Novel Techniques to Characterize Pore Size of Porous Materials

Thesis by

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ABSTRACT

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Ali Jasim Alabdulghani

Porous materials are implemented in several industrial applications such as water desalination, gas separation and pharmaceutical care which they are mainly governed by the pore size and the PSD. Analyzing shale reservoirs are not excluded from these applications and numerous advantages can be gained by evaluating the PSD of a given shale reservoir. Because of the limitations of the conventional characterization techniques, novel methods for characterizing the PSD have to be proposed in order to obtain better characterization results for the porous materials, in general, and shale rocks in particular. Thus, permporosimetry and evapoporometry (EP) technologies were introduced, designed and utilized for evaluating the two key parameters, pore size and pore size distribution. The pore size and PSD profiles of different shale samples from Norway and Argentina were analyzed using these technologies and then confirmed by mercury intrusion porosimeter (MIP). Norway samples showed an average pore diameter of 12.94 nm and 19.22 nm with an average diameter of 13.77 nm and 23.23 nm for Argentina samples using permporosimetry and EP respectively. Both techniques are therefore indicative of the heterogeneity of the shales. The results from permporosimetry are in good agreement with those obtained from MIP technique, but EP for most part over-estimates the average pore size. The divergence of EP results compared to permporosimetry results is referred to the fact that the latter technique measures only the active pores which is not the case with the former technique. Overall, both techniques are complementary to each other which the results from both techniques seem reasonable and reliable and provide two simple techniques to estimate the pore size and pore size distributions for shale rocks.
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<th>Description</th>
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<tbody>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>EIA</td>
<td>US Energy Information Administration</td>
</tr>
<tr>
<td>EP</td>
<td>evapoporometry</td>
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<tr>
<td>ESEM</td>
<td>environmental scanning electron microscopy</td>
</tr>
<tr>
<td>FESEM</td>
<td>field emission scanning electron microscopy</td>
</tr>
<tr>
<td>FIB-SEM</td>
<td>focused ion beam scanning electron microscopy</td>
</tr>
<tr>
<td>GAD</td>
<td>gas adsorption/desorption</td>
</tr>
<tr>
<td>GRI</td>
<td>Gas Research Institute</td>
</tr>
<tr>
<td>IPA</td>
<td>isopropyl alcohol</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>LDP</td>
<td>liquid displacement porometry</td>
</tr>
<tr>
<td>MFC</td>
<td>mass flow controller</td>
</tr>
<tr>
<td>MIP</td>
<td>mercury intrusion porosimetry</td>
</tr>
<tr>
<td>MWCO</td>
<td>molecular weight cutoff</td>
</tr>
<tr>
<td>PAS</td>
<td>positron-annihilation spectroscopy</td>
</tr>
<tr>
<td>PSD</td>
<td>pore size distribution</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
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<tr>
<td>USGS</td>
<td>US Geological Survey</td>
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Chapter 1: Porous Media

1.1 Background

Porous materials, or sometimes so-called porous media, constitute mainly of solid matrix and voids which usually are filled with a fluid. The definition of porous materials might be vague for most people despite its existence in several visual daily-life examples just as honeycombs. The structure of a honeycomb can be obviously pictured and seen with the naked eyes since it is based on centimeter scales. Atoms, however, are not densely packed because of the presence of voids in their structures but of course at micrometer and nanometer scales. Most natural and synthetic materials such as organic, inorganic and polymeric materials have porous structures. Otherwise, the material will be considered as a dense material which has no voids on its structure. The ratio of voids to the total bulk varies from one material to another depending on numerous influences including chemical composition, pores regularity, compaction pressure and preparation method [1]. Measuring the pore size and porosity of any porous material will provide valuable information regarding the physical properties such as density, thermal conductivity and mechanical stability. Porous materials with different pore sizes have the potential to be implemented on a quite large number of scientific and industrial fields such as but not limited to membranes, catalysts and catalytic processes wherein the concept of pore size and porosity are introduced excessively in those fields and their applications [1]. However, preparing a dense material is considered as a major obstacle for scientists and researchers. The industrial importance of evaluating the pore size can be leveraged to optimize most conventional techniques and processes and also for providing better understanding of the chemical reactivity influence and the physical interaction of solids with other phases. [2]
1.2 Porous Material Classifications

Many studies have revealed various classes to sort out the porous materials into different categories such as The International Union of Pure and Applied Chemistry (IUPAC), Dubinin, Cheremskoj and Kodikara. The way of defining the pores whether as the physical frames, pore origin, structure, size and accessibility to surroundings is what generates various classifications. The IUPAC classification of pores, commonly used by researchers and scientists, relies on the pores accessibility to surrounding as depicted in Figure 1. [3]

![Figure 1: Schematic representation of a porous structure.](image)

Pores are found in different forms with respect to the external surface based on their communication to the surroundings. Open pores are either open at both ends or open only at one end as shown in the figure above in (b), (c), (d), (e) and (f). The accessibility of pores at only one side is described as blind or dead-end pores and this type is shown in (b) and (f). Others have no communication and association to the surroundings are named as closed pores as in (a). The latter type has the potential to affect the mechanical properties of solid materials.
Pores can also be described based on their shapes as in (c) is cylindrical open, (f) is cylindrical blind, (b) is ink-bottle-shaped, (d) is funnel shaped and (g) is roughness.

Table 1: IUPAC classification for porous materials.

<table>
<thead>
<tr>
<th>IUPAC Pore Classification</th>
<th>Pore Size Range</th>
</tr>
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<tbody>
<tr>
<td>Macropores</td>
<td>&gt; 50 nm</td>
</tr>
<tr>
<td>Mesopores</td>
<td>2-50 nm</td>
</tr>
<tr>
<td>Micropores</td>
<td>&lt; 2 nm</td>
</tr>
</tbody>
</table>

The IUPAC-based pore classification categories the pores into three main domains in which each domain is dependent on the mass transport mechanism through porous media. Table 1 outlines the pore size range based on the IUPAC classification which is the most common classification used for scientific purposes [3]. The nanopore range might be defined in several fields in the literature but it is not outlined in the IUPAC scheme. The latter range has been introduced by Loucks et al [4] through the Nanopore scheme in which it is based on pores that are less than 1000 nm. Figure 2 shows a graphic comparison between IUPAC and Nanopores classifications. The main difference between the two classifications is concerning the macropore domain of the IUPAC which is well-defined and subdivided in the Nanopore classification. [5]
Briefly, the transport theory of porous materials is described either as pore-flow model or as solution-diffusion model [6]. The concept of the solution-diffusion model is referred to the permeant that is dissolved in the membrane material and then diffuses across the other side due to the concentration gradient wherein the material solubility is the key parameter in this model. The pore-flow model, in contrast, is a filtration process based on pressure difference where the transport of permeants happens at the tiny pores of the porous materials. The aforementioned models are correlated to Fick’s law, concentration-based correlation, and Darcy’s law, pressure-based correlation, respectively [6]. Thus, porous materials, following the pore-flow model, are described by the IUPAC scheme while the solution-diffusion model (i.e. processes such as reverse osmosis and pervaporation) describes the materials that have no visible pores as
commonly named as dense materials [6]. The association between pore size and diffusion mechanism is demonstrated as the interaction and collision of gas molecules through the porous media depending on the behavior of the diffused gas. Multiple diffusion mechanisms can occur such as molecular sieving, viscous diffusion and Knudsen diffusion. The latter mechanism can be described as the ratio of the gas mean free path to the particle pore size and this mechanism occurs on mesoporous materials. Molecular sieving, however, denotes to the relative motion of diffusing gas species and it governs the total diffusion process wherein the mean free path of the gas molecules is at least one order of magnitudes higher than the pore size of media. Schematic representations for both diffusion patterns are shown in Figure 3. [7]

![Knudsen diffusion mode (left side), molecular diffusion mode (right side).](image)

**1.3 General Definitions and Terminologies**

Porous materials might have the same porosity but they fall in a different pore size domain. Hence, to avoid any confusions, the important definitions regarding porous media will be illustrated in this section. Definitions such as porous material, pore volume, pore size or width, pore size distribution and porosity are sometimes sounds alike but each term is different. Thus, to differentiate between them, this section will address the definitions of the aforementioned terminologies.
**Porous solid** means a solid that has pores as cavities, channels or interstices in which the pores are deeper than their widths. One of the important parameters is used to characterize porous materials is the **density**. The concept of density is subdivided into three different density parameters which are true density, apparent density and bulk density. The first term is referred to the solid network without counting the effect of pores and interparticle voids. Closed and inaccessible pores are included in apparent density while bulk density evaluates the pores and voids of the material. **Pore volume** ($V_p$) is basically the volume of the pores and this value can be measured via several techniques mainly by pressure intrusion and the wavelength of the radiation. **Pore size** is the distance between two opposite pore walls and sometimes this parameter is referred to pore width or diameter and the way that pores are categorized has already been investigated. **Pore size distribution** can be represented by the wall area derivative ($\frac{dA_p}{dr_p}$) or the pore volume derivative ($\frac{dV_p}{dr_p}$) where the pore radius ($r_p$) is generally assumed to have a cylindrical shape. **Surface area** is defined as the accessible area of solid surface per unit mass. **Porosity** ($\varepsilon$) is the ratio of the total pore volume to the bulk volume of the material. Numerous methods are applied for measuring this parameter where the accuracy varies from one technique to another depending on the measuring mechanism. **Tortuosity** ($\tau$) denotes to the length of the average pores relative to the sample thickness. Further details will be addressed later in this paper.

1.4 Applications

1.4.1 Pharmaceutical Care

The design of solid dosage in pharmaceutical fields requires comprehensive knowledge of the physical properties and the nature of the designated dosage. Characterizing parameters such as
disintegration, dissolution and stability are very crucial for system evaluations and therefore meaningful interpretations of these parameters can be obtained directly by measuring the porosity. Several studies have disclosed the significance of determining the pore size and pore size distribution for controlling the disintegration and dissolution processes at the initial stages especially when the solvent penetrates through the porous medium. Other factors including drug stability, diffusion mechanism and adsorption process are influenced proportionally towards the pore size and porosity. [8]

1.4.2 Membrane Processes

The importance of membrane characterization is essentially demonstrated in the following domains; (i) membrane fabrication, (ii) membrane morphology and (iii) attaining the desired membrane performance. The scope and potential of characterized membranes can be utilized for many purposes such as modification on membrane processes, membrane selection and developing new materials. Thus, physical morphology characterization, chemical composition characterization and membrane fouling characterization are the main classes that are meant by characterizing porous materials. [9]

One of the major challenges in the membrane field is to obtain a homogeneous morphology of fabricated porous materials. Therefore, optimizing the morphology of a certain porous structure will enhance the physical properties of the modified material. [10]

Membrane processes including reverse osmosis, microfiltration, ultrafiltration and nanofiltration are classified based on the membrane pore size. For each industrial application, certain membrane specifications must be achieved to obtain the desired outcomes. The industrial market of membrane processes has occupied and replaced large portions of the
conventional processes particularly in gas and liquid separation processes, water desalination and pharmaceutical concerns. Such an enormous move towards this field can be referred to its effectiveness with lower expenses compared to the other techniques. Hence, many attempts have been conducted in this area to optimize the industrial processes. The key parameter in fabricating a certain membrane is to make a membrane has no defects or cracks on it. In order to overcome such a challenging task, powerful characterization techniques are needed to have conclusive information about the nature of the material you are dealing with. [11]

1.4.3 Catalyst and Adsorbent Implementations

Over 80% of chemical and petroleum-refining industries are based on solid-catalyzed reactions. A wide range of daily-use applications are dependent on catalytic processes such as plastics, fertilizers and commodity chemicals. The behavior of catalysts in terms of how they interact with molecules and how to be selective towards specific sites on the surface can be analyzed by determining their chemical nature. Generally, solid catalysts are composed of three components wherein they are the active agents, the support and the promoter. The characteristics of a given catalyst are influenced by the support material and therefore it is recommended to select a porous material as a support to provide a large surface area and also to sustain its chemical and mechanical properties at severe operating conditions. The impact of these characteristics can be reflected in understanding the behavior of catalysts in order to implement and optimize them in a reactor accordingly. Pore size distribution, for example, is considered as a valuable parameter in this field as it indicates of how fast the active sites can be occupied by the reactant’s molecules and consequently determining the reaction rate. However, the chemical and mechanical properties of catalysts are implicitly related to the physical characterization.
Therefore, proceeding in this field for better understanding is depending on overcoming the flaws of how the catalysts are fabricated. [12]

