017), and Nitrogen (N\textsubscript{2}) adsorption-desorption have used to estimate the surface area (SA) and the pore size distribution (PSD) in clays and shales by Kuila and Prasad (2011). Nitrogen adsorption-desorption is used for the characterization of a wide range of porous materials, it is used in multiple disciplines such as chemistry (Groenendijk and Van Wunnik, 2021), civil engineering (Paz-Ferreiro et al., 2016), and the petroleum industry (Cavelan et al., 2019), in this regard, nitrogen adsorption-desorption method have performed in this present research paper to characterize the pore network of non-conventional shale reservoir taking a Silurian shale of the Ahnet basin as an example.

2. Materials and Methods

2.1. The Study Area

The Ahnet basin, which has a surface area of 75000 km\textsuperscript{2}, is the subject of this study. It is situated in the western-central region of the Saharian platform, between the geographic coordinates of 01° 00' 00" and 03° 00' 00" East and 24° 00' 00" and 27° 00' 00" North, in the southern part of Algeria. This basin is characterized by a depression and is categorized as a Paleozoic intracratonic basin. The first research on this basin has performed in 1880 by the first geological synthesis of the Austrian Oscar Lenz, during the 20th century. Several types of research have been performed (Beuf, 1971; Gautier, 1905; Menchikoff, 1949; Menchikoff, 1930; Meyendorff, 1938), oil prospecting has been launched in these zones in the 1950s. The first discovery of gas in the Sahara have confirmed in a well from the Cambro-Ordovician and Devonian formations in 1953. The Ahnet basin considers the first basin where gas has been discovered and confirmed in the Saharian platform. There are 45 wells of dry gas accumulations confirmed by Sonatrach among the 150 wells that have been completed in the Ahnet basin, of various sizes, from 1 to 250 BCM, with a proven gas potential estimated at 760 BCM, with possible reserves of over 600 BCM. The Ahnet basin is bounded by the Djoua Saddle in the north, the Hoggar shield in the south, the Idjerane spur and Mouydir basin in the east, the Azzene ridge and Azzel Matti saddle in the west. It has a lithostratigraphic column, is made up of Paleozoic deposits, and lies in a major unconformity on the bedrock with the absence of the Permian. The Hercynian unconformity separates the Paleozoic from the Mesozoic and the Cenozoic occupies the top part (Fig.1). The source rocks present in the Ahnet basin are the basal part of the Silurian and the clay-carbonate series of the Givetian and Frasnian, the reservoir rocks are The Quartzites of Hamra. The Sandstones of El Golea, Gedinnian (Lochkovian) Reservoirs, Siegenian Reservoirs (Pragian), Emsien Reservoirs, Tournaisian Reservoirs, concerning the cap rocks, there are Silurian clays with thick series reaching 500 m, The Frasnian-Famennian Khenig Clays, and the Tournaisian clays (Fig.2).
Fig. 1. Geologic situation of the Ahnet Basin

Fig. 2. Typical lithostratigraphic column of the Ahnet Basin
2.2. Sampling

Six drill formation cutting samples from the Hot shales, Argillaceous Silurian, and Siluro-Devonian passage formations were collected for this study from the same section in different depths to account for the vertical lithology heterogeneity. The depths of the samples range from 2580 m to 3100 m, based on their clay content they are divided into upper (ranging between 57.74 and 58.88 %) and lower (ranging between 50.25 and 52.92 %) section samples. Table 1 lists the samples’ depth, ID, and other parameters. To characterize the pore network parameters, such as pore type, pore shape, SA, PV, PSD, the nitrogen (N₂) adsorption-desorption method has been applied to the chosen samples.

Table 1. Sample ID with their depths of the upper and lower Silurian shale section samples

<table>
<thead>
<tr>
<th>Group of Section</th>
<th>Sample ID</th>
<th>Measured Depth (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper Section</td>
<td>AHTT-1</td>
<td>2580</td>
</tr>
<tr>
<td></td>
<td>AHTT-6</td>
<td>2680</td>
</tr>
<tr>
<td></td>
<td>AHTT-16</td>
<td>2800</td>
</tr>
<tr>
<td></td>
<td>AHTT-18</td>
<td>2910</td>
</tr>
<tr>
<td>Lower Section</td>
<td>AHTT-22</td>
<td>2970</td>
</tr>
<tr>
<td></td>
<td>AHTT-27</td>
<td>3100</td>
</tr>
</tbody>
</table>