1.4.4 Shale Rocks

Oil and gas production is classified into two categories; conventional and unconventional depending on the method used to extract the trapped oil and gas. Shale gas is fallen in the latter class and it is primarily natural gas trapped in the pore structure of the shale rocks as kerogen with small traces of other gases such as CO$_2$ and N$_2$. Kerogen is the major source of hydrocarbons in the shale reservoirs and it is insoluble in organic solvents because of its structure. Kerogen is made up of high molecular weight organic geopolymer with a partial association with bitumen and pyrite (FeS$_2$). The chemical composition of kerogen is not fixed since it is dependent on several chemical and biological factors. Figure 4 shows the composition of a common structure of the vitrinite maceral existed in the kerogen. [5]

![Figure 4: Structure of one of the common vitrinite maceral in kerogen.](image)
Unconventional reservoirs are known as low permeability reservoirs and have to be stimulated in order to enhance the permeability and then to collect the natural gas [13]. Conventional reservoirs, however, are like a sponge in terms of structure and this is why the gas can be easily collected [13]. The procedure for both technologies is almost the same but the recent improvements in the technologies that are implemented in the oil field over the few past years is what have made shale gas feasible economically. [14]

Shale gas production provides an alternative abundance resource of natural gas supply since most leading countries are harnessing natural gas to generate power [15]. According to the US Geological Survey (USGS), there are approximately 3 trillion barrels of proven oil shale reserves worldwide which is considerably higher than the globe’s crude oil resources [16]. Production of shale gas has increased exponentially in the recent years in several countries around the world such us but not limited to United States, China, Jordan, Australia and Brazil. As stated earlier, the reason behind this boom in shale gas production in the 21st century might be referred to the improvements in technologies which could make the production cost of this type of gas resources is feasible. [17]

The result of low permeability shales is related to the stored shale gas within the shale matrix which act as a flow barrier [5]. In order to capture the gas that is trapped in the shale rocks, a fluid, most often water, at high pressure is pumped in the reservoir to create narrow fractures and then release the natural gas. This process is called hydraulic fracturing or fracking [14]. This process has been used for over six decades and cumulative production of natural gas and oil barrels have exceeded 600 trillion cubic feet and 7 billion barrels respectively [13]. Also, the extraction of liquid and gaseous hydrocarbons from oil shales can be done by heating
and/or treating the rock with solvents [18]. The operating temperature to decompose the kerogen into oil and gas, known as pyrolysis process, is in the range of 480 – 520°C. [16]

Another technology to produce natural gas from shales is known as horizontal drilling. The concept of this technology is similar to the drilling method applied in conventional reservoirs. The process commences with vertical drilling up to the section where the shales are formed which usually located between 5000-10000 feet in depth. Just before this layer, the well deviates from vertical to horizontal. The advantage of this technology is mainly referred to creating additional pathways and maximizing the number of fractures that allow the gas to escape from the shales. [13]

As a result, a wide number of studies has been conducted in geological porous media such as reservoir rocks to investigate and understand the mechanisms of fluid storage and diffusion mechanism. Also, determining the hydrocarbon capacity is considered as a significant economic parameter to evaluate the reservoirs’ quality [19]. The nature of shale rocks and reservoirs, such as high compressibility and low porosity and permeability, is gained and affected by the hydraulic and mechanical properties of the rocks.

1.5 The Paper’s Objective

Several studies and numerous characterization techniques have been conducted to determine the pore size distribution (PSD) but the full spectrum of pore sizes cannot be obtained using the current techniques. The focus of this paper is to;

- Design and optimize the permporosimetry and evapoporometry methods.
- Characterize commercial membranes to validate the setups.
- Evaluate the pore size and pore-size distribution of shale reservoirs.
1.6 Outline of Thesis Chapters

This research thesis contains the following chapters:

**Chapter 1:** The main goal of this study is to characterize the pore size and pore size distribution of porous materials, in general, and shale rocks, in particular. Therefore, Chapter 1 is used to discuss the basic knowledge concerning the porous media and their importance in scientific and industrial purposes. Then, important terminologies related to the pore structure have been introduced and defined such as pore size and distribution, porosity and pore volume. Also, various grouping criteria for the porous materials are outlined and then the basis of the IUPAC classification is explained. Finally, some industrial applications that are utilizing porous materials have been addressed.

**Chapter 2:** Most conventional techniques, to determine the pore size and size distribution, have been addressed in this chapter. Mechanism, equation used, pore size limitations, pros and cons for each technology have been investigated extensively and then summarized briefly in a table.

**Chapter 3:** The process description, theory and procedure to analyze the raw data using permoporosimetry technique is investigated in this chapter. Also, the justifications of the assumptions have been discussed including the helium and hexane selections as non-adsorbing and condensable gases respectively. The system validation has been conducted for commercial Anodisc membranes and then confirmed by SEM images.

**Chapter 4:** Evapoporometry is the 2nd main setup that will be under the microscope in this paper. Thorough and clear details, from its principle to validation, have been studied in this
chapter. Moreover, the experimental design and specifications are described in an easy way including the core components such as the unit cell and the chamber. As this technology follows Kelvin equation and it is based on evaporation mass rate, a very detailed mathematical derivation is conducted to determine the pore size and size distribution. Similar to permporosimetry, commercial Anodisc membranes have been tested to validate the system.

Chapter 5: A brief introduction of shale rocks is addressed firstly and then elaborating on the main parameters for petrophysical evaluation and the current available techniques to determine the pore size and permeability. After this introductory part, the raw data for the Norway and Argentina shale samples will be outlined and analyzed using the permporosimetry, evapoporometry and mercury intrusion porosimeter to measure the average pore diameters. Data, including the relative pore size and pore size distribution, are also investigated in this chapter.

Chapter 6: Results obtained from permporosimetry, evapoporometry and mercury intrusion porosimeter are compared in this chapter and then discussed for possible explanations. Also, a few comments for better PSD calculations is investigated. Finally, some future remarks are suggested for improving the PSD results using permporosimetry and EP techniques.
Chapter 2: Pore Size and Pore Size Distribution

2.1 Background

Porous materials that are implemented in several industrial applications such as water desalination, gas separation and pharmaceutical care are mainly governed by the pore size and the pore size distribution (PSD). The performance of a certain material could be enhanced by determining the pore size. Accurate methods for the PSD measurements of porous materials have to be proposed in order to obtain better characterization results. Accordingly, characterized samples are fitted on certain applications, including but not limited to water desalination and membrane processes, depending on how they behave under certain circumstances and operating conditions which are primarily controlled by their evaluated properties. Analyzing shale reservoirs are not excluded from these applications and numerous advantages can be gained by evaluating the PSD of the rocks. [20-22]

2.2 Pore Size Characterization Methods

The current applied methods for determining the PSD are principally classified into direct observation methods and indirect methods. The former class, which sometimes so-called radiation methods, comprises the microscopy techniques that are based on light or electron wavelength such as scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM), environmental SEM (ESEM), atomic force microscopy (AFM) and others. The characterization potential of transmitted and reflected light microscopy, on the other hand, is controlled by the light wavelength and therefore smaller pores cannot be detected [23]. Also, the magnification power is about 1000x for the ocular lens while it is 500,000x for
the electron-based microscopies [23]. Characterizing porous materials using SEM and FESEM requires special sample treatments in which non-conductive samples cannot be analyzed immediately and have to be coated with a thin conducting layer to overcome this issue. Also, exposing the sample into a high vacuum is essential to remove the trapped moisture and then obtain the morphology of the sample. However, coating and drying the sample might change the pore structure and hence the PSD accuracy. Charging and drying effects can be resolved using ESEM since it is equipped with gas-ionizing detector and therefore the coating and vacuuming steps are avoided. The drawback of this technique is the image resolution will not be as good as the SEM image. For AFM, the characterization does not require special treatment or preparation. Nevertheless, these techniques are limited by the scanning area which is less than 1 μm² and therefore the results will not be comprehensive and well-defined for the entire sample. Moreover, the pore size limitations using microscopes is controlled by the resolution of the used technique and they are very expensive to afford. [20-22]

The indirect methods, which are commonly referred to fluid invasion methods, are divided into two main classes in terms of the equation used; Young-Laplace equation and Kelvin equation. Liquid displacement porometry (LDP) and mercury intrusion porosimetry (MIP) are examples for those are based on the former equation. The principle of LDP is basically to intrude an immiscible fluid, gas or liquid, after immersing and saturating the sample in a wetting liquid. MIP, on the other hand, is aimed to intrude a nonwetting liquid, which is mercury, through the evacuated pores. Both techniques are governed by the applied pressure in which the pores will be filled progressively from the largest to the smallest. Obviously, higher pressure allows smaller pores to be detected and since LDP and MIP are commercially available, they are controlled by the maximum adjusted pressure. Thus, LDP has the potential to characterize
pores in the meso-domain, typically larger than 10 nm, while MIP can reach up to 3.6 nm which is theoretically equivalent to 60,000 psi as it follows Washburn’s equation. The major downside of these techniques is the applied pressure might distort the structure of the material if the pressure is very high. Also, MIP is considered as a destructive and expensive technique but numerous parameters can be obtained from this method including the surface area, porosity and pore volume [24]. Additionally, conducting experiments using this method has to be under caution since it is based on mercury (Hg) which is a toxic material to deal with. Generally, the morphology of the sample will be altered due to the high pressure applied and the sample has to be fine-powder or small solid pieces which are considered as common features for the techniques those are classified as indirect methods. The ultimate difference between Hg porosimetry and LDP is the way of conducting the analysis in which Hg porosimetry cannot discriminate between continuous and dead pores. [20-22]

Kelvin equation, however, relates the vapor pressure to the curvature at the liquid-gas interface in a pore. This equation can be applied in several methods such as gas adsorption/desorption (GAD) and permporosimetry. GAD method is based on capillary condensation which the adsorption step launches by increasing the pressure of a gas and then reduced for the desorption step. Pores are occupied from the largest to the smallest as dictated by Kelvin equation. Thereby, the minimum pore size can be measured is limited to the kinetic diameter of the gas molecules used for the analysis whether it is N\textsubscript{2} (~ > 2 nm) or CO\textsubscript{2} (~ < 2 nm) [23]. Information such as surface area, pore volume and PSD are determined using this method. Similar to MIP, GAD cannot discriminate between the continuous and dead-end pores which therefore gives inaccurate PSD profiles [20-22]. Permporosimetry, on the other hand, is a special type of GAD in which the dead-end pores will be excluded from the analysis but it requires special protocol.
The principle of permporosimetry system relies on measuring helium gas permeance through the sample as a function of relative pressure of a condensable hydrocarbon such as n-hexane, benzene or p-xylene. Theoretically, increasing the relative pressure means larger pores are occupied by following Kelvin equation. In general, this technique aims to measure the pore sizes between 4 nm and 100 nm, whereas the recent modifications on this technique allows the system to measure the pore size from 0.3 nm to 4 nm. Permporosimetry system is utilized to study the contribution of micropores in the sample. The system and surrounding temperature must be maintained precisely since the vapor pressure of the helium-hexane stream is very sensitive to it. The tested sample is not required to be crushed to get fine powder out of it which this pretreatment step is mandatory to conduct the analysis using LDP, MIP and GAD. More details about this system will be addressed later in Chapter 3. [25, 26]

Recently, Greenberg et al. have developed and patented [27] a novel method to characterize flat sheet membranes that is named as evapoporometry (EP) [20]. The EP technique is based on Kelvin equation which relies on measuring the vapor pressure of a wetting liquid. Also, it has the potential to measure the PSD of hollow fiber membranes as stated by Akhondi et al. [21]. Numerous factors are made the EP method more attractive among most direct and indirect techniques. Considering a non-destructive method, which has the capability to provide realistic data, is what makes this technique distinguishable compared to the other methods. Pores larger than 4 nm are measured precisely using this setup. More details about this technology will be discussed in Chapter 4.

Another indirect method is called thermoporometry which is based on the Gibbs-Thomson equation. The concept of thermoporometry is fundamentally measuring the heat arises due melting the frozen liquid after saturation the sample. This system is referred to the curvature at
the solid-liquid interface in a pore at the freezing point temperature. The main drawback of thermoporometry is that the PSD cannot be determined accurately at very small pores because of the limitations in measuring the heat input and a correction for the submicron layer of unfrozen liquid has to be accounted. [20, 21]

Additionally, molecular weight cutoff (MWCO) and positron-annihilation spectroscopy (PAS) can be used to calculate the PSD of porous materials. Determining the PSD using the former technique is not straightforward and its aim is to measure the amount of rejected solute by a certain membrane. The latter system, however, utilizes the annihilation of a positron beam. The disadvantages of this method are mainly expressed as the difficulty to interpret the data and this system is very expensive [22].