2.3. Nitrogen (N₂) adsorption-desorption

Dewar (1904) and Ramsay (1905) are the earliest reporters of the adsorption of nitrogen and other gases at liquid air temperature (77K) in their investigations of the composition of the atmosphere and the separation of the noble gases (Sing, 2001). Multiple previous studies have used the Nitrogen (N₂) adsorption-desorption method in their methodology to characterize the unconventional reservoir such as shale reservoir (Kuila and Prasad, 2013; Loucks et al., 2017; Chen et al., 2019; Whitelaw et al., 2019; Wang et al., 2020; Xu L. et al., 2020; Xu S. et al., 2020; Shi et al., 2021). This method uses for the characterization of porous material either natural or artificial, it is used in many specialities, and it can measure a wide range of pore diameter or width, analysis of the selected samples have performed using a Micromeritics ASAP-2020 Plus apparatus at a temperature of 77 K, at this temperature nitrogen gas will physically adsorb on the surface of the sample, and a relative pressure (P/P₀) ranged from 0.05 to 0.99 to quantitatively characterize pores size ranging from 1.7 nm to 300 nm. Before the analysis, the shale samples were crushed into powder with particles size of 12-35 mesh, then degassed automatically at 105 °C under vacuum for 21 h using Micromeritics VacPrep 061 Sample Degas System apparatus, to remove adsorbed moisture and volatile matter (Fig.3).

Fig. 3. Micromeritics ASAP-2020 Plus apparatus for Nitrogen adsorption-desorption with Micromeritics VacPrep 061 degasser
2.3.1. Pore type and shape

An adsorption isotherm is usually recorded as the volume of gas adsorbed (cc/g @ STP) versus relative pressure P/P0, the relative pressure is scaled from 0 to 1, a relative pressure of 1 represents a completely saturated sample. The new International Union of Pure and Applied Chemistry (IUPAC) classification of physisorption isotherms (Thommes et al., 2015) shows in Fig.4, the nitrogen adsorption isotherms types are I(a), I(b), II, III, IV(a), IV(b), V, and VI. Noting that I(a) and I(b) types are mainly micropores solids, and type II is non-porous or macroporous solids, type III is typical for Bromine adsorption on silicate at 352 K and nitrogen adsorption on polyethylene, for IV(a) and IV(b) types are mainly mesoporous solids, for type V is typical for mesoporous solids with low adsorption capacity, and lastly, type VI Stepwise multilayer adsorption on a uniform non-porous surface. In the context of physisorption, the IUPAC classify pores according to their sizes as follows:

- Macropores pores with widths exceeding about 50 nm.
- Mesopores of widths between 2 nm and 50 nm.
- Micropores pores with widths not exceeding about 2 nm.

The hysteresis loop occurs in the adsorption isotherm due to the phenomenon of condensation inside capillaries of mesoporous structures, the IUPAC classification of hysteresis loop shown in Fig.5, the hysteresis loop types are H1, H2(a), H2(b), H3, H4, and H5, their types are related to the pore shape, where H1 is related to cylindrical pores, H2 (a and b) are related to ink-bottle pores, H3 is related to slit-shaped pores, H4 is related to narrow slit-like pores.

![Fig. 4. Classification of physisorption isotherms types (Thommes et al., 2015)](image-url)
2.3.2. **BJH pore volume (PV\textsubscript{BJH})**

This method proposed by Barret, Joyner, and Halenda (BJH), it assumed that the initial relative pressure is close to unity, with the full filling with liquid of all pores, the BJH equation is as follows (Barrett et al., 1951):

\[
V_p = R_n (\Delta V)_n - R_n \Delta t_n \sum_{i=1}^{n-1} c_i A_t \quad \text{where} \quad c = (t_p - t_f)/t_p
\]

Where: \(V_p\): the pore volume (cc/g), \((\Delta V)_n\): Volume of liquid adsorbate removed from the pores in the desorption (cc/g), \(t\): multilayer thickness (Å), \(r_p\): pore radius (Å), \(\Delta t\): thickness of the adsorbed layer of nitrogen (Å), \(A\): area exposed by the pore from which the physically adsorbed gas is desorbed (m\(^2\)/g), \(t_r\): thickness of the physically adsorbed layer at the corresponding value of \(P/P_0\) in (Å), \(R\) and \(c\): constants.