Lastly, gas pycnometry is a modern technique to evaluate the PSD and can handle all sorts of samples. This technology is based on determining the true and apparent densities of the tested sample by displacing a gas, helium or argon, across the sample under very thorough procedure and conditions. The porosity and PSD are then evaluated accordingly from the density. Also, porous and non-porous materials can be both analyzed through this setup but it is designed mainly to evaluate the porosity and density. A graphic comparison of the most conventional techniques for pore size characterization is shown in Figure 5. [5, 28, 29]
In summary, a brief description for each technique is presented in Table 2.

2.3 Pore Structure

Although the aforementioned techniques are meant to evaluate the pore structure through the porous medium, the collected raw data from each method might not match with each other. Inconsistency in data could be referred to several reasons such as irregular pore network, limitation of certain models and other geometric assumptions. Depending on the methods’ mechanism, the determined pore size is either the pore throat, sometimes is called pore neck, or the pore body as depicted in Figure 6. [30]
Generally, the evaluated pore size through techniques based on measuring the permeate gas are defined as pore throat since the gas molecules have passed through the accessible path. Mercury intrusion porosimetry is also fallen in that category but closed pores will be counted and therefore miscalculation in determining the pore size and porosity might occur. Methods based on sorption mechanism are grouped in the ones that determine the pore body. [24]

Numerous reviews have been conducted to resolve this issue and provide accurate measurements in determining and evaluating the PSD particularly in micropore domain. As a result, Everett [31] had proposed the effective pore size term which is defined as the outer surface of the smaller pores and this term is assumed to be negligible at larger pores. Afterwards, Horváth and Kawazoe had successfully developed a model to calculate the effective pore size at the smaller pores. More information will be addressed in Chapter 3. [31]

2.4 Kelvin Equation Limitations

The relationship between the vapor pressure and the mean curvature radius of a liquid is based on thermodynamics equilibrium and was derived initially by Lord Kelvin. This derivation is what has led to the well-known form of Kelvin Equation.

\[
r_k = \frac{2\gamma V_m \cos \theta}{RT \ln \left( \frac{P}{P_o} \right)}
\] (Ch. 2 – 1)

where \( r_k \) is the Kelvin radius, \( \gamma \) is the surface tension, \( V_m \) is the molar volume of the liquid, \( \theta \) is the contact angle, \( R \) is the gas constant, \( T \) is the absolute temperature and \( P/P_o \) is the relative pressure. Scientists and researchers have applied equation (Ch. 2-1) to several applications for pore size determinations. The validity of Kelvin equation at smaller pores was and still a big question mark needs to be answered. No consensus agreement has been reached on the
accuracy of using Kelvin equation on the micropore domain. Harris had compared the pore size obtained from the Kelvin equation with another model, named as Gurvitch procedure, and the results showed that Kelvin equation data were inaccurate at pores below 4 nm. The reason for that, as stated by Harris, is because the assumption of constant surface tension and molar volume. Gubbins et al had confirmed Harris’s results by computer simulations of the fluid behavior in pores. Fisher and Isrealachvili, however, reported contradictory outcomes which the equation is valid at the pores below 4 nm. Takei et al. [32] had conducted low pressure nitrogen adsorption to investigate the validity of Kelvin equation and they concluded that the liquid nitrogen behaves differently because of the physical properties are changed at very narrow pores (below 4 nm). [20, 32]

In this paper, the pores below 4 nm will be excluded from the analyses for the raw data obtained from the evapoporometry technique.
Table 2: Summary of the most techniques used for pore size characterization

<table>
<thead>
<tr>
<th>Technique</th>
<th>Equation Used</th>
<th>Pore Size Limits</th>
<th>Mechanism</th>
<th>Drawbacks</th>
</tr>
</thead>
</table>
| Permporosimetry    | -Kelvin equation

\[ d_k = -\frac{4\gamma V_l}{RT \ln(P_r)} \]

-Mainly for mesopore range (~ > 4 nm).

-Can go below 4 nm but another equation is used.

-Helium-hexane adsorption technique

-Kelvin equation limitations.

-Difficult to maintain the relative pressure above 0.9

-Temperature and relative pressure must be maintained.

| Evapoporometry     | -Kelvin equation

\[ d = -\frac{4\gamma V}{RT \ln\left(\frac{\chi_{40}}{\chi_{A0}}\right)} \]

-Mainly for mesopore domain (~ > 4 nm).

-Pores below 4 nm can be determined but inaccurate data might be obtained.

-Evaporative mass loss over saturated pores.

-The limitation of using Kelvin equation below 4 nm and no other equation is available.

-Cannot discriminate between dead-end pores and continuous pores. |
| Mercury Intrusion Porosimetry | - Young-Laplace Equation  
\[ \Delta P = \frac{2\gamma \cos \theta}{r_{\text{pore}}} \] | - Mainly for macro- and mesopore domains. 
- Theoretically, 3.6 nm is the minimum pore size can be detected. | - Intrusion and extrusion of mercury by applying pressure | - Cannot discriminate between the continuous and dead-end pores. 
- Time consuming and expensive method. 
- High pressure might alert the surface compaction. 
- Destructive Method. |
| Gas Sorption (Adsorption/Desorption) | - Kelvin equation  
\[ d_k = -\frac{4\gamma V_i}{RT \ln(P_r)} \] | - Range from 1.7 nm – 200 nm. 
- Depends on the gas used. 
- Commonly used for mesopore size range. | - Based on capillary condensation which a gas condenses in pores at pressure less than the saturation pressure. | - Cannot discriminate between the continuous and dead-end pores. 
- Slow and expensive. 
- Sample has to be crushed. |
<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Liquid Displacement Porometry</strong></td>
<td>- Young-Laplace Equation [ \Delta P = \frac{2 \gamma \cos \theta}{r_{pore}} ]</td>
<td>- Commonly for pores larger than 10 nm. - Allowing an immiscible fluid to pass through saturated pores under high pressure. - The morphology might be changed due to the high pressure.</td>
</tr>
<tr>
<td><strong>Microscopic Techniques</strong></td>
<td>- Not applicable.</td>
<td>- Mainly for macro- and mesopore ranges. - Cannot go below 1 nm.</td>
</tr>
<tr>
<td><em>(SEM/AFM/EFSEM)</em></td>
<td></td>
<td>- Based on the instrument used, the image of the surface will be obtained.</td>
</tr>
<tr>
<td><strong>Thermoporometry</strong></td>
<td>- Gibbs-Thomson equation [ r = \frac{2 T_0 \gamma V}{\Delta T_m \Delta h_b} ]</td>
<td>- Mainly for mesopore range. - Based on the melting point shift of a liquid. - Limitations in measuring the heat input.</td>
</tr>
</tbody>
</table>

Chapter 3: Permporosimetry

3.1 Background

Permporosimetry, as it is also called porosimetry and perporosimetry, had been designed initially to handle a short list of materials and was limited only to meso- and macroporous materials as different non-adsorbing gases and condensable hydrocarbons were chosen for pore size characterization [22, 33]. Further modifications were introduced later to this technology by Deckman et al. [25] for determining the defects of zeolite membranes that fell in the mesopore range. Currently, permporosimetry is considered as one of the powerful methods used for measuring the pore size and size distribution over the other conventional techniques because of its potential in utilizing a broad range of porous materials and more importantly of being a non-destructive method which means the morphology of the characterized sample will not be affected. Materials, such as inorganic materials, ceramic membranes, γ-alumina membranes and hollow fiber membranes, are all subjected to be directly characterized by this system [26, 34].

3.2 Process Principles and Justifications

Permporosimetry system is based on the combination of capillary condensation with gas permeation. The principle of the latter system relies on measuring the permeance of a non-adsorbing gas, such as helium or any inert gas, as a function of relative pressure (P/Po) of a condensable adsorbing hydrocarbon. Experiments must be conducted at constant temperature without exceeding the dew point temperature to avoid streams condensation inside the system. The dew point is defined as the point where the first
condensation drop of gaseous mixture is observed which can be calculated using Raoult’s law and Dalton’s law. [25, 26, 35-40]

In this paper, helium and n-hexane are chosen as the non-adsorbing gas and the condensable hydrocarbon respectively. The justifications of these choices are related to the objective of occupying the pores in the micropore range since the helium molecules have the smallest kinetic diameter (~ 2.6 Å [41]) which can diffuse and penetrate through smaller pores easily. The advantage of choosing helium is clearly reflected on low-permeability samples. For the selection of the condensable hydrocarbon, n-hexane was chosen because it has lower physical properties compared the other hydrocarbons. As shown in Table 3, n-hexane can access smaller pores at the same relative pressure which implies lower pore size limits.

Table 3: Corresponding pore size at different relative pressure and component at room temperature

<table>
<thead>
<tr>
<th>Component</th>
<th>Surface Tension ((\gamma)) (N/m)</th>
<th>Molar Volume ((V_m)) (m(^3)/mol)</th>
<th>Relative Pressure ((P/P_0))</th>
<th>Pore Size Range (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexane [40]</td>
<td>(1.54 \times 10^{-2})</td>
<td>(1.36 \times 10^{-4})</td>
<td>0.10</td>
<td>Micropores</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.25</td>
<td>2.44</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.90</td>
<td>32.11</td>
</tr>
<tr>
<td>Benzene [40]</td>
<td>(2.51 \times 10^{-2})</td>
<td>(1.36 \times 10^{-4})</td>
<td>0.10</td>
<td>2.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.25</td>
<td>3.97</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.90</td>
<td>52.33</td>
</tr>
<tr>
<td>p-Xylene [25]</td>
<td>(2.83 \times 10^{-2})</td>
<td>(1.23 \times 10^{-4})</td>
<td>0.10</td>
<td>2.44</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.25</td>
<td>4.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.90</td>
<td>53.36</td>
</tr>
</tbody>
</table>
3.3 Theory of Permporosimetry

Permporosimetry method is governed by Kelvin equation to determine the pore diameter which is expressed as follows;

\[
\ln\left(\frac{P_v}{P_{sat}}\right) = -\frac{4\gamma V_l \cos \theta}{d_k RT}
\]  

(Ch. 3 – 1)

where \(P_v\) is the equilibrium vapor pressure, \(P_{sat}\) is the saturation vapor pressure, \(\gamma\) is the surface tension, \(\theta\) is the contact angle, \(d_k\) is the Kelvin diameter, \(V_l\) is the molar volume of liquid, R is the gas constant and T is the absolute temperature. The contact angle is assumed to be equal to 0 and that means the curvature radius is equal to the capillary radius. Thus, equation (Ch.3-1) can be re-written as follows;

\[
d_k = -\frac{4\gamma V_l}{RT \ln(P_v)}
\]  

(Ch. 3 – 2)

where \(\gamma\) and \(V_l\) for n-hexane at 19°C are equal to \(1.85\times10^{-2}\) N.m\(^{-1}\) and \(1.36\times10^{-4}\) m\(^3\).mol\(^{-1}\) respectively and Pr is the reduced pressure \((\frac{P_v}{P_{sat}})\). Since the surface tension is a strong function of the temperature, the following correlations are used to determine this parameter for n-hexane based on the adjusted system temperature T(K) [42];

\[
\gamma(mN/m) = 5.553 \times 10^{-5}(P_c)^{2/3}(T_c)^{1/3}F(1 - T_r)^{11/9}
\]  

(Ch. 3 – 3)

\[
F = \frac{T_{br}[\ln(P_c) - 11.5261]}{1 - T_{br}} - 1.3281
\]  

(Ch. 3 – 4)
where $P_c$ is the critical pressure (3.02×10^6 Pa), $T_c$ is the critical temperature (507.6 K), $T_r$ is the reduced temperature $(\frac{T}{T_c})$, $T_{br}$ is the reduced boiling temperature $(\frac{T_b(=342K)}{T_c})$ and F is the factor in surface tension equation.

Equation (Ch.3-2) is used to characterize mesoporous materials (2 nm - 50 nm) because of the Kelvin equation limitations. Several studies have been conducted to evaluate the equation at different ranges but no conclusive results were proposed so far. One of the reasons behind this limits is related to the surface tension ($\gamma$) and the molar volume ($V_l$) in which they are assumed to be constant. Therefore, Horváth-Kawazoe (HK) equation is proposed as an alternative equation to determine the pore size in the micropore range (< 2 nm). The HK equation is expressed as follows; [35, 40]

$$RT\ln\left(\frac{P}{P_0}\right) = \frac{\Delta H_{ADS}}{(d - d_o)} \left[\frac{\sigma^{10}}{9d_o^9} - \frac{\sigma^4}{3d_o^3} - \frac{\sigma^{10}}{9(2d - d_o)^9} + \frac{\sigma^4}{3(2d - d_o)^3}\right] \quad (Ch. 3 - 5)$$

$$d_o = \frac{d_s + d_a}{2} \quad (Ch. 3 - 6)$$

$$\sigma = 6\sqrt{0.4d_o} \quad (Ch. 3 - 7)$$

$$d_i = 2d - d_s \quad (Ch. 3 - 8)$$

where $d_i$ is the width of pores, $d_s$ is the diameter of a surface atom of the sample, $d_a$ is the diameter of the adsorbate (4.3×10^{-10} m for n-hexane), d is the slit pore half width, $\sigma$ is the zero interaction energy distance and $\Delta H_{ADS}$ is the isosteric heat of adsorption (71.8 kJ/mol for n-hexane).