2.3.3. **BET surface area (SA\textsubscript{BET})**

The BET method is derived from the first name of three researchers that has defined the equation, they are Brunauer, Emmett, and Teller (BET), this method is the most common procedure used for the determination of the surface area of solid materials, the BET equation is as follows:

\[
\frac{1}{W\left(\frac{P}{P_0}\right) - 1} = \frac{1}{W_m c} + \frac{c - 1}{W_m c \left(\frac{P}{P_0}\right)}
\]

Where: \(W\) is the weight of gas adsorbed at a relative pressure \((P/P_0)\), and \(W_m\) is the weight of adsorbate as a monolayer of surface coverage. \(C\) is the BET constant. The BET equation requires a linear plot of \(1 / \left[\frac{(P/P_0)}{} - 1\right]\) against \(P/P_0\). Nitrogen is used as adsorbate for the most solids material, it is
commonly known that the region of adsorption isotherm in the relative pressure \( \frac{P}{P_0} \) range of 0.05 to 0.35, whereas in the microporous materials, this linear region is shifted to lower relative pressure \( \frac{P}{P_0} \).

2.3.4. Pore size distribution (PSD)

Commonly, the pore size distribution (PSD) calculated from physisorption isotherms assumed that: the pores are rigid and of a regular shape, the absence of micropores, the size distribution does not extend continuously from the mesopore into the macropore range, it is determined by plotting \( \Delta V_p/\Delta r_p \) vs \( r_p \) where \( V_p \) is the total pore volume, and \( r_p \) is the radius of cylindrical pores; \( r_p = r_k \) (Kelvin radius) + \( t \) (multilayer thickness) (Sing, 1985).

3. Results

This section may be divided into subheadings. It should provide a concise and precise description of the experimental results, their interpretation, and the experimental conclusions that can be drawn.

3.1. Pore Type and Pore Shape

Nitrogen adsorption-desorption isotherms of the six samples; upper and lower section samples; are shown in Fig. 6.

![Fig. 6. N\(_2\) Adsorption-desorption isotherms of upper and lower section Silurian shale samples of the Ahnet Basin](image-url)
all the isotherms of both upper and lower section samples have the same diagram plotting, this requires that all the isotherms belong to the same type IV(a) based on IUPAC classification of physisorption isotherms types, in result, the studied samples are mesopore powdered samples. Due to the capillary condensation in the larger pores phenomenon, a sharp increase occurred in 0.9 of relative pressure (P/P₀) in all the studied samples. Based also on the IUPAC classification of the hysteresis loops types, both upper and lower section samples of Silurian shale are in the H3 hysteresis loop type, which means the pores are related to slit-shaped pores.

3.2. BJH Pore Volume (PV_{BJH})

The BJH pore volume results of the studied samples are shown in Table 2, the sample which has the highest value of BJH pore volume is the AHTT-6 sample of 0.046 cm³/100 g, with the lowest nanoparticle size of 540.62 nm, whereas the lowest value of BJH pore volume belongs to the AHTT-1 sample of 0.014 cm³/100 g, with the highest nanoparticle size value of 1589.22 nm, the rest samples exhibit a similar BJH pore volume with an average value of 0.03 cm³/100 g and with an average value of nanoparticle size of 785 nm, it is clear that the nanoparticle size has a significant effect on BJH pore volume of the upper and lower section samples of the Silurian shale.

Table 2. BET Surface area, BJH pore volume, nanoparticle size of Silurian shale samples with their depths

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Depth (m)</th>
<th>SBET (m²/g)</th>
<th>VBJH (cm³/100g)</th>
<th>Nanoparticle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AHTT-1</td>
<td>2580</td>
<td>3.7754</td>
<td>0.014391</td>
<td>1589.2229</td>
</tr>
<tr>
<td>AHTT-6</td>
<td>2680</td>
<td>11.0984</td>
<td>0.046399</td>
<td>540.62</td>
</tr>
<tr>
<td>AHTT-13</td>
<td>2800</td>
<td>8.7436</td>
<td>0.031875</td>
<td>686.2144</td>
</tr>
<tr>
<td>AHTT-18</td>
<td>2910</td>
<td>6.3685</td>
<td>0.025313</td>
<td>942.1298</td>
</tr>
<tr>
<td>AHTT-22</td>
<td>2970</td>
<td>7.9815</td>
<td>0.03134</td>
<td>751.7415</td>
</tr>
<tr>
<td>AHTT-27</td>
<td>3100</td>
<td>7.8689</td>
<td>0.033528</td>
<td>762.4963</td>
</tr>
</tbody>
</table>