The Kelvin diameter, equation (Ch.3-2), must be corrected by considering the thickness of the adsorbed layer (the so called t-layer) in order to calculate the actual pore diameter:
\[ d = d_k + 2t \quad (Ch. 3 - 9) \]

where \( d \) is the actual diameter and \( t \) is the t-layer thickness that represents the thickness of adsorbed layer of n-hexane on pore walls. The latter parameter depends on the relative pressure. The thickness calculation, however, is very tedious since homogenous non-porous reference surfaces with the same chemical properties are required for that purpose [43]. Nevertheless, several approaches and correlations were provided to approximate the influence of the t-layer and therefore the Harkins-Jura (HJ) equation was used [44]:

\[ t = \sqrt{\frac{C}{B - \log(P/P_0)}} \quad (Ch. 3 - 10) \]

where \( B \) and \( C \) for n-hexane are equal to -0.04 and 16.77 Å² respectively [40].

The helium permeance through the pores can be obtained by using the following:

\[ \Pi_l = \frac{F_t \cdot \rho_{He}}{6 \cdot 10^9 \cdot A \cdot \Delta P \cdot MW_{He}} \quad (Ch. 3 - 11) \]

where \( \Pi_l \) is the He permeance (mol/(s.m².Pa)) at its corresponding relative pressure, \( F \) is the flow rate (ml/min), \( A \) is the active area of the sample in the unit cell (m²) which is equal to 2.38×10⁻⁴ m² in this paper, \( \Delta P \) is the pressure gradient (bar), \( \rho \) is the He density (kg/m³) and \( MW \) is the molecular weight of He (g/mol). Since the general transport behavior follows Knudsen diffusion mechanism, the flux through the pores can be described and calculated by Fick’s law using the following equations; [35]

\[ J_{total} = -\frac{D_k \Delta P}{RT \delta} \quad (Ch. 3 - 12) \]
\[ D_k = \frac{3.068 \times \varphi \rho r_i}{\tau} \sqrt{\frac{RT}{M}} \]  

(Ch. 3 – 13)

where \( D_k \) is the Knudsen diffusion coefficient \((m^2/s)\), \( M \) is the molecular weight \((kg/mol)\), \( \delta \) is the sample thickness \((m)\), \( \varphi \) is the constriction factor which represents the cross-sectional area change normal to the diffusion path \([45]\), \( \tau \) is the tortuosity and \( r \) is the half of average pore width. Lastly, the pore size distribution (PSD) can be evaluated by measuring the area of pores at each pore size interval utilizing the following equation \([40]\):

\[ A_i = \frac{F_i - F_{i+1}}{J_{total}} \]  

(Ch. 3 – 14)

where \( F_i \) and \( F_{i+1} \) represent the helium flow rate at the corresponding relative pressure \( P_i \) and \( P_{i+1} \) respectively. Alternatively, the PSD can be determined with respect to the specific pore volume using the following equation; \([39]\)

\[
f(r) = \frac{-3\delta \tau}{2Ar} \sqrt{\frac{\pi M RT}{8000} \times \frac{d\Pi}{dr} (10^{-9})}
\]  

(Ch. 3 – 15)

Where \( f(r) \) is the pore size distribution \((1/m^3)\), \( r \) is the actual pore radius \((nm)\) and \( \frac{d\Pi}{dr} \) is the drop in helium permeance at a fixed pore interval \( \sim dr = 5 \text{ nm} \). The data analyses in this paper using permoporosimetry were conducted for both equations to evaluate the PSD.

### 3.4 Experimental Setup and Procedure

The relative pressure is increased gradually from 0 (pure helium) to \( \sim 0.9 \) by controlling the flow of helium gas. At low relative pressure, smaller pores are occupied while the
larger ones are blocked progressively by increasing the relative pressure as dictated by Kelvin equation. The permeating helium flow rate depends on the relative pressure and inherently depends on the pore size, such that the permeance decreases with increasing relative pressure due to the adsorbed hexane. A schematic diagram of permporosimetry system is shown in Figure 7.

Prior to running an experiment, all the gas lines and the sample are evacuated overnight (In addition, the sample is degassed beforehand at 120°C under vacuum for 2-3 days prior to being loaded in the membrane module, to ensure the removal of the moisture/gas
trapped within the sample). Following this, helium flow is adjusted using mass flow control (MFC) (Alicat scientific model) wherein different flow range controllers are equipped in the system to achieve certain relative pressure. The pure helium stream \((\frac{p}{p_0}=0)\) is mixed with n-hexane at relatively low temperature (~ 17-19°C) in order to avoid condensation and to enhance the amount of n-hexane that will be carried in the stream where the association between temperature and relative pressure is clearly described using Antoine equation. As the pure helium stream is mixed with n-hexane in a saturator, which is controlled primarily by MFC 1, the stream coming out from the saturator is assumed to be fully saturated (~ 1). Therefore, MFCs 2 and 3 are used to dilute the saturated stream and as explained previously, the adsorption process is followed by capillary condensation launching from the finest pores.

The permeate helium flow rate through the sample is recorded using a digital bubble flowmeter, Humonic Optiflow 520 model, which the experiment commences with flowing pure helium. In this manner, it is required to control flow ratio \((\text{He}:\text{C}_6\text{H}_6)\) as 3:1 in order to maintain the relative pressure at 0.25 and as 1:1 to adjust it at 0.50 and so on. The amount of hexane adsorbed within the sample might be measured by running a GC analysis for the feed and permeate streams. The driving force across the sample is the pressure and it should be maintained throughout the experiment and this achieved by the back pressure regulator.

3.5 Data Validation

To test and validate the results from the permporosimetry setup, pore size distribution for commercial 20 nm Anodisc membranes (Whatman®) were measured and calculated. The system was maintained at 19°C and degassed overnight. Anodisc membranes are very
permeable and therefore the exposed area was reduced using epoxy resin in order to maintain the pressure difference across the membrane. As explained earlier, the first measurement was recorded by flowing only helium (P/P₀=0) and then the relative pressure was increased gradually by saturating the helium stream with hexane vapor and diluting the saturated stream to the desired relative pressure. The tabulated data in Table 4 shows the measured permeance (also shown in Figure 8) as a function of relative pressure for Anodisc, using the permporosimetry method, along with the corresponding pore sizes calculated using Kelvin equation.

Table 4: Data obtained for 20 nm Anodisc membrane.

<table>
<thead>
<tr>
<th>P/P₀</th>
<th>Flow Rate (ml/min)</th>
<th>Pore Size (nm)</th>
<th>He Permeance (mol/(s.m².Pa))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>12.65</td>
<td>-</td>
<td>3.41E-05</td>
</tr>
<tr>
<td>0.05</td>
<td>12.24</td>
<td>2.08</td>
<td>3.33E-05</td>
</tr>
<tr>
<td>0.15</td>
<td>11.38</td>
<td>3.05</td>
<td>3.15E-05</td>
</tr>
<tr>
<td>0.20</td>
<td>11.06</td>
<td>3.51</td>
<td>2.95E-05</td>
</tr>
<tr>
<td>0.50</td>
<td>9.16</td>
<td>7.42</td>
<td>2.49E-05</td>
</tr>
<tr>
<td>0.75</td>
<td>7.15</td>
<td>16.82</td>
<td>1.94E-05</td>
</tr>
<tr>
<td>0.85</td>
<td>4.07</td>
<td>29.49</td>
<td>1.12E-05</td>
</tr>
<tr>
<td>0.90</td>
<td>2.41</td>
<td>49.06</td>
<td>6.49E-06</td>
</tr>
<tr>
<td>0.95</td>
<td>0</td>
<td>-</td>
<td>0.00E+00</td>
</tr>
</tbody>
</table>

As can be seen from Figure 8, the helium permeance decreases with increasing relative pressure indicating hexane adsorption in pores and thus subsequent blocking of those
pores to gas flow. The profile, shown in Figure 8, provides an indication of the major pore bin range in the sample. It can be clearly seen from Figure 8, that there is a sharp drop in the He permeance between relative pressure of 0.75 and 0.95 (which is equivalent to 16.82 nm and 49.06 nm pores), indicating that majority of pores are in this size range. At very high relative pressure (≥0.95), no He flow was detected implying that all pores are blocked by adsorbed hexane.

![Figure 8: Helium permeance versus relative pressure profile of 20 nm Anodisc membrane. Trial 1 and 2 refers to the experiment done on the same membrane.](image)

Based on the permeance data, the pore size distribution of the 20 nm Anodisc membrane sample was calculated using equation (Ch.3-15) and the results are presented in Figure 9. The average pore size of this sample calculated to be 19.79 and 19.42 nm (manufacturer nominal value for pore size is 20 nm) from the two trials conducted on the same sample. Based on this result, it can be said that the permporosimetry system provides reliable data for measuring the pore size distribution for porous materials.
3.6 SEM Observation

To further corroborate the above data, SEM image was taken for 20 nm Anodisc membrane using Nova™ NanoSEM 630. Figure 10 depicts the SEM image and it is clearly shown that various pore sizes were observed in the 15-50 nm range (no distribution analysis was done) similar to the range we obtain using permporosimetry (Figure 9). Based on these results, it can be confirmed that the designed permporosimetry set-up is reliable and accurate.

Figure 9: PSD of 20 nm Anodisc membrane.

Figure 10: SEM image of 20 nm Anodisc membrane.
Chapter 4: Evapoporometry (EP)

4.1 Process Principle

EP is an indirect method based on Kelvin equation and it is considered as a genuine technique because it has the potential to characterize porous materials over the entire pore size domains from macro-scale to nano-scale. The basic idea of EP method is to correlate the pore size to the evaporation rate of the wetting liquid in the sample, through Kelvin equation. Thus in essence, EP relies on evaporating a wetting volatile liquid from a pore at conditions where the vapor at the surface of the pore is saturated in terms of pores from which the liquid is draining and supersaturated with respect to all other pores that are not draining (i.e. smaller pores). Unlike permporosimetry, evaporation commences from the largest to smallest pores. The evaporation rate in turn, can be related to the mass loss as the wetting liquid is evaporating, thus making it a simple technique where only mass loss as a function of time is measured.

Figure 11: Schematic representation of the test cell (left) and EP setup (right). [21]
4.2 Experimental Setup Design

As shown in Figure 11, the design of EP setup is relatively easy but many parameters have to be considered in the design for accurate measurements. The two core components in the EP setup are the test cell and the microbalance. For the test cell part, the dimension specifications are noted in Figure 12 in which the cell was fabricated from Teflon since this material is lighter than aluminum. The advantage of the weight reduction is reflected on the readability of the balance (resolution) as will be stated later in this section. The cell is a cylindrical shape which is open from one side and sealed from the other side. Different sort of configurations are considered depending on the thickness and the nature of the sample (i.e. flat sheet or hollow fiber materials).

![Figure 12: Dimension specifications for the EP test cell.](image)
The upper part of the test cell has an outside diameter of 20 mm and a length of 100 mm while the bottom side of the cell holds the sample on the inner-circular hole (~21.50 mm) where the diameter of the exposed area, which will be covered with the wetting volatile liquid (d_c), is equal to 12 mm. The two parts of the cell are attached to each other and sealed using nut/bolts and O-ring, so as to prevent any lateral vapor leakage from the evaporating liquid. The length of the tube-side of the unit cell governs the resistance of the mass-transfer coefficient as will be discussed further later in this chapter.

The other core component is the microbalance where the setup was equipped with Sartorius balance, CPA225D model, which has the capability to read up to 5 decimal digits depending on the weight of the test cell and the sample together (~ 100 mg). Also, the microbalance has to be placed on an isothermal chamber to maintain the temperature and pressure where the chamber is located on an anti-vibrating table to obtain precise readings of the evaporative mass loss.