3.3. BET Surface Area (SA_{BET})

Table 2 shows us the results of the BET surface area of the studied samples, similarly to the BJH pore volume, the highest value of BET surface area for the AHTT-6 sample, is about 11.1 m²/g, whereas the lowest value of the BET surface area is for AHTT-1 sample, it is about 3.8 m²/g, so the nanoparticle size is the significant factor that affects the BET surface area of the powdered samples, and this factor affects directly the properties of the solids or powdered materials. Table 2 shows us the results of the BET surface area of the studied samples, similarly to the BJH pore volume, the highest value of BET surface area for the AHTT-6 sample, is about 11.1 m²/g, whereas the lowest value of the BET surface area is for AHTT-1 sample, it is about 3.8 m²/g, so the nanoparticle size is the significant factor that affects the BET surface area of the powdered samples, and this factor affects directly the properties of the solids or powdered materials.

3.4. Pore Size Distribution (PSD)

Pore size distribution values of the studied samples are shown in Figs.7 and 8 show us the BJH desorption pore volume (cm³/g) vs pore diameter (nm), it is clear that all the samples have a large amount of pore volume of pores with a diameter ranging from 3 nm to 10 nm, with a high increase in the amount of cumulative pore volume in pores with diameter 3 nm Fig.7. In Fig.8, the BJH desorption cumulative pore volume of the samples is mainly contributed by pores with diameters ranging from 1.7 nm to 10 nm, where there is a flat plot in pores diameters range from 1.7 nm to 4 nm explains the sharp increase in a plot of the PSD shown in Fig.7.
Fig. 6. The pore size distribution (PSD) of the upper and lower Silurian shale section samples
3.5. Nanoparticle Size Correlations

The correlation of BET surface area ($SA_{BET}$) versus the nanoparticle size is shown in Fig. 9, it is clear that the correlation is strongly negative with a Pearson’s $r$ coefficient is about -0.94, this result indicates that the nanoparticle size affects an inverse relationship the surface area (SA), so that the smaller the nanoparticle size, the greater the surface area (SA), or in the inverse proportion, the greater nanoparticle size, the smaller the surface area (SA). This relationship results from a decrease in the size of the nanoparticle size, which represents the creation of larger available spaces where the nitrogen molecules will stick. The correlation of pore volume ($PV_{BJH}$) versus the nanoparticle size is shown in Fig. 10, a strong negative correlation has recorded with a strong negative Pearson’s $r$ coefficient, which
reaches -0.92, similar to the previous correlation of nanoparticle size versus surface area, nanoparticle size affects in an inverse relationship the pore volume (PV), the smaller nanoparticle size, the greater pore volume will generate, whereas the greater nanoparticle size, the smaller pore volume (PV), meanwhile this relationship will affect directly the amount of storage capacity in the reservoir.

Fig. 7. Negative correlation between the nanoparticle and the surface area (SA)

Fig. 8. Negative correlation between the nanoparticle and the pore volume (PV)
4. Conclusions

Porosity in the Hot shales, Argillaceous Silurian, and Siluro-Devonian passage formations samples are mainly mesopores with slit-like shaped pores, with PV ranging from 0.014 to 0.046 cm³/100 g similar to thermal neutron porosity (NTPH) values logged in the same depths ranging from 0.3 to 0.39 m³/m³, the surface area (SA) ranging from 3.8 to 11.1 m²/g, and the PSD covers a range of 1.7 nm to 40 nm with high values of density ranging from 0.05 to 2.9 g/cm³. Nanoparticle size range from 540 nm to 1589.2 nm, it has a strong effect in an inverse relationship on both pore volume and surface area, this is confirmed with high gamma ray values of this well ranging from 149.3 to 258.3 API. Theses findings show that the studied formations with lower nanoparticle size are more favorable to the adsorption of gases due to their high surface area in the adsorbed gas form, also for the storage of gases in the pore volume due to their high pore volume in the free gas form. In general, these formations have appropriate pore structure parameters qualified it as an unconventional reservoir with profitable accumulations of hydrocarbons.

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