Since EP method is based on evaporation rate, the higher temperature means the higher mass loss. So, two light bulbs, 50 W each, were attached on the top of the chamber to heat up the whole system to the desired temperature (usually around 30°C). In addition, these two bulbs with a cooling fan were both controlled with a temperature controller, Hanyoung Nux model, to keep the temperature uniform on all the chamber’s levels. To avoid accumulation of vapor pressure inside the chamber, adsorbent material, such as carbon source, was located nearby the test cell. The need of humidity sensor depends on the wetting volatile liquid used, which in this case for isopropanol, it is not required to attach such a sensor to record the humidity. In case of water, however, recording the humidity is mandatory since the evaporation rate will be affected accordingly.
4.3 Theory of Evapoporometry

Since EP follows Kelvin equation, Krantz et al. [20] have used the following expression to explain the curvature of the liquid-gas interface in a pore;

\[
\ln \left( \frac{P'_A}{P^o_A} \right) = -\frac{\gamma V_A}{RT} \left( \frac{1}{r_1} + \frac{1}{r_2} \right)
\]

where \( P' \) is the instantaneous vapor pressure of liquid A, \( P^o \) is the normal vapor pressure of a liquid layer on the liquid-saturated sample which represents the behavior of the free-standing liquid as will be addressed later, \( \gamma \) is the surface tension, \( V \) is the liquid molar volume, \( R \) is the gas constant, \( T \) is the absolute temperature and \( r \) is the principal radius of curvature of the liquid-gas interface. The relation between the pore size and the vapor pressure can be expressed to the following form by assuming a completely wetting liquid in pores with a circular opening having diameter \( d \);

\[
\ln \left( \frac{P_A}{P^o_A} \right) = -\frac{4\gamma V_A \cos \theta}{RTd}
\]

where \( P_A \) is the partial vapor pressure at the sample surface at any time and \( \theta \) is the contact angle of the liquid at the sample surface. Usually, the contact angle is assumed to be zero whenever the sample is fully wetted by the liquid. Equation (Ch.4-2) can be reformed in terms of vapor phase mole fractions which also referred to the evaporation rates;

\[
d = -\frac{4\gamma V}{RT \ln \left( \frac{x_A}{x^o_A} \right)} = -\frac{4\gamma V}{RT \ln \left( \frac{W_A}{W^o_A} \right)}
\]
where $x_{A_0}$ and $W_{A_0}$ represent the vapor phase mole fraction and the evaporation rate (which is calculated from the mass loss) from the pores at the liquid-gas interface as evaporation is taking place, respectively; while $x_{oA_0}$ and $W_{oA_0}$ represent the same parameters for free standing liquid layer.

Kelvin equation, as discussed previously, has limitations in terms of pore size range in which the relation might not be suitable for determining pores below 4 nm. Thus in EP, pores with sizes less than 4 nm will be excluded from the pore size analyses.

Data obtained using EP method depends on which side of the sample is facing the open side of the cell. In order to get reliable result, the upward side, which is facing the open side, has to be consisting the smallest pores in which the wetting liquid will be drawn upward the pores. Otherwise, the wetting liquid will be drawn downward and hence the PSD result will be inaccurate. Moreover, the downside of the sample must be dried to ensure accurate gravimetric readings.

### 4.4 Mass Transfer Diffusion through the Unit Cell

As stated earlier, the pore size of porous materials can be obtained using Kelvin equation (Ch.4-3). Since this technique is based on measuring the evaporative mass loss, the mass diffusion of the wetting liquid must be analyzed and hence correlated to the pore size characterization. Many assumptions have been raised in order to derive the evaporation rate equation such as isothermal condition, one-dimensional binary diffusion, steady state condition, no reaction occurs and circular cross-section at the mouth of the pores. Thus, the conservation of mass species can be written as follows;
\[
\frac{\partial C_A}{\partial t} + u \cdot \nabla C_A = D_{AB} \nabla^2 C_A + R_A \quad (Ch. 4 - 4)
\]

where \( \frac{\partial C_A}{\partial t} \) is the rate of accumulation term, \( u \cdot \nabla C_A \) and \( D_{AB} \nabla^2 C_A \) are the net rate of convective transport and diffusive transport respectively and \( R_A \) is the rate of production term. Equation \((Ch.4-4)\) can be expressed in another form by emerging the diffusive and convective terms together where \( N_A \) is referred to the absolute transport rate;

\[
N_A = \text{Convection} + \text{Diffusion} \quad (Ch. 4 - 5)
\]

\[
\frac{\partial C_A}{\partial t} = -(\nabla \cdot N_A) + R_A \quad (Ch. 4 - 6)
\]

Applying the aforementioned assumptions, equation \((Ch.4-4)\) can be cast into the following equation;

\[
\nabla \cdot N_A = \frac{1}{r} \frac{\partial}{\partial r} (r N_A r) + \frac{1}{r} \frac{\partial N_{A\theta}}{\partial \theta} + \frac{\partial N_{AZ}}{\partial z} = 0 \quad (Ch. 4 - 7)
\]

Knowing that \( \frac{\partial}{\partial r} \) and \( \frac{\partial}{\partial \theta} \) terms in equation \((Ch.4-7)\) are assumed to be zero as the diffusion is considered in one direction. Therefore, equation \((Ch.4-7)\) is reduced to the following correlation;

\[
\frac{\partial N_{AZ}}{\partial z} = 0 \quad (Ch. 4 - 8)
\]

Fick’s law can be used to describe equation \((Ch.4-5)\) in the following expression;

\[
N_A = C_A u^M + \left(-D_{AB} \frac{dC_A}{dz}\right) = C_A \left(\frac{N_A + N_B}{C}\right) - D_{AB} \frac{dC_A}{dz} \quad (Ch. 4 - 9)
\]

where \( C_A \) is the concentration of the wetting liquid, \( u^M \) is the molar average velocity, \( z \) is the spatial coordinate measured upward from the sample surface and \( D_{AB} \) is the
diffusivity coefficient. Further mathematical manipulation is applied to obtain equation (Ch.4-12);

\[ N_A = x_A(N_A + N_B) - D_{AB}C \frac{dx_A}{dz} \] (Ch. 4 – 10)

\[ N_A = x_A N_A - D_{AB}C \frac{dx_A}{dz} \] (Ch. 4 – 11)

\[ N_A = -\frac{C D_{AB}}{(1 - x_A)} \frac{dx_A}{dz} \] (Ch. 4 – 12)

In order to proceed in determining the pore size as a function of vapor pressure, boundary conditions must be specified. For this method, the following two conditions are proposed;

1] \( x_A = \frac{P_A^*}{P} \) at \( z = 0 \)

2] \( x_A = 0 \) at \( z = L \)

Combining equations (Ch.4-8) and (Ch.4-12) with each other in order to formulize the differential equation and then integrate it based on the conditions that have been specified previously.

\[ \frac{d}{dz} \left( \frac{C D_{AB} \ dx_A}{1 - x_A} \right) = 0 \] (Ch. 4 – 13)

Equation (Ch.4-13) can be integrated twice to get equation (Ch.4-14) and (Ch.4-15) progressively.

\[ \frac{1}{1 - x_A} \frac{dx_A}{dz} = A \] (Ch. 4 – 14)

\[ -\ln(1 - x_A) = Az + B \] (Ch. 4 – 15)
Consequently, substituting the boundary conditions on the equations (Ch.4-14) and (Ch.4-15) in order to obtain the final net transport rate as a function of vapor pressure.

\[
\frac{1 - x_A}{1 - \frac{P_A}{p}} = \left( \frac{1}{1 - \frac{P_A}{p}} \right) \left( \frac{z}{L} \right) \quad (Ch. 4 - 16)
\]

\[
N_A = -\frac{CD_{AB}}{L} \ln(1 - \frac{P_A}{p}) \quad (Ch. 4 - 17)
\]

The evaporation rate is obtained by multiplying the molar flux with the cross sectional area \(S_c\);

\[
W_A = N_A * S_c \quad (Ch. 4 - 18)
\]

\[
W_A = -\frac{CD_{AB}S_c}{L} \ln(1 - \frac{P_A}{p}) \quad (Ch. 4 - 19)
\]

\[
W_A = -\frac{k_x \pi d^2}{4} \ln(1 - x_A) \quad (Ch. 4 - 20)
\]

where \(k_x\) is the mass transfer coefficient and \(d\) is test cell diameter. The former parameter is assumed to be constant at a fixed temperature and pressure and hence the value will be the same for all pores. Equation (Ch.4-21) is expressed to evaluate the instantaneous mole fraction as a function of evaporation rate;

\[
x_A = 1 - e^{-\frac{4W_A}{k_x \pi d^2}} \quad (Ch. 4 - 21)
\]

As expressed in equation (Ch.4-3), the pore size is determined based on the ratio of the mole fraction of IPA. Thus;

\[
\frac{x_{AO}}{x_{AO}^0} = 1 - e^{-\frac{4W_A}{\pi d_x^2 k_x}} \quad (Ch. 4 - 22)
\]
Equation (Ch.4-22) does not depend explicitly on the temperature or vapor pressure while the evaporation rate does. This equation might be reduced further by applying Taylor series for the exponential terms as follows [20]:

\[
\frac{x_{AO}^0}{x_{AO}} = \frac{1 - e^{-\frac{4W_A}{\pi d_x^2 k_x}}}{1 - e^{-\frac{4W_A^0}{\pi d_x^2 k_x}}} \approx -\left(\frac{4W_A}{\pi d_x^2 k_x}\right) + \frac{1}{2}\left(\frac{4W_A}{\pi d_x^2 k_x}\right)^2 - \cdots \approx \frac{W_A}{W_A^0} \quad (Ch. 4 - 23)
\]

Achieving the same operating conditions for each run is not easy and therefore different binary diffusion coefficient of IPA in air (D_{AB}) might be obtained for the same sample. As a result, Sherwood number, which is the dimensionless mass-transfer coefficient as expressed in equation (Ch.4-24), is preferred to be calculated and should be giving almost the same value for each run. [20]

\[
Sh = \frac{k_x L}{c D_{AB}} \quad (Ch. 4 - 24)
\]

where L is the tube-side length of the cell and c is the gas molar density.

**4.5 Experimental Procedure**

First of all, the microbalance has to be calibrated and validated before running any experiment. Then, the sample is wetted by immersing it overnight (~ 6 to 7 hours) in isopropyl alcohol (IPA) to ensure complete wetting. Afterward, the wetted sample is placed in the test cell without any underlying support to avoid any cooling effects that might occur during evaporation. A layer of IPA (around 0.5 ml) is spread on the sample (such that it forms a uniform thin layer on the sample) after it is enclosed in the test cell. The chamber temperature must be maintained to obtain accurate data since the evaporation rate is strongly dependent on the temperature. The higher temperature means higher evaporation rate and hence it is recommended to run the experiment at least under
29°C. The surface tension and molar volume for the chosen volatile liquid (IPA) at the adjusted system temperature (~ 30°C) are equal to $21.7 \times 10^{-3}$ N/m and 76.34 cm$^3$/mol respectively [20].

The vapor pressure is measured by recording the mass loss of IPA using a microbalance that is placed on the anti-vibrating table to provide accurate readings. IPA is selected as a wetting liquid because it has relatively lower boiling point compared to water and the initial vapor pressure can be assumed to be zero while this assumption is not valid in case of water if the humidity is quite high. Excess of IPA is added through the open-end side of the test cell to overlie on the sample surface. The diffusion of vapor IPA will occur vertically only and the evaporation commences progressively from the largest pores to smaller ones.

The recorded gravimetric measurements from the microbalance are acquired and stored on a PC every 10 seconds using programmed LabView software. The pore size of a given sample is measured as follows (Microsoft Excel and OriginPro were used for analyzing the raw data);

1] Record the mass loss every 10 seconds. Also, system temperature and pressure are recorded.

2] Calculate $W_A$ from the slope of a fixed number of consecutive reading sets (mass versus time) and assign this value to the midpoint time. For example, the slope of the data set from 0 to 60 sec is assigned to 30 sec; the next value represents the data set from 10 to 70 sec and it is assigned to 40 sec and so on.

3] Plot $W_A$ values versus time and then determine $W_A^0$ from the average value of $W_A$ of the free-standing liquid evaporation segment as depicted in Figure 13.
4] Determine the standard deviation (\(\delta\)) over the same time period. The following equation is used for this manner;

\[
\delta = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (W_{Ai} - W_{Ao})^2}
\]

(Ch. 4 – 25)

where N is the number of points located in the 2\textsuperscript{nd} segment and \(W_A\) is the evaporation rate.

5] Calculate the vapor pressure of IPA at the sample’s surface (\(P_o\)) based on the temperature of the system using Antoine equation (which is basically equivalent to mole fraction in the gas phase when it is divided by the system pressure).

\[
\ln P_o \text{(bar)} = 15.3026 - \frac{5418.45}{T(K)}
\]

(Ch. 4 – 26)

6] Evaluate the mass-transfer coefficient \(k_x\) from the value of \(W_o^A\) and \(x_o^A\) using;

\[
k_x = \frac{-4W_o^A}{\pi d_c^2 \ln(1 - x_A^o)}
\]

(Ch. 4 – 27)

where \(d_c\) is the active diameter of the open-side cell. The value of \(k_x\) is assumed to be constant at a fixed temperature and pressure, therefore, the same value is applied for all points in order to determine the instantaneous mole fraction from the evaporation rate at the 3\textsuperscript{rd} segment (shown in Figure 13) by applying equation (Ch.4-21).

7] Calculate the pore size when the evaporation from the pores commences using equation (Ch.4-3) in which it occurs when \(W_A\) deviates from \(W_o^A\) by more than three times the standard deviation.
8] Determine the average pore diameter of two consecutive pore diameter sets and assign this value to the difference between two consecutive readings of mass loss.

9] Sort the values of average pore diameter into bins having a width of 5 nm or any fixed range (i.e. the pores between 5 nm and 10 nm are associated to the 10 nm bin).

10] Add up the mass loss values that belong to the same bin and assign the value to its corresponding bin and finally plot the graph of percentage of mass loss versus pore size bin to get the distribution.

11] Finally, the mass-average pore diameter and standard error are calculated statistically.

As observed, several sample properties, such as tortuosity, constriction factor and geometric parameters, are not considered on the previous calculations which is an advantage for the EP technique. So, the measured pore diameter is called mass-average pore diameter. In case to account for the aforementioned parameters, mass-average diameter has to be converted to number-average pore diameter which is not a part of this study.
4.6 Data Validation

4.6.1 100 nm Anodisc Membrane

The pore size distribution of 100 nm Anodisc membrane was determined using the EP system. The temperature was maintained at 31.5°C. The collected raw data were acquired and plotted as a function of time as shown in Figure 14. These data were converted into evaporation rate $W_A$, as depicted in Figure 15, to break down the evaporative mass loss into three segments namely; the startup segment, evaporation of the free standing IPA layer and the evaporation from the pores (see Figure 13). The average evaporation rate $W^o_A$ and standard deviation ($\delta$) were determined from the 2nd segment where the overlying volatile liquid, IPA, had begun to evaporate.
From Figure 15, the values of $W^o_A$ and $\delta$ were $8.5 \times 10^{-8}$ mol/s and $6.72 \times 10^{-10}$ mol/s respectively. The evaporation of IPA from the pores ($W_A$) had started when the rate was equal to $8.25 \times 10^{-8}$ mol/s (i.e. when the evaporation rate $W_A$ deviated from $W^o_A$ by more than three times the standard deviation). The instantaneous mole fractions and pore
diameters were measured accordingly in this regime in order to evaluate the PSD of this sample as shown in Figure 16. The average pore size calculated for this sample was about 112.88 nm (manufacturer value is 100 nm).

4.6.2 20 nm Anodisc Membrane

Same procedure as described above for 100 nm sample was repeated for the 20 nm sample, except the temperature in this case was maintained at 32.5°C. From Figure 13, the average value of evaporation rate of the overlying liquid (from the 2nd segment), $W_A^o$ was about to $9.22 \times 10^{-8}$ mol/s while the evaporation from the pores commenced from $8.95 \times 10^{-8}$ mol/s. The mass transfer coefficient was calculated to be equal to $4.15 \times 10^{-7}$ mol/(cm$^2$.s) at the system temperature. The same steps mentioned in the procedure section has been followed for determining the average pore size and size distribution of 20 nm Anodisc membrane. As a result, the profile of this sample is shown in Figure 17 with average pore size equal to 24.94 nm.
Thus for the 100 nm and 20 nm Anodisc membranes, the estimated average pore diameters from EP are close to the manufacturer value. Comparing the measured mean pore size of the 20 nm Anodisc, we can see that the average pore size estimation of ~19.7 nm from permporosimetry agrees well with the manufacturer data but EP overestimates the average pore size (24.94 nm). This disparity could be due to one of the following reasons:

1. The variation in the samples as two different samples from different batches were used for the two set-ups.

2. EP includes dead end pores in its analysis while permporosimetry does not, although this would not be true for Anodisc as they are very thin membranes (0.5 micron active layer) to have any dead end pores.

Figure 17: PSD of 20 nm Anodisc membrane using EP.
3. The most plausible explanation could be the fact the Anodisc are highly asymmetric membranes with ~59.5 micron thick support (200 nm pore size) and 0.5 micron thick active layer (20 nm pore size) and thus the IPA could have wetted the support too and its evaporation would erroneously be accounted for in the pore size distribution.

But overall the results from permporosimetry and evapoporometry seem reasonable and reliable and provide two simple techniques to estimate the pore size distributions for shale rocks as it will be discussed in Chapter 5. At the same time, the set-ups are being continually optimized (temperature control, humidity control etc.) to minimize the errors in the pore size estimation.
Chapter 5: Pore Size Results of Shale Rocks

5.1 Petrophysical Properties of Shale Rocks

The current projection of the unconventional oil reservoirs concerning the oil and natural gas production is quite vague so far. Quantifying shale resources is extremely controlled by the current technologies used for exploration and extraction and these estimations might be changed with time as additional information will be discovered in this field.

Shale rocks are fine-grained sedimentary rocks which are mainly made up from mud which consisted of random percentage of clay and silt-sized particles. Although shales are classified as mudstones, they have special properties compared to the other mudstones in terms of structure which shales are fissile and laminated. The latter term means that the rock is composed of several thin layers while the former term describes its potential of obtaining thin pieces along with the laminations. [18]

The concept of porosity is basically defined as the volume of void spaces within the rock that can be filled with a fluid (i.e. oil, gas and water). Thus, the amount of fluid stored in the rock can be determined using the porosity value, which can be divided into total porosity and effective porosity. The former parameter determines the total pore volume divided by the bulk volume and the latter parameter refers to the active pores volume divided by the bulk volume. The effective porosity is linked to the fractures that are required to perform in a given reservoir in order to collect the natural gas (i.e. methane-dominated) [5]. Variation in porosity from one rock to another is dependent on mineralogy, organic contents, degree of water saturation and fabric (i.e. clay, carbonate,
biogenic and detrital). As the total organic carbon (TOC) contents, for instance, is increasing in a certain shale reservoir, the porosity of that reservoir will be declining [46]. Also, shales can be found in different colors from greens to blacks depending on many factors such as depositional environment and material composition in which the properties of a given rock can be predicted from its color [47]. In general, black shales indicate that they contain organic materials and highly probable to hold a significant amount of natural gas or oil within insoluble organic matter which is commonly called as kerogen [14].

Natural gas might be stored in various phases inside the shale matrix as free gas, adsorbed gas and dissolved gas. The molecules in phase one are in steady random motion which allows the gas molecules to propagate and then fill the pores within the rock due to continuous collisions with each other [5]. The second phase is basically the adherence of particles to the surface of the shale due to weak chemical bonds as it is known as adsorbed gas. The adsorbed gas phase is organically rich shale and might be the dominant source of natural gas [48]. The third phase is described as low molecular weight gas that is dissolved in a reservoir fluid such as water and oil [5]. The accumulation of natural gas in shales is depicted in Figure 18. [14]
Another important parameter is the permeability which relates the cracks and pores in the rocks to the production flow of natural gas and oil. The permeation through shale reservoirs relies on many factors such as pore size, the structure of the rock-building grains, grain grading and cementation and the fracture pathways [14]. Generally, the unit of permeability is described by Darcy (D) which is commonly used by the geologists and petroleum engineers to represent the fluid flow in an oil field. Darcy is not an SI unit and it is referred to squared length. The Darcy’s law can be expressed as follows:

\[ k = \frac{Q \mu l}{A \Delta P} \]  

(Ch. 5 – 1)

where \( k \) is the permeability (cm\(^2\) or Darcy), \( Q \) is the flow rate (cm\(^3\)/s), \( \mu \) is the viscosity (cp), \( l \) is the sample thickness (cm), \( A \) is the sample area (cm\(^2\)) and \( \Delta P \) is the pressure gradient (atm) [49].

Defining general relationships between permeability and porosity to evaluate the petrophysical properties of shale rocks is quite challenging since the latter is anisotropic,
heterogeneous and highly clay contents dependent. Nevertheless, several studies have published a few empirical correlations to estimate the porosity such as the weak power law relationship between porosity ($\phi$) and permeability. [50]

5.2 Pore Size and Permeability of Unconventional Reservoirs

Characterizing the key parameters for unconventional reservoirs is very complicated since the rocks are heterogeneous. The pore size distribution is related directly to the porosity and therefore to the permeability. Thus, a correlation between porosity and permeability can be found to evaluate a certain rock [51]. The petrophysical properties of conventional reservoirs, which are made up of sandstones or carbonates, in terms of porosity and permeability of unfractured rocks are in the range of $10^{-40\%}$ and $10^{-13}$-$10^{-11}$ m$^2$ respectively, while it is $0.1$-$20\%$ and $10^{-23}$-$10^{-19}$ m$^2$ for unconventional reservoirs considering TOC up to $20\%$ and clay up to $70\%$. The lower values of unconventional compared to the conventional will affect other properties such as pore size distribution and the mechanical properties. [50]

The limitations of the conventional characterization techniques have led the researchers and scientists to combine multiple techniques in order to analyze the pore systems of shale reservoirs. Numerous studies have been conducted to measure the porosity and permeability of shales but most analyses were limited as discussed in Chapter 2.

Luffel et al. [52] have developed GRI method, named after Gas Research Institute, also known as helium pycnometry for characterizing shales. This technique, however, requires quite extensive pretreatment steps and divergence in the obtained raw data is highly
probable due to the lack of step-by-step procedure for characterizing [19]. Also, neither pore size nor permeability are measured in this technology where only the porosity is calculated through the density using this method. The other technique that has been used extensively is the mercury intrusion porosimetry, mainly Micromeritics’ AutoPore IV 9500 Series, which has the potential to apply high pressure to access the smaller pores. The limitations of this technique are discussed broadly in Chapter 2. Other techniques have been utilized in this field but since the shale rocks are heterogeneous and have irregular pores across the surface, evaluated pore sizes are not representative to the entire reservoirs.

To have the full spectrum and deep understanding of how the shale rocks behave and form, it is necessary to evaluate the two key parameters, pore size and permeability. Several observations in this area have revealed that evaluating the properties of various shale rocks from mineral grains to the order of lithological variability is quite challenging due to the necessity of more advanced technologies that have the potential to discover more in micro- and nano-scale [14].

In this paper, pore size distribution analyses were conducted, using the two techniques described above, on shale samples received from Argentina (Neuquen basin well) and Norway.

5.2.1 Argentina Shales (Neuquen Basin)

Shale gas reservoirs are located on several spots around the world including Argentina where it is considered as the third largest producer according to the US Energy Information Administration (EIA). The majority of the produced shale gas and oil
resources are mainly from Neuquen basin, located in west-central Argentina (shown in Figure 19). Shales in Neuquen basin are characterized as thick, organic-rich, marine-deposited black rocks in which the production has been estimated to be around 180 to 600 bbl/day with approximately 50 vertical wells. This basin is grouped under Los Molles and Vaca Muerta based on the depth of the shale reservoir and geological age. The average TOC of the collected shales is about 5.0% and they consist of low-to-medium percentage of clay. [48]

Figure 19: Sedimentary basins located on Argentina.

5.2.2 Norway Shales

No further information, such as the exact location and depth, was provided concerning the samples that were collected from Norway.
5.3 Sample Preparation

The advantage of permporosimetry and evapoporometry techniques to analyze shale rocks lies in the fact that for the pore size distribution analysis, the sample need not be crushed or grinded into fine-powder as well as that these techniques are non-intrusive or destructive. To do the analysis, the samples were cut and polished into a 21.5 mm diameter disk (with thickness of 1-2 mm) so that they can be installed in the test cell/module. Since chunks of irregular shaped rocks were collected from Norway and Argentina basins, the following steps were carried out to make uniform shale samples.

First of all, a cutter equipped with diamond blade, IsoMet® Low Speed Saw Buehler, was used to get smaller pieces of shale rocks. For pieces greater than 22 mm in diameter, they were polished by a polishing machine using different grit size sanding papers, to obtain uniform disc shapes. The smaller rock samples were shaped in a required disk form and dimensions by using impermeable epoxy resin around the edges as shown in Figure 20.

Figure 20: Different shale samples for characterization using permporosimetry and EP.
Afterwards, the samples were placed in a vacuum oven operated at relatively high temperature (\(\sim 120 \, ^\circ C\)) to remove any adsorbed gas and moisture. 12 different samples were made and characterized using the permporosimetry and evapoporometry techniques and their details are outlined in Table 5. Samples 1 to 9 were collected from Norway (sample # 4 is not shown here) and the remaining samples were from Argentina.

Table 5: Shale rock details.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Location</th>
<th>Uniformity*</th>
<th>Thickness (mm)</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Norway</td>
<td>Yes</td>
<td>2.11</td>
<td>0.47</td>
</tr>
<tr>
<td>2</td>
<td>Norway</td>
<td>Yes</td>
<td>1.54</td>
<td>0.60</td>
</tr>
<tr>
<td>3</td>
<td>Norway</td>
<td>Yes</td>
<td>1.85</td>
<td>0.85</td>
</tr>
<tr>
<td>5</td>
<td>Norway</td>
<td>No</td>
<td>1.85</td>
<td>0.84</td>
</tr>
<tr>
<td>6</td>
<td>Norway</td>
<td>No</td>
<td>2.08</td>
<td>0.49</td>
</tr>
<tr>
<td>7</td>
<td>Norway</td>
<td>No</td>
<td>1.95</td>
<td>0.43</td>
</tr>
<tr>
<td>8</td>
<td>Norway</td>
<td>No</td>
<td>1.62</td>
<td>0.43</td>
</tr>
<tr>
<td>9</td>
<td>Argentina</td>
<td>Yes</td>
<td>1.99</td>
<td>1.20</td>
</tr>
<tr>
<td>10</td>
<td>Argentina</td>
<td>No</td>
<td>1.77</td>
<td>0.87</td>
</tr>
<tr>
<td>11</td>
<td>Argentina</td>
<td>Yes</td>
<td>1.81</td>
<td>1.48</td>
</tr>
<tr>
<td>12</td>
<td>Argentina</td>
<td>No</td>
<td>1.92</td>
<td>1.45</td>
</tr>
</tbody>
</table>

* Uniformity describes the exposed area, whether it represents the actual rock or shaped with epoxy.
5.4 Permporosimetry Results

The geometric parameters, including tortuosity and constriction factor, were assumed to be equal to 1 and 0.8 respectively. Seven Norway samples were tested using permporosimetry technique but permeate flow was observed for only 3 of them. The helium permeance profile versus relative pressure for these samples is shown in Figure 21.

![Figure 21: Helium permeance versus n-hexane relative pressure profile for Norway samples.](image)

The drop in helium flow with increasing relative pressure means that n-hexane has started blocking the pores (i.e. adsorbing in the pores). Hence, the pore area could be determined using equation (Ch.3-14), which in turn can provide the average pore size of a given pore. Also, Knudsen diffusion mechanism for gas flow was assumed in order to calculate the relative pore area since the average pore diameters fall in the mesopore range. The data for sample 1 is outlined in Table 6 and it can be clearly seen that the majority of pores lie between 2.5 to 7.5 nm range (based on the pore area for this range).
Table 6: Permporosimetry results for sample 1.

<table>
<thead>
<tr>
<th>P/Po</th>
<th>He Permeance (mol/(s.m².Pa))</th>
<th>Pore Diameter (nm)</th>
<th>Average Pore Diameter (nm)</th>
<th>Relative Pore Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.34E-09</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.10</td>
<td>1.26E-09</td>
<td>2.59</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.50</td>
<td>1.11E-09</td>
<td>7.42</td>
<td>5.00</td>
<td>0.051</td>
</tr>
<tr>
<td>0.75</td>
<td>7.21E-10</td>
<td>16.82</td>
<td>12.12</td>
<td>0.003</td>
</tr>
<tr>
<td>0.85</td>
<td>5.62E-10</td>
<td>29.49</td>
<td>23.16</td>
<td>0.002</td>
</tr>
<tr>
<td>0.90</td>
<td>4.97E-10</td>
<td>49.06</td>
<td>39.27</td>
<td>0.007</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>Total 0.063</strong></td>
</tr>
</tbody>
</table>

Alternatively, equation (Ch.3-15) was utilized to obtain the pore size distribution of the same sample and the distribution is depicted in Figure 22 which indicates an average pore size of 16.38 nm.

![Sample 1](image)

Figure 22: PSD of sample 1 using permporosimetry.
Results for samples 2 and 3 are shown in Tables 7-8 and Figures 23-24. The average pore diameter of sample 2 and 3 are about 16.59 nm and 5.85 nm respectively.

Table 7: Permporosimetry results for sample 2.

<table>
<thead>
<tr>
<th>P/Po</th>
<th>He Permeance (mol/(s.m².Pa))</th>
<th>Pore Diameter (nm)</th>
<th>Average Pore Diameter (nm)</th>
<th>Relative Pore Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>4.11E-09</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.10</td>
<td>3.63E-09</td>
<td>2.59</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.50</td>
<td>3.09E-09</td>
<td>7.42</td>
<td>5.00</td>
<td>0.066</td>
</tr>
<tr>
<td>0.75</td>
<td>2.67E-09</td>
<td>16.82</td>
<td>12.12</td>
<td>0.004</td>
</tr>
<tr>
<td>0.85</td>
<td>2.36E-09</td>
<td>29.49</td>
<td>23.16</td>
<td>0.002</td>
</tr>
<tr>
<td>0.90</td>
<td>2.08E-09</td>
<td>49.06</td>
<td>39.27</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Total 0.081</td>
</tr>
</tbody>
</table>

Figure 23: PSD of sample 2 using permporosimetry.
Table 8: Permporosimetry results for sample 3.

<table>
<thead>
<tr>
<th>P/Po</th>
<th>He Permeance (mol/(s.m².Pa))</th>
<th>Pore Diameter (nm)</th>
<th>Average Pore Diameter (nm)</th>
<th>Relative Pore Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>2.96E-08</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.25</td>
<td>1.10E-08</td>
<td>4.00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.50</td>
<td>5.90E-09</td>
<td>7.42</td>
<td>5.71</td>
<td>0.485</td>
</tr>
<tr>
<td>0.75</td>
<td>0.00E+00</td>
<td>16.82</td>
<td>12.12</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td></td>
<td></td>
<td>0.485</td>
</tr>
</tbody>
</table>

Figure 24: PSD of sample 3 using permporosimetry.

The helium permeance profiles for the Argentina samples are shown in Figure 25. Tables 9-12 and Figures 26-29 are shown the data concerning the relative pore area and pore size distribution.
Table 9: Permporosimetry results for sample 9.

<table>
<thead>
<tr>
<th>P/Po</th>
<th>He Permeance (mol/(s.m².Pa))</th>
<th>Pore Diameter (nm)</th>
<th>Average Pore Diameter (nm)</th>
<th>Relative Pore Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>7.07E-10</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.05</td>
<td>6.19E-10</td>
<td>2.08</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.20</td>
<td>5.48E-10</td>
<td>3.51</td>
<td>2.79</td>
<td>0</td>
</tr>
<tr>
<td>0.50</td>
<td>5.51E-10</td>
<td>7.42</td>
<td>5.47</td>
<td>0.028</td>
</tr>
<tr>
<td>0.75</td>
<td>3.85E-10</td>
<td>16.82</td>
<td>12.12</td>
<td>0.001</td>
</tr>
<tr>
<td>0.90</td>
<td>3.47E-10</td>
<td>49.06</td>
<td>32.94</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>Total 0.035</strong></td>
</tr>
</tbody>
</table>
Table 10: Permporosimetry results for sample 10.

<table>
<thead>
<tr>
<th>P/Po</th>
<th>He Permeance (mol/(s.m².Pa))</th>
<th>Pore Diameter (nm)</th>
<th>Average Pore Diameter (nm)</th>
<th>Relative Pore Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>3.93E-09</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.10</td>
<td>3.11E-09</td>
<td>2.59</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.50</td>
<td>2.29E-09</td>
<td>7.42</td>
<td>5.00</td>
<td>0.093</td>
</tr>
<tr>
<td>0.75</td>
<td>1.50E-09</td>
<td>16.82</td>
<td>12.12</td>
<td>0.028</td>
</tr>
<tr>
<td>0.85</td>
<td>9.51E-10</td>
<td>29.49</td>
<td>23.16</td>
<td>0.024</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td></td>
<td></td>
<td><strong>0.145</strong></td>
</tr>
</tbody>
</table>
Table 11: Permporosimetry results for sample 11.

<table>
<thead>
<tr>
<th>P/Po</th>
<th>He Permeance (mol/(s.m².Pa))</th>
<th>Pore Diameter (nm)</th>
<th>Average Pore Diameter (nm)</th>
<th>Relative Pore Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>3.38E-09</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.05</td>
<td>3.15E-09</td>
<td>2.08</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.25</td>
<td>2.99E-09</td>
<td>4.00</td>
<td>3.04</td>
<td>0.086</td>
</tr>
<tr>
<td>0.50</td>
<td>2.39E-09</td>
<td>7.42</td>
<td>5.71</td>
<td>0.051</td>
</tr>
<tr>
<td>0.75</td>
<td>1.90E-09</td>
<td>16.82</td>
<td>12.12</td>
<td>0.007</td>
</tr>
<tr>
<td>0.85</td>
<td>1.73E-09</td>
<td>29.49</td>
<td>23.16</td>
<td>0.034</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td></td>
<td></td>
<td>0.178</td>
</tr>
</tbody>
</table>
Figure 28: PSD of sample 11 using permporosimetry.

Table 12: Permporosimetry results for sample 12.

<table>
<thead>
<tr>
<th>P/Po</th>
<th>He Permeance (mol/(s.m².Pa))</th>
<th>Pore Diameter (nm)</th>
<th>Average Pore Diameter (nm)</th>
<th>Relative Pore Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>3.18E-09</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.25</td>
<td>2.90E-09</td>
<td>4.00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.50</td>
<td>2.39E-09</td>
<td>7.42</td>
<td>5.71</td>
<td>0</td>
</tr>
<tr>
<td>0.75</td>
<td>2.42E-09</td>
<td>16.82</td>
<td>12.12</td>
<td>0.018</td>
</tr>
<tr>
<td>0.90</td>
<td>1.91E-09</td>
<td>49.06</td>
<td>32.94</td>
<td>0.028</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Total 0.046</td>
</tr>
</tbody>
</table>
5.5 Evaporoporometry (EP) Results

EP results are tabulated for both Norway and Argentina shale samples in Table 13. The duration for each run was from 24 to 48 hours depending on the amount of IPA overlying the sample and the actual pore size distribution.

Table 13: Summary of EP results for all shale samples.

<table>
<thead>
<tr>
<th></th>
<th>Nor #1</th>
<th>Nor #2</th>
<th>Nor #3</th>
<th>Nor #5</th>
<th>Nor #6</th>
<th>Nor #7</th>
<th>Nor #8</th>
<th>Arg #9</th>
<th>Arg #10</th>
<th>Arg #11</th>
<th>Arg #12</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W_a \times 10^8$ (mol/min)</td>
<td>4.93</td>
<td>7.02</td>
<td>5.13</td>
<td>5.59</td>
<td>5.06</td>
<td>6.29</td>
<td>5.19</td>
<td>7.82</td>
<td>5.49</td>
<td>5.33</td>
<td>8.22</td>
</tr>
<tr>
<td>$\delta \times 10^9$ (mol/min)</td>
<td>1.67</td>
<td>1.40</td>
<td>1.06</td>
<td>1.30</td>
<td>3.35</td>
<td>1.04</td>
<td>0.70</td>
<td>1.16</td>
<td>0.80</td>
<td>1.57</td>
<td>1.65</td>
</tr>
<tr>
<td>$W_k \times 10^8$ (mol/min)</td>
<td>4.43</td>
<td>6.60</td>
<td>4.81</td>
<td>5.19</td>
<td>4.05</td>
<td>5.98</td>
<td>4.98</td>
<td>7.48</td>
<td>5.25</td>
<td>4.86</td>
<td>7.73</td>
</tr>
<tr>
<td>$k_\phi \times 10^{-3}$ (mol/min/m²)</td>
<td>5.36</td>
<td>7.09</td>
<td>5.18</td>
<td>5.64</td>
<td>5.10</td>
<td>6.35</td>
<td>5.24</td>
<td>7.90</td>
<td>5.54</td>
<td>5.38</td>
<td>8.30</td>
</tr>
<tr>
<td>$d_{avg}^\pm \sigma$ (nm)</td>
<td>18.01±2.00</td>
<td>24.04±2.59</td>
<td>16.13±2.44</td>
<td>23.44±2.45</td>
<td>8.50±1.43</td>
<td>17.12±3.28</td>
<td>27.33±2.63</td>
<td>29.98±4.61</td>
<td>22.15±2.45</td>
<td>18.19±2.07</td>
<td>22.59±2.63</td>
</tr>
</tbody>
</table>
The typical raw data obtained from EP is basically mass loss of IPA (both the overlying IPA layer and IPA from pores) as a function of time. Figure 30 presents the raw data for Sample 3, showing a continual loss in mass which is due to the obvious reason that IPA is evaporating. The flat data line in the end means that all the IPA has evaporated and that mass corresponds to the weight of sample.

![Figure 30: Raw data of sample 3 using EP.](image)

Following the data analysis procedure as described in Chapter 4, the mass loss can be converted into the evaporation rate and the results are shown in Figure 31 for all Norway samples.
Based on the evaporation rates, the pore size distributions for the Norway samples, from sample 1-8, are calculated and shown in Figures 32-38.

Figure 31: The evaporation rate profiles with respect to time for Norway samples.

Figure 32: PSD of sample 1 using EP.
Figure 33: PSD of sample 2 using EP.

Figure 34: PSD of sample 3 using EP.
Figure 35: PSD of sample 5 using EP.

Figure 36: PSD of sample 6 using EP.
Similarly, Argentina samples were analyzed by conducting the same procedure protocol. The evaporation rate profiles for these samples are shown in Figure 39 while the PSDs are presented in Figures 40-43.
Figure 39: The evaporation rate profiles with respect to time for Argentina samples.

Figure 40: PSD of sample 9 using EP.
Figure 41: PSD of sample 10 using EP.

Figure 42: PSD of sample 11 using EP.
Mercury Intrusion Porosimetry (MIP) Results

In addition to the permporosimetry and EP techniques, MIP analyses were performed on both the shale samples using an AutoPore™ IV 9500 Porosimeter, manufactured by Micromeritics Corporation, which has the capability to reach up to 60,000 psi in terms of applied pressure and around 3 nm in terms of pore throat diameter, to verify and compare the results from permporosimetry and EP techniques. The samples were crushed and grinded to powdered form to do MIP analysis. About 0.77 g of Norway sample and 0.62 g of Argentina sample were introduced in the penetrometer for each run. Figures 44 and 45 show the results for the pore size distributions for both samples using MIP. The average pore diameter of the Norway sample was about 16.50 nm while it was 14.70 nm for the Argentina sample.

Figure 43: PSD of sample 12 using EP.

5.6 Mercury Intrusion Porosimetry (MIP) Results
Figure 44: PSD of the Norway sample using MIP.

Figure 45: PSD of the Argentina sample using MIP.
5.7 Scanning Electron Microscopy (SEM) Results

Two samples, one per location, were analyzed using FEI Magellan 400 XHR Scanning Electron Microscope. Both samples were coated with iridium to suppress the charging issue.

Figure 46: SEM images for Norway sample.
As shown in Figure 46, the SEM images for the Norway sample show pores (~ 12-19 nm) which are in agreement with the result reported using the above-mentioned techniques.

![SEM images for Norway sample](image1)

The Argentina sample is more representative than the other sample, as shown in Figure 47, in which the surface of the sample can be classified mainly into three zones: A, B, and C. Zone A represents the dark spots and zone C refers to the rough areas (lighter spots) while zone B is the edge of the two zones. Smaller pores (i.e. pore ~ 6-10 nm) are located in zone B and larger ones in zone C (i.e. pores ~ 10-40 nm). Zone A, however, is flat area and they have no pores on their

![SEM images for Argentina sample](image2)

Figure 47: SEM images for Argentina (sample#11).
surfaces. Nevertheless, pores in zone B is more likely to be dead-end pores. Further studies should be investigated in the future to understand the surface roughness variation, although, the sample was polished uniformly by conducting focused ion beam milling.
Chapter 6: Discussion & Final Remarks

6.1 Comparison of Results

Table 14 shows the comparison for the average pore size estimated from permporosimetry, EP and MIP for the shale samples. For MIP analysis, only two samples, one each of Norway and Argentina were used.

Table 14: Pore diameter results using permporosimetry, EP and MIP.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Location</th>
<th>Permporosimetry (nm)</th>
<th>EP (nm)</th>
<th>MIP (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Norway</td>
<td>16.38</td>
<td>18.01</td>
<td>16.50</td>
</tr>
<tr>
<td>2</td>
<td>Norway</td>
<td>16.59</td>
<td>24.04</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Norway</td>
<td>5.85</td>
<td>16.13</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Norway</td>
<td>-</td>
<td>23.44</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Norway</td>
<td>-</td>
<td>8.50</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Norway</td>
<td>-</td>
<td>17.12</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Norway</td>
<td>-</td>
<td>27.33</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Argentina</td>
<td>11.89</td>
<td>29.98</td>
<td>14.70</td>
</tr>
<tr>
<td>10</td>
<td>Argentina</td>
<td>11.76</td>
<td>22.15</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Argentina</td>
<td>12.74</td>
<td>18.19</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Argentina</td>
<td>18.68</td>
<td>22.59</td>
<td></td>
</tr>
</tbody>
</table>

From Table 14, it can be seen that the results from permporosimetry are in good agreement with those obtained from MIP technique, but EP for most part over-estimates
the average pore size. Also, it can be seen that there are variations in average pore size for the all the samples even if they are from same batch i.e. from Norway and Argentina. For example, samples from Argentina exhibited pore size from 11 to 18 nm (permoporosimetry) and 18 to 29 nm (EP) even though they were cut from the same rock stub. These results are therefore indicative of the heterogeneity of the shales.

As indicated above, EP over-estimates the average pore size and this could be due to the fact the, in case of EP, we did not take into account the contribution from pores smaller than 4 nm (due to limitation of Kelvin equation) and this would lead to overestimation of the pore size. At the same time, EP analysis also accounts for dead end pores while permoporosimetry accounts only for open pores, which could lead to disparity between the two systems. In addition, the pores from epoxy used to shape the samples in disk form may have been accounted for in EP analysis whereas in case of permoporosimetry it does not affect the analysis as it only accounts for open pores (epoxy is impermeable to gases, but may have dead end pores). This hypothesis is currently under investigation. One way to circumvent this issue that we are currently trying is to cut the disks using laser cutter and fabricate modules that can accommodate different diameter disks.

6.2 Kelvin Limitations for EP Results

As stated earlier, pores below 4 nm were excluded from the analyses since there is no alternative equation has been proposed as in permoporosimetry technique. Shales, however, are generally fallen in the microporous material category and the contribution of those pores are definitely influencing the skewed distribution of data. This might be considered as one reason of obtaining higher average mass-pores diameter using EP compared to the permoporosimetry. Since some studies have suggested the validity of
Kelvin equation at pores from 2 nm and higher, Table 15 is outlined the effect of excluding the smaller pores from the pore size calculations. Permporosimetry, on the other hand, provides HK equation to account for the pores below Kelvin limits and therefore this point might not be as important as in EP technology.

Table 15: Influence of smaller pores on the average mass-pores diameter in EP method.

<table>
<thead>
<tr>
<th></th>
<th>Nor #1</th>
<th>Nor #2</th>
<th>Nor #3</th>
<th>Nor #5</th>
<th>Nor #6</th>
<th>Nor #7</th>
<th>Nor #8</th>
<th>Arg #9</th>
<th>Arg #10</th>
<th>Arg #11</th>
<th>Arg #12</th>
</tr>
</thead>
<tbody>
<tr>
<td>d$_{avg}$ (nm) [&gt;4 nm]</td>
<td>18.01</td>
<td>24.04</td>
<td>16.13</td>
<td>23.44</td>
<td>8.50</td>
<td>17.12</td>
<td>27.33</td>
<td>29.98</td>
<td>22.15</td>
<td>18.19</td>
<td>22.59</td>
</tr>
</tbody>
</table>

6.3 Relationship between Relative Pore Area and Total Mass

Measuring the relative pore area is a common feature associated to the permporosimetry technique while total mass is related to the EP system. The relationship between these two parameters is not clear as tabulated in Table 16.

Table 16: Summary of total mass and pore area for shale samples.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Permeance [mol/(s.m$^2$.Pa)]x10$^{-9}$</th>
<th>Total Mass (g %)</th>
<th>Relative Pore Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.34</td>
<td>0.96</td>
<td>0.063</td>
</tr>
<tr>
<td>2</td>
<td>4.11</td>
<td>1.01</td>
<td>0.081</td>
</tr>
<tr>
<td>3</td>
<td>29.60</td>
<td>0.45</td>
<td>0.485</td>
</tr>
<tr>
<td>5</td>
<td>0.00</td>
<td>0.77</td>
<td>0.000</td>
</tr>
<tr>
<td>6</td>
<td>0.00</td>
<td>0.24</td>
<td>0.000</td>
</tr>
<tr>
<td>7</td>
<td>0.00</td>
<td>0.50</td>
<td>0.000</td>
</tr>
<tr>
<td>8</td>
<td>0.00</td>
<td>1.02</td>
<td>0.000</td>
</tr>
<tr>
<td>9</td>
<td>0.71</td>
<td>2.43</td>
<td>0.035</td>
</tr>
<tr>
<td>10</td>
<td>3.93</td>
<td>0.80</td>
<td>0.145</td>
</tr>
<tr>
<td>11</td>
<td>3.38</td>
<td>0.64</td>
<td>0.178</td>
</tr>
<tr>
<td>12</td>
<td>3.18</td>
<td>1.11</td>
<td>0.046</td>
</tr>
</tbody>
</table>
The ideal relationship between the total mass and the relative pore area should be stated as both parameters are directly proportional to each other which means obtaining high relative pore area indicates high value of total mass too. However, this is not the case as shown in Table 16. Several reasons might be linked to this inconsistency:

1] Tortuosity and sample’s thickness are significant key factors for determining the pore size using the permporosimetry while these geometric factors are not accounted for EP analyses. Also, these parameters were assumed to be constant for all shale samples (i.e. Norway and Argentina samples) but this is not the case since the shale samples have heterogeneous structures.

2] The reported EP results were concerning the mass-average pore diameter with proportionality of \((d^2)\) for cylindrical pores (equation \((Ch.4-2)\)). To convert these values into number-average pore diameter, the proportionality should be doubled \((d^4)\) which basically indicates lower values compared to the reported data [20, 21].

3] The effect of forming additional layer on top of the sample, as it is known by t-layer, is considered on the permporosimetry data for the entire pore size domains as suggested by Koreleskiy et al. Some studies have considered the contribution of this layer at specific pore size domain.

4] The exposed area is not the same for both permporosimetry and EP technologies which is 17.6 mm and 12 mm in terms of diameter respectively.

6.4 Modifying the Sample Preparation Process

As observed earlier, the sample preparation steps are very essential to conduct pore size analysis using permporosimetry and EP. The process, which has been followed in this
study, is consisted of several steps; (1) using a diamond blade cutter, (2) polishing the sample and (3) modifying the shape with epoxy resin. Steps (2) and (3) are repetitive and the sample must be dried right after each step. Therefore, the characterization results might not be accurate if the steps were not the same for each sample. Also, this issue influences the quality of the microscopic. To overcome this problem, an ultra-fast, advanced PCB laser etching, manufactured by LPKF Laser & Electronics, has been proposed for sample preparation. The purpose of this machine is mainly etching circuitry and drilling holes via focusing an ultraviolet laser with a 20 μm beam diameter. Thus in essence, the propagation of cracks on shale rocks will be contained since the laser beam can easily penetrate the shale rocks. Implementing the laser-based cutter is fairly genuine in this field and will provide better characterization measurements.

It is recommended to perform focused ion beam milling imaging (FIB-SEM) to provide clear evidences of the heterogeneity and examine the porosity of shale samples by taking multiple cross-sectional area shots for the sample and also to support the idea of dead-end pores.
**Conclusion**

Porous materials are implemented in several industrial applications such as water desalination, gas separation and pharmaceutical care which they are mainly governed by the pore size and the PSD. Analyzing shale reservoirs are not excluded from these applications and numerous advantages can be gained by evaluating the PSD of a given shale reservoir. Several studies have investigated this field utilizing the microscopic techniques, mercury intrusion porosimeter and helium pycnometry. Because of the limitations of the conventional characterization techniques, novel methods for characterizing the PSD have to be proposed in order to obtain better characterization results. Thus, permporosimetry and EP technologies were introduced, designed and utilized for evaluating the two key parameters, pore size and pore size distribution. The pore size and PSD profiles of different shale samples from Norway and Argentina were analyzed using these technologies and then confirmed by mercury intrusion porosimeter. The results of Norway and Argentina samples from permporosimetry are in good agreement with those obtained from MIP technique, but EP for most part over-estimates the average pore size, though, they were cut from the same rock stub and this could be due to the fact the, in case of EP, we did not take into account the contribution from pores smaller than 4 nm (due to limitation of Kelvin equation). In addition, the pores from epoxy used to shape the samples in disk form may have been accounted for in EP analysis whereas in case of permporosimetry it does not affect the analysis as it only accounts for open pores. One way to circumvent this issue that we are currently trying is to cut the disks using laser cutter and fabricate modules that can accommodate different
diameter disks. Nevertheless, both techniques are reliable and provide simple data interpretations to estimate the pore size distributions for shale rocks.
REFERENCES


14. Dyrka, I. *Petrophysical properties of shale rocks*. Available from: 